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Biofuels

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Edited by Krzysztof Biernat

BIOFUELS - STATE OF DEVELOPMENT

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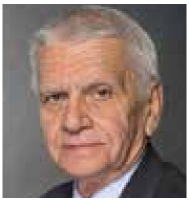
Meet the editor



Prof. Krzysztof Biernat, PhD (Mech. Eng.), is acting as the head of the Department of Fuels and Bioeconomy, is a coordinator of the Polish Technology Platform for Biofuels, and is also a member of the Coordination Committee of Polish Technology Platform of Bioeconomy. He is also a lecturer at the Cardinal Stefan Wyszynski University. He is a member of the Scientific Board of Automotive Industry Institute as the chairman of the science commission. He is a leading expert in the International Renewable Energy Agency and an expert in the International Energy Agency and many operational programs. He specializes in chemical thermodynamics of environmental processes as well as obtaining technologies, quality evaluation and use of exploitative liquids, including biofuels, and biorefinery systems. He received many national and foreign distinctions, decoration and orders for scientific and pro-innovative activities. He is an author of above 250 publications in the area of properties and exploitative conditionings of fuels, biofuels and other liquids as well as environmental protection.

Contents

Preface

The intention of the publisher was to present the book covering a wide review of biofuels, mainly, in the area of the current status and future perspectives of their development. Biofuels, as energy carriers, are located in the group of alternative fuels designed mainly for powering the engines as a means of transport or as bioliquids for fueling any types of stationary devices. Depending on the region or country, the advancement of research of the development of biofuels is dictated mainly by raw materials, environmental aspects, local legal conditions, research potential and, most importantly, demand and social acceptance. Therefore, the proposals of chapters submitted by the authors did not always meet the expectations of the publisher, due to the varying degree of advanced work on the development of biofuels, represented by specific research centers. Currently, in the highly industrialized countries, there is a clear trend in the transition from the production of so-called first-generation biofuels (conventional) to work on the development of the second and higher generations of biofuels (advanced biofuels), which results mainly from environmental and raw material reasons as well as from the requirements of modern internal combustion engines in relation to energy carriers, because fuels, including biofuels and other alternative fuels intended for supplying combustion engines and heating devices, must meet specific requirements directly related to process evaporation and combustion of fuel and indirectly with ensuring proper efficiency, fuel consumption and environmental protection as well as in general ensuring rationality of exploitation.

As already mentioned, the presented book is based on selected materials that take into account the state and stage of research, production and use of biofuels in the countries represented by the authors. These materials, therefore, are not only informative but also cognitive, although they mainly concern conditions in the field of conventional biofuels. It should be expected that the next book will cover the issues of advanced biofuels described above, which will pass from the demonstration or pilot stage in the stage of common production.

In the field of systematics regarding the naming and technology of biofuels, especially advanced biofuels, there are various divisions and classifications, not always consistent with the current state of knowledge in this field. Research experiences and experiments carried out on pilot and demonstration installations have led to the development of correct taxonomy and even to the creation of strict and unambiguous definitions, applicable especially in European Union countries. Therefore, the book contains the first section as an introduction in which there is an introductory chapter, defining types of biofuels, their distribution and future biofuels, including methods of obtaining them. This is particularly important in the field of defining biofuels, both the third and fourth generations, which in many publications are defined and described in a not very precise, and even incorrect way. This chapter is a synthesis of previous publications of the author of this chapter.

The essential 12 chapters were accepted from the submitted materials, which were grouped in the next four sections. The second section, which includes gas biofuels, contains two chapters (Chapters 2 and 3) covering the production processes of biogas from waste substances on the example of Mexico and the very important issues for the use of biomethane in transport.

The third section is represented by Chapter 4 on the possibility of using waste fruit palm tree (EFBOPT) for the production of second-generation bioethanol and Chapter 5 containing considerations in the field of high biomass/bagasse from sorghum and Bermuda grass as a raw material for the production of second-generation bioethanol.

Due to the generality of production and the degree of utilization, the fourth section on biodiesel includes Chapters 6–10, which include, inter alia, a review of catalytic transesterification methods, description of ultrasonic methods in the production and analysis of biodiesel and kinetics of transesterification processes. This section also contains Chapter 9 dedicated to the research on the nitrogen oxide emissions of B20-fueled engines and the final chapter of this section, which discusses the systems of modern bioreactors for the cultivation of algae as raw materials for the production of second-generation biodiesel.

The fifth section includes Chapter 11 defining the potential for the use of biofuels in Turkey and Chapter 12 covering the very prospective biorefinery technology in the field of production technology for biodegradable biomass-derived plastics. The last chapter, Chapter 13, goes somewhat beyond the thematic area of the book and defines the environmental conditions for obtaining synthetic gas from natural gas. This chapter has been included in the book, because in both our own research and literature data, it can be expected that synthesis gas in the future, including waste biomass, may prove to be a universal raw material for biofuel production and depending on the origin also for the production of effective and adaptable alternative fuels.

Finally, on behalf of the authors and my own, I would like to thank Mrs. Maja Bozicevic, Author Service Manager from IntechOpen Publishing House, for the patience, understanding and, most importantly, effective coordination of the complex publishing process of this book.

I dedicate this book to my daughter Ewa, who stimulated and mobilized me to work on the edition of this book. I hope that Ewa's knowledge of her specialization, which is psychology, will allow us in the future to develop a book on the psychological determinants of the processes of biofuels and other alternative fuels, which may be important for the development prospects and social acceptance of these energy carriers.

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Section 1

Introduction

Introductory Chapter: Prospective Biofuels

Krzysztof Biernat

Additional information is available at the end of the chapter

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1. Introduction

The development and modifications of the drives of modern engines therefore require appropriate fuels for these drives, so that the main requirements set out above are met. These requirements are defined by engineers and vehicle manufacturers, while guaranteeing the durability and reliability of engines powered by appropriate fuels. To ensure the correct quality of fuels for spark-ignition and self-ignition engines meeting the requirements of internal combustion engines and environmental protection, leading global car concerns have established World-Wide Fuel Charter (WWFC) [1, 2]. Due to the increasingly stringent environmental requirements, the fifth edition of the WWFC was introduced, which introduced, in addition to the current four, additional, fifth categories of both motor gasolines and diesel oils. In the fifth edition of the WWFC, in the same way for all five motor gasolines categories, it is permissible to add up to 10% (v/v) of ethanol, with the ban on methanol being sustained, and for diesel oils, the permissible addition of up to 5% (v/v) FAME to fuels in categories 1–4, while in the top category 5, the content of this biocomponent is not allowed. In Category 5 of diesel oils, it is permissible to use other biocomponents originating from "hydrotreated vegetable oil" (HVO) and "biomass to liquid" (BtL) processes, provided that the resulting mixture meets all normative requirements for conventional diesel fuels.

2. Types of biofuels

It is anticipated that the prospective raw materials for the production of biofuels will be all waste substances (biodegradable at the beginning), including waste biomass (lignocellulosic feedstock) and in the long-term waste carbon dioxide, and even water vapor. Due to environmental conditions, we should carefully approach energy crops as a raw material.

The modern state of knowledge defines as relatively safe crops (cultivations) of Jatropha, Arnica, halophytes, and algae, which can be raw materials for biofuels. The need to look for new raw materials necessary for the production of biofuels (as well as bioliquids—energy carriers for industrial applications) is particularly important in European countries. In these countries, the need to introduce biofuels has been legally sanctioned, and at the same time, there has been a development of waste biomass recycling technology. Taking into account significant environmental conditions, limiting the use of all biomass for industrial purposes, it is necessary, especially in European countries, to import biofuels and raw materials for their production.

From many tests, including engine tests, it is clear that use as additives (first-generation biocomponents) is not beneficial for the operation of combustion engines, and fuels with biocomponents cannot be practically stored, and in some cases, the use of biofuels. The first generation not only does not close the balance of carbon dioxide, but unfortunately it is characterized by the positive emissivity of this gas. In addition, the use of food for energy purposes is considered to be unethical ("food competition"), and in turn, energy crops can cause disturbances in "biodiversity" and the occurrence of scarcity of land for cultivation for the agri-food industry, the so-called "land hunger" ("ground competition"). Therefore, it should be considered technical, operational, and environmental, as the right way to replace first-generation biofuels with second-generation and higher-generation biofuels [3–7].

In the second generation of biofuels, as before, the following fuels are located:

- bioethanol, biobutanol, and mixtures of higher alcohols and their derivatives obtained as a result of advanced processes of hydrolysis and fermentation of lignocellulose derived from biomass (excluding raw materials for food);
- synthetic biofuels that are products of biomass processing through gasification and appropriate synthesis for liquid fuel components in BtL processes and resulting from the processing of biodegradable industrial and municipal waste, including carbon dioxide in WtL processes;
- fuels for self-ignition engines derived from the processing of lignocellulose from biomass in Fischer-Tropsch processes, including synthetic biodiesel derived from the composition of lignocellulosic products;
- biomethanol obtained as a result of lignocellulose transformation processes, including Fisher-Tropsch synthesis and also using waste carbon dioxide;
- biodimethylether (bio-DME) obtained in thermochemical processes of biomass processing, including biomethanol, biogas, and synthesis gases being derivatives of biomass transformation processes;
- biodiesel, as a biofuel or fuel component for self-ignition engines obtained as a result of hydrogen refining (hydrogenation) of waste, derived from waste vegetable oils and animal fats;
- biodimethylfuran (bio-DMF) derived from sugar processing processes, including cellulose in thermo- and biochemical processes, derived from the processing of waste raw materials;

- biogas as synthetically produced natural gas—biomethane (SNG), obtained as a result of lignocellulose gasification processes, and appropriate synthesis as a result of agricultural biogas, landfill, and sewage sludge treatment processes [8];
- biohydrogen obtained as a result of gasification of lignocellulose and synthesis of gasification products or as a result of biochemical processes.

As part of the developed documents characterizing further perspectives in the development of biofuels, it was also proposed to separate the next generation of biofuels, i.e., the third one, which would contain biofuels obtained from genetically modified biomass, in order to facilitate conversion processes with known technologies. The fourth category would include biofuels produced from biomass, whose genetic modification would additionally increase the absorptivity of carbon dioxide in the photosynthesis process. In the available literature, biofuels obtained from algae are very often included in the third generation of biofuels. It is definitely not correct, because the division of biofuels into the third and fourth generation has been clearly defined by the former Directorate General for Energy and Transport of the European Commission [9]. Based on previous experience, it turned out that there is a need to develop more efficient ways to obtain biofuels, which resulted in the separation of third-generation biofuels, obtained by similar methods as second-generation fuels, but from a properly modified raw material. The raw material for the production of third-generation biofuels should be made of biomass, modified at the stage of cultivation, among others by means of molecular biological techniques. The purpose of these modifications is to improve the conversion of biomass to biofuels by, for example, growing trees with low lignin content, growing crops with enzymes built in. Biofuels that are completely obtained by biochemical methods such as biohydrogen, biomethanol, or biobutanol can also be included in this generation of biofuels.

A prospective fourth generation of biofuels has been separated due to the need to close the carbon dioxide balance or to eliminate its impact on the environment. Therefore, the fourth-generation biofuel technologies should take into account carbon capture and storage (CCS) processes, i.e., carbon capture and storage at the stage of raw materials and production technologies of these biofuels. So, raw materials for the production of biofuels of this generation can be plants with increased, even genetically assimilated, CO_2 during cultivation, and the technologies used must take into account the uptake of carbon dioxide in appropriate geological formations by bringing to the carbonate stage or storage in oil and gas workings. To avoid creating further divisions of biofuels that may arise in the future, the International Energy Agency proposes to group these fuels as conventional ("conventional biofuels") and future-oriented ("advanced biofuels"). The proposed division of biofuels by IEA is increasingly used.

3. Perspective biofuels

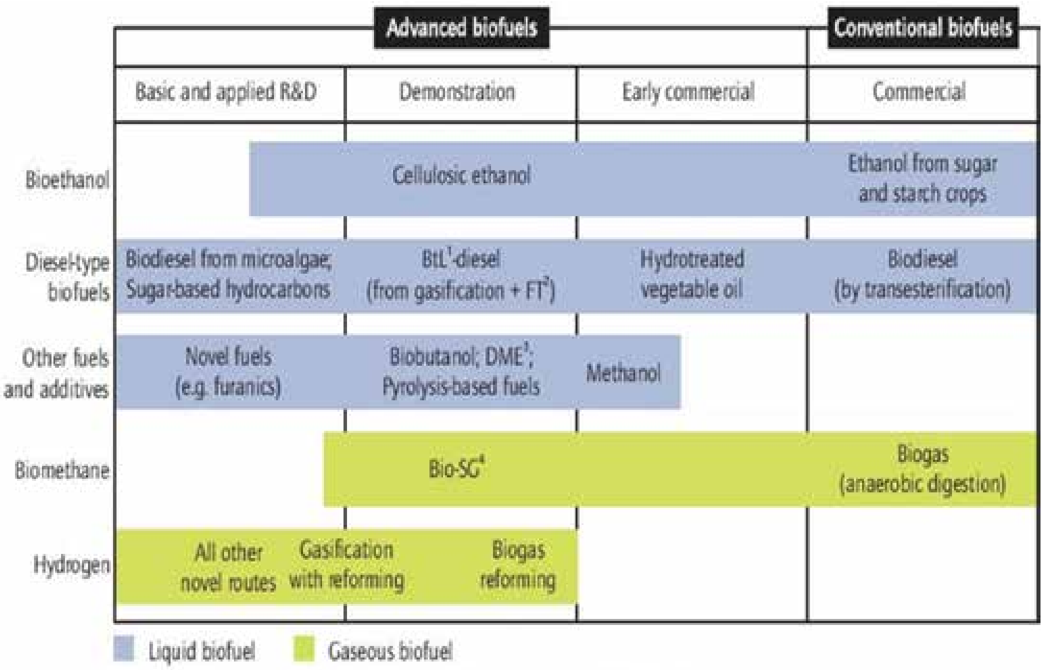
Research into the processes of obtaining substitutes for previously used fuels, referred to as "alternative fuels" for motor gasolines, diesel fuels, and even aviation fuels is being conducted intensively in the world. An alternative gas fuel for SI engines is already manufactured in the world, DME (dimethylether) or bio-DME, where DME can be produced from coal, and bio-DME from lignocellulosic biomass, and even from waste substances. Biofuels should also be included in the group of alternative fuels. It is planned to purify biogas to almost pure biomethane and compress it to form gaseous fuel with similar qualitative characteristics as compressed natural gas (CNG). In the field of liquid fuels, technologies for the production of second-generation bioethanol from lignocelluloses (waste biomass or specific energy crops) or from waste substances are being implemented. Also tested is biobutanol from fermentation processes and DMF (dimethylfuran) obtained from cellulose and starch, also considered solar fuels, obtained in the processes of thermal decomposition of biomass or waste. The processes of converting biomass into liquid fuels are referred to as "biomass to liquid" processes (BtL), and obtained from waste—"waste to liquid" processes (WtL). Alternative fuels are also considered, being properly composed mixtures of synthetic hydrocarbons obtained from various raw materials—so-called XtL processes. A prospective raw material may be synthesis gas obtained from very different thermal and thermocatalytic processes of waste substances, including biomass and energy crops, and also, what is new, derived from the synthesis of water vapor and carbon dioxide. Various types of hydrocarbons can be obtained from syngas whose compositions will correspond to the composition of gasolines, diesel fuels, or aviation fuels. Synthesis gas, in the light of recent studies, the results of which are already implemented on a demonstration scale, can also be subjected to a fermentation process, leading to the production of bioethanol, and hydrocarbons from C2 to C5. In the perspective, hydrogen or biogas obtained from synthesis gas or other biomass transformation processes is referred to as a universal energy carrier, but it is envisaged to use it as a carrier in fuel cells (for example, supplying electric cars). The future of alternative fuels in the world up to 2050 was outlined in a document prepared by the International Energy Agency ("Technology Roadmap—Biofuels for Transport"). The document also presents the current division and prospects for the development of biofuels, as shown in **Figure 1**.

An analogous document, "Innovation Outlook: Advanced Liquid Biofuels," was developed by the International Renewable Energy Agency (IRENA) in 2016, where the state and prospects for biofuels were also characterized with the current TRL levels. The division of biofuels according to IRENA is shown in **Figure 2**.

Therefore, taking into account environmental, operational, and logistic conditions, it is necessary to gradually pass biofuel production processes from processes using typical agro-food products to biomass, mainly waste—BtL processes, waste substances—"waste to liquid" processes (WtL), vegetable fat waste, and animal oils (frying oils), nonedible vegetable oils—HVO processes, production of biomethane from biogas using waste carbon dioxide for industrial algae breeding (microalgae). The future is the work started in the USA on the production of "solar fuels,", furan fuels, and work on the gasification of various waste substances in XtL processes, followed by the production of so-called "synthetic hydrocarbons," i.e., biorefinery processes also in the beginning become the main European program "Bio-economy for Europe."

Taking into account the demand for biofuels that meet the requirements of future sources of propulsion for means of transport, including air transport, as well as limiting carbon dioxide emissions, in terms of future fuels, the following biofuels will be preferred along with the technological paths of their production [1, 3–7]:

- **Fuels from BtL processes** (synthetic hydrocarbon compositions), obtained by rapid pyrolysis, biomass heating to a temperature between 400 and 600°C, followed by rapid cooling, whereby unstable compounds can be converted into liquids (HTU process) as a fuel HTU-diesel or deoxidized (HDO process), distilled, and refined for fuel compositions. The remainder of the so-called bio-char (charcoal) as a by-product can be used as a solid fuel, or used as a means for carbon sequestration and soil fertilization;
- **Diesel oil from processes BtL**, so-called FT-diesel, obtained by conversion to synthesis gas and catalytic Fischer-Tropsch synthesis (FT) in a wide range of liquid hydrocarbons, including synthetic diesel and JET biofuels;
- **Hydrotreated vegetable oil (HVO)** as fuel for self-ignition engines or fuel oil produced by hydrogenation of vegetable oils or animal fats (nonfood and waste). The first large plants were launched in Finland and Singapore, but the processes have not yet been fully commercialized;
- **Cellulosic bioethanol** produced from lignocellulosic raw materials by biochemical conversion of cellulose and hemicellulose leading to the fermentation of sugars (IEA, 2008a, [16]). Cellulose ethanol has a better energy balance in terms of greenhouse gas emissions and land-use requirements than starch ethanol;
- **Biogas** obtained through anaerobic digestion of raw materials such as organic waste, animal waste, and sewage sludge, and/or energy plants. Purified for biomethane (SNG) by



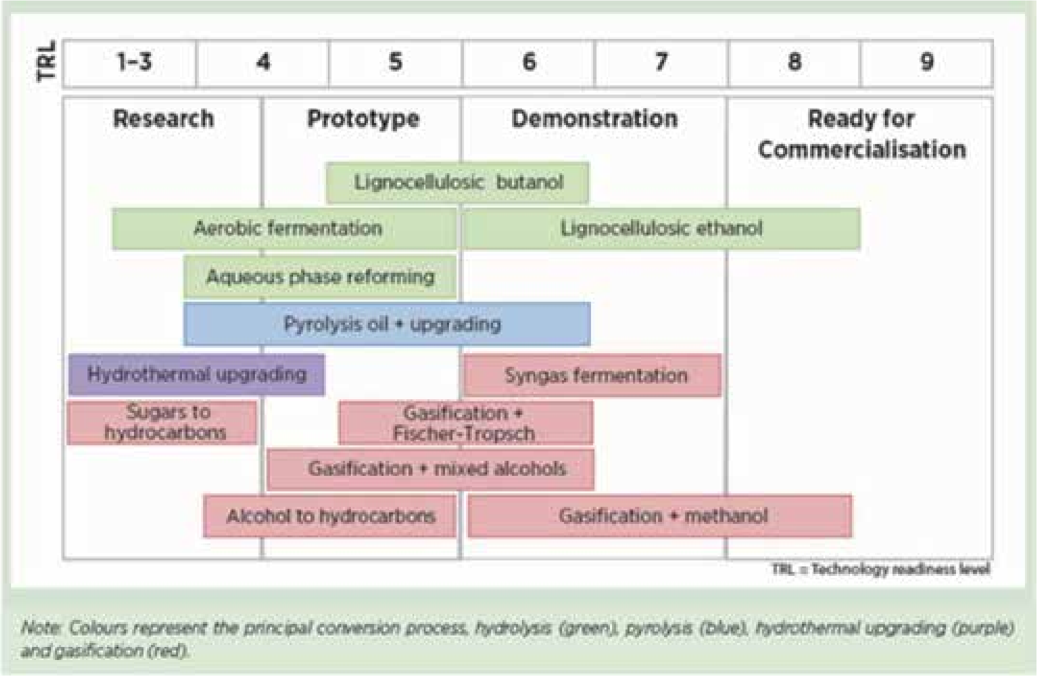
1. Biomass-to-liquids; 2. Fischer-Tropsch; 3. Dimethylether; 4. Bio-synthetic gas.

Source: Modified from Bauen *et al.*, 2009.

Figure 1. The division of biofuels and their advancement in production according to IEA [10].

removing carbon dioxide (CO_2) and hydrogen sulfide (H_2S), it can be a motor fuel or a hydrogen source, also for cell fuel;

- **Dimethyl ether (bio-DME)** as a gaseous fuel for self-ignition engines, obtained from methanol in the process of catalytic dehydration, from synthesis gas by gasification of lignocellulose and other biomass. The production of bio-DME from biomass gasification is in a demonstration phase (September 2010 in Sweden, Chemrec);
- **Biobutanol** with higher energy density and more favorable than ethanol in motor gasolines (MG). It can be distributed via the existing BS network. Biobutanol can be produced by fermenting sugars with *Clostridium acetobutylicum*. Demonstration plants operate in Germany and the USA, while others are under construction;
- **Furan fuels**, for which polysaccharides of the type cellulose and starch, constitute a raw material, obtained in defragmentation processes of multisugar chains leading to glucose, then converted into fructose, by isomerization using enzymatic catalysts. Fructose in the dehydration process changes into 5-hydroxymethylfurfural (HMF), which in the process of hydrogenolysis, in the presence of a copper-ruthenium catalyst, is converted into DMF (dimethylfuran), a fuel for spark-ignition engines with advantages over ethanol, without its disadvantages as a component fuel;
- **Solar fuels** [12] obtained by gasification of biomass for syngas using heat generated by the concentration of solar energy, which potentially improves conversion efficiency and



Note: Colours represent the principal conversion process, hydrolysis (green), pyrolysis (blue), hydrothermal upgrading (purple) and gasification (red).

Figure 2. Division and level of technological readiness of biofuels according to IRENA [11].

ensures greater reduction of greenhouse gas emissions. They can also be obtained as a result of the decomposition of water (steam) and the use of carbon dioxide to produce synthesis gas, catalytically converted to fuel fractions. The production of these fuels may also include so-called "artificial leaf";

- **Biorefinery systems** [13] for the production of liquid fuels and chemical intermediates. These processes are preferred in each of the five "value chains" set started in 2014. Bioeconomy for Europe, as a prospective, waste-free, biofuels, biomaterials (biochemicals).

In the area of the most promising raw materials for future biofuels, taking into account the so-called "land hunger" and requirements for reducing CO_2 emissions, cultivation of algae, niknik, Jatropha, and halophytes is preferred. To increase the amount of possible biomass resources to be used, technologies such as sunless (dark) photosynthesis and marine membrane systems for the production of algae, and technologies for the production of biomethanol as a raw material are also being developed.

4. Conclusion

The future of biofuels as alternative energy carriers for transport and bioliquids for stationary devices will depend on many factors. The main determinant is the availability of raw materials and the efficiency of both production technology and direct exploitation and, most importantly, the reduction of greenhouse gas emissions, including mainly carbon dioxide, throughout the life cycle assessment cycle (LCA). Taking into account the degree of development of various biomass waste processing technologies, it seems that the most effective and efficient gasification technologies are not only waste biomass for biofuel production in BtL processes but also gasification processes for industrial waste, mainly plastics leading to the production of alternative fuels in WtL processes [14], which prefers to jointly run XtL processes as processes significantly affecting the improvement of the environment. It seems, therefore, that future synthesis gas can be treated as a universal energy carrier. The confirmation of this thesis may be synthesis gas fermentation processes [13] enabling the production of bioethanol and other C2 to C5 hydrocarbons, i.e., acetic acid, isopropanol, dimethylketone, 2,3-butenediol, butane, isobutane, succinic acid, as well as isoprene structures important in the processes of economy on a closed circuit. In the field of alternative fuel production, with significant co-operation of the author's team, a patented thermolysis technology for plastic waste has been developed, which under atmospheric pressure conditions allows to obtain hydrocarbon fractions that can meet components of both motor gasolines and diesel oils compliant with the quality requirements of European fuel standards as "drop in alternative fuels" [15]. The catalyzed technology for producing synthesis gas from waste carbon dioxide and water vapor, which also has a significant negative impact on climate change, can also be considered as prospective. Therefore, one should strive to develop effective technologies of gasification processes of any waste raw materials, of course with regard to biomass, to obtain energy carriers adaptable by modern engines, both transport and stationary destination.

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Section 2

Biogas and Biomethane

The Potential for Biogas Production from Agriculture Wastes in Mexico

Salvador Carlos Hernandez and
Lourdes Diaz Jimenez

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Abstract

An important objective of the Mexican Energy National Strategy (ENS) is to produce around 35% of energy from clean technologies in 2024. This goal implies challenges from scientific and technologic perspectives. Besides solar and wind energies, different initiatives have been implemented to promote biofuels, mainly, biodiesel, bioethanol and biogas. Agriculture and livestock wastes are being used as biogas source to produce energy in small and medium scale. Also, some industries use biogas to provide a part of the energy required in their processes. But in general, the potential of biomethane production is not well seized yet. In the context of the ENS, biogas should be considered as an important topic due to the existence of several economical activities producing a lot of organic wastes. In this document, an analysis of the biogas from agricultural wastes is performed in order to identify the current status and opportunities for the next years.

Keywords: waste to methane, biofuel, agri-waste

1. Introduction

1.1. Objective of this study

The main sources of energy in Mexico are fossil fuels since there are, in some regions of the country, important reserves of oil, natural gas and even shale gas. However, from some years ago, a recurrent concern is the depletion of fossil fuels and the necessity of alternatives to provide the increasing energy demand.

From some years ago, renewable sources are considered as a real alternative to deal with the society requirements. In 2010, the National Strategy for Energy (NSE) has been designed in order to state directives concerning the generation and management of the energy. An important objective of this strategy is to produce around 35% of energy from clean technologies in 2024. This goal implies challenges from scientific and technologic perspectives. Besides solar and wind energies, different initiatives have been implemented to promote biofuels, mainly, biodiesel, bioethanol and biogas. Agriculture and livestock wastes are being used as biogas source to produce energy in small and medium scale. Also, some industries use biogas to provide a part of the energy required in their processes. But, in general, the potential of biomethane production is not well seized yet. In the context of the ENS, biogas should be considered as an important topic due to the existence of several economical activities producing a lot of organic wastes.

In this work, an analysis of the biogas from agricultural wastes is performed in order to identify the current status and opportunities for the next years in Mexico. Agriculture is an economic activity all around the country; besides products (fruits, vegetable, fodder), a large amount of wastes is generated in each stage of this activity: raising, harvesting and distribution. Only in the harvesting, it is estimated a production of 75 Mt of agricultural wastes. Many of them are traditionally used as fodder; some others are left in crop lands in order to promote the soil recovery and to improve the soil production. A few of them are studied as raw material to synthesize chemical products at industrial level. Then, only a small part of agricultural wastes is available as raw material for biogas production. However, it is necessary to assess the biomethane potentials in the national and international energy context.

1.2. Anaerobic digestion for biogas production

Anaerobic digestion (AD) is the process for wastes transformation into biogas. It is a natural mechanism of Earth to re-integrate organic wastes into the ecosystem dynamics. This process has been studied from many years ago, nowadays is well known and it is an active scientific topic [1–3]. AD is developed by many interdependent micro-organism communities, living in an environment free of oxygen, to transform complex substrates in four main stages: hydrolysis, acetogenesis, acidogenesis and methanogenesis; each stage has specific dynamics and three main phenomena are involved: physicochemical, hydrodynamic and biological. In optimal conditions, AD produces a biogas mainly composed of methane (50–80%) and carbon dioxide (48–18%); depending on the substrate, some other components (NO_x, SO_x) are also present in low concentration (1–2%).

It has been determined that hydrolysis and methanogenesis are the limiting steps of AD. Hydrolysis is the stage where most complex substrates should be transformed, if there is an excess of complex molecules, the hydrolytic bacteria may become saturated and then inhibited; a consequence of this situation is the stopping of the complete AD process. On the other side, methanogenesis is the slowest stage and then the most important for the process stability; it is very sensitive to variations in the operating conditions such as: pH, temperature, overload on substrate concentration, etc. Then, these two stages receive special attention in order to improve them and consequently enhance the global methane production yields.

AD imposes several challenges in different aspects of the process; some of them, which are specially related to transformation of agriculture wastes, are [3–6]:

- Wastes composition
- Combination of substrates for co-digestion
- Development on solid-state anaerobic digestion
- Reduction of inhibitory components.

2. Methods

The information used to develop the analysis was taken from official organisms such as:

- Ministry of Environment and Natural Resources (SEMARNAT)
- Ministry of Agriculture, Livestock, Rural Development, Fisheries and Food (SAGARPA)
- Agrifood and Fisheries Information Service (SIAP)
- Ministry of Energy (SENER)
- Federal Electricity Board (CFE)
- National Water Board (CONAGUA)
- National Institute of Statistics and Geography (INEGI).

Also, a workshop was organized in order to verify and complement the official information; the participants of the workshop were specialized people such as industrialists, farmers and stockbreeders from different regions of the country.

Four topics were considered in order to assess the biogas situation as follows:

a. Feedstock. The production of agriculture wastes is computed from data provided by official organisms (usually until 2015). Three kinds of wastes are included since it is considered that its gathering is technically and economically feasible: i) rising and harvest wastes: products which are lost in the raising and harvest due to mechanical damages or products selection, ii) postharvest wastes: products that do not reach the market standards or that perish before the sell points and iii) foliage: biomass and all organic matter which is leaved in soil in the harvest stage.

b. Potential for biogas production. The assessment of the energy potential is done considering the amount of wastes and the efficiency reported from experiments of biogas transformation in different regions of the country; when this efficiency is unknown a typical one (from specialized literature) is used.

c. Technology for biogas utilization. The mechanisms currently used for biogas utilization were obtained directly from users.

d. Perspectives. Alternatives and strategies to implement systematically the biogas technology are presented.

3. Results and discussion

3.1. Feedstock

The available surface for agriculture in Mexico is around 27 Mha and it is distributed all around the country. Due to the weather and geographic conditions, a large diversity of plants is raised: fruits, vegetables, grains, ornamental plants, etc. According with the SIAP, there were 326 crops in 2015 with a global production of around 677.76 Mt.

A relative classification of these products is presented in **Figure 1**. The most abundant are fruits and ornamental plants: 69 different kinds of fruits are raised, corresponding to 22% of the agriculture products; a similar amount is obtained for ornamental plants. Besides, the categories vegetables and grain and seeds concentrate 32% of products, aromatic herbs and fodder correspond to 15%. The item Other includes products such as agave, Christmas tree

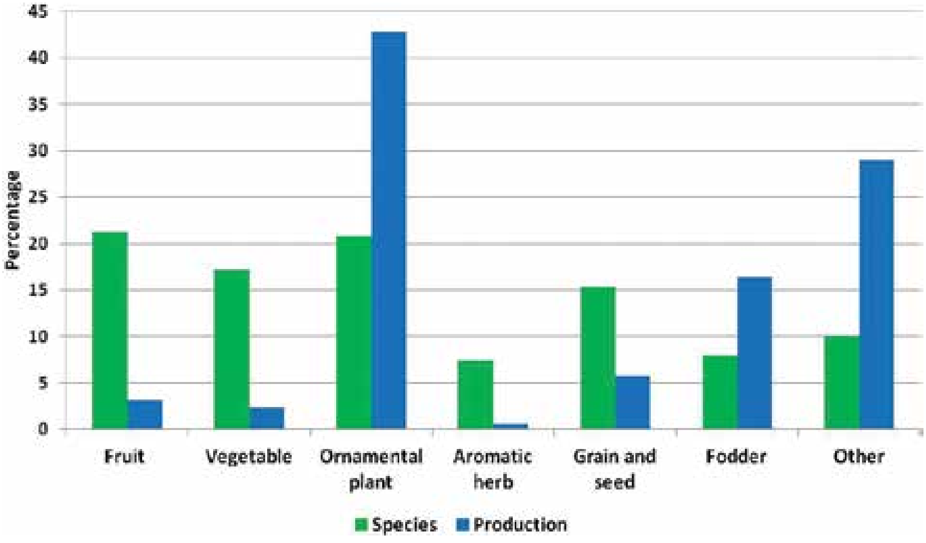

Figure 1. Relative classification of products from agriculture in Mexico.

and medicinal plants. Concerning the mass production, 290 Mt of ornamental plants were obtained in 2015, which correspond to the 40% of the total agriculture production in that year.

The categories which are not considered as raw material for biomethane production are Aromatic herb, Grain and seed, Fodder and Other. The reason for this exception is since either the wastes production is negligible (the case of most of aromatic herbs) or the wastes are used for specific applications. For example, most of wastes from grains crops are used as fodder. Also, most of those wastes are hard to be transformed into biogas due to the low moisture and high fiber content.

Although it is possible to transform these kinds of wastes into biogas by anaerobic digestion, they are better situated for other type of processes, such as thermochemical ones (combustion, pyrolysis and gasification), or fermentation with a previous treatment.

As said before, although there is a large production of wastes, only a fraction of them could be available for biomethane production. In the case of aromatic herbs, almost all the plant is profitable; that means, the organic wastes production is negligible. Besides, most of wastes from grains and seeds crops are used as fodder either in small or large scale. Also, an amount of the produced wastes from crops of fruits, vegetables and even fodder are left in the soil in order to protect the surface and to keep the productivity. In addition, it is not possible to collect all the produced wastes.

Then, a selection of crops was done considering the generation of wastes, the feasibility to collect them and its suitability to be transformed into biogas. On the basis of these criteria, 36 species were considered as source of wastes for biomethane production. The selected species are among fruits, vegetables and ornamental plants.

An estimation of the wastes production from these crops is done by using Eq. (1).

$$AW = AP \cdot WF \tag{1}$$

where AW is the agricultural wastes, AP is the agricultural production and WF is a waste factor which determines the amount of wastes produced from a specific crop. Then, the total waste production (AW_T) is obtained with:

$$AW_T = \sum_i AP_i \cdot WF_i \tag{2}$$

The respective waste factors were deduced from information reported in different works [7–14]. Based on an analysis of the reported information, in this work a general formula to calculate the waste factors is proposed as follows:

$$WF = 0.5 \cdot W_H + 0.5 \cdot W_{PH} + 0.6 \cdot W_{FB} \tag{3}$$

where W_H represents the wastes obtained in the harvesting stage, W_{PH} the wastes generated in the post-harvest stage and W_{FB} the wastes from plants foliage. It has been considered that 50% of the wastes from harvest and post-harvest stage are available for biogas production; the other 50%

could be used as traditionally. Besides, foliage which could be collected and transformed into biogas is around 60% and the other 40% can be used as nowadays. The amount of foliage (W_{FB}) is computed on the basis of the harvesting index, which relates the total biomass in a plant [14–16]. The wastes generated in the post-harvesting stage (W_{PH}) are estimated according with [7]. Also, the next expression to estimate the wastes from harvesting stage is proposed:

$$W_H = P \cdot \left(\frac{100}{100 - WI} - 1\right) \tag{4}$$

WI is the waste index, which is deduced from information reported in [7].

The information corresponding to the agricultural wastes produced from the selected species is presented in **Table 1**.

The Production column contains the reported production on the official records of SIAP. The Harvest, Post-harvest and Foliage columns include the estimation of wastes on the corresponding stage. The last column presents the estimation of wastes available for biogas production. A total of 12.7 Mt of wastes from the considered crops was estimated. This amount could provide either fuel or electricity to cover a fraction of the energy demand in the agriculture activities, as shown below.

3.2. Potential for biogas production

There exist different works related to biogas production from agriculture wastes [17–24], the yield depends on specific operating conditions and raw materials. In order to ease the data processing, in this study, the estimation of the biogas production from the selected agriculture wastes is done by following an experimental method developed for energy production from wastes in an herbalist facility [25]. This is based on the total solids, the biodegradable solids on the raw material (the fraction of biomass which can be transformed into biogas by anaerobic bacteria) and a conversion efficiency factor. Then, the estimation of biogas is done with the next equation:

$$V_{biogas} = \gamma \cdot VBS \tag{5}$$

where V_{biogas} is the estimated biogas production, VBS the biodegradable volatile solids in the raw material and γ the conversion efficiency factor. VBS are computed as follows:

$$VBS = \alpha_1 \cdot \alpha_2 \cdot TS \tag{6}$$

where TS is the total solids and α_1 and α_2 are coefficients related to the fraction of volatile solids in total solids and the fraction of biodegradable solids in volatile solids, respectively.

On the other side, the estimation of the energy content on the produced biogas is done considering a concentration of 50% of methane. This value is easily reached in anaerobic digestion processes. The equation to obtain the potential of energy generation (E_{biogas}) is:

$$\mathrm{E}_{biogas} = CH_4 \cdot HV_{methane} \cdot V_{biogas} \tag{7}$$

Species	Production	Harvest	Post-harvest	Foliage	Available
Apple	750324.85	187581.21	60025.99		123803.60
Apricot	1086.55	271.64	86.92		179.28
Asparagus	198075.04	49518.76	15846.00	222315.00	166071.38
Avocado	1644225.86	411056.47	131538.07		447229.43
Banana	2262028.25	565507.06	180962.26		615271.68
Broccoli	449185.37	112296.34	35934.83	1310124.00	908252.82
Dragon fruit	4542.28	1135.57	363.38		1235.50
Cabbage	226702.39	56675.60	18136.19	343680.00	267871.05
Cauliflower	68832.29	17208.07	5506.58	5490.43	22016.64
Carrot	318365.81	47571.90	41387.56	314500.00	264006.32
Chayote	163743.50	40935.88	13099.48	66525.00	84453.23
Courgette	456570.28	114142.57	36525.62	658025.00	519002.12
Cucumber	817799.83	204449.96	65423.99	658025.00	617256.55
Grapefruit	424315.36	106078.84	33945.23		115413.78
Green tomato	683984.96	170996.24	54718.80	1681234.00	1194784.31
Guava	294422.68	73605.67	23553.81		80082.97
Lettuce	437561.70	109390.43	35004.94	30356.80	137230.86
Mammee apple	18321.03	4580.26	1465.68		4983.32
Mandarin orange	291078.27	72769.57	23286.26		79173.29
Mango	1775506.77	443876.69	142040.54		482937.84
Melon	561891.31	140472.83	44951.30	457650.00	427424.44
Ornamental plants	358799.76			71759.95	71759.95
Orange	4515520.33	1128880.08	361241.63		1228221.53
Papaya	883592.54	220898.14	70687.40		240337.17
Peach	176302.74	44075.69	14104.22		47954.35
Pear	24679.04	6169.76	1974.32		6712.70
Pineapple	840486.46	210121.62	67238.92		228612.32
Plum	72206.82	18051.71	5776.55		19640.26
Potato	1727345.51	258109.10	224554.92	1228180.00	1145494.70
Prickly pear cactus	408445.05	102111.26	32675.60		111097.05
Rambutan	8840.97	2210.24	707.28		2404.74
Sapota	17167.30	4291.83	1373.38		4669.51
Spinach	39738.91	9934.73	3179.11		10808.98

Species	Production	Harvest	Post-harvest	Foliage	Available
Soursop	16620.91	4155.23	1329.67		4520.89
Strawberry	392625.19	98156.30	31410.02	99650.00	166584.05
Tangerine	195111.08	48777.77	15608.89		53070.21
Tomato	3098329.41	774582.35	247866.35	1936556.00	2004679.20
Watermelon	1020268.73	255067.18	81621.50	863525.00	795628.09
Total	**25644645.13**	**6115714.51**	**2125153.20**	**9947596.18**	**12700876.13**

Table 1. Production of wastes from agriculture (t).

where CH_4 is the methane concentration in biogas and $HV_{methane}$ is the heat value of pure methane, which is 8840 kcal (36.9 MJ). The results of this estimation are presented in **Table 2**.

The biogas which could be produced from these agricultural wastes is estimated on 4953 × 10^9 m^3 and the energy content is around 100 GJ. The production of electricity considering typical efficiency of internal combustion engines and electric generators is around 8300 GWh. This amount of energy is a little value in comparison of the total primary consumption in the country, which is near to 11,000 PJ per year. However, a systematic transformation of biomass for biogas production could be an interesting alternative not only for the energy generation but also for the environmental sector since it represents a mechanism for wastes management.

At present time, different biogas processes have been identified at different production scales. Some examples of them are shown in **Table 3**.

3.3. Technology

Biogas is a versatile fuel which can be transformed into energy by following different pathways [26, 27]. **Figure 2** includes a schematic representation of the biogas applications in the context of agriculture wastes transformation.

Thermal and electrical energy are the main alternatives to take advantage of biogas. The former can be employed for heating services either in farms or in residential applications; also, it can be used as energy source for food cooking and even for lighting through lamps fueled by biogas. The last one can be used to provide energy for household applications. In a larger scale, it is feasible to inject it to the national energy grid in order to be managed by the National Energy Board in Mexico (CFE); this is nowadays possible thanks to the recent modifications to the energy management laws. In next paragraphs, technologies currently used, and some alternatives, to profit the biogas potentials in Mexico are briefly described.

3.3.1. Thermal energy

Thermal energy is obtained from a biogas combustion process; the technology depends on the final applications. Among the alternatives, it is possible to find burners, stoves and lamps.

Species	Wastes (t)	Biogas (m^3)	Energy (MJ)
Apple	123803.60	48283404.10	979911686.16
Apricot	179.28	69919.49	1419016.10
Asparagus	166071.38	64767838.82	1314463288.93
Avocado	447229.43	174419479.23	3539843330.95
Banana	615271.68	239955956.76	4869906142.44
Broccoli	908252.82	354218599.07	7188866468.22
Dragon fruit	1235.50	481845.06	9779045.54
Cabbage	267871.05	104469709.53	2120212754.94
Cauliflower	22016.64	8586490.41	174262822.90
Carrot	264006.32	102962465.54	2089623238.04
Chayote	84453.23	32936760.48	668451553.94
Courgette	519002.12	202410825.30	4107927699.51
Cucumber	617256.55	240730055.97	4885616485.84
Grapefruit	115413.78	45011373.39	913505822.93
Green tomato	1194784.31	465965880.56	9456777545.90
Guava	80082.97	31232357.89	633860703.47
Lettuce	137230.86	53520036.34	1086189137.44
Mammee apple	4983.32	1943494.86	39443228.23
Mandarin orange	79173.29	30877582.88	626660544.58
Mango	482937.84	188345758.16	3822477161.89
Melon	427424.44	166695530.16	3383085784.69
Ornamental plants	71759.952	27986381.28	567983608.08
Orange	1228221.53	479006396.61	9721434819.13
Papaya	240337.17	93731496.64	1902280724.37
Peach	47954.35	18702194.66	379561040.61
Pear	6712.70	2617952.56	53131347.27
Pineapple	228612.32	89158803.68	1809477920.62
Plum	19640.26	7659699.47	155453600.65
Potato	1145494.70	446742934.57	9066647857.10
Prickly pear cactus	111097.05	43327850.90	879338734.10
Rambutan	2404.74	937850.10	19033667.73
Sapota	4669.51	1821107.18	36959370.30
Spinach	10808.98	4215503.57	85553645.01
Soursop	4520.89	1763146.13	35783050.77

Species	Wastes (t)	Biogas (m^3)	Energy (MJ)
Strawberry	166584.05	64967780.16	1318521098.25
Tangerine	53070.21	20697383.37	420053395.42
Tomato	2004679.20	781824887.81	15867136098.16
Watermelon	795628.09	310294956.88	6297436149.85
Total	**12700876.13**	**4953341689.58**	**100528069590.05**

Table 2. Estimation of the biogas production from agricultural wastes.

Raw material	Escala	Potential biogas (m^3 m^3)	Potential electricity kWh m^{-3}
Mango wastes	Laboratory	3.14	7.74
Residuos de cultivo de jitomate	Laboratory	0.911	2.24
Residuos de papaya	Semi-pilot	1.59	3.92
Residuos de plátano	Semi-pilot	4.6	11.35
Residuos de brócoli	Pilot	40	100
Nopales	Commercial	68.75	197
Algas	Laboratory	85.5	85.7

Table 3. Processes for biogas production from agriculture wastes identified in Mexico.

3.3.1.1. *Burners*

There exist commercial biogas burners which provide heat in conditioning thermal systems. For example, EcoFlam and Sayercen. EcoFlam is an Italian enterprise offering medium- and large-scale burners employing gaseous fuels including biogas. The thermal power is ranged from 7 kW to 25 MW. They can be easily adapted for households and industrial applications such as boilers, calefaction and drying systems, furnaces, greenhouses and heat regeneration systems, among others. Besides, Sayercen is a Mexican enterprise focused on the management of organic wastes in farms for production and utilization of biogas. They have integrated different technologies to produce, heat, steam and flames which are employed in farms and slaughterhouses.

In addition, biogas could be used by devices designed for natural gas applications; in this case, the injection conditions should be modified. Due to the different composition and lower calorific value of biogas, a larger input flow is required; also, the air content should be more than 20% and the pressure should be among 7 and 20 mbar.

3.3.1.2. *Stoves*

Biogas stoves are an interesting alternative for small facilities, e.g. rural towns and small farms. There are not national commercial devices, but there exist different Chinese organizations, such as Puxin, Xunda, Huamei and Taiyangyan, offering biogas stoves.

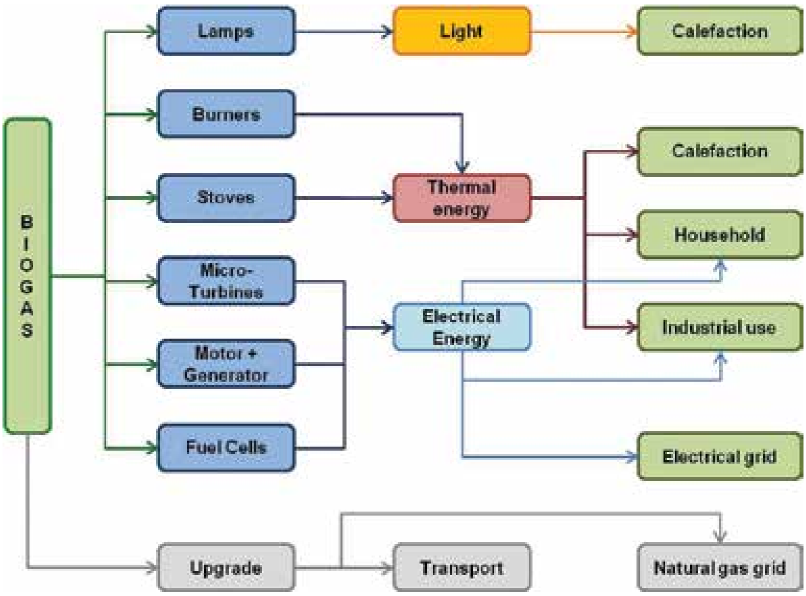

Figure 2. Biogas to energy alternatives.

On the other side, the adaptation of natural gas stoves to biogas is not complex [27]. Two alternatives are identified in order to allow the biogas to produce a similar flame as the one from natural gas: adaptation or replacement of burners. First one requires to increase the diffuser vent diameter and to regulate (decrease) the air in the mix biogas/air to reach a good flame quality. Replacement of burner implies also a replacement of the biogas pipeline; either stainless steel or PVC pipes are better situated for biogas flows since they are more tolerant to corrosive elements on biogas. As for the previous case, it is necessary to regulate the relation biogas/air.

3.3.2. *Lighting*

Lighting is produced by biogas lamps. Its efficiency is low (30–50%); however, this is a good alternative to facilities outside the national electrical grid coverage, and also for some specific situations in farms. Light is produced from the luminosity properties of materials such as lanthanum, cerium and thorium when they are exposed to high temperature (provided in this case from the biogas combustion). With these materials, it is possible to obtain light in the range of 400 and 500 lm, which is similar to 25–75 W. There are some commercial alternatives of biogas lamps, such as Puxin, Xunda, Taiyangyan, Rupak and Huamei. Coleman offers a variety of gas lamps, which could be adapted for biogas.

3.3.3. *Electrical energy*

Electricity from biogas can be obtained by two alternatives: electromechanical systems and electrochemical devices. Electromechanical systems require the combustion of fuels to produce mechanical energy which is transformed in electricity by the electromagnetic induction

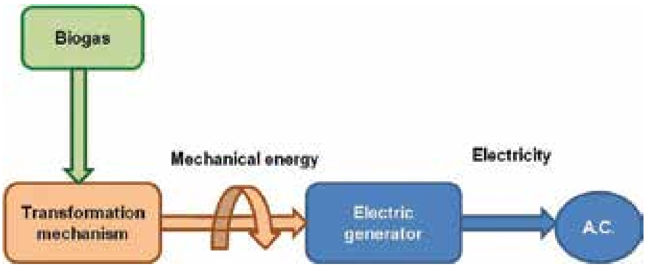

Figure 3. Electricity production from electromechanical devices.

principle (**Figure 3**). The alternatives for biogas transformation into mechanical are internal combustion engines, Stirling engines and turbines. In Mexico, internal combustion engines are preferred for electricity generation in comparison with the other two options.

3.3.3.1. Internal combustion engines

These engines have been studied from many years ago. They operate under the ignition by compression (Diesel cycle) or spark (Otto cycle).

The oil and diesel engines are modifiable to operate with biogas [28]. The injection system should be adapted to allow a larger gas flow and reach the adequate relation in the mixture fuel/air. In addition, it is necessary to synchronize the injection with the compression stage. Another alternative is to purify biogas in order to separate the CO_2 and to allow the methane to be the only component in the mix fuel/air for the thermodynamic cycle.

There are several commercial biogas engines for electricity generation. In Mexico, the most used are Mopesa, Cummins (adapted), Guascor and Jenbacher:

- Mopesa offers power plants of 30 and 60 kW, 220 V and 60 Hz known as Econogas Power Plants; the first system includes a 4.07 L 4 cyl biogas engine coupled to a synchronous generator of 30 kW; the second one uses a 5.8 L 6 cyl biogas engine with a 60 kW synchronous generator.
- Cummins. Diesel engines have been adapted to operate with biogas and they are connected to Marathon electric generators; the power is ranged among 40 and 100 kW and they are designed to be connected to the federal grid. The required biogas should content at least 55% of methane in order to reach the claimed efficiency.
- Guascor. These engines have been designed specifically to operate with biogas. The power capacity is ranged from 150 to 1240 kW. The biogas Guascor engines have been implemented in cogeneration or single generation configurations.
- GE-Jenbacher. Even if these engines are designed to operate with biogas from landfills and wastewater treatment plants, they are an alternative for biogas from other kind of wastes. The production power is ranged from 250 kW to 3 MW; that means, the engines are ideal for large scale applications. This technology could be employed either in single generation or in cogeneration operation modes.

- Caterpillar. The electric power plants offered by Caterpillar are fuel-flexible; then, they can operate with biogas. The main detected applications are in power generation with biogas from landfills, wastewater treatment plants and animal wastes; however, they could operate with any biogas containing the adequate methane concentration. The power generation is ranged from 64 to 3770 kW.

Table 4 includes a relationship of the equipment implemented in Mexico for electricity generation from biogas.

From this information, it can be deduced that the commercial power electric plants are available for more than 30 kW. This implies an approximate consumption of biogas of 12 $m^3 h^{-1}$. For applications less than 30 kW (a fewer capacity to produce biogas), other alternatives should be explored. For example: a) the adaptation of small either diesel or oil engines to allow them to operate with biogas; after that, it is advisable to connect them to small electric generators. Even if the conversion efficiency decreases, it is a feasible option to produce electricity from biogas at small scale; b) the use of biogas only to produce thermal energy; for low biogas production, the thermal energy is the best option since only a combustion process is required and there are not large lost of the potential energy and c) the methane up-grade in biogas, this allow to get a better quality fuel since the calorific value increases; a direct benefit of this situation is the reach large efficiencies at low scale. Nevertheless, this alternative requires more research at technological transfer: in fact, it is necessary to develop efficient devices to up-grade biomethane in biogas.

3.3.3.2. *Stirling engines*

External combustion engines can be used for energy production with biogas [29]. The Stirling cycle is based on the work produced form the expansion and contraction of a gas from a cold point to a hot one. The temperature on the hot point can be provided by the combustion of biogas, which takes place outside the engine.

Equipment	Number of implemented engines	Installed capacity
Mopesa	11	720 kW
Jidoka	16	1095 kW
Cummins	1	100 kW
Jenbacher	13	13.68 MW
Guascor	3	2.85 MW
Caterpillar	5	4.3 MW
Confidencial	3	1.28 MW
Other	107	6.42 MW

Table 4. Biogas engines coupled to electric generators implemented in Mexico.

Only one Stirling engine operating with biogas to energy production has been identified in Mexico. This use the biogas obtained from animal wastes. These kinds of engines are easy to design and to operate. Then, they present clear opportunities from scientific and technologic developments.

3.3.3.3. *Microturbines*

Turbines are well-known technology to produce energy at large scale. The fundamentals of them are based on the transformation of the kinetic energy of a fluid (water, steam, gas) into a mechanical energy. Nowadays, there are commercial developments which can operate at medium scale. Biogas is a feasible fuel for this kind of technology [30].

There are different commercial microturbines, such as Capstone and Siemens, which can be considered as an alternative to take advantage of biogas for a power production (more than 30 kW).

In Mexico, a beer company obtains biogas from the produced wastes in the beer production processes; the biogas is used to produce 6% of its energy consumption. The transformation is done by using biogas and steam in a cogeneration system.

3.3.3.4. *Fuel cells*

Fuel cells are electrochemical devices, which allow the energy of a chemical reaction to be transformed directly into electricity; they operate while being supplied with fuel and oxygen, then they do not neither become ended nor require to be recharged like conventional batteries. A basic operation principle of fuel cells is shown in **Figure 4**.

Research on this type of devices has made remarkable progress in recent years. Specifically, solid oxide (SOFC) cells have received special attention because they offer very high efficiency with relatively low sensitivity to the chemical composition of the fuel. The high operating temperature (700–1000°C) allows flexibility in relation to the fuel to be used. This implies that it is possible to use biogas, which cannot be used in other types of cells. SOFCs can be used in small power applications, stand-alone systems and remote systems [31]. Different research teams in Mexico deal with fuel cells.

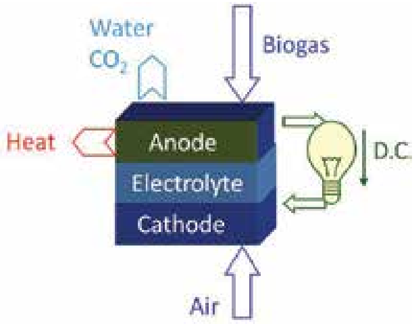

Figure 4. Electricity generation principle from electrochemical devices.

3.4. Perspectives

The potential of biomass for energy production in Mexico is large; besides agriculture, there are many other activities producing organic wastes. Since a single biogas production scheme may require high investment and operational costs some other complementary approaches should be explored. In this context, a national strategy should be implemented in order to achieve an optimal use of organic wastes, not only for energy production but for added value product generation. Based on the experience of some other countries all around the world, among the main topics which should be systematically addressed in Mexico the next could be considered: biorefinery approaches, biomethane upgrading, energy crops and technology development. This is schematized in **Figure 5**.

3.4.1. Biorefinery approaches

The schemes for integral revalorization of biomass, known as biorefineries, are considered as a promising alterative to develop a global industry based on biomass [32]. These schemes combine different biomass conversion processes in order to produce biofuels and chemical products in an analogue structure of oil refineries. Anaerobic digestion has been identified as a biological pre-treatment that ease the subsequent transformation of the diverse components of biomass. Then, biogas can be only one of the multiple products which can be synthesized. Some other biofuels such as ethanol, hydrogen and butanol could be obtained. Besides, chemical products or precursors such as organic acids, biopolymers and biofertilizers are possible to be produced [33].

At current time, there are several reports concerning the development of biorefineries in Mexico [34]. Most of them are in the conceptualization stage; there are different efforts related to experimental studies in order to identify the best operating conditions. Some of them are

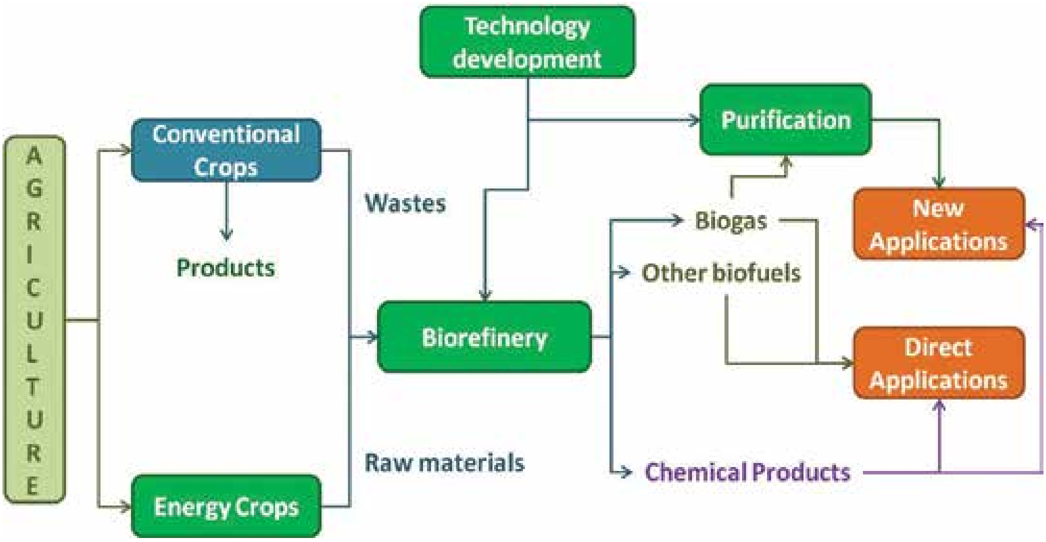

Figure 5. Strategy for transformation of agriculture wastes and energy crops products.

briefly described. The Nerixis project has been developed by an interdisciplinary work team, and the objective was to develop the concept of a based agriculture wastes biorefinery; the structure included pre-treatment, saccharification, fermentation, separation, biogas, hydrogen and electricity co-production, enzyme enhancement, synthesis of lignine-based products, plant design and life cycle assessment (LCA); the considered raw material was wheat including streams of wastewater [35]. Additional schemes have been implemented from this project [36]. Other work explores the wastes of algae from a biodiesel productions process as raw material for ethylene and bioplastic production [37]. Mango wastes have been employed as raw material for bioethanol and food supplement production in a biorefinery scheme [38]. Other research deals with the evaluation of biohydrogen production from agro-industrial wastewaters and by-products; six different wastewaters and industrial by-products coming from cheese, fruit juice, paper, sugar, fruit processing and spirits factories were evaluated [39].

Besides the technical feasibility analysis, the economic, environmental and social aspects of biorefineries should be assessed. This is a topic considered in different Mexican studies. A multi-feed biorefinery (MPB10) for producing bioethanol from lignocellulosic residues and simultaneously treating agro-industrial wastes (cheese whey and tequila vinasses) was proposed. It was concluded that the most important sustainability indicators were the End-use Energy Ratio for the environmental aspect and Yield together with total production cost (TPC) per energy unit produced for the economic domain [35]. Other work is related to the sustainability assessment of a switchgrass-based biorefinery. Among the main results, it can be mentioned that some indicators such as the employment extent and raw materials consumption need to be improved in order to avoid risks; increasing operational jobs within the plant, increasing crop productivity or increasing the cropland surface may lead to better results on these indicators. Indicators concerning social domain are difficult to set on a sustainability scale, because commonly there is no possible definition for the ideal sustainability and/or the critical value [40].

Even if more research is required to consolidate the biorefineries topic, the next step in Mexico is the knowledge transfer for scaling up of processes. This is not an easy task since many factors should be in synchronization: government, farmers and academic sector.

3.4.2. Biogas purification

As said previously, biogas composition depends on the raw materials. The presence of compounds other than methane reduces the calorific value. The elimination of those compounds is a research topic with scientific and technologic interest. There are two main approaches relating biogas purification: biomethane upgrading and biogas cleaning [41].

The increase in the methane grade, known also as upgrading or enrichment, refers to the separation of the methane from the biogas in order to have a compound with higher energy potential. The idea is to recover methane in order to conserve the material representing the highest calorific value in biogas. There are different methods for this effect:

- Adsorption is known as pressure swing adsorption (PSA).
- Absorption with water traps.

- Absorption with organic solvents.
- Membrane technology.

Concerning biogas cleaning, the issues are related with the elimination of corrosive compounds, which affect the equipment used in the energy generation stage. Among the harmful agents, most commonly found in biogas are sulfur and nitrogen compounds. Methods to remove these chemical compounds are studied. The compound that receives most attention is H_2S due to its impact on the mechanical parts of the devices as well as on the environment:

- Biological desulfurization.
- Chemical precipitation with ferrous compounds.
- Chemical reaction using iron compounds.
- Combination of adsorption and catalytic oxidation.

Biogas cleaning and upgrading is few addressed in Mexico; however, it is an important issue which could diversify the use of biogas and even to promote the transformation of agriculture waste into biogas.

3.4.3. Technology development

Although there is some equipment designed for national entrepreneurs, most of the commercial technology associated to the biogas life cycle is foreign. At present time, commercial globalization and the international free trade agreements allow to get low prices for several products. However, since the biogas topic is not really spread at small and medium size, the importation of technology increases the initial investment for projects.

Then, the development of technology is a topic which should be addressed in Mexico, especially for small applications such as burners, furnaces, stoves, lamps, small engines for mechanical energy, and power plants for a generation less than 30 kW.

Due to the geographic characteristic of the country, the production of agriculture wastes is not uniformly distributed. This implies an additional issue on the collection stage for large size biogas facilities. Then, it is advisable to consider a distributed generation approach; that means, to implement small-scale facilities transforming small quantities of biomass and producing small quantities of energy, but near to the final users. This allows a better management of resources. Then, the distributed structures are designed to avoid logistic problems for transportation which demand energy, time and other resources. For this reason, the availability of technology for medium and small size is an important aspect to be considered.

3.4.4. Energy crops

Energy crops should be also a developing topic for biogas production, preferentially in biorefinery schemes.

Currently, there exist around 5 nopal (*Opuntia*) crops for electricity production; the selected plant is not edible specie which has been modified to eliminate thorns and make it easier to handle. Also, some studies have been carried out to evaluate the potential of the species *Opuntia* spp. for the production of biofuels. It has been reported that 1 ha of nopal can produce more than 100 t of biomass [42]. Experimental results show that a methane content of more than 70% can be achieved when a mixture of nopal and manure is used in a 3:1 ratio at a temperature of 30°C. Another study indicates a biogas production of 0.861 $m^3 kg^{-1}$ of volatile solids with 58.2% of methane [43, 44].

On the other side, algae have been also identified as feasible plants for energy crops [45]. In Mexico, this raw material is mainly studied for the production of hydrogen, biodiesel and bioethanol. The production of biogas from algae is little studied; however, the potential is important, especially in biorefinery schemes. Currently, different laboratory experiments have been carried out using substrates that include algae. Different aspects of the transformation are considered such as the sequestration of carbon dioxide (CO_2) from different industrial emissions to use as a nutrient in the growth of algae, the selection of the site for the installation of biorefineries as well as transportation costs [46]. Other project is developed in order to evaluate the performance of a biorefinery at laboratory and pilot plant level producing biogas, biodiesel from microalgae and hydrogen from algae residues, using municipal wastewater.

There are different plants which could be produced in energy crops such as jatropha, moringa, savage castor oil plant and others. Even if these plants do not involve a direct food competition, they induce an indirect food competition due to the soil and resources requirements. For these reasons, more studies should be addressed in order to take appropriate decisions concerning the implementation of energy crops.

4. Conclusions

Among more than 300 species cultivated in Mexico, 39 were selected for this assessment due to its characteristics, production amount and availability for biogas production. It was deduced that around 12.7 Mt of wastes available for biogas are produced. From those wastes, a total of 450 GWh could be produced from these wastes.

Currently, the generation of energy from agricultural wastes is less than 10% of the estimated potential.

The main applications of biogas are thermal and electric energy generation. However, some other potential applications should be explored, such as light and heat for cooking at low size and the obtaining of added value products from biorefinery schemes at larger scales.

It is important to remark that a national strategy is required to take advantage of the potential of biogas. Some independent efforts have been done: government has promoted new legislations to motivate the development of biofuels; academic sector addressed from different perspectives the knowledge generation related to bioenergy; enterprises are searching for alternatives to implement bioenergy projects. However, an integrated strategy is necessary for more strong and efficient collaboration. The adequate transfer of technology and knowledge is essential, which requires a dynamic collaboration between academy, productive sector and government.

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Chapter 3

Biomethane as Transport Fuel

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Ewa Krasuska

Additional information is available at the end of the chapter

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Abstract

In the European Union (EU), the demand for energy in transport is growing, and at the same time, transport is almost entirely dependent on oil and is responsible for more than 30% of greenhouse gas (GHG) emissions in Europe. Biomethane is one of promising options for sustainable mobility. Technical requirements applied for biomethane in transport in both countries and at the EU level are presented as well as short overview of the main upgrading technologies. Sweden and Germany may serve as examples of effective implementation of biomethane in transport sector; however, it is done in different ways (Sweden (non-grid transport use) and Germany (mainly via injection to gas grid)). Their experience can be useful for countries starting development of biomethane production and use, e.g., Poland.

Keywords: biomethane, transport, quality requirements, good practices, Sweden, Germany, Europe

1. Introduction

In the European Union (EU), the demand for energy in transport is growing, and at the same time transport is almost entirely dependent on oil and is responsible for more than 30% of greenhouse gas (GHG) emissions in Europe, and related emissions will double by 2050 [1]. In the medium and long term, significant changes are needed regarding transport means (sustainable mobility); the implementation of biofuels (including biomethane) and renewable alternative fuels is a short-term solution.

Experts' reports prepared at the request of the European Commission (EC) clearly indicate natural gas and its renewable equivalent, biomethane, as a bridging fuel between conventional

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fuels and advanced biofuels of the next generations [2]. Methane fuels are perceived as an important supplement to the fuel market, especially during the transition period between the first generation of liquid biofuels and the commercial implementation of advanced biofuels.

Biogas upgraded to the quality of natural gas—**biomethane**—has the same advantages as natural gas but is more friendly for the environment from sustainable point of view (higher reduction of GHG emissions, use of local substrates, positive link with waste management). Several European projects (GasHighWay [3], Biogasmax [4], Biomaster, etc.) have shown that biomethane produced and used locally has a positive impact on local sustainable development (reduction of negative impacts connected with transport sector such as smog, creation of new markets, generation of news jobs, etc.). Biomethane and natural gas are recommended as fuels in urban traffic; the advantages of methane fuels related to noise reduction and emissions of harmful substances predispose them to be used in such fleets of vehicles as buses, municipal and delivery vehicles, and taxis. Moreover, biomethane is currently the only biofuel with the same chemical composition as the fossil fuel it replaces. It can therefore be mixed with natural gas in any ratio, without negative consequences for the engine.

In the EU about 11% of energy of the produced biogas is used for transport sector [5]. In 2015 in Sweden, the use of biomethane for vehicles amounted to 1124 GWh and in Germany 580 GWh, respectively. Globally, the leading position belongs to the United States with the use of biomethane for vehicles twice more compared to Sweden [6].

1.1. Technical options for natural gas vehicle (NGV) filling with biomethane

Biomethane for transport can be used in several different technical options, as presented in **Figure 1**. Option 1 is a biomethane filling station established directly at the biomethane plant.

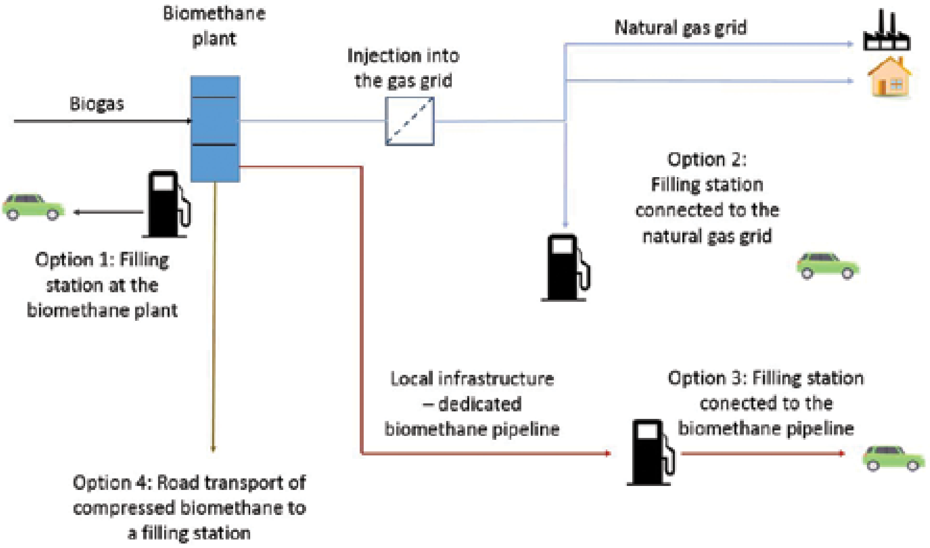

Figure 1. Technical options of filling biomethane for vehicles.

Option 2 is feeding biomethane into the grid of natural gas; then, a mixture of biomethane and natural gas is supplied to filling stations. This technical solution is very common, for example, in Germany, where the grid of natural gas is well developed and a significant number of CNG filing stations are established. In option 3 biomethane is transported by a local infrastructure to a filling station—a dedicated biomethane pipeline is constructed. In option 4 compressed biomethane is transported in containers via road vehicles to the filling station. Options 3 and 4 are common in Sweden.

2. Examples of biomethane markets in selected EU countries

In many European countries, the production and use of biomethane have increased within the last 10 years. In the end of 2016, biomethane was produced in nearly 500 plants in 16 countries [7, 8]. Germany is still the biggest European biomethane producer, the United Kingdom (UK) with 80 running plants has become the second largest biomethane producer, and Sweden is in third position. In the UK nearly all the plants have been created in the last 5 years due to extensive support policies, such as the introduction of an attractive Renewable Heat Incentive (RHI) providing a bonus paid on top of the market value of the gas injected [9].

In the following subsections, more details will be provided on biomethane markets in Germany (as the European leader in biomethane production) and Sweden (as the European leader in the transport use of biomethane).

2.1. Biomethane in Germany

Germany has a strong biogas industry with more than 10,000 biogas plants and is the EU leading country in terms of biomethane production. In 2016 there were 193 biomethane plants connected to the natural gas grid with a total estimated capacity of 1.71 billion m^3 of raw biogas processed [10]. It is an equivalent to about 940 million m^3 of biomethane fed into the German gas grid. This contributes to about 12.3% of the natural gas production or 1% of natural gas consumption in Germany.

Biomethane fed into the gas grid is primarily used in CHP systems for combined heat and power production, i.e., more than 90% of total biomethane volumes, about 4% is used for transport sector and 3.5% for heat production. In Germany there are currently (September 2017) about 900 CNG filling stations which sell a mixture of natural gas and biomethane with different mixture ratios [11]. The current total number of NGV amounts at some 100,000.

One interesting example of promoting biomethane as a transport fuel is in Berlin. Biogas production from 60,000 tons of selectively collected biowaste from households is upgraded into biomethane, which is used to fuel 150 waste collection tracks [11].

Biomethane has higher production costs than natural gas. The support for biomethane market in Germany is realized particularly in the electricity sector which was the key driver for development of biogas installations in recent years [5]. Currently, feed-in tariff is offered for systems with a capacity of up to 100 kW and a market premium for systems with a capacity up to 20 MW. The change in the past feed-in tariff system of 2011 resulted in a strong fall in the development of new installations.

In transport sector a tax reduction is offered till 2018 for the use of natural gas; however, for biomethane used as a transport fuel, no tax benefits are granted since January 2016 [12]. There is also no incentive to feed-in biomethane into the natural gas grid anymore. The main instrument in the transport sector in Germany is currently the GHG quota, which in 2015 replaced the biofuel quota obligation [11]. The GHG quota is an annual target for GHG emission reduction as a "decarbonization strategy" for transport sector. The use of biomethane offers a mean to achieve this. Biomethane and other biofuels have to fulfill the national regulations established by the Biofuel Sustainability Ordinance.

With regard to a relatively slow rate of the GHG emission reduction in the transportation sector, the German government gave more attention to the increased use of natural gas and biomethane for transport. The Round Table for Natural Gas Mobility set a goal to reach 4% share of natural gas in transport by 2020 and 20% share of biomethane in the natural gas used for transport [12].

2.2. Biomethane in Sweden

Biomethane has quickly found a place in Sweden because Sweden's natural gas prices have always been higher than in Europe and Sweden does not have an extensive gas network.

Sweden has well developed non-grid-based transportation of biomethane. The biomethane is transported mainly not only in compressed form in mobile storage units but also in liquefied form or by local gas grids [13].

In Sweden the most of the biogas is produced from sewage treatment plants, and the amount of landfill gas decreases due to EU regulations (since 2005, the ban on landfill for organic waste has been in force in Sweden). The growing sector is centralized biogas plants that process organic waste, including food waste separated at the source [14]. Food waste collection is growing: in 2016 already 212 municipalities from 290 introduced such systems.

In Sweden natural gas and biomethane are complementary fuels; in 2016 almost 70% of the produced biogas was upgraded and used as transport fuel. In the end of 2016, there were in the operation 62 biogas upgrading plants: 43 water scrubbers, 6 PSA, 11 amine scrubbers, and 2 membrane units [15].

At the end of 2016, Swedish natural gas vehicle (NGV) fleet had 54,439 light duty vehicles, 2331 buses (18% of national market), and 821 HD trucks (in that 50 LNG trucks) [15].

Sweden as the first country in Europe has reported to the European Commission the consumption of biomethane in transport in the annual reports on the implementation of the biofuel directive (2003/30/EC) to the European Commission [16].

Biomethane is the very interesting option with a lot of opportunities for municipalities, because local governments are responsible, among others, for waste management (biowastes—the potential source of biogas) and municipal services such as transport (potential user of biomethane as a fuel). Therefore, they have possibilities to create local supply and demand. Municipalities can use locally produced fuel in their own vehicles, municipal buses, and waste trucks. Swedish experience showed that municipalities were creating local markets with a lot of benefits for their communities [17, 18].

Besides using their existing companies, municipalities were active in establishment of new ones for this sector, e.g., gas enterprises Svensk Biogas and Fordonsgas. Local governments implemented effectively public purchasing policy not only for procurements of vehicle purchases (e.g., city buses and waste trucks) but also for municipal services. New expertise has arisen for local enterprises—production of equipment for upgrading systems (e.g., Malmberg, Purac) and production of gas engines and vehicles (e.g., Scania and Volvo).

In the regions of Västra Götaland (Western Sweden) and Skåne (Southern Sweden), the impressive development of the biogas sector resulted from a unique interaction between research, local governments, and industrial partners [19, 20]. Their experience may be used as an example of good practices in developing local biogas and biomethane deployment strategies in other regions and countries, e.g., in Poland.

In Kristianstad (capital of Skåne), digestion of organic matter into biogas has become the most important way to reduce the negative environmental impacts of waste and instead use it as an energy resource. The biogas plant, as well as the units for upgrading gas, is owned by the municipal company, Kristianstad Biogas, which is a part of the municipal energy company. In **Figure 2** biomethane filling station for buses located nearby Kristianstad biogas plant is presented. The municipality is aiming to have a fossil fuel free fleet by 2020, mainly running on biogas [21].

Figure 2. Biomethane filling station for buses in Kristianstad (photo by M. Rogulska).

3. Technical requirements for biomethane use in transport

Development of **technical standards** is important for market introduction of advanced biofuels, in that biomethane. Standards for biomethane need to meet not only requirements of automotive industry and vehicle users but also requirements of the natural gas sector.

For the use of natural gas and biomethane in transport especially, following issues are important [22]:

- *Hydrogen sulfide* as a toxic gas has high corrosive properties. The sulfur contained in it is converted to sulfur oxides, which have a negative impact on the natural environment.
- *Sulfur* has a huge impact on the size and type of exhaust emissions from the car and the corrosive properties of the fuel. Failure to meet the required sulfur content limit shortens the lifetime of the catalyst and consequently, in many modern engines, disruption of the fuel dose control system and problems with proper engine operation. There is also the danger of engine corrosion. Sulfur compounds are among the most technologically and environmentally troublesome.
- *Mercury* has been recognized as a metal that poses a significant threat to the natural environment and human health, and its specific behavior in various ecosystems makes it difficult to fully anticipate the ecological and health effects of contamination with this metal. Mercury in natural gas usually occurs in elemental form, and it can also exist in the form of HgCl2, CH3HgCH3, C2H5HgC2H5, and ClHgCH3. Mercury from aluminum creates amalgams which can cause damage to the materials it comes in contact with.
- *Smell*. Natural gas is lighter than air, is colorless, and does not have an odor, so it is odorized with a special chemical that gives it a characteristic smell, to detect even very low concentrations of gas from leaks (before the gas reaches a dangerous concentration in the air). Gas in combination with air can form an explosive mixture. The explosion limit is 5–15%.
- *Heat of combustion* is the amount of energy that is released during the combustion of a given substance. If the product of combustion is water vapor, the heat of combustion also includes the heat of condensation of water vapor. Of course, we assume that all fuel will be burned (total combustion) and that combustion is complete (i.e., no combustible substances in the exhaust). When *the heating value* is considered, we are dealing with the same amount of energy, but we do not take into account the condensation of water vapor. As they are similar in terms of definition, but quite different numerically, it is important to pay attention to all tables or statements on which quantity is given.
- *Water*. The most important safety requirement for BioCNG/CNG is the very low value of the water dew point, excluding the formation of liquid water. For this reason, the water dew point temperature in the gas fuel at the exit from the refueling station should be adequately lower than the lowest ambient temperature at which the refueling station and vehicles used will operate.
- *Liquid water* is a precursor to the formation of corrosive compounds because it combines with natural gas components such as carbon dioxide and hydrogen sulfide. The combination of

corrosive components and variable pressure caused by fuel consumption and subsequent refilling of the fuel tank can cause metal cracks leading to damage and failure. Liquid water can also be harmful, creating liquid or permanent blockages in the fuel system.

- The supplied gas fuel should be technically *dust*-free.
- The content of *oil* in supplied gas should not have an adverse effect on the safe operation of the vehicle. If necessary, filters and separators can be used. A small amount of oil can have a beneficial effect on tank protection and lubrication of the injectors.
- *Oxygen* together with hydrogen sulfide can react, in particular with copper, which is detrimental to the installation.

Minimizing the content of pollutants to the limit values given in the standards is important due to their unfavorable effect on the combustion process in car engines.

3.1. Swedish technical regulations

Sweden has developed a standard for biomethane as a fuel; it has included biomethane in its legal regulations on transport fuels. The Swedish standard SS 155438 "Motor fuels – Biogas as fuel for high-speed Otto engines" developed in 1999 was the first standard regulating the use of biomethane as a fuel for vehicles in European countries [16, 23].

The guidelines contained therein are presented in **Table 1**. Values for type A biometric relate to fuel for engines without regulation of the lambda mixture composition ratio used in heavy vehicles, such as trucks and buses. Values for type B biomethane relate to fuel for engines with controlled mixture composition, used for stoichiometric combustion, e.g., passenger cars [23].

Parameter	Unit	Biomethane (type A)	Biomethane (type B)
The Wobbe index	MJ/m^3	44.7–46.4	43.9–47.3
Methane content	% vol.	97 ± 1	97 ± 2
Dew point at the highest storage pressure (t—the lowest average daily temperature over the month)	0°C	t-5	t-5
The maximum water content	mg/m^3	32	32
The maximum $CO_2 + O_2 + N_2$ content	% vol.	4.0	5.0
with oxygen maximum	% vol.	1.0	1.0
Maximum total sulfur content	mg/m^3	23	23
Total maximum content of nitrogen compounds (excluding N_2) calculated as NH3	mg/m^3	20	20
The maximum particle size	μm	1	1

Table 1. Swedish requirements for biomethane use in transport [23].

3.2. German technical regulations

In Germany the successful biomethane injection to grid was possible thanks to the fact that clear regulations have been included in the Gas Network Access Ordinance (Gas NZV) [24].

Technical regulations concerning the quality properties of biomethane and natural gas are provided in worksheets G 260 and G 262 published by the German Technical and Scientific Association for Gas and Water (DVGW)—a standardization body for the gas and water industry [11, 25]. The basic requirements for the quality of gas from renewable sources are given in the worksheet G 262. If the gas is to be fed into the public gas grid, it needs to meet the regulations of DVGW worksheet G 260.

Table 2 presents the quality requirements for the biogas injection to the gas grid according to DVGW G 260 [25].

Technical requirements for design, construction, and operation of biogas and biogas upgrading installations specify worksheet DVGW G 265. Technical requirements are defined separately for:

- Biogas plant: production of biogas from organic raw materials through methane fermentation.
- Biogas treatment plant: removal of hydrogen sulfide, carbon dioxide, and other trace gases and drying.
- Installations injecting biomethane to the gas grid: calibrated measurement of quality and quantity for billing purposes, if necessary, increases the pressure to the network pressure, conditioning with liquefied hydrocarbon gas and odorization.
- Recovery systems: an increase in gas pressure in order to transfer to a higher-level network.

Parameter	**Unit**	**Value**
The Wobbe index	MJ/m^3	48.96–56.52
Heating value	MJ/m^3	30.24–47.16
Relative density		0.55–0.75
Total sulfur content	mg/m^3	<8 (short term to <30)
Hydrogen sulfide content	mg/m^3	<5
Water content	mg/m^3	< 50 in grid> 10 bar < 200 in grid ≤10 bar
Hydrogen content	%(v/v)	< 2 in exceptional cases to <10
CO_2 content	%(v/v)	In gas grids L < 10 In gas grids H < 5
Oxygen content	%(v/v)	<3 injection to a dry network <0.5 injection to wet network

Table 2. Quality requirements for biomethane injection to grid in Germany [11].

The biomethane supplier is responsible for the warranty of the gas compositions stated in the worksheets.

3.3. European technical regulations

Standardization is important for market access as it brings legal and technical security. Countries producing biomethane have introduced standards, respectively, for injection (e.g., Germany) or vehicle fuel use (e.g., Sweden), but they were very different. To solve this problem, the European Commission (EC) has given to the European Committee for Standardization (CEN) the mandate M/475 for elaboration of European biomethane standards for grid injection and vehicle fuel use. Technical Committee CEN TC 408 formed on this basis started to work in 2011, and final result of their work was published in 2016 (Part 1) and 2017 (Part 2) [26].

Due to the differences in the legal acts and standards regarding the quality of biomethane for transport applications and for injection into the gas grid as well as the expectations of both the gas and automotive industries, it was decided to prepare a standard subdivided into two parts. Developed norms are not looking on the biomethane production pathways (e.g., biomass fermentation process or gasification process) nor origin of the substrates.

In 2016, Part 1 of the European standard EN 16723–2 *Natural gas and biomethane used in transport as well as biomethane injected into the natural gas network* was published. This part concerns the requirements of biomethane injected into the network [27].

Part 2 published in 2017 refers to the specification for fuels for motor vehicles. This standard specifies the requirements and test methods for natural gas (group L and H), biomethane and blends of both at the point of use as vehicle fuels and applies to these fuels irrespective of the storage state (compressed or liquefied). In **Table 3** requirements, limit values and related test methods for natural gas and biomethane use as vehicle fuel are presented [28].

The technical requirements and safety conditions for the use of biomethane-powered vehicles are identical as those for CNG vehicles, so also their use must be in compliance with regulations and standards such as EN ISO 15403–1:2010: Natural gas—Natural gas for use as a compressed fuel for vehicles—Part 1: Designation of the quality [22].

The standard provides manufacturers, vehicle users, service station operators, and other entities associated with the natural gas vehicle (NGV) industry with information on the quality of fuel for NGV vehicles necessary for the efficient development and operation of gas-fueled equipment.

It is recommended that fuels meeting the requirements of this part of ISO 14503 enable:

- To ensure the safe operation of vehicle and equipment used to refuel and service
- To protect the fuel system against corrosion, poisoning, and secretion of sediments or liquids
- To achieve satisfactory operation of the vehicle in all climatic and road conditions

Parameter	Unit	Limit values[a]		Test method
		Min	Max	
Total volatile silicon (as Si)	mgSi/m^3		0.1 or 0.5[b]	EN ISO 16017-1:2000 TDS-GC-MS
Hydrogen	% mol/mol	—	2	EN ISO 6974-3 EN ISO 6974-6 EN ISO 6975
Hydrocarbon dew point temperature (from 0.1 to 7 MPa absolute pressure)	°C	—	−2 (as in EN 16726)	ISO 23874 ISO/TR 11150 ISO/TR 12148
Oxygen	% mol/mol	—	1	EN ISO 6974 series EN ISO 6975
Hydrogen sulfide + carbonyl sulfide (as sulfur)	mg/m^3	—	5 (as in EN 16726)	EN ISO 6326-1 EN ISO 6326-3 EN ISO 19739
S total	mgS/m^3		[c]	EN ISO 6326-5 EN ISO 19739
Methane number	Index	65[d] (as in EN 16726)		Annex A of EN 16726
Compressor oil			[e]	ISO 8573–2
Amine			10	VDI 2467 Blatt 2:1991-2008

[a] Limit values are absolute, and the number of the decimal places shall not imply the accuracy of the test method.

[b] A silicon content of <0.1 or 0.5 mg/m^3 is considered as a safe level. Further research is needed for a decision whether a higher limit value is acceptable.

[c] Currently, there is a difference between the automotive industry needs for sulfur content (10 mgS/m^3 including odorization) and the values, and the gas industry can provide (30 mg/m^3 including odorization) (see Annex B). It is possible to cover this parameter in a national foreword.

[d] The methane number depends on the composition of the distributed natural gas.

[e] The fuel shall be free from impurities other than "de minimis" levels of compressor oil and dust impurities. In the context of this European standard, "de minimis" means an amount that does not render the fuel unacceptable for use in end-user applications.

Table 3. Requirements, limit values, and related test methods for natural gas and biomethane use as vehicle fuel [28].

The operator of the refueling station for vehicles is responsible for any changes in the composition of natural gas supplied to refueling stations to meet these requirements and complements ISO 15403-1.

4. Biogas upgrading technologies

Biogas upgrading is a process of removing carbon dioxide (CO_2) from the initial mixture, which increases the methane content (CH_4) in the gas obtained, and purifying it from hydrogen sulfide, water, and other trace constituents. The treatment allows to adjust the quality parameters of biogas to natural gas parameters.

The selection of an effective and economically attractive method for the purification of biogas from compounds that are toxic to the environment and damaging the engines, combined with the adjustment to natural gas parameters, is a key element for the successful introduction of biomethane into the gas grid and/or transport sector.

There are four main types of commercially available biogas upgrading technologies: (i) absorption methods (scrubbing), (ii) membrane separation, (iii) pressure swing adsorption (PSA), and (iv) cryogenic separation. Upgrading should take place with the lowest possible biomethane losses and low energy input.

The share of different biogas upgrading technologies in Europe in the end of 2016 is presented in **Figure 3** [7, 29]. The most popular method of biogas upgrading is water scrubbing, which belongs to absorption methods [8]. Membrane separation is the second most commonly applied technology. Then, chemical scrubbing and PSA come, and the next is physical scrubbing. The cryogenic treatment has so far the lowest market contribution [29]. In Germany, in 2016 taken as a separate year, 11 new upgrading plants were established, of which 6 were different scrubbing methods, 3 membrane separation method, 1 PSA, and 1 biological methanation [30].

4.1. Water scrubbing and physical scrubbing

The most popular biogas upgrading method is water scrubbing, which is based on the difference of the solubility of CO2 and CH4 in water in lower temperatures. In the water scrubbing column, CO2 dissolves in water, while the concentration of methane in the gas phase increases. In the absorption column, there is also the process of H2S removal. Commonly, raw biogas is compressed to the absorption pressure of 4 to 10 bar and then cooled to increase the efficiency of the gas mixture separation process. Biogas is introduced in the lower part of the column, in which the flowing water absorbs carbon dioxide and hydrogen sulfide. Water is a harmless, low-cost solvent that is easy to handle. In physical scrubbing technologies, organic solutions are used (e.g., polyglycol) instead of water.

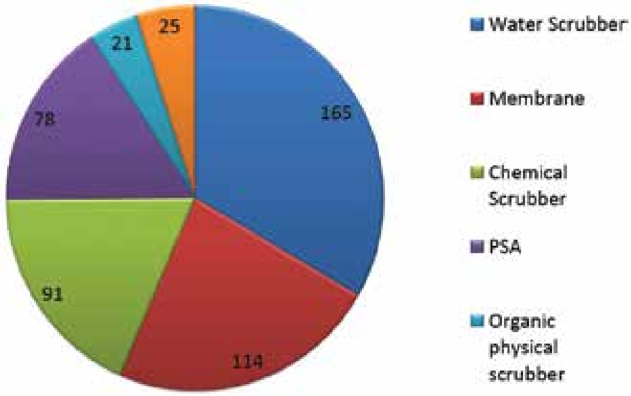

Figure 3. Biogas upgrading technologies in Europe, data for 2016 [7, 29].

The scrubbing technologies assume the regeneration of an aqueous solution (or organic) in the desorption column by depressurizing or passing the stream of air in a countercurrent (stripping). Passing the air stream is not recommended at higher levels of H_2S, because the precipitating elemental sulfur causes operational problems of the installation. The scrubbing technologies in general do not require the supply of heat to the process and the use of chemicals, while they assume heat recovery and minimization of water consumption. Depending on the design of the column, the efficiency of upgrading with water scrubbing method is at the level of 90–99% of pure biomethane in the output gas [11].

4.2. Chemical absorption

This technology is purifying biogas by absorption and chemical binding of carbon dioxide in aqueous solutions of amines (most often monoethanolamine (MEA) or dimethylethanolamine (DMEA)). Due to the high selectivity of the reaction of CO_2 with amines, the process is more efficient than physical absorption. The gas obtained contains methane in an amount above 99% (even 99.4%), and methane losses can be limited to <0.1%. Raw biogas is pretreated with activated carbon to reduce the sulfur content (up to 0.5 ppm). In the case of increased H_2S content, an additional pretreatment plant is needed.

The process requires the use of heat, but does not require elevated pressure, so only the gas leaving the installation is compressed, which allows for a significant saving of energy. The amine solutions are regenerated by heating (110–160°C), and some of the heat is recovered.

4.3. Membrane separation

Biogas can be purified from both carbon dioxide and hydrogen sulfide with the application of a membrane technique. Membranes are typically combined in a tube bundle to provide maximum surface area. Typical operating pressures are 7 to 20 bar. The membrane acts selectively, i.e., only one component of the mixture passes through the filter freely, while the others are retained due to their size or affinity. Transport through membranes, as in the case of osmosis, occurs on the principle of difference of the potentials on both sides of the membrane. The difference of potentials stimulates the speed at which the particles pass through the membrane in order to compensate the concentration, pressure, or temperature.

Membrane separation is a relatively new technology for biogas purification and, within the last 10 years, has been significantly developed. The efficiency of one membrane is too low for biogas to achieve natural gas quality properties, so more than one membrane or additional purification technology should be used to achieve higher methane concentration. Moreover, in order to increase the separation efficiency, it is possible to recirculate the gas to be purified.

4.4. Pressure swing adsorption (PSA)

Pressure swing adsorption has been for years used in a gas industry, and recently it has been adapted for biogas upgrading. In this technology carbon dioxide is removed from biogas by adsorption on the surface-activated carbon, or on zeolite molecular sieves or carbon molecular sieves. CO_2 molecules are smaller than methane molecules and thus CO_2 accumulate on the surfaces or in the pores to a much greater degree than CH_4. The latter remains primarily in the gas phase. Adsorption is higher in higher pressures and in low temperatures. Biogas is cooled down to about 70°C and fed into the adsorption column. The biogas must be pre-purified in order to remove hydrogen sulfide and water vapor, which could, however, result in the deactivation of the active bed. The adsorption is a batch process and takes place in several columns. The methane loss is between 1.5 and 2.5% [11].

4.5. Cryogenic separation

Cryogenic separation is a new biogas upgrading technology. The process takes place under conditions of very low temperatures (up to −100°C) and high pressures (40 bar). Carbon dioxide condenses or sublimes and can be separated from biogas in the liquid or solid form, while methane remains in the gas phase. There are many options for the adjustment of temperature and pressure in order to perform the separation. Cryogenic separation can also be combined with other gas treatment methods. The advantage of the cryogenic separation is high methane purity with low losses. A disadvantage of cryogenic treatment is the energy required for refrigeration.

5. Conclusions

Biomethane is an attractive fuel, available now for support of the transition from the conventional fuels to sustainable low-emission mobility (advanced biofuels, e-fuels, hydrogen, etc.).

The use of biomethane is connected with very low GHG emissions if produced through biomass gasification or even with negative GHG emissions when produced from substrates such as organic municipal wastes or manure (otherwise emitting methane during its decomposition process).

The potential for development is huge when looking only on biogas sector: in Germany less than 2% of biogas units (around 190 units) are biomethane production plants; in France it is less than 3% (around 30 units), while in other EU countries, this rate varies between 4% and 12%. Only in Sweden 21% of biogas plants produce biomethane (62 units) [7].

In Sweden and Germany, biomethane markets are well established so they can serve as good examples for analyzing pros and cons of solutions and models implemented by them. Automotive Industry Institute (PIMOT) together with national stakeholders and international partners (e.g., Swedish-Polish Sustainable Energy Platform) is involved in promotion and development of biomethane market in Poland.

Nomenclature

Biomethane	biogas upgraded to the quality of natural gas.
The Wobbe index (W)	used as an indicator for the assessment of gas utilization properties—is a determinant of gas "calorific value"; it is the quotient of the Qc gas combustion heat in MJ/m^3 and square root of the relative density d. The change in Wobbe's number may affect the power and operation of the engine.

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Section 3

Bioethanol

Pretreatment Empty Fruit Bunch of Oil Palm Tree for Improving Enzymatic Saccharification

Sutikno Sutikno and Muhammad Kismurtono

Additional information is available at the end of the chapter

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Abstract

Empty fruit bunch of oil palm tree (EFBOPT), solid waste of palm oil industries, is potential for raw materials of biofuel especially bioethanol production because of its cellulose and hemicellulose contents. There are four steps to produce bioethanol, called the second generation bioethanol, from EFBOPT or other lignocellulosic materials. The steps are (a) pretreatment of lignocellulose biomass into cellulose/hemicellulose, (b) hydrolysis of cellulose/hemicellulose into monosaccharides, (c) fermentation of monosaccharides into bioethanol, and (d) recovery of bioethanol from medium fermentation broth. Pretreatment steps are the key success factor to convert lignocellulosic materials into bioethanol. This paper will review EFBOPT and pretreatment steps, including physical pretreatments, physicochemical pretreatments, and biological pretreatments.

Keywords: bioethanol, biomass, empty fruit bunch of oil palm tree, lignocellulose, pretreatment

1. Introduction

Depletion of fossil fuels, increasing of climate changes, and improvement of world energy consumption [1] have directed towards the development of biofuel production [2]. Biofuels are able to replace petroleum-based fuels, decrease greenhouse gas emission [3], and have significant potential sustainability [4]. Biofuels can be as gaseous (methane or hydrogen) or liquid (biodiesel, biobutanol, or bioethanol) forms and are commonly generated from agricultural materials. Either agricultural commodities or agricultural waste materials can be used for developing biofuels; for example, vegetable oil [5, 6] is used for biodiesel and agricultural

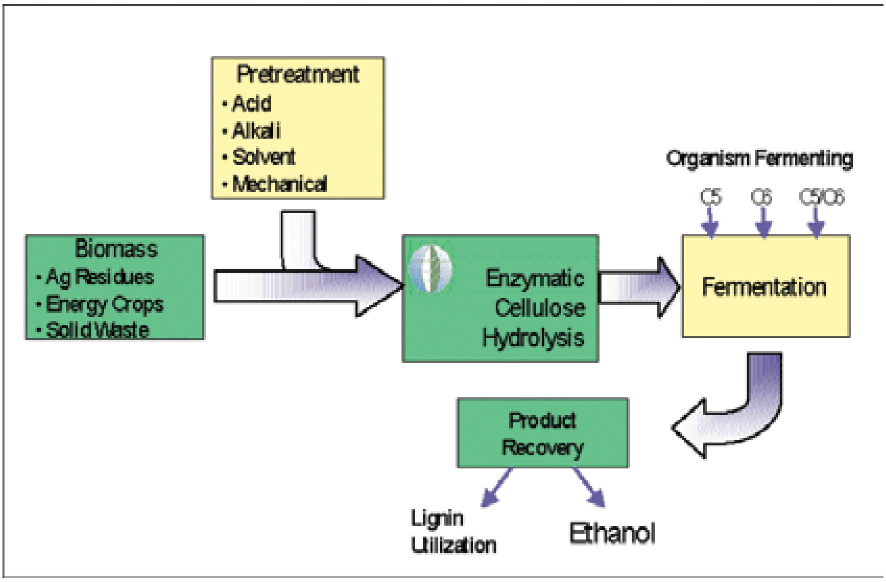


Figure 1. Steps of second generation bioethanol production from agricultural waste biomass. Source available from [30]: Knauf and Moniruzzaman.

wastes [7, 8] were processed for developing methane or hydrogen gases. Meanwhile, bioethanol can be produced either from agricultural high starch/sugar-containing commodities such as corn [9] and sugarcane [10] or from agricultural solid wastes such as non-edible parts of cassava [11], banana peels [12], cocoa-pod waste [13], rice straw [14, 15], sugarcane bagasse [16–19], sorghum bagasse [20], and empty fruit bunch of oil palm tree (EFBOPT) [21–24]. Bioethanol produced from starch/sugar containing commodities is called the first generation bioethanol, and one produced from agricultural solid wastes or lignocelluloses is called the second generation bioethanol.

Among agricultural materials, oil palm tree (*Elaeis guineensis* Jacq.) is considered as a major source of biofuel. In the world, oil palm tree is planted in about 43 developing countries and plantation area increased eight time in the past four decades to over 12 million ha in 2009 [25]. In a good condition, oil palm tree can yield about 4.5 ton oil and 7–8 ton EFBOPT/ha/year. Unlike palm oil which can be processed directly into biodiesel, EFBOPT has to be pretreated before converted into bioethanol [26].

There are four steps to produce bioethanol, called the second generation bioethanol, from lignocellulosic materials [27–29] such as EFBOPT. They are (a) pretreatment of lignocellulose biomass into cellulose/hemicellulose, (b) cellulose/hemicellulose hydrolysis into monosaccharides, (c) monosaccharides fermentation into bioethanol, and (d) bioethanol recovery (**Figure 1**) [30]. The key success factor to convert EFBOPT into bioethanol is pretreatment step [31]; therefore, this paper will review the EFBOPT pretreatment and discuss recent research results which significantly enhanced enzymatic saccharifications.

2. Empty fruit bunch of oil palm tree

EFBOPT is solid waste residue generated from palm oil factories. Fresh fruit bunches are harvested from oil palm tree (**Figure 2**) and then sterilized in a steam sterilizer for inactivating enzymes that present in pericarp and loosening fruits from bunches. The sterilized bunches are then fed into a rotary drum thresher to separate the sterilized fruit from bunches without fruit, which are called as empty fruit bunch of oil palm tree (EFBOPT). The sterilized fruits are further processed for palm oil production and the EFBOPT (**Figure 3**) are conveyed to the damping ground and left unused. It was reported that each 100 ton of fresh fruit bunches yielded 14 tons oil-rich fiber and 20–22 tons of EFBOPT [32]. EFBOPT is dry and brown; its shape is not uniform with low bulk density; and its length and width can vary from 17 to 30 cm long and 25 to 35 cm wide depending on the size of fresh fruit bunch [32].

Like other lignocellulose materials, native EFBOPT fiber is mainly constructed from a complex matrix of three main polymers (**Figure 4**) [33], namely cellulose, hemicellulose, and lignin. The EFBOPT fiber consists of 44.2–50.0% cellulose, 22.0–33.5% hemicellulose, and 20.4–21.0% lignin [34, 35].

Cellulose, a major constitutes of FEBOPT, is closely associated with hemicelluloses and lignin, and the separation of the cellulose from hemicelluloses and lignin requires intensive physical and chemical treatments. Cellulose is a linear polymer of D-glucopyranose units bound by β-1-4-glycosidic linkages (**Figure 5**). The successive glucose units are rotated by 180° relative to each other to form a cellobiose unit as a repeating unit of cellulose chains ended by a hydroxyl group. The hydroxyl (OH) groups in the cellulose act as functional groups which are able to interact each other or with O-, N-, and S-groups forming hydrogen bonds. Hydrogen bonds also occur between the OH-group of cellulose and water. Through hydrogen bond, cellulose chains are packed together to set up highly crystalline microfibrils. An individual microfibril contains ten of glucan chains in a parallel orientation [36]. This microfibril fraction can be hydrolyzed into glucose either by enzymatic or by chemical methods [37].

Figure 2. Oil palm tree (A) with fresh fruit brunches (B). Source available from: http://www.thestar.com.my/~/media/online/2014/09/07/08/01/str2_ma_0809_p10a-lead-pic.ashx/?w=620&h=413&crop=1&hash=B2A67ABD156961DCE9E42C52EA4D72C3F9503686 (accessed on February 25, 2018).

Figure 3. Empty fruit bunch of oil palm tree (EFBOPT) on damping ground. Source available from: https://s3-ap-southeast-2.amazonaws.com/ecostore-static-assets/Page+images/Palm+Oil+Page/Empty-fruit-bunches.jpg (accessed on February 25, 2018).

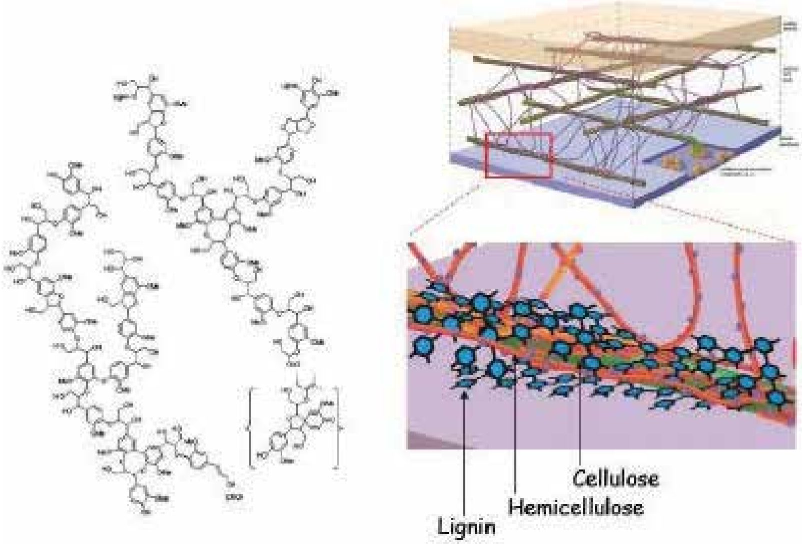
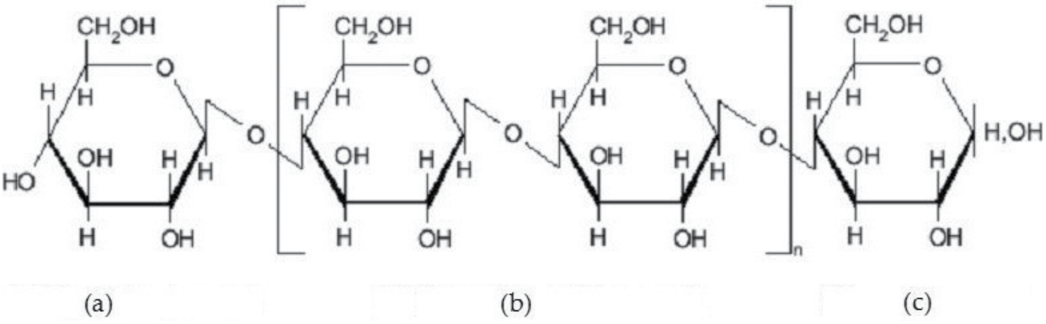


Figure 4. Polymer structure of lignocellulosic biomass. Source [33] Quintero-Ramirez.

Hemicellulose is a polymer consisting of heteropolymers of D-xylose, D-mannose, D-glucose, D-galactose, and L-arabinose, in the form of linear and branched (**Figure 6**). Its structure is not crystalline and is, therefore, easier to hydrolyze than cellulose [38]. Hemicelluloses usually form cross-linked to other polysaccharides, proteins, or lignin. Xylans are considered to be the main interface between lignin and other carbohydrates [39].

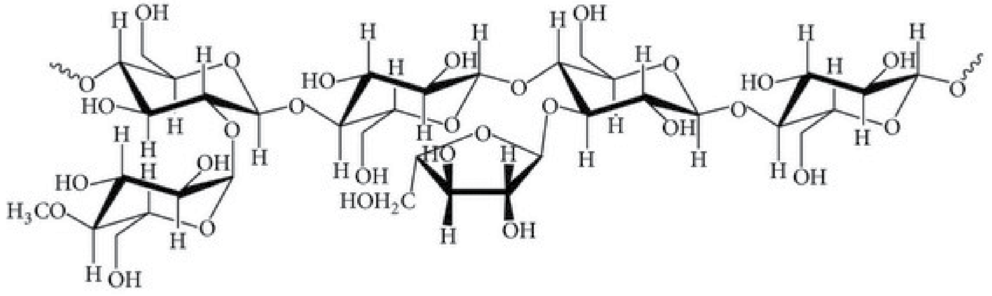
Lignin is a cross-linked aromatic, hydrophobic, and complex polymer consisting of three different phenyl-propane precursor monomer units which are very difficult to biodegrade (**Figure 7**). Lignin is mostly observed as an integral part of the plan cell wall, embedded in a polymer matrix of cellulose and hemicellulose. Thus, lignin is the most non-biodegradable component of the plant cell wall [36].



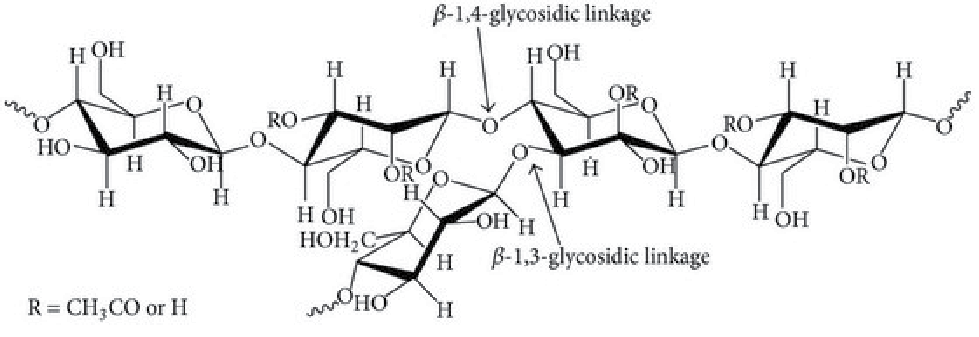
(a) (b) (c)

Figure 5. Chemical structure of cellulose. Source: available from https://www.intechopen.com/books/cellulose-fundamental-aspects/cellulose-microfibril-angle-in-wood-and-its-dynamic-mechanical-significance (accessed on February 26, 2018).

(i) Xylan



(ii) Glucomannan



R = CH$_3$CO or H

Figure 6. Chemical structure of hemicellulose. Source: available from https://www.researchgate.net/figure/Chemical-structure-of-hemicellulose-compounds-xylan-and-glucomannan-are-the-most_fig4_266026683 (accessed on February 26, 2018).

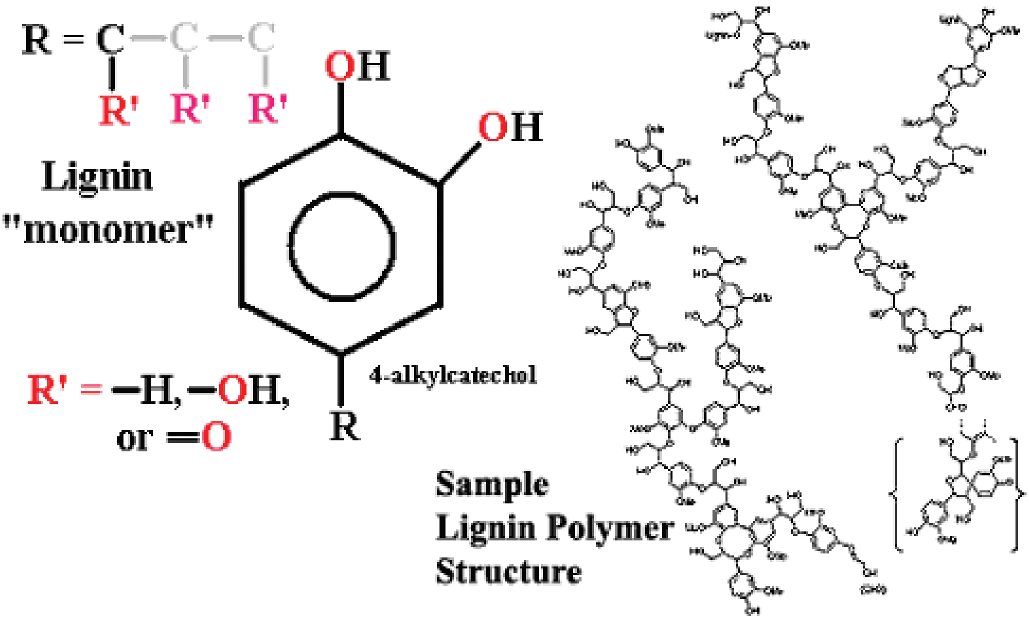


Figure 7. Chemical structure of lignin. Source: available from http://palaeos.com/plants/glossary/images/Lignin.gif (accessed on February 26, 2018).

3. Pretreatments

Pretreatment is actions given to biomass materials such as EFBOPT for enhancing the cellulose reactivity with cellulase enzymes and for increasing the yield of fermentable sugars. There are eight requirements for effective and economical pretreatment; they are (a) producing higher reactive cellulose fibers for enzymatic attachment, (b) producing less residues, (c) avoiding formation of compound inhibitors for hydrolytic enzymes and fermenting microorganisms, (d) avoiding destruction of celluloses and hemicelluloses, (e) reducing of material cost for setting upper-treatment reactors, (f) minimizing the energy demand, (g) reducing the cost of size reduction for feedstock, (h) consuming little or no chemical, and (i) using a cheap or no chemical [40]. The goal of pretreatment is to disrupt the crystallinity of cellulose, to open lignin and hemicellulose protection, to increase EFBOPT surface accessibility, and to decrease the degree of hemicellulose acetylation [41]. Pretreatment can increase significantly bioethanol or biogas yield and productivity. Effects of pretreatment on the degrading enzyme accessibility, bioethanol or biogas yield, and productivity from lignocellulosic materials were diagrammatically (**Figure 8**) shown by Taherzadeh and Karimi [40].

Based on actions given to biomass materials, pretreatment methods are classified into three groups, namely physical, chemical and physicochemical, and biological pretreatment methods [40]. The physical methods include milling (ball milling, colloid milling, hammer milling, two-roll milling, and vibrant energy milling), irradiation (electron-beam irradiation, gamma-ray irradiation, and microwave irradiation), and expansion, extrusion, high pressure, hydrothermal,

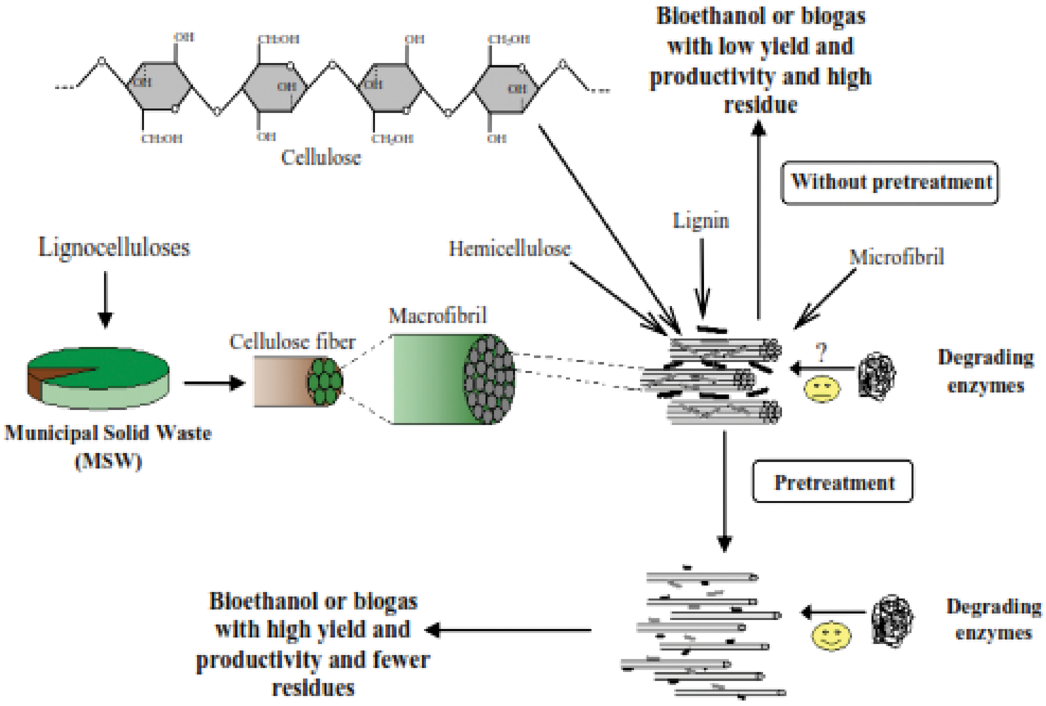


Figure 8. Effects of pretreatment on degrading-enzyme accessibility, and bioethanol or biogas yield and productivity. Source: available from Taherzadeh and Karimi [40].

and pyrolysis. The chemical and physicochemical pretreatments consist of acid (hydrochloric acid, phosphoric acid, and sulfuric acid), alkali (ammonia and sodium hydroxide), explosion (ammonia fiber explosion/AFEX, CO_2 explosion, SO_2 explosion, and steam explosion), gas (chlorine dioxide, nitrogen dioxide, and sulfur dioxide), oxidizing agents (hydrogen peroxide, ozone, and wet oxidation), and solvent extraction of lignin (benzene-water extraction, butanol-water extraction, ethanol-water extraction, ethylene glycol extraction, and swelling agents), and biological. Biological pretreatments commonly utilize fungi and actinomycetes as microbial producing enzymes which can degrade lignin compounds. Advantages and disadvantages of some different pretreatments are well tabulated (**Table 1**) by Brodeur et al. and Maurya et al. [42, 43].

3.1. Acid pretreatments

The main objective of the acid pretreatment is to solubilize lignin and hemicelluloses chemically so that the cellulose is more accessible to enzymes. Either diluted or concentrated acid can be utilized to perform this acid pretreatment. The diluted acid pretreatment method is more attractive because of less inhibitor compound formation, such as furfural, 5-hydroxymethylfurfural, phenolic acids, and aldehydes. In addition, diluted acids are less toxic, corrosive, hazardous, and corrosive, as well as more feasible for industrial scale. The diluted acid pretreatment methods have been developed in different types of reactors including percolation,

Pretreatment method	**Advantages**	**Disadvantages**
Acid	• Yield of glucose is high • Hemicellulose is solubilized	• Costs of acids are high • Acid recovery is needed • Costs of corrosive resistant equipment are high • Fermentation inhibitors are formed
AFEX	• Effectiveness for herbaceous material is high • It is suitable for low lignin content biomass • Cellulose becomes more accessible	• Recycling of ammonia is needed • Process effectiveness decreases with increasing biomass lignin content
	• Formation of inhibitors is low	• Lignin structure changes • Costs of ammonia are high
Alkali	• Lignin is efficiently removed • Formation of inhibitors is low	• Costs of alkaline catalyst are high • Alteration of lignin structure
Ammonia recycle percolation	• Majority of lignin is removed • Cellulose content after pretreatment is high • Herbaceous materials are most affected	• Energy costs and liquid loading are high
Biological	• Energy requirements are low • Lignin is removed • Degree of cellulose polymerization is reduced • Hemicelluloses are partial hydrolyzed • Chemicals are not required • Environmental conditions are mild	• Process rate is slow • Treatment rate is very low • It is not very effective for commercial application
CO_2 explosion	• Accessible surface area increase • Inhibitory compounds are not formed • It is non-flammability and relatively cheap • Recovery after extraction is easy • It is environmentally acceptable	• Pressure requirements are very high
Liquid hot water	• Hemicellulose is separated from rest of feedstock • It is no need for catalyst • Hemicellulose is hydrolyzed	• Energy/water input is high • Solid mass left over will need to be dealt with (cellulose/lignin)

Pretreatment method	Advantages	Disadvantages
Milling	• Cellulose crystallinity and degree of polymerization are decreased • Particle size decreases • Specific surface area and pore size increase	• Power and energy consumptions are high
Steam explosions	• It is low cost • Lignin transforms • Hemicellulose is solubilized • Yield of glucose is high	• Partial hemicellulose degrades • Acid catalyst is needed to make process efficient with high lignin content material • Toxic compound is formed
Wet oxidation	• Majority of hemicellulose and lignin are solubilized • Inhibitor compounds are avoided	• Costs of oxygen and alkaline catalyst are high

Table 1. Advantages and disadvantages of different pretreatment methods of lignocellulosic biomass [42, 43].

plug flow, shrinking-bed, batch, flow-through reactor and countercurrent reactors [40]. There are two approach processes of dilute acid pretreatment methods, namely (a) high temperature (e.g., 180°C) during a short period of time and (b) lower temperature (e.g., 120°C) for longer retention time (30–90 min). The most widely used acid is dilute H_2SO_4 which provides high hydrolysis yields [37, 44]. Other acids used for cellulosic material pretreatments are acetic acid, $C_2H_4O_3$, formic acid, hydrochloric acid (HCl), maleic acid, oxalic acid, phosphoric acid, and nitric acid [45–49].

3.2. AFEX pretreatment

AFEX is one of the physicochemical pretreatments which treated lignocellulosic biomass with liquid ammonia at relatively moderate temperature (90–100°C) for about 30–60 min, then followed by a rapid pressure release [50]. A rapid expansion of the liquid ammonia causes swelling and physical disruption of lignocellulosic fibers and partial reduction of cellulose crystallinity. AFEX process is able to either modify or effectively decrystallization of cellulose and lignin fractions [51]. AFEX removes the least acetyl groups of biomass by deacetylation process, so that the digestibility of lignocellulosic biomass increases [52, 53]. The main advantage of the AFEX is that it does not produce inhibitors for the downstream biological processes, so water wash is not needed. AFEX is more effective for agricultural residues [54]. The AFEX process conditions (ammonia loading, temperature, blowdown pressure, moisture content of biomass, and residence time) have been optimized [55]. At the optimal conditions, AFEX can convert over 90% cellulose and hemicellulose to fermentable sugars for a broad variety of biomass materials including EFBOPT. Due to high volatility, ammonia is easy to be recovered and recycled [56], and leaving the dried biomass ready for enzymatic hydrolysis [57]. After pre-pretreatment, ammonia must be recycled in order to reduce the cost and protect the environment [56].

3.3. Alkali pretreatment

Alkali pretreatment is commonly utilized ammonium, calcium, sodium, and potassium hydroxides at certain temperature and pressure. The main advantage of this pretreatment is that lignin is efficiently removed from the biomass (**Table 1**). This process eliminates acetyl and uronic acid groups at hemicelluloses; as a result, the accessibility of enzyme that degrades hemicellulose increases [58]. Xylan ester linkages on hemicellulose residues are also hydrolyzed [56]. The advantages of alkali pretreatments are able to largely improve the cellulose digestibility, solubilize lignin more effectively, exhibit less cellulose, and hemicellulose solubilization compared to the acid pretreatments [59]. Alkali pretreatments can also be performed at lower temperature, pressure, and time ranging from hours to days. NaOH solution is more effective than other alkalis [60, 61]. Alkali pretreatments were shown to be more effective on decreasing the degree of polymerization and crystallinity, increasing the internal surface area of cellulose, and disrupting the lignin structure [41].

Besides NaOH, $Ca(OH)_2$ (lime) is another alkali widely used. It also eliminates lignin-carbohydrate ester and acetyl groups, and enhances cellulose digestibility [37]. Lime pretreatment has been proven successful for several biomass pretreatments, such as wheat straw, poplar wood, switchgrass, and corn stover [61, 62]. This pretreatment has lower reagent cost and less safety requirements compared to NaOH or KOH pretreatments. In addition, lime can be easier recovered from hydrolysate by reaction with CO2 [37]. The air/oxygen addition to the alkaline pretreatments (NaOH or lime) can increase lignin removal [59].

3.4. Ammonia recycle percolation

Ammonia recycled percolation (ARP) is an another type of ammonia-based pretreatment in which aqueous ammonia (5–15 wt %) passes through a packed of bed reactor along with biomass materials at high temperature (140–210°C) for 90 min and the rate of percolation is maintained at 5 mL/min [56, 64]. ARP can remove hemicellulose and lignin from the biomass as the liquid phase [31] although requires high liquid loading or process temperature. To reduce energy cost, soaking in aqueous ammonia (SAA) at lower temperatures (40–90°C) for longer reaction times has been used. This approach can preserve most of the glucan and xylan in the biomass samples which are then fermented using the simultaneous saccharification and cofermentation (SSCF) method [63].

3.5. Biological pretreatment

Biological pretreatments are treatments to biomass materials with microbes such as white rot fungi. Like conventional physicochemical methods, the objectives of biological pretreatments are to degrade lignin. The biological pretreatment is considered as a cheap, ecofriendly, and efficient method [64]. This method is carried out using cellulolytic and hemicellulolytic microbes, such as filamentous fungi which are ubiquitous and can be isolated from soil, living plants or lignocellulosic waste material [65, 66]. The most effective microorganisms for the pretreatment of most of the biomass materials are white-rot fungi [52], such as Ceriporia lacerata, Ceriporiopsis subvermispora, Cyathus stercoreus, Phanerochaete chrysosporium, Pleurotus ostreatus, Pycnoporus cinnabarinus, and P. chrysosporium. These fungi produce lignin peroxidases—lignin-degrading enzymes and manganese-dependent peroxidases—which show high delignification efficiency on various biomass materials [52, 67]. Some advantages of biological pretreatments include low-capital cost, low energy requirement, no chemical requirement, and mild environmental conditions (**Table 1**). However, the main drawback of the biological methods is that hydrolysis rate is very low [56]. To solve this drawback, some researches have to perform to find out isolates which have ability to delignify the biomass materials more quickly and efficiently.

3.6. CO_2 explosion pretreatment

CO_2 explosion pretreatment utilizes CO_2 as a supercritical fluid. The fluid displays gas like mass transfer properties and a liquid-like solvating power. This method can remove lignin effectively so that enzymes can digest biomass materials effectively [68]. Supercritical CO_2 has been mostly used as an extraction solvent because of its several advantages including easy recovery after extraction, environmental acceptability, non-toxicity, non-flammability, and relatively low cost (**Table 1**) [69]. In aqueous solution, CO_2 reacts with H_2O to form carbonic acid and increases hydrolysis rate. Because of their small size, CO_2 molecules are able to penetrate small pores accessible to ammonia and water molecules. In this pretreatment, cellulose and hemicellulose structures disrupt so that the surface area of the substrate increases and can easily attack by the digestive enzymes. For several substrates, the CO_2 explosion pretreatment is more cost-effective than ammonia expansion and produces lower inhibitors than steam explosion [70].

3.7. Liquid hot water pretreatment

Liquid hot water (LHW) is one of the hydrothermal pretreatment without rapid decompression and any catalyst or chemical additions and performs under high pressure in order to maintain the water in the liquid state at high temperatures. It is usually carried out at temperature range between 170 and 230°C and pressure (5 MPa) [71]. LHW eliminates hemicellulose from biomass materials so that the cellulose is more accessible to enzymatic attack (**Table 1**). After pretreatment, the obtained slurry is able to be filtered to yield two fractions, namely a solid cellulose-enriched fraction and a liquid fraction containing high hemicellulose derived sugars. Better pH (4–7) of this pretreatment can be controlled in order to minimize the non-specific degradation of polysaccharides and also to avoid the formation of inhibitors [37]. To promote more effective contact between the biomass materials and the liquid water, three methods have been developed, namely co-current, countercurrent, and flow-through methods. In co-current method, water and biomass slurry are heated to the desired temperature and held at the pretreatment conditions for a certain residence time before being cooled. Countercurrent method is designed to move water opposite to biomass through the pretreatment system. Hot water flows through passage system over a stationary bed of biomass which hydrolyzes and dissolves biomass components and brings them out of the system [72, 73]. LHW pretreatments are generally preferred because it is required lower costs due to no need chemicals and corrosion-resistant materials for hydrolysis reactors. In addition, the LHW pretreatments produce lower concentration of the solubilized hemicellulose and lignin products due to high water input (**Table 1**). Lower formation of inhibitory components and higher pentose recovery can be achieved in this LHW pretreatment compared to the steam explosion. However, this method has not yet developed at a commercial scale due to higher water demand and high energy input.

3.8. Milling pretreatment

Milling pretreatment is commonly used for reducing size biomass and altering the inherent ultrastructure of biomass and degree of crystallinity so that the biomass can be easier accessed by cellulase enzymes [74]. This pretreatment is performed prior to enzymatic hydrolysis or even other chemical pretreatment processes [74, 75, 76, 77]. There are several kinds of milling, such as ball, tow roll, hammer, colloid, and vibro energy millings [40]. Milling is able to improve susceptibility to enzymatic hydrolysis because of reducing the biomass size [78], decreasing the biomass crystallinity, [79] and increasing the biomass area.

3.9. Steam explosion pretreatment

Steam explosion pretreatment is a treatment with high pressure saturated steam for few seconds (30 s) to several minutes (20 min), and then pressure is suddenly reduced. These pretreatments are the most commonly used for treating biomass materials [80, 81]. Steam explosion—typically a combination of mechanical forces and chemical—is able to hydrolyze (autohydrolyze) acetyl groups of hemicellulose. At high temperatures (160–260°C), autohydrolysis occurs and produces acetic acid from acetyl groups of the biomass materials [82, 83]. In addition, water is also able to act as an acid at high temperatures. Reducing pressure suddenly produces explosive decompression so that biomass fibers separate each other. This process is able to degrade hemicellulose and lignin because of explosive decompression, and thus increase the potential of cellulose hydrolysis [82].

Steam explosion processes have several advantages compared to other pretreatment methods (**Table 1**). The advantages include high sugar recovery, less hazardous process chemicals and conditions, lower environmental impact, lower capital investment, possibility of using larger chip size, no acid catalyst additions except for softwoods, more efficient in energy usage, and significant improvement in enzymatic hydrolysis as well as its feasibility at industrial scale [84]. The main drawbacks of steam explosion pretreatment are the partial degradation of hemicelluloses producing inhibitor compounds that can affect the enzymatic hydrolysis and fermentation process [85, 86]. Thus, an inhibitor compound separation becomes necessary (e.g., addition of activated charcoal, over liming, and ion exchange) and will increase the overall process cost [31, 87].

3.10. Wet oxidation pretreatment

Wet oxidation is treated biomass materials with water and air/oxygen at temperatures higher than 120°C for 30 min [88]. This wet oxidation pretreatment is suitable for pretreatment of biomass materials containing high lignin content. The most effective parameters in the wet oxidation process are temperature, reaction time, and oxygen pressure [87]. This pretreatment yields acid compounds from the hydrolytic processes and oxidative reactions of biomass materials.

Wet oxidation pretreatments affect all three main components of lignocellulosic materials, namely, cellulose, hemicellulose, and lignin. The hemicelluloses are extensively hydrolyzed to low molecular weight sugars that become soluble in water. Lignin is cleaved and oxidized, and cellulose is partly degraded and becomes highly susceptible to enzymatic hydrolysis. Addition of some alkaline compounds, such as sodium carbonate make easier to hydrolyze hemicellulose components and also minimizes the formation inhibitor compounds, such as furan-based degradation products [89].

The main advantage of wet oxidation is efficient lignin removal and less inhibitor formations (**Table 1**). The main disadvantage of this method is requirements for high temperature and pressure maintenances and the presence of strong oxidizing agents such as H_2O_2. These requirements cause to high costs of maintenance and also require large-scale reactors. Therefore, application of this process is limited in large-scale pretreatment of biomass materials.

4. Conclusions and future perspectives

Empty fruit bunch of oil palm trees have been described in terms of their physical and chemical characteristics. As solid waste products of palm oil factories, physical EFBOPT characteristics are brown, not uniform, low bulk density, varying in length from 17 to 30 cm, and varying in width from 25 to 35 cm depending on the size of fresh fruit bunch. EFBOPT fiber is mainly constructed from a complex matrix of three main polymers, namely, cellulose, hemicellulose, and lignin. The main chemical component of EFBOPT is cellulose (44.2–50.0%) and the others are hemicellulose (22.0–33.5%) and lignin (20.4–21.0%) which should be removed through pretreatments before the cellulose is hydrolyzed enzymatically.

There are three kinds of pretreatment methods, namely, physical, chemical, and physicochemical and biological pretreatment methods. The various pretreatment methods for biomass materials have been described to improve enzymatic saccharifications and ethanol production. Each method has its advantages and disadvantages. There is no one treatment method yielding 100% conversion of biomass into fermentable sugars. There is always a loss of biomass materials, which affects the final yield and increases the cost of finished product, i.e., bioethanol. Although a combination of two or more pretreatment methods has indicated promising results, we still feel that there is a need for extensive researches in this area so that either a new efficient treatment method is discovered or an existing method is upgraded to yield better results. Predictive models will enable the selection, design, optimization, and process control of pretreatment methods that are suitable for biomass materials.

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Chapter 5

Conversion of High Biomass/Bagasse from Sorghum and Bermuda Grass into Second-Generation Bioethanol

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Abstract

Sorghum (Sorghum bicolor) and Bermuda (Cynodon dactylon) grass are examples of annual and perennial forage crops produced throughout the globe. These crops should be harvested at the peak of biomass production when the levels of lignin are relatively low. The high biomass sorghum, sweet sorghum bagasse (2 cuts or crops year^{-1}) or Bermuda grass capable of yielding up to 50, 60 and 27 tons of dry forage ha^{-1} year^{-1} rich in cellulose and hemicellulose can be efficiently transformed into bioethanol using second-generation technologies consisting of milling, pretreatment (chemical and/or enzymatic) and fermentation with microorganisms capable of transforming C5/C6 sugars to obtain ethanol. An alternative process contemplates the extrusion aimed toward the physical disruption of cell walls minimizing the use of considerable amounts of water and chemicals commonly used during pretreatment. Extruded feedstocks treated with fiber-degrading enzyme cocktails had conversion efficiencies between 60 and 78% of the hemicellulose and cellulose similar to the ones achieved after acid/enzyme hydrolyses. The chief advantages of this continuous process are that hydrolysates are practically free of enzymes and yeast inhibitors. These feedstocks can produce up to 310 L anhydrous bioethanol dry t^{-1} and have a great potential for widespread use.

Keywords: high biomass sorghum, sorghum bagasse, Bermuda grass, second-generation bioethanol

1. Introduction

The family of true grasses, botanically known as *Gramineae* or *Poaceae*, is a large group of genus and species commercially grown and distributed practically in all places around the globe. These monocotyledonous flowering plants are the most common sources of food for mankind and forages for domestic animals. The value of these plants is that they produce kernels rich in starch and protein that constitute the main staple for most cultures around the globe. Furthermore, these grasses provide most of the fiber consumed by ruminant domestic animals that provide mankind with milk and meat. The family contains about 10,000 domesticated and wild species, which represent the fifth largest plant family. Grasslands make up one-fifth of the vegetation cover of the globe and are considered as one of the chief sources of fibrous rich feedstocks. Annual and perennial grasses are classed into three broad categories: bunch-type, stoloniferous and rhizomatous. The success of the various types of grasses is mainly attributed to their morphological and physiological diversity. According to the physiological activity and more specifically to the photosynthetic pathways for carbon fixation, grasses are divided into C3 or C4 plants. The C4 plants have a photosynthetic pathway that particularly adapts them to hot climates and atmospheres low in CO_2 [1]. The commercial cereal grains are annual whereas most of the grasses that provide forages perennial. The chemical composition of these forages is affected by genotype, maturity and soil fertility. However, independently of the source, these feedstocks are highly attractive for biorefineries because of their abundance, relative low cost and quality of the fiber that it can be successfully converted into second-generation bioethanol, lactic acid, or other high value chemicals.

According to the Renewable Fuels Association, the world biorefineries generated more than 100 billion L of bioethanol in 2016. The USA is the major producer with approximately 58% of the present production (57.7 billion L) followed by Brazil with 27% of the total production. The contemporary fuel ethanol production is based chiefly on maize and sugarcane [2] and the use of these feedstocks triggers concerns related to food security especially as world population surpasses 7600 million people [3]. More biofuels production is particularly expected in the USA where the Energy Independence Act mandates the manufacturing of 136 billion L of bioethanol and biodiesel by year 2022. In order to meet these expectations, biorefineries will convert lignocellulosic biomass to energy using forages and dedicated energy crops such as high biomass sorghum, switchgrass and Miscanthus, which could be planted in marginal zones or alternatively serve to protect ecosystems especially from soil erosion.

The C4 sorghum (*Sorghum bicolor* L. Moench) plant has been identified as one of the best potential bioenergy crops. This member of the Gramineae family poses considerable potential as a dedicated lignocellulosic crop because of its broad genetic diversity, which provides plant breeders the opportunity to develop high biomass types adapted to different environments under dryland or irrigated conditions or sweet sorghums varieties, which can be effectively converted into first- and second-generation bioethanol [4]. The annual or short perennial high biomass sorghums can grow to a height of 6 m tall, depending on the genotype and growing conditions. This capacity has been boosted by intensive plant breeding programs focused in the design of new genotypes that can be effectively converted into second-generation ethanol [5, 6]. Sorghum is resistant to both abiotic and biotic stress factors such as drought, soil salinity and alkalinity and insects. Besides, this cultivar possesses one of the best rates of carbon incorporation (50 g m^{-2} d^{-1}), which promotes its fast growth and enhanced rate of CO_2 utilization [7]. The sorghum growth cycle regularly lasts 3–5 months, and therefore, it can be produced twice or even three times throughout the year instead of only one crop obtained with sugarcane. Bermuda grass (*Cynodon dactylon*) is also a C4 perennial season forage crop, mainly used in the United States and northern of Mexico for ruminant feed and soil remediation from animal wastes. This grass has a short growth period and is usually cut monthly during the spring and summer seasons. The grass is highly susceptible to cold temperatures so it passes the winter inactive. The optimum growth conditions are 24–37°C maintaining a well biomass yield under water-stress conditions [8]. Together with these characteristics, the Bermuda grass is composed of a high amount of holocellulose (>50%) and low amounts of lignin (up to 20%) [9].

The aim of this review is to describe conversion technologies of sweet sorghum bagasse, high biomass sorghum and perennial grasses like Bermuda into second-generation fuel bioethanol.

2. Ethanol production from high biomass or sorghum bagasse and Bermuda grass

Among annual cultivars, the high biomass and sweet sorghums offer the most efficient and fastest means of producing large quantities of usable biomass [1, 3, 6, 10], whereas the perennial Bermuda grass is a good example of a forage crop which can be effectively converted into second-generation bioethanol using currently available technologies. High yielding sweet sorghums planted in good soils and with adequate agronomic practices are able to produce 3500 L of anhydrous ethanol ha^{-1} from sweet juice, 3000 from the spent bagasse and 500 L from the starchy kernels (a total of about 7000 L) after 4 months of sowing, whereas high biomass dedicated crops up to 5600 L of second-generation ethanol ha^{-1}.

Amosson et al. [6] estimated dry yields of high biomass sorghum planted on dryland and irrigated areas in 8 and 18.5 t ha^{-1}. Likewise, Habyarrimana et al. [11] evaluated the biomass yield and drought resistance in field conditions of Italian sorghum genotypes. This study which evaluated 75 lines and two hybrids concluded that tropical sorghum landraces yielded total aboveground dry biomasses of 33–51 t ha^{-1} under irrigation and 20–29 t ha^{-1} under rain-fed conditions. Dryland and irrigated high biomass sorghum planted in the high plains of Texas was capable of yielding from 2400 to 5600 L ethanol ha^{-1}, respectively, assuming that one ton of dry biomass yields approximately 300 L of second-generation ethanol. The estimated cost of producing 1 ton of dry weight on the dryland and irrigated lands was estimated at 76.6 and 82 US dollars, respectively [6].

The short rotational sweet sorghums yield high sugar in their stalks, whereas the high biomass sorghums developed for second-generation bioethanol are mainly composed of fibrous chemical compounds. In terms of conversion into ethanol, the extracted sweet juice can be easily and highly efficiently converted into bioethanol leaving the spent bagasse as other potential feedstock for second-generation ethanol manufacture. Vencor Green [12] reported that the cost of ethanol production from sweet sorghum juice was 20% lower than either sugarcane or corn. According to Serna Saldivar et al. [1], the mature stems of sweet sorghum contain about 73% moisture and 27% solids which are manly comprised of structural and non-structural carbohydrates. Approximately 13% of the solids are non-structural carbohydrates composed of the disaccharide sucrose and monosaccharides glucose and fructose, in variable amounts according to cultivar, maturity stage and harvesting season [13, 14]. The sweet sorghum cultivars are classified based on their juice sugar composition into sugar and syrup types. The first is rich in sucrose while the second in glucose and fructose. According to the same authors, Wray, Keller and H173 sweet sorghum cultivars harvested post-anthesis yielded an average of 10, 7 and 4 t ha^{-1} of fermentable sugars. Other studies [15, 16] reported sugar yields varying from 4.5 to 18 t ha^{-1}. These sugars are considerably highly fermentable and able to yield approximately 46% ethanol after 48 h fermentation. Therefore, the conceivable production of anhydrous ethanol fluctuates from 1000 to 8000 L.

On the other hand, an established perennial Bermuda grass field is capable of producing from 6 to 27 t ha^{-1} year^{-1} of dry forage [8], which can be converted into 1200–5400 L fuel ethanol. The large yield variability is due to water availability, nitrogen fertilization, soil fertility and number of monthly cuts during the year. Generally, the Bermuda grass is cut monthly except during the cold season of the year.

2.1. Second-generation ethanol from high biomass or sorghum bagasse and Bermuda grass

2.1.1. Fiber composition

The high biomass forage or sorghum bagasse leftover after juice extraction of sweet cultivars is a fiber-rich feedstock with some variation in composition according to intrinsic and extrinsic factors such as genotype, maturity or degree of lignification and climatic conditions.

Nagaiah et al. [17] determined the structural composition of six high biomass sorghums differing in plant height (3.9–6.2 m) and yield (53.6–90.5 t of fresh stalks). The cultivars contained from 27 to 52% cellulose, 17 to 23% hemicellulose and 6.2 to 8.1% lignin (**Table 1**). According to Woods [18], from 12 to 17% (average 15%), 15% of the total sweet sorghum plant weight is constituted by the fibrous portion. Typically, the sweet sorghum harvested at optimum time yields half juice and half bagasse after milling or crushing the stalks. The spent bagasse with 52% moisture contains 5.4% residual fermentable sugar, 17% cellulose, 11.9% hemicellulose and 8.5% lignin [19, 20]. Heredia-Olea et al. [20], evaluating the fiber and structural carbohydrate composition of sweet sorghum bagasse, concluded that the main structural carbohydrates were cellulose derived β-glucans and xylans and arabinans related to hemicellulose. The quantity of lignin of 13.5% (dwb) was similar to that assayed by Gnansounou et al. [19] and

Crop	Composition (%)		
	Cellulose	Hemicellulose	Lignin
High biomass sorghum[2]	27–52	17–23	6.2–8.1
Sweet sorghum bagasse[3]	31–34	18–25	10–18
Bermuda grass[4,5]	31–35	26–30	14–23

[1] Composition and yields are expressed on dry matter basis.

[2] Nagaiah et al. [17].

[3] Stenberg et al. [27], Heredia-Olea et al. [20].

[4] Canizo et al. [22].

[5] Lee et al. [9].

Table 1. Chemical composition of high biomass sorghum, sweet sorghum bagasse and Bermuda grass[1].

slightly higher compared to the value (11.1% dwb) reported by Prasad et al. [7]. Importantly, lignin is directly related to plant maturity and thus inversely correlated to the proneness of the other fiber components to hydrolysis and ethanol production.

According to Lee et al. [21], the Bermuda grass contains 30.4, 22.6, 4.9 and 23.2% of glucans, xylans, arabinans and lignin, respectively. On the other hand, Canizo [22] determined a similar composition of the potentially fermentable sugars but a slightly lower lignin content (**Table 1**).

2.2. Second-generation ethanol production

2.2.1. Pretreatments and sugars yields

Production of lignocellulosic anhydrous ethanol consists of five sequential steps: milling of the feedstock, chemical or physical pretreatment, enzyme catalysis or saccharification, fermentation of resulting C6 and C5 sugars and ethanol distillation-dehydration [4]. Cellulose and hemicellulose upon hydrolysis yield the C6 and C5 fermentable sugars, respectively. The effectiveness of the process is strongly affected by the availability of cellulose and hemicellulose which must be separated from lignin, which hinders rate of hydrolysis and therefore ethanol yields.

The lignocellulosic residue is usually milled in hammer or rotary mills with the objectives of reducing the particle size and disrupt cell walls so fiber components are more prone to subsequent chemical, enzymatic and fermentation treatments. Then, the ground feedstock is hydrolyzed using chemicals such as acid, alkalis and ammonia and/or a set of fiber-degrading enzymes. Generally, the chemical or physical hydrolysis precedes the enzymatic in order to further release C6 and C5 sugars [4].

Extrusion cooking and steam explosion are two alternative types of physical pretreatments that are used to expose cellulose and hemicellulose associated with lignified cell walls. The first has been effectively used to disrupt fiber components especially hemicellulose minimizing the use of water [23, 24]. Heredia-Olea [25] effectively employed a thermoplastic twin extruder to modify the fiber structure of ground sorghum bagasse. Results indicated that that thermoplastic extrusion additionally reduced the particle size of the ground feedstock and exposed cellulose which was more susceptible to fiber-degrading enzymes. The extruded feedstock treated with the kit of fiber-degrading enzymes had conversion efficiencies of 77.5 and 60 of cellulose and hemicellulose, respectively. These conversion rates are comparable to rates attained when acid and enzyme hydrolyses. The main benefits of the continuous extrusion process are that hydrolysates are virtually free of yeast inhibitors such as acetic acid, furfural and hydroxymethyl furfural [1, 24].

Steam explosion consists of placing the feedstock in a pressurized reactor where steam is injected. The reactor's operation temperature is in the range of 170–210°C [26, 27]. After a 2–10 min holding cycle, the blown down valve suddenly opens and the resulting pressure variation disrupts the fiber matrix [27]. Sipos et al. [26] achieved an extraction of 89–92% of cellulose associated with sweet sorghum after the use of this technology. The same authors documented an impregnation process for ground sorghum bagasse with up to 3% w/w SO_2 in plastic bags for up to 30 min. The SO_2 impregnated bagasse prior to steam pretreatment improved the subsequent saccharification step [27]. The ammonia fiber explosion process known as AFEX is a novel pretreatment that disrupts the internal fiber structure and molecular characteristics of the raw material without the production of liquid. Lee et al. studied the effectiveness in terms of fermentable sugars generation of autohydrolysis or AFEX applied to coastal Bermuda grass [9]. The AFEX process conducted at 100°C for 30 min yielded 94.8% sugars of the theoretical possible value, whereas autohydrolysis at 170°C for 1 h yielded just 55%. The study clearly demonstrated that the proposed AFEX pretreatment enhanced significantly the enzymatic accessibility of the Bermuda grass.

The most employed chemical pretreatment employed for second-generation ethanol production is acid hydrolysis because it is relatively cheap, releases significant quantities of sugars and improves the susceptibility of disrupted fiber components to the next stage of the process consisting of treating the biomass with fiber-degrading enzymes [28]. The major advantage and disadvantage of acid hydrolysis is that it enhances cell wall delignification and generates relevant quantities of known yeast inhibitors. Sulfuric, hydrochloric, hydrofluoric or acetic acids have been used. The process involves adding diluted acid solution (0.1–10% mass fraction) to the milled feedstock followed by pressure-cooking in a reactor. The major control points of acid hydrolysis are the strength of the acid solution, the pressure and temperature and the processing time.

Several investigators have researched the effectiveness of acid hydrolysis of sweet sorghum bagasse. Kurian et al. [29] pressure-cooked sorghum bagasse with sulfuric acid at a concentration of 5 g kg^{-1} for half an hour and obtained an extract with 92 g L^{-1} of total sugars, whereas Ban et al. [28] treated the same raw material at a solid-liquid ratio of 10% with 80 g phosphoric acid L^{-1} at 120°C for 80 min. These authors reported 302 g kg^{-1} bagasse of reducing sugars after applying this specific acid treatment. Recently, Heredia-Olea et al. [20] researched through surface response methodologies two different acid pretreatments (sulfuric or hydrochloric acid) and one blend of these acids on ground sweet sorghum bagasse harvested post-anthesis. Resulting acid hydrolysates were treated with calcium hydroxide in order to detoxify hydrolysates. The sweet sorghum bagasse free of the sweet juice contained 41.2% cellulose and 24.5% hemicellulose. The response variables were production of C5 and C6 sugars and the three major inhibitors of yeast (acetic acid, 5-hydroxymethylfurfural, and furfural). Results indicated that the different acid pretreatments produced similar quantities of fermentable carbohydrates. These pretreatments liberated from 56 to 57% of the total sugars present in the sorghum bagasse (390–415 mg sugar g^{-1} bagasse) and from 44 to 61 mg total inhibitors g^{-1} (**Table 2**). Among the three pretreatments, the HCl treatment was the best alternative due to its relatively lower hydrolysis time (less energy expenditure) and satisfactory yield of C5 and C6 fermentable sugars.

On the other hand, the use of strong alkalies breaks ester bonds of cross-linked lignin and xylans producing an enriched cellulose and hemicellulose fraction. The preferred alkalis are sodium hydroxide, ammonia and calcium hydroxide or lime. The alkaline pretreatments are regularly conducted at relatively lower temperatures, pressures and times compared to other technologies. The main withdraw of chemical treatments is the production of known yeast inhibitors divided into three categories: organic acids (i.e. acetic, formic and levulinic), furans (furfural and 5 hydroxymethylfurfural) and phenolics such as *p*-hydroxybenzoic acid released from lignin moieties [28]. The concentration of these hydrosoluble compounds is known to upset cell physiology and viability and thus the efficacy of ethanologenic microorganisms. According to Amartey and Jeffries [30], the removal of these inhibitors before fermentation can reduce approximately 25% the production cost.

Wang and Cheng investigated the efficiency of lime or calcium hydroxide pretreatment in order to enhance reducing sugar recovery in coastal Bermuda grass [31]. These authors studied the effects of temperature (21–121°C) and lime loadings (0.02–0.2 g/g of dry biomass) followed by biocatalysis with cellulases and cellobiases. The best pretreatment combinations removed approximately 20% of the original total lignin content, which was over twice more than that from the untreated counterpart. The best total fermentable sugar yield for the lime pretreated Bermuda grass (100°C, 15 min, and 0.1 g lime g^{-1} dry biomass) was 78% of the theoretical maximum. Moreover, this specific pretreatment converted 87%, and 68% of the

Compound (%)	**Sweet sorghum bagasse**[4]			**Bermuda grass**[5]	
	HCl hydrolysis	**HCl hydrolysis + enzymatic hydrolysis**	**Extruded + enzymatic hydrolysis**	**H_2SO_4 hydrolysis**	**H_2SO_4 hydrolysis + enzymatic hydrolysis**
Glucose	52.2	82.2	66.5	20.9	90.5
Xylose	53.3	75.7	94.1	66.6	84.6
Arabinose	42.6	50.2	28.7	90.0	90.0
Total sugar yield[3]	55.6	80.6	67.5	40.9	89.2

[1] The compounds are percentage of sweet sorghum bagasse or Bermuda grass.

[2] Results are in dry matter basis.

[3] Sugars yield = total sugars (mg/g)/[1.11× glucans (mg/g) + 1.14 (xylans (mg/g) + arabinans (mg/g))].

[4] Heredia et al. [25].

[5] Canizo et al. [22].

Table 2. Sugars and second generation ethanol generated from sorghum bagasse or Bermuda grass after different pretreatments[1,2].

glucan and xylan into glucose and xylose, respectively. A microwave-assisted alkali pretreatment of coastal Bermuda grass followed by enzyme hydrolysis proved to be an effective technology to improve fermentable sugars. Pretreatments were performed by immersing the feedstock in different dilute alkalis and microwaving the resulting slurries at 250 W for 5–20 min [32]. Sodium hydroxide was the most effective alkali for microwaving of the coastal Bermuda grass. Approximately 87% glucose and 59% xylose yields were achieved after the hydrolysate previously treated with 2% NaOH and microwave treated for 10 min was treated with the fiber-degrading enzymes. For pretreated Bermuda grass, the hypothetical yields of ethanol based on glucose or glucose and xylose were 147 and 208 L ton^{-1}, respectively.

Heredia-Olea et al. [20] assayed the quantities of furfural, hydroxymethyl furfural and acetic acid produced after diverse acid hydrolyses. These compounds were generated in higher extents in hydrolysates obtained with higher acid concentrations and processed for longer periods of time. The principal inhibitor was acetic acid which was freed from hemicellulose covalently bound by acetic moieties to lignin [33, 34]. The different sorts of acids broke these linkages generating this acid inhibitor. Detoxification strategies are commercially used to lower inhibitors. The most usual approaches are the use of calcium hydroxide (lime) or activated carbon which entraps phenolic compounds from lignin, ion-exchange resins and enzymes such as laccase [4]. Heredia-Olea et al. [20] successfully detoxified with lime different sorts of acid hydrolysates obtained from sorghum bagasse. Results indicated that the lime treatment removed 19% of the acetic acid and 38% of the hydroxymethylfurfural.

2.3. Enzymatic hydrolysis and fermentation

The enzyme hydrolysis of fiber is one of the fundamental steps for second-generation alcohol production. Normally, this biocatalysis is performed in chemically treated biomass or alternatively and less frequently with ground untreated fiber. This last process is more recommended for feedstocks low in lignin and has the advantages of saving energy, processing time. Besides the sole utilization of enzymes without the chemical pretreatment is less harmful for the environment. There are several enzymes normally utilized to convert cellulose and hemicellulose into fermentable carbohydrates. They consist of blends of endo and exocellulases, cellobiase, hemicellulases, pectinases, xylanases, B-glucosidase and others [4]. Cellulose is more effectively hydrolyzed by the synergistic activity of endo and exo-acting enzymes (exoglucanases). Nowadays, it is common practice to employ enzyme kits consisting of seven or more cell wall degrading enzymes which act synergistically. Heredia-Olea et al. [25] investigated the efficacy of two concentrations of a fiber-degrading enzyme kit supplemented directly to ground sorghum bagasse and concluded that the higher concentration produced about 20% more fermentable sugars. The main soluble carbohydrates generated during the enzymatic treatment were glucose and xylose. Moreover, the thermoextruded feedstock treated with the fiber enzyme complex was effective when applied in a SSF system. This combination yielded hydrolysates with high amounts of fermentable sugars employing less energy and processing time.

Production of ethanol from physically, chemically and/or enzymatically treated hydrolysates is feasible with the utilization of osmotolerant and C5 (pentose) yeast or bacterial strains. The recent advances in biotechnology has generated numerous genetically modified or engineered yeast and bacteria proficient of fermenting hydrolyzates containing significant amounts of

C5 and C6 sugars. The most important and applicable are strains of *Saccharomyces cerevisiae*, *Kluyveromyces marxianus*, *Pichia stipitis*, *Klebsiella oxytoca*, *Klebsiella planticola*, *Candida shehatae*, *Flammulina velutipes* and *Issatchenkia orientalis.* These microorganisms have been innoculated alone or in blends at temperatures around 37°C and pH varying from 5.2 to 6 [1, 32].

Heredia-Olea et al. [20] fermented detoxified sweet sorghum bagasse worts obtained after acid and/or enzyme treatments with a genetically-engineered *S. cerevisiae* or *I. orientalis* which were modified so they were able to metabolize C5 and C6 sugars. *S. cerevisiae* and *I. orientalis* were able to produce 18.4 and 20.9 g ethanol·100 g^{-1} dry sweet sorghum bagasse, respectively, and were capable of fermenting 64.4 and 73.3% of the fermentable sugars. Remarkably, most of the bioethanol was produced during the first day of fermentation. Likewise, Ballesteros et al. [35] obtained 16.2 g ethanol L^{-1}(10% solids) from sweet sorghum bagasse hydrolyzates fermented with *K. marxianus*, whereas Kurian et al. [29] working with *P. stipitis* produced 38.7 g ethanol L^{-1} with a theoretical conversion of 82.5%.

Although similar pretreatments have been also applied to Bermuda grass (alkaline, hot water, ozonolysis, steam explosion), the diluted acid hydrolysis had better effectiveness in terms of releasing monomeric sugars, specially xylose [23]. Canizo et al. [22] concluded that H_2SO_4 hydrolysis (121°C, 75 min, 1.25% acid concentration, and 12.5 solid to liquid fraction) released 20.9% glucose, 66.6% xylose and 90% arabinose. Likewise, Ballesteros et al [35] used a hydrolysis scheme with more acid concentration (1.5% w/w) and time (90 min) achieving 66 and 52% xylose and glucose yield, respectively. Wang and Cheng studied the efficiency of lime pretreatment and enzyme hydrolysis in terms of reducing sugar production and bioethanol yield of costal Bermuda grass [31]. The highest total reducing sugar production of 449.8 mg/g of raw biomass was attained using the pretreatment conditions of 0.1 g of lime/g of dry biomass, 100°C, and 15 min. Fermentation tests of the hydrolysates indicated that more than 99% glucose was converted by the yeast with ethanol yields of approximately 95% of the theoretical maximum. Assuming that the annual production of coastal Bermuda Grass was 14.8 tons/ha, on the basis of the theoretical ethanol yield from raw Bermuda grass of 167 L/dry ton of biomass for only glucose fermentation or 273 L/dry ton of biomass for co-fermentation of glucose and xylose, could be 2056–2755 L/ha. Redding et al. [36] employed higher temperatures (140°C for 30 min) achieving hydrolysis rates of 83% of total xylose and 28.3% glucose. A significant improvement in fermentable carbohydrate yield from Bermuda grass is documented after using a fiber-degrading enzyme complex [23]. Likewise, Canizo et al. [22] hydrolyzed Bermuda grass solids after separating the acid pretreated hydrolysate using 27 FPU celullase g^{-1} cellulose, 0.6% β-glycosidase and 0.5% xylanase for 168 h at 50°C, pH 4.8 and 150 rpm and concluded that the dual technology released 90.1% of glucose from cellulose and 18% xylose from hemicellulose. Thus, the dual treatment yielded 89.2% of the total sugars from the Bermuda grass cell walls (**Table 2**). Sun and Cheng [37] used 25 FPU g^{-1} cellulase plus 75 IU g^{-1} cellobiase to increase approximately 20% the yield of glucose. Likewise, Redding et al. [36] used 40 FPU g^{-1} cellulase plus 70 IU g^{-1} cellobiase in order to obtain 95% of the theoretical fermentable sugar yield.

With the estimated ethanol yield obtained by Canizo et al. [22] is feasible to attain a theoretical amount of 180 mg of ethanol g^{-1} of dried Bermuda grass. This means a theoretical ethanol yield between 1.08 and 4.86 t ha^{-1} $year^{-1}$ (**Figure 1**).

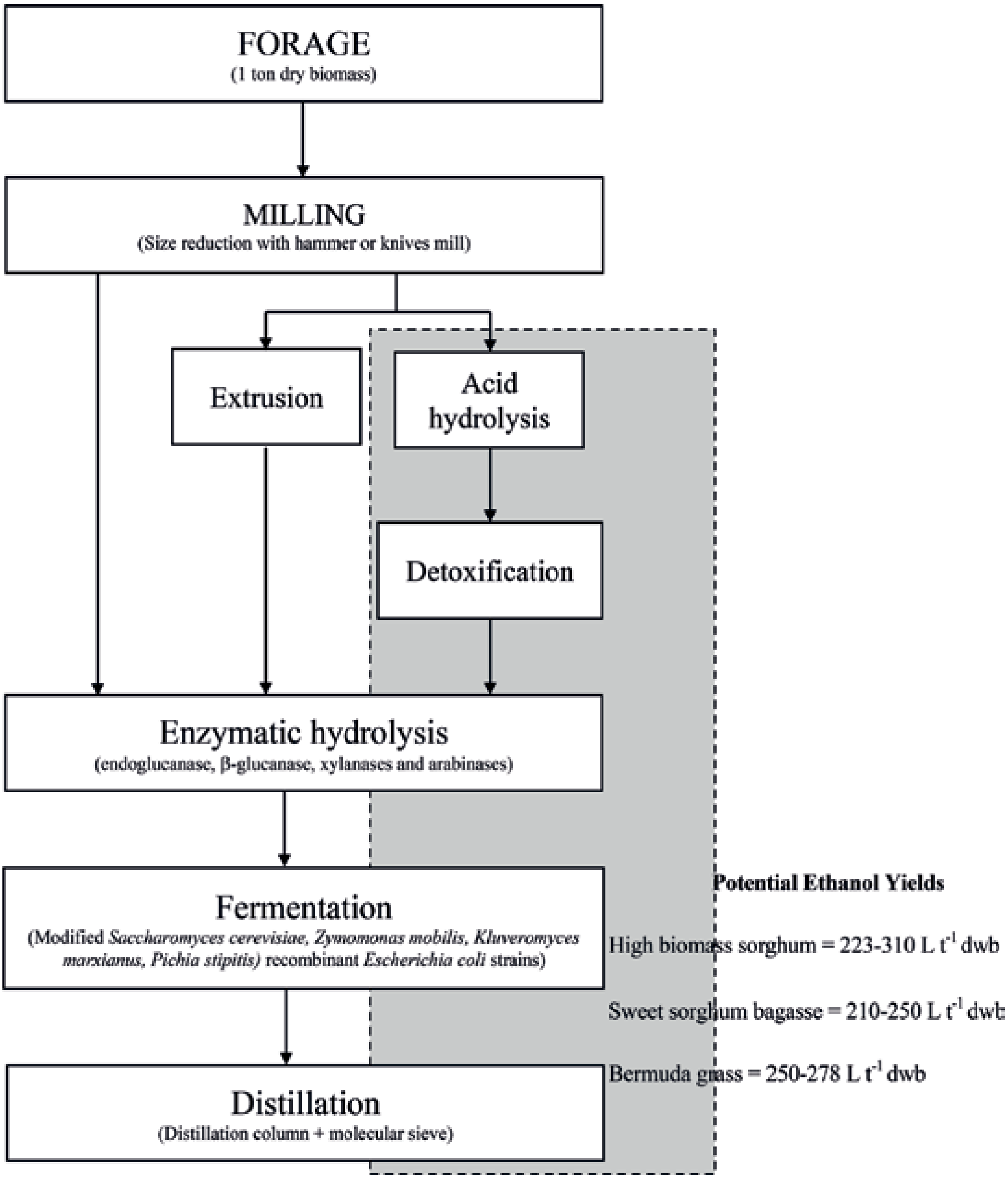

Figure 1. General schemes for production of second-generation ethanol from high biomass sorghum, sweet sorghum bagasse or Bermuda grass.

3. Conclusions

Both biomass sorghum and Bermuda grass adapted to tropical, subtropical and temperate agriculture regions of the world can be effectively converted into second-generation bioethanol due to the composition of the fiber rich in cellulose and hemicellulose and low in lignin.

Sweet and biomass dedicated sorghums can yield up to 60 tons of dry forage ha^{-1} year $^{-1}$, whereas the perennial Bermuda grass up to 20 tons of dry forage ha^{-1} year.

These lignocellulosic feedstocks can be converted into bioethanol using the conventional process of milling and pretreatment (chemical and/or enzymatic) with the aim of producing both C5 and C6 sugars in preparation for fermentation with yeast or genetically modified microorganisms capable of fermenting these sugars. After fermentation, the fermented broth is distilled in order to obtain high concentrated ethanol, which is further dehydrated in order to get anhydrous alcohol. An alternative process contemplates the use of thermoplastic extrusion aimed toward the physical disruption of the cell walls of the biomass minimizing the use of considerable amounts of water and chemicals commonly used during pretreatment. These feedstocks can yield up to 310 L anhydrous ethanol dry t^{-1} and have a great potential for general use.

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Section 4

Biodiesel

Review of Catalytic Transesterification Methods for Biodiesel Production

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Additional information is available at the end of the chapter

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Abstract

Attempts for improving the synthesis procedure of catalysts for fatty acid methyl ester production have been progressing for a considerable length of time. Biodiesel lessens net carbon dioxide emissions up to 78% with reference to conventional fuel. That is the reason for the improvement of new and operative solid catalysts necessary for inexhaustible and efficient fuel production. Homogenous base catalysts for transesterification is risky in light of the fact that its produces soap as byproduct, which makes difficult issues like product separation and not temperate for industrial application. In comparison, heterogeneous process gives higher quality FAME which can be effectively isolated and facilitate costly refining operations that are not required. A focus of this review article is to study and compare various biodiesel synthesis techniques that are being researched. The catalytic strength of numerous heterogeneous solid catalysts (acid and base), specially earth and transition metal oxides were also appraised. It was observed that catalytic proficiency relied upon a few factors, for example, specific surface area, pore size, volume and active site concentration at catalyst surface. This review article will give assistance in assortment of appropriate catalysts and the ideal conditions for biodiesel generation.

Keywords: biodiesel, heterogeneous catalyst, fatty acid methyl ester, transition metals, vegetable oil, transesterification

1. Introduction

Fatty acid methyl ester (FAME) commonly called biodiesel is a fuel derived from renewable sources suitable for use in conventional compress ion-ignition engines. The interest and development of biofuels has grown exponentially over the last few years in response to the need to develop sustainable energy resources and to address climate change. Currently, biodiesel are the most successful fossil fuel supplements. Notwithstanding limited market share, biodiesel has several strong traits to make a considerable influence to energy portfolio propose that its usage will continue to raise in the forthcoming years. Many countries are promoting the use of biodiesel through government incentives and targets, and the production of biodiesel is increasing worldwide. Besides the obvious economic benefits, renewable fuels are also offering environmental benefits by reducing the greenhouse gas emission and increase the energy security of the country by plummeting necessity on foreign oil.

FAME is synthesized through the transesterification reaction of triglyceride and methanol. Transesterification is the process by which an ester is converted into another product over the exchange of the alkoxy moiety.

Vegetable oils are attractive promising substitute to diesel fuel since they are inexhaustible in nature and can be produced locally and eco-friendly as well. All unsaturated fat sources, such as animal fats or plant lipids can be used in biodiesel production [1–5]. Edible vegetable oils like canola, soybean and corn have been utilized for biodiesel generation and observed to be great as a diesel substitute [6, 7]. The non-consumable vegetable oils such as *Madhuca indica*, *Jatropha curcas* and *Pongamia pinnata* are observed to be suitable for biodiesel synthesis under the test conditions researched. In perspective of the few focal points, vegetable oils have an incredible potential to supplant oil-based powers over the long haul [7–9].

2. Transesterification methods

Catalysis of transesterification can be done by catalytic, non-catalytic and enzymatic [8–11]. Non-catalytic transesterification mechanism takes place at supercritical conditions. These conditions entail a greater temperature and higher pressure, which is not an economically viable choice, for this reason catalytic transesterification approaches for biodiesel production are more commonly used and more vastly preferred [12]. Homogeneous catalysis may be basic, acidic or enzymatic in which basic catalysis of oils comprise alkaline, for example, potassium and sodium hydroxide, alkoxides summary of catalytic methods are given in **Figure 1**. At low temperature and pressure, basic catalysts have extraordinary activity rate in transesterification. Sulfuric, hydrochloric and sulfonic acids are the major acid catalysts [13, 14]; whereas homogeneous acids and bases have well-defined chemical properties; heterogeneous acid and bases exhibit a variety of sites; while heterogeneous catalysts can be categorized by the Bronsted or Lewis nature of sites, acid or base strength of sites and the texture of support [15, 16].

The base catalyzed transesterification process is primary viable heterogeneous process practiced now a days [11]. It has various mechanism which converts the triglycerides (TG) to FAME with the liberation of glycerol such as a byproduct [17, 18]. Specialists are seeking after new catalyst. Additionally, the limpidness of the required feedstock, reaction kinetics and postreaction processing is relying on the used catalyst [19].

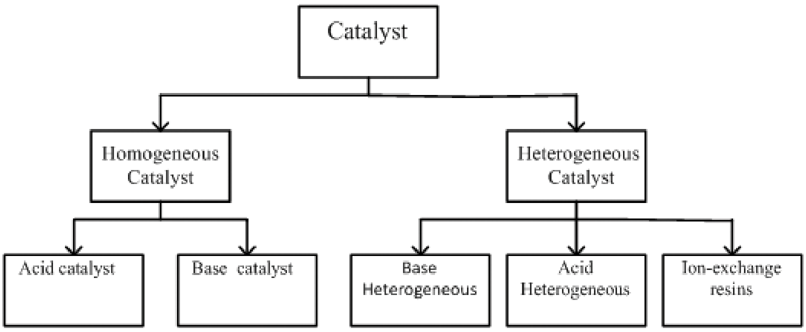

Figure 1. Catalytic methods.

3. Heterogeneousversus homogenous catalysis

Catalyst fundamentally has a place with the classifications of homogeneous or heterogeneous. Homogeneous catalyst act in a soluble stage from the blend, while heterogeneous catalyst act in an alternate stage from the response blend. The outline of reactant process is given in **Figure 2**. Being in an alternate stage, heterogeneous impetuses have the upside of simple partition and reuse [17].

Heterogeneous catalyst is supplanting homogeneous catalyst because of hurdles in catalyst separation and waste disposal. [18]. The need for the neutralization step and subsequent disposal of neutralized salt in acid and base catalyzed reactions could be eliminated by replacing

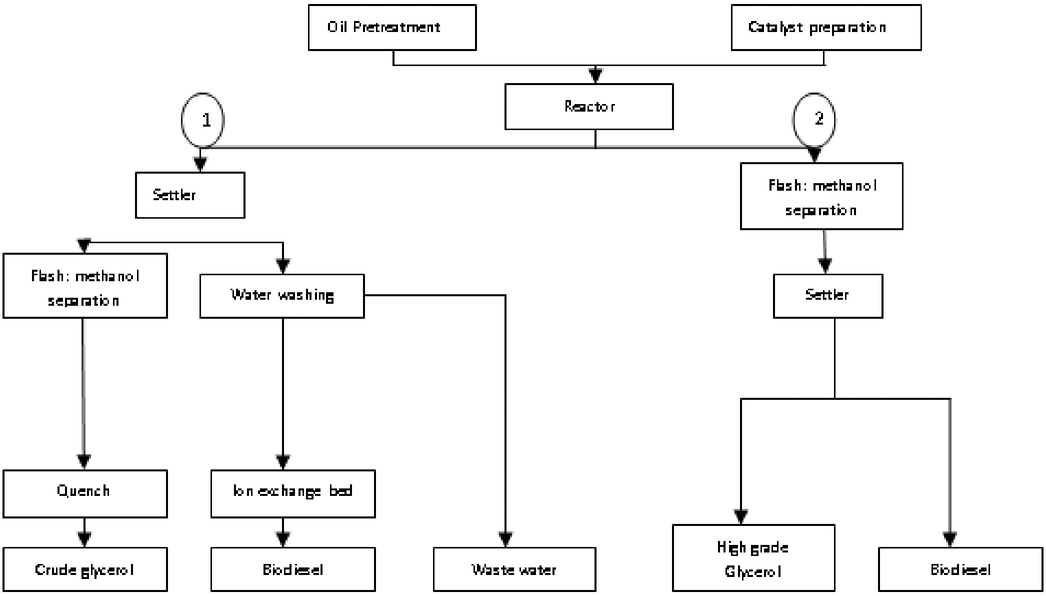

Figure 2. Biodiesel production path way by heterogeneous and homogeneous process.

a homogeneous acid or base by a heterogeneous catalyst. This trend to switch homogeneous catalysts with heterogeneous catalysts is part of the drive toward green chemistry which in turn minimize waste and eliminate the need for harmful reactants. Comparison of catalysis for biodiesel production is given in **Table 1** which reveals that many industrial processes now operate with solid acid catalysts [19]. But fewer processes operate with solid bases, as solid bases are less prevalent than solid acids [20].

Type	Homogeneous catalysts	Enzymatic catalysts	Heterogeneous catalysts
Advantage	Modest operation conditions Base catalyst give favourable kinetics: high activity and give high yield in short time Base catalysts are 4000 times faster reaction than acid catalyzed transesterification Basic methoxides are more effective than hydroxides Acid catalysts can be used for both esterification and transesterification simultaneously Acid catalyst are preferred for low grade oils and are insensitive to FFA and water	Very selective FFA are converted to biodiesel Low reaction temperature, insensitive to water Ease of separation products Higher yield than base catalysts Can be implemented as homogeneous or heterogeneous catalysts	Environmentally benign, noncorrosive, recyclable, fewer disposal problems Ease separation of products, higher selectivity, longer catalyst life Acid heterogeneous catalyze both esterification and transesterification simultaneously and insensitive to FFA and water Comparatively cheap Can be used in continuous fixed bed reactors
Disadvantages	Separation of waste problem after reaction Saponification, emulsion formation Catalyst reuse not possible Limited to batch type of reactors Basic catalysts are sensitive to the presence of FFA and water High production cost compared with heterogeneous type Acid catalysts are corrosive and give very small reaction rate Acid catalysts require higher molar ratio of methanol to oil, higher temperature, concentration acid and more waste from neutralization reaction	Expensive Enzyme is inhibited in the presence of methanol and may require additional supportive solvents to be used as a medium	Currently moderate conversion compare to high active basic homogeneous Mass transfer limitation due to the presence of three phase and need well mixing Basic catalysts require low FFA and anhydrous condition and pretreatments is required for high FFA feedstock High alcohol to oil ratio required, high temperature and pressure Acidic catalysts: low acid site concentration, low microporosity, and high cost compared with basic types
References	[17, 24–27]	[13, 17, 25, 28, 29]	[13, 17, 24, 30–33]

Table 1. Comparison of homogeneous, heterogeneous and enzymatic catalysis for biodiesel production.

The homogeneous catalysts, commonly utilized for commercial processes, have some disadvantages, such as they cannot recycle, large amounts of waste water is being produced, produce low grade glycerol as byproduct. In other hand, the heterogeneous catalysis offers easy production and purification process with reference to economic and environment. Truth is told, a few scientists have announced the potential monetary focal points of the heterogeneous reactant process over the option homogeneous one [21–23].

Cost of biodiesel production by heterogeneous catalysts is 4–20% less then homogeneous catalysts. Preparation of new long-lasting heterogeneous catalysts with anticipated physical and chemical properties is one of the most important and eye-attracting emphases of the latest studies. This is the main reason for the production of new heterogeneous catalysts which are suitable for pure biodiesel from different type of fatty acids that have been produced and appraised for FAME synthesis processes [24–26].

However, numerous additional thought-provoking issues endure to be resolved until highly proficient solid catalysts can be industrialized. However, with a specific end goal to build up a superior comprehension of impetus outline for the transesterification procedure, distinctive heterogeneous incentive utilized for biodiesel generation has been considered and examined in this article. It can be concluded that each of these catalyst properties have remarkable effect on the transesterification reaction. The application of catalysts is for various kinds of oils, reaction parameters and there for stability of the catalysts are also incorporated in this discussion. It can be inferred that each of these catalyst properties have significant influences on the transesterification process.

4. Biodiesel production with alkaline metal oxides and derivatives

4.1. Acid catalyzed transesterification

Homogeneous Lewis acid (H_2SO_4) and carboxylates ($PbCH_3COOH$) have been used as catalyst for biodiesel production from oil even if it have high concentration of FFA [13, 27, 28]. Several heterogeneous acids were also used and reported in literature (ion-exchange resin, metal oxides, heteropolyacids, etc.). However, three main drawbacks reported for the use of carboxylates catalyst are its work under high temperature and pressure ($T > 190°C$, $P > 20$ bar); purification of product is costly and not economical for industrial application. Supported sodium and potassium on larger surface area zeolite and alumina had given upto 85% conversion of fame which is still lower as compare to solid base catalyst [6, 29, 30].

4.2. Base catalyzed transesterification

Presently, there are various alkali-based catalysts have been utilized as homogeneous and heterogeneous transesterification. Base catalyzed transesterification is substantially less time consuming with respect to acid catalyzed transesterification and it is regularly used technique for commercial purpose. Numerous solid alkali base metal oxides and there substrate have

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
Li/CaO	3	60	100	[87]
Li-Al HTA	1	65	83	[88]
$LiNO_3/Al_2O_2$	1	60	91.6	[90]
H_2SO_4:NaOH	6	60	96.4	[39]
NaOH	1	60	97	[79]
Na/NaOH/γ-Al_2O_3	1	25–65	89	[85]
KOH/NaY	3	60	91.1	[64]
Na/NaOH	1	60	70	[91]
$NaOH/Al_2O_3$	2	60	65	[91]
$NaNO_3/Al_2O_3$	4	60	24.7	[90]
NaO/NaX	1	65	28	[85]
Ki/NaX	2	65	12.9	[6]
Al_2O_3/Na/NaOH	2	60	83	[91]
KI/SiO	8	70	90.9	[47]
KNO_3/Al_2O_3	6	65	84	[26]
K_2CO_3/MgO	2	70	99	[26]
$KAlSiO_4$ doped in Li	2 min	120	100	[92]
KOH/MgO	7	100	99.4	[93]
KNO_3/Al_2O_3	7	70	87	[47]
KI/Al_2O_3	3	60	96	[47]
KF/Al_2O_3	3	65	90	[66]
KOH/Al_2O_3	2	60	91.1	[60]
KCO_3/Al_2O_3	5	65	48	[47]
KNO_3/Al_2O_3	5	65	84–87	[94]
KOH/Al_2O_3		65	80.2	[47]
KOH/NaX		60	82	[85]
KX		60	82	[85]
KI/ZnO		60	72.6	[47]
Kf/ZnO		60	80	[47]
Ki/ZrO		60	78.2	[47]
Al_2O_3/KNO_3	7	60	83	[47]
Al_2O_3/KI	8		96	[16]
ZnO/KF	9	65	87	[47]

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
ZnO/Ba	1	65	95	[47]
Na/hydrotalcite with pure oil	8	60	88	[90]
Na/hydrotalcite with used oil	8	60	67	[90]
KF/hydrotalcite	5	65	92	[76]
KF/Ca–Al hydrotalcite	3	65	99	[77]

Table 2. Alkaline metal oxides catalysts used for the transesterification of oils.

been used for homogeneous catalyzed transesterification (**Table 2**). The benefit of alkali base catalysis requires a little amount in catalysis [8].

Basic metal alkoxide, hydroxide and sodium and potassium carbonates are utilized as a part of alkali-based catalyzed transesterification process [31–37]. With virgin vegetable oil, basic catalyst typically show high performance. If oil have critical amount of unsaturated fats then these free unsaturated fats respond with the basic catalyst to produce soap that inhibit glycerol that restrain the division of biodiesel, glycerin and wash water [16, 38]. NaOH or KOH are generally utilized as catalyst for transesterification of triglycerides at atmospheric pressure and temperature. Evacuation of these catalyst is in fact troublesome and it adds additional cost to the final product [39, 40]. It was reported in may researches that alkaline metal are less expensive than metal alkoxides, however the action of alkaline metal alkoxides (CH_3ONa for the methanolysis) is more dynamic as catalyst, then soluble metal hydroxides (KOH and NaOH since the previous) give high yield in short time than the last mentioned.

Homogeneous base catalyst catalyzed transesterification of oil into FAME fast. Freedman et al. observed that only 1% sodium hydroxide gives 94% conversion of oil at the temperature of 333 K for 0.1 h. The reaction is very vigorous between a plant oil and CH_3NaO, when alcohol is being used as solvent. It takes 2–3 min for complete transesterification of triglycerides at room temperature (293–298 K) by using CH_3NaO as catalyzed. While if we use homogeneous acid and base for transesterification, it takes 60–360 min at 303–338 K. Freedman et al. stated that only 1% sodium hydroxide gives about 94% of FAME [41–45].

However, water which is produced as byproduct caused during soap formation, as a result it becomes hard to recover catalyst and purification the products. Therefore, NaOH and KOH catalysts become slowly got replaced in coming eras by environmental friendly and long-lasting heterogeneous catalysts. However, these catalysts exhibit remarkable activity in esterification of FFA, but on the other hand they are not good in glycerides transesterification. Moreover a huge number of these catalysts get leached into product [46, 47]. In lot of cases, catalyst undergo fouling due to impurities in reaction mixture [48, 49].

Now a days, alkali oxides, alkaline oxide earth metals supported over large surface area are used for biodiesel production [50].

It was reported that alkaline metal are economical than metal alkoxides, but the activity of alkaline metal alkoxides (CH_3ONa for the methanolysis) is higher then KOH and NaOH, since the former gives high yield in short reaction time than the latter. In industries, biodiesel is synthesized, now a days, by transesterification of oils in presence of solvent along with NaOH and NaOMe. The advantage of the homogeneously base catalyzed transesterification is that the reaction of transesterification is very fast and performed at room temperature. Glycerol and FAME are being separated by settling after catalyst neutralization followed by purification of crude glycerol and biodiesel [51].

However, during the transesterification reaction, certain amount of water is produced as byproduct which causes ester hydrolysis along with soap, as a result it become hard to purify product by separating the catalyst. Therefore, it is assumed that heterogeneous catalyst will replace conventional homogeneous catalysts. Homogeneous catalysts show good performances in FFA esterification, while their performance for glycerides transesterification is not suitable. Another drawback is that this catalyst leached into reaction mixture and showed rapid deactivation [66, 67]. Alkali salts supported on metal oxide such as KOH/Al_2O_3 KF/MgO exhibited good results for transesterification [52, 53].

Recently, numbers of heterogeneous catalysts such as ion-exchange resin CaO, alkylguanidines, KI/Al_2O_3, $Na/NaOH/Al_2O_3$, ionic liquid and lipase have been reported in literature for catalyzed transesterification of vegetable oils in presence of methanol [54–63].

Gao et al. prepared KF supported on hydro calcite by using co-precipitation techniques. It was observed that the formation of $KMgF_3$ and $KAlF_4$ enhance catalytic activity of catalyst. KF/hydro calcite gives 92% fame yield with 12:1 (alcohol to oil) molar ratio in 5 h reaction time at 65°C.

Gao et al. also study the percentage activity of KF supported at Ca–Al hydro calcite. He observed that catalytic activity is very satisfactory, about 99.7% yield can be obtained. It was assumed that this high output of 99.74% was due to the new crystal phases $KCaF_3$, $KCaCO_3F$ and $CaAl_2F_4(OH)$ [64, 65]. KI loaded at mesoporous silica has been used as heterogeneous catalysis for conversion of TG in to FAME. It was observed that increase in reaction temperature and time enhances yield up to 90.09%. This highest yield ware obtained at 70°C, 15 wt.% of KI, within 8 h by using 5.0% by weight of the oil [34].

It was reported that biodiesel could be effectively produced by two-step process with ultrasonic radiation in less time. Xin deng in 2010 investigated two-step esterification and transesterification of jatropha oil in ultrasonic reactor. He used NaOH and H_2SO_4 as catalyst at 60°C the reaction temperature. It was observed that 96.4% yield can be obtain just in 1.5 h by esterification of oil with H_2SO_4 for 1 h and then subsequent transesterification by NaOH for 0.5 h [66].

Umer et al. used alkali catalyst for transesterification of sunflower oils to alkyl esters. They get 97.1% yield at 60.8°C by using 1%W catalyst. However, he observed that increase in catalyst concentration above 1 wt% has no effect at yield but it could add extra costs of production [67]. Sulfuric acid or hydrochloric acid used as homogeneous catalyst does not produce soap but the main problem in using these catalyst is corrosiveness and downstream purification and separation of product is costly and not economical. On the other hand use of heterogeneous acid catalyst can overcome this problems and could reduce economic issues and better profitability of the biodiesel production process [68–70].

Hamed et al. reported the use of RSM response surface methodology as a statistic tool for study instruction among experimental variables and optimizing reaction condition [71]. Jeong et al. had reported 98% conversion of fame [54]. He used RSM to study animal fat transesterification at 65°C for 20 min, KOH (1.25 wt% 7.5:1 molar ratio of methanol and fat) [72].

According to literature, the production of methyl ester with extraordinary yield not only the choice of catalyst but also experimental conditions should be concerned, optimization of some reaction parameters and the application of those parameters are essential. Solid base catalyst synthesized by loading KNO3 aluminum oxide calcinated at 773 K for 5 h gives only 75% conversion by using 3.5% catalyst. While same method was used by Supper et al. in 2004 for preparing Na/NaOH/γ-Al_2O_3 catalyst. Supper et al. reported high conversion of soybean oil by using 1–3% w at 25–65°C and 1–3% w/w catalyst was found to attain conversion rate that was more then two orders of magnitude [73].

Heterogeneous catalysts possessing dual acidic and basic sites had been examined which could simultaneously esterify FFA and transesterify triglycerides (TG) to biodiesel [74]. Catalytic activity of Li/CaO has been stated by Watkins et al., where 100% FAME has been achieved 3 h at 60°C [75]. Shumaker et al. reported that Li-Al HTA was found to work efficiently and gives 65% yield only in 1 h reaction time [76]. Hernandez et al. used incorporated sodium hydrotalcite in Mg–Al mixed oxide. Sodium was incorporated as sodium acetate in Mg–Al mixed oxide calcite at 500°C for 8 h. He found that incorporation of sodium enhances the activity and it works at a low temperature (60°C) and with pure and used soybean oil. This catalyst gives 88% conversion for pure soybean oil and 67% for used soybean oil [77].

5. Biodiesel production with alkaline earth metals and metalloids

Several attempts had been made in search for promising solid base alkali earth oxides catalyst such as CaO, SrO and BaO [78–81]. Magnesium oxide and salts based catalyst have been examined in past by different research. Early research has not showed satisfactory output, but far ahead on CaO and MgO were modified to acquire 99% yield and conversion of biodiesel. It was observed that preparation method, calcination and time of reaction and temperature and oil to methanol molar ratio have a great impact at biodiesel yield. Wang et al. used nano-magnesium oxide for transesterification of vegetable oil at 250°C reaction temperature for 0.3 h reported biodiesel yield was 98% [82].

MgO is very reactive at supercritical reaction condition giving upto 99% methyl ester. It was observed that reaction is finished in 10 min at 300°C by using methanol to oil molar ratio of 39.6:1. [83, 84].

Venkat Reddy et al. used noncrystalline CaO for the conversion of poultry fat triglyceride into biodiesel. He observed 100% conversion of fame at 25°C with temperature with 1 mmol of 1 wt% catalyst). The reaction was performed for 7 h by using 70:1 molar ratio of methanol to triglyceride [85].

Li et al. used MgO supported silica as a solid heterogeneous catalyst at 220°C for 5 h reaction time gives 96% biodiesel yield [80]. Additionally, magnesium oxide supported at high surface are metal like lanthinum, zirconium and aluminum have been screened for biodiesel production. Babu et al.l reported that magnesium oxide supported at zirconium oxide showed 100% yield in 30 min just at 65°C reaction temperature [86, 87].

Furthermore, Ngamcharussrivichai et al. used $CaMg(CO_3)_2$ as a catalyst for esterification of plant oil. They remarked that under 60°C in 3 h, the catalyst yielded optimum biodiesel yield of 99.9% [88, 116]. Takagaki et al. and Li et al. studied catalytic activity of magnesium- and aluminum-based metal oxides such as Mg-Al HTA, Mg/Al/Zr, Mg/Al HT, Mg/Al and MgO/Al_2O_3 in the methanolysis of plant oil. Batch reactor was used for reaction for different combination at 65–130°C. The reaction time was from 1 to 4 h, resulting in yield of 65–90.5%. It was observed that Mg-Al HTA show high durability, ester product more than 90.5% and can be effectively used as heterogeneous base catalysts [89–91].

Serio et al. described the kinetics of MgO heterogeneously catalyzed methanolysis of soybean oil by using MgO/Al_2O_3, MgO/Cao as catalyst. He observed 92% yield in the transesterification of soybean oil at 60°C within 2 h reaction time MgO/Cao catalyst [92]. Ochoa et al. and Liu at et al. used CaO as heterogeneous catalyst. It was observed that when CaO was calcination at 550°C temperature, 98% yield can be obtained at 60°C within reaction temperature and in 2 h reaction time [93, 94].

Nakatani et al. had used oyster shell as CaO source. He obtained 96% conversion of fame at 65°C for 4h reaction time. While Boey et al.l used mud crab shell as heterogeneous catalyst for transesterification of palm olein, the results showed 98% yield in 150 min at 65°C reflex temperature. Sarin et al. used seashell and eggshells as CaO source for TG conversion from different feed stocks. All this catalyst shows 98% FAME yield only in 60 min of reaction time [59, 95–97].

Albuquerque et al. used mesoporous silica supported by CaO as solid base catalyst for biodiesel production and gets 95% conversion in 5 h reaction at 60°C reaction temperature [98].

$CaMg(CO_3)_2$ and $Ca(NO_3)_2/Al_2O_3$ were used as solid base catalyst by Ngamcharussrivichai et al., Benjapornkulaphong et al., for palm kernel oil transesterification at 60°C reaction temperature. They get 99.9 and 94% yield, respectively, after 3 h reaction time [26, 88]. Summary of alkaline earth metals and metalloids is given in **Table 3**.

Kouzu et al. [98] investigated the use of CaO as catalyst in a batch reactor at methanol reflux temperature for 2 h and achieved 93% biodiesel production. Kawashima et al. also discussed calcium oxide activity as catalyst along with its derivatives such as $Ca(OCH3)_2$, $CaTiO_3$, $CaMnO_3$,$Ca_2Fe_2O_5$, $CaZrO_3$ and $CaO–CeO_2$ for rapes oil transesterification of rapeseed oil. CaO were activated by methanol at 25°C for 1.5 h to increase basic strengths. The reaction mixture was refluxed for 10 h at 60°C. It was observed that $Ca(OCH_3)_2$ gives 98% yield among other derivatives the reason for highest yield of $Ca(OCH_3)_2$ is it had a remarkable basic strength in the range of 11.1–15.0 and these results demonstrated the reasons why $Ca(OCH_3)_2$

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
Mgo	0.3	250	98	[99]
Mgo/SiO_2	5	220	96	[125]
MgO-$MgAl_2O_4$	10	65	57	[99]
Mgo-La_2O_3	2.2	25	100	[104]
MgO-ZrO_2	0.5	65	100	[103]
MgO/CaO	1	60	92	[105]
Mg-Al HTA	4	65	90.5	[125]
Mg/Al/Zr	1.5	70	74	[91]
Mg/Al HT	1	100	75	[91]
Mg/Al	1	130	65	[91]
MgO	1.5	75	12.1	[109]
MgO-SBA-15	5	220	96	[125]
MgO/Al_2O_3	3	180	92	[108]
MgO/Al_2O_3	2	65	66	[108]
MgO/Cao	1	60	92	[108]
Mgo-CaO	2	60	92	[114]
CaO	1.5	75	91.1	[109]
CaO	2	65	98	[110]
Oyster shell	4	65	96	[111]
Mud crab shell	2.5	65	98	[112]
Egg shell	2	60	90	[113]
Cao/SiO_2	5	60	95	[114]
$CaMg(CO_3)_2$	3	60	99.9	[105]
$Ca(OCH_3)_2$	10	65	98	[115]
$CaTiO_3$	10	60	79	[115]
$CaMnO_3$	10	60	92	[115]
$CaFe_2O_5$	10	60	92	[115]
$CaZrO_3$	10	60	88	[115]
$Ca(NO_3)_2/Al_2O_3$	3	60	94.3	[39]
$CaCeO_3$	10	60	89	[115]
SrO	0.5	65	95	[96]
$Sr(NO_3)_2$/ZnO	5	65	96	[119]
CaO/ZnO	0.5	65	93.5	[105]

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
Mg–Al hydrotalcite	9	65	67	[6]
Mg–Al–CO_3hydrotalcite	3	180–200	99	[122]
Mg–Al hydrotalcites	4	65	90	[124]
Mg–Al hydrotalcite	6	100	96	[124]
Mg–Co–Al–La	5	200	97	[125]

Table 3. Alkaline earth metals and metalloids catalysts used for the transesterification of oils.

exhibited a greater catalytic activity than CaO and $Ca(OH)_2$ for others the resulting yield is from 79 – 90%. $CaZrO_3$ and CaO–CeO_2 exhibit high durability and it can be used in future as heterogeneous catalyst [99].

Application of strontium oxide- and nitrate-based catalyst is also reported in literature, there reported order of activity observed to be BaO > SrO > -CaO > MgO [100].

In past, the activity of MgO, CaO and SrO were are studied by different researcher for biodiesel productions and the observed conversion efficiency of followings ranging from 90 to 95% Liu et al. reported the use of SrO for transesterification of soybean oil. It is examined that SrO gives 95% yield in just 30 mins reaction time and at 65°C temperature as reported by Liu et al.[86, 101–103].

The catalytic efficiency of activated $Sr(NO_3)_2$/ZnO was also examined by Yanz et al., the catalyst was prepared by using 2.5 mmol of strontium nitrate $Sr(NO_3)_2$/g on ZnO by wet impregnation process followed by calcination at 600°C for 5 h. Transesterification of soybean oil was carried out in batch reactor at 65°C 12:1 methanol:oil molar ratio. Under this condition, reaction was complete in 5 h by giving 96% conversion of FAME [104].

Alkali metal hydrotalcite is another group catalyst which has been used extensively for triglyceride conversion into FAME. Hydrocalcite are important as their acidic and basic properties can be monitored by fluctuating their composition and hence can be used for fatty acid methyl ester production. Helwani et al. and Zabeti reported use of hydrotalcites as catalyst for the production of biodiesel. Magnesium-based hydrotalcite are common and mostly synthesized by co-precipitation method [24, 50, 105].

Most commonly hydrocalcite has three groups of basic sites, like weak basic site(OH), medium basic site (oxygen in metal oxide) and strong basic sites (O_2 anions) present in hydrocalcite [106].

Hydrocalcite possesses large pore than the normal metal oxides, the large pro size of this hydrocalcite results in higher catalytic then normal common metal oxides. Magnesium and aluminum-based hydrocalcite have been reported in literature. Mg-based hydrocalcite showed optimum activity from 350 to 600°C calcination temperature. Xie et al. reported Mg-Al-based hydrocalcite for transesterification of plant oil. It was observed that at high calcination temperature catalyst become deactivated. The hydrocalcite calcinated at 500°C temperature for 8 h, 67% conversion of fame ware reported at 9 h reaction time with methanol to oil ratio of 15:1. While Barakos reported 99% conversion of oil by using Mg–Al–CO_3 hydrotalcite as catalyst. He has calcinated Mg–Al–CO_3 hydrotalcite calcinated at 350°C temperature for 6 h and methanol to oil molar ratio of reaction was 6:1 at 200°C reaction for 3 h [6, 91, 107–110].

6. Biodiesel production from transition metals, lanthanide actinides and their derivatives

Transition metal oxides and chlorides are widely examined in several chemical reactions concerning their activity in plant oils transesterification. Transition metal complexes are also been studied in literature as active materials for esterification reactions. [111].

In literature, the best reported catalytic activity and strength were detected for the $CaZrO_3$ and $CaOCeO_2$ heterogenized catalysts. It is found that Zr and Ce catalyst endured highly active up to 7th, and gave up to 80% yield in methyl esters were obtained within in 60 min reaction at 60°C by using 6:1 oil to methanol ratio. Possessing of variable Lewis acidity, metal oxidation state and ion radius size makes transition metal oxides and Oxo salts more suitable for transesterification catalysts. Due to their acidic properties, a lot of transaction metals like zinc, zirconium and titanium oxide are best among the transition metal oxides which are famous and broadly used for biodiesel synthesis. Past molybdenum- and tungsten-containing solids have been accounted in various reactions in which the acidity profile assumes essential parts in isomerization, cyclic alkene oxidation, alcohol dehydration and plant oils transesterification [16, 29, 112].

There have been a few research provided details regarding the utilization of sulfated zirconia as a strong catalyst for triglyceride conversion of various oils, because of its strong acidity it was discovered that the causticity is advanced when the surface of this zirconia metal contains anions of sulfate and tungstate. Catalytic activity of SO4 2-/ZrO2 was studied by Lam et al., and WO_3/ZrO_2 was studied by Sunita. It was accounted for that the specific surface area and active site number assume to be an essential part in the catalytic action.. Sulfated zirconia showed more activity in less time for conversion of oil into biodiesel than tungstated zirconia [113, 114].

Zinc(II) Shiff base complexes have been reported by martino as catalysts for biodiesel production from waste oil. He demonstrated that zinc(II) species can work in mild condition for catalyzing the triglyceride conversion of plant oil and activity could modified by a fine choice of the anions of the metals on the ancillary bidentate ligand. Homogeneous acid catalyst was widely studied in literature. Despite they have lower activity, yet strong acid catalyst have been utilized as a part of numerous modern commercial process since they contain a variety of acid sites with various quality of Bronsted or Lewis acridity. Nafion-NR50, tungstated, sulfated zirconia and zirconia possesses sufficient acid site and had been used in transesterification. Nafion were found to be the best, among these catalyst, because of their acid Nafion has hindrances of high cost and lower activity contrasted with liquid acids so it is not exceptionally practical catalyst for commercial application [115–117].

Most transition metal are expensive and heterogeneous catalyst of these metal need high temperature and pressure to achieve high conversion of oil. It was found that pure and mixed ZnO exhibits the conversion efficiency ranging from 90 to 95%. while strontium loaded at fly ash ZnO-La_2O_3 and zinc aluminate have been reported. WO_3/ZrO_2 and $Sr(NO_3)_2/ZnO$ have been used for the canalization of plant activity of zirconium and tungsten oxide investigated by Lopez et al. had found that the calcination temperatures impact on synergist properties of catalyst, concluded that more strong catalyst could be acquired after calcination at 800°C (with the development of Bronsted acid sites centralization of 161 μmol/g). At 2.5 h reaction time at 200°C reaction temperature, the methyl ester yields within the sight of WO3/ZrO2/MCM-41 were 85% [38, 111, 118–120].

A variety of transition metal-based solid acids SO_4/ZrO_2–Al_2O_3 SO_4/ZrO_2, WO_3/ZrO_2, SO_4/TiO_2, and Nafion had already been tested for esterification and their catalytic efficiency for esterification and transesterification of free fatty acid and triglycerides [112, 121–126].

According to the literature, microwave heating along with barium, alumina, silica, zinc aluminate and zirconium-based catalysts are good catalyst for biodiesel production (Portnoff et al., 2005; Bournay et al; Ondrey et al., 2004). By using different approach, utilization of sulfated transition metal oxides such as SO_4/TiO_2, SO_4/ZrO_2, SO_4 2-/SnO_2 + Fe_3O_4 and SO_4/SnO_2 is also reported in literature as a good catalyst [116]. Zhai et al. reported 90% activity of SO_4 2-/SnO_2 + Fe_3O_4 catalyst at 60°C reaction temperature for 8 h reaction while Lam et al. reported 90% activity of SO4 2-/ZrO2 catalyst 200°C in 1 h reaction time [113, 127–129]. In acid catalyzed reaction, heteropoly tungstate was found as active catalysts for pure and waste oil. Zirconia (ZrO_2), silica (SiO_2) and alumina (Al_2O_3) support could be used to produce heterogeneous HPAs. HPAs supported at Cs+, NH4+ are also very active and useful as acid catalyst. Chai et al. who investigated the activity of Cs25H3PW12O40 has reported 96% conversion of FAME in 65°C reaction for 1 h [115, 116, 129–131]. In previous research, the activity of acids fall in CsHPW >20%WO_3/ZrO_2 > 20%HPW/Al_2O_3 > 20%HPW/ ZrO2 > 20%HPW/SiO2 order [47, 131–134].

Zirconium, hafnium and antimonium-based transition metal catalyst were also being studied by researchers in past for transesterification. Porous zirconia, titania and alumina microsphere stabilized chemically, thermally and mechanically have been investigated by Clayton et al. [30]. Yan et al. tested Fe–Zn catalyst methanolysis of vegetable oil (using 1:15 molar ration of methanol at 170°C, by using catalyst in amount of 3 wt.% showed TG conversion more than 99% within 5 h of reaction). It was assumed that the catalyst activity was endorsed due to the Lewis acid active sites of probably Zn2+ on the surface of catalyst [135].

Serio et al. studied solid acid vanadium phosphate catalyst for biodiesel synthesis, it was observed that the methyl ester yields reached 80% at 150°C within 60 min using 0.2 wt.% of the catalyst under and 1:1 of alcohol/oil molar ratio. However, the catalyst could be recycled after regeneration at high temperature [15].

Lee and Shiro used ZnO–La_2O_3, which combines acid (ZnO) and base sites (La_2O_3) for transesterification of oil they got high conversion of 96% TG in 180 min. Yan el al. used calcium oxides modified with lanthanum (La_3O_3/CaO) and observed that this catalyst is particularly effective for transesterification at 65°C and attain a remarkable yield exceeded 94.1% at a reaction time of 1 h [136, 137]. Summary of biodiesel production from transition metals, lanthanide actinides is given in **Table 4**.

Thitsartarn et al. examined the use of CeO_2-CaO mixed oxides as catalysts for biodiesel production. They had studied several reaction parameters carried out at optimal transesterification. They concluded that CeO_2-CaO mixed oxides gives best catalytic activity at 85°C in 2 h with 97% yield [138].

Catalyst	**Reaction time in hour**	**Reaction temperature, °C**	**Yield, %**	**Reference**
ZnO/CaO	1	60	94.2	[105]
ZnO-Al_2O_3	0.5	200	99	[153, 154]
ZrO_2	1	200	64.5	[131]
SO4 2-/ZrO_2	1	200	90	[128]
SO4 2-/TiO_2	1	20	40	[127]
SO4 2-/SnO_2	3	180	65	[155]
SO4 2-/SnO_2+Fe_3O_4	8	60	90	[142]
SO4 2-/SnO_2+Al_2O_3	3	180	80	[128]
SO4 2-/ZrO_2-TiO_2/La^{3+}	5	60	95	[128, 156]
ZrO_2/Al_2O_3	Continuous run	250	97	[81]
WO_3/ZrO_2	5	200	97	[129]
TiO_2/ZrO_2	Continuous run	250	95	[16]
MnCex	5	140	87	[157]
WO_3/ZrO_2/Al_2O_3	Continuous run	200	90	[158]
WO_3/ZrO_2/MCM-41	2.5	200	85	[159]
H3PW12O40/ZrO2	10	200	77	[130]
H3PW12O40/Ta2O5	24	65	65	[160]
Cs25H3PW12O40	1	65	96	[131]
MnO-TiO	0.35	260	92	[161]
Fe-Zn	5h	170	99	[150]
$CaMnO_3$	10	60	75	[75]
Al_2O_3/PO4 3-	5	200	69	[162]
Al_2O_3/ZrO_2/WO_3	20	75	85	[163]
$VOPO_4{\cdot}2H_2O$	1	150	80	[15]
La_3O_3/CaO	1	60	94.3	[126]
CeO_2-Cao	2	85	97	[164]

Catalyst	Reaction time in hour	Reaction temperature, °C	Yield, %	Reference
La_2O_3	2	200	97.5	[165]
Eu_2O_3/Al_2O_3	8	70	63.2	[166]
Sulphonated carbon	2.5	260	90	[167, 168]
Sulphonic/SiO_2	5	150	60	[169]
Sulphonic acid/SBA-15	8	180	96	[170]

Table 4. Transition metals, lanthanide actinides based catalysts used for the transesterification of oils.

Bancquart et al. investigated the activity of La_2O_3 for glycerol transesterification to investigate the relationship between activity and basicity. It was reported that at high temperature of 200°C, the fame yield was 97.5% in 2 h. On the other hand, both these metals are very expensive and not economical for the production of biodiesel [139].

Li et al. studied the activity of a novel solid super base of Eu_2O_3/Al_2O_3 complex for transesterification triglycerides with alcohols, he observed 63.2% yield of FAME in 8 h reaction at 195°C [140].

Currently, due to the believe that solid base catalyst are more environmental friendly and could replace acid catalyst, researches are focusing at the synthesis of novel, stable and economical solid acid catalysts for transesterification reaction [68].

7. Bio catalyst

The utilization of lipases (triacylglycerol acyl hydrolases) as biocatalyst for the production of biodiesel has become more appealing since the ease of glycerol recovery (byproduct) and purification of FAME [141]. Plethora of research reports demonstrated the used of lipase as a catalyst for production of biodiesel; however, this technology has not received much commercial attention due to the high cost of enzyme [141]. To overcome the drawback of free lipases, recent research efforts have been made toward the immobilization of lipases on solid support (such as zeolite, Celite, silica gel, inorganic nanoparticles, acrylic resin and textile membrane etc.) which not only reduce the cost in terms of reusability but also increases the number of available active sites [142]. Crosslinking, covalent bonding, adsorption and entrapment are the most common approaches that are involved in immobilization of lipase onto the solid support [143–145].

Casimir et al. stated that enzymes can be used as biocatalyst for transesterification reaction, for example, Candida antarctica lipase many enzyme like *Pseudomonas fluorescens* Rhizomucor miehei and Chromobacterium viscosum [146] and Rhizopus oryzae lipase [147] have been used as enzyme catalyzed transesterification reactions. Immobilized lipase have been used by Tan et al. for biodiesel synthesis covalent bonding, crosslinking, encapsulation, entrapment and adsorption have also being reported in literature to rise the stability of lipase in FAME synthesis.

It was investigated that recombinant DNA technology can be used to produced large quantities of lipases. Casimir et al. recommended that the utilization of immobilized lipase may diminish the general cost of biodiesel production and lower downstream preparing issues and this is ecologically suitable with respect to other conventional methods. Watanab et al. built up a three-advance methanolysis process for biodiesel synthesis by utilizing Candida antarctica lipase for persistent generation of biodiesel fuel from vegetable oil. It was observed that 95% yield can be gotten by utilizing 4% immobilized Candida lipase as a catalyst at 308°C reaction time in a 20-or 50-ml screw-topped vessel with The 1:2 molar amount of methanol against the aggregate unsaturated fats. Hideki et al. additionally reviewed utilization of enzymatic-catalyzed transesterification to reduce problems associated with homogeneous catalysis. The author revealed the use of immobilized antarctica lipase (Novozym-435) for high FFAs feed stock for biodiesel production [147].

Additionally, Shah et al. used lipase for synthesis of biodiesel from jatropha oil. He used solvent-free system for screening of pancreas porcine, C*andida rugosa* and Chromobacterium viscosum for the production of biodiesel. 0.5 g of jatropha seed oil in a vessel having 1:4 molar ratio of ethanol and 50 mg of enzyme was introduced and incubated at 40°C with constant stirring at 200 rpm. They observed 62–71% yield of ester by free-tuned enzyme of lipase (Chromobacterium viscosum) in a process time of 8 h at 40°C.

8. Conclusion

The generation and utilization of biodiesel have seen a quantum bounce in the current century because of advantages related to its capacity to relieve ozone depleting substance (GHG). There is a huge number of non-edible plants oil use for biodiesel synthesis through transesterification of fats, a stable catalysts in terms of, catalytic life, recyclability and lower cost are critical as these directly affect the general cost of the overall process. The different choices of heterogeneous strong catalysis were accounted for the particular research results of transesterification on heterogeneous catalysis majorly centered on examining the suitable oil source, methanol to oil molar proportion, and assessing the accessibility of catalyst. Unlike homogeneous, heterogeneous catalyst are cost effective and environmental friendly can easily be reused and recovered.

As lower reaction rate and side reactions make the use of catalyst limited, solid acidic catalysts for biodiesel synthesis. Solid acid catalyst are very useful in term or their ability to work in one step and are able to convert oils with high amount of free fatty acids (FFA) into biodiesel.

Presence of water in feedstock obstructed the activity of the basic heterogeneous catalyst. Be that as it may, strong base work quicker and gives higher TG conversion then an acid catalyst. Amendment of the catalyst by monitoring different aspects makes catalyst more suitable for transesterification and makes it more energy intensive. Mutual esterification and transesterification could be simultaneously done by using acid-base catalysts. On the other hand enzymatic catalysts are highly promising but enzymes carried out transesterification reaction in very slow rate. On the other hand heterogeneous catalyst work smoothly when reaction temperature, pressure and molar ratio of alcohol to oil is considerably high.

Efficiency of catalyst also depends upon calcination time and temperature. Calcination leads to alteration of the starting reactant into new compound possessing high catalytic activity then original compound. It is because calcination increases basicity, pore size and pore volume specific surface area and active site concentration could at catalyst.

Only few researches specify the industrial level production of FAME by implementing the heterogeneous catalyst method. In past, a lot or researches were done to explore and exploit synthesis and use of novel heterogeneous catalysts in the production of FAME. Some of the reasons for the recent growth and development of heterogeneous catalysts include among others are biodiesel yield of 98 wt% and simplicity in catalyst separation process, high-purity byproducts, less cost of separation and low energy.

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Chapter 7

Ultrasound Methods for Biodiesel Production and Analysis

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Abstract

Ultrasonic techniques have been widely used in biodiesel production, since the acoustic cavitation is a phenomenon capable of accelerating potentially the transesterification reactions. The equipment employed in such approach was simply equipment available in any regular laboratory of chemistry. Further developments introduced the ultrasound as an important tool to produce biodiesel. The main advantage is increasing the conversion of esters at reduced reaction times, with significantly lower production costs. As a method for characterization and analysis of materials, ultrasound has been used since several decades ago. However, ultrasonic analytical methods based on metrological principles are fairly recent investigated. Using ultrasound as physical principle to interrogate biodiesel is a promising field of research, with some remarkable outcomes produced so far. The aim of this chapter is to demonstrate advances of using ultrasonic techniques in production and characterization of biodiesel, as well as an appraisal of the current technology status, and provide insights into future developments.

Keywords: ultrasound, metrology, chemical kinetics, real-time reaction monitoring, biodiesel production

1. Introduction

Biodiesel production has achieved increasing importance worldwide due to the potential depletion of oil reserves and the environmental impacts caused by gases of fossil fuel. Biodiesel is a renewable fuel composed of alkyl esters of fatty acids, which are derived from triglycerides (vegetable oils or animal fats). There are several routes for biodiesel production, but the most common is the transesterification, which is the reaction between triglycerides and a short chain alcohol in the presence of a catalyst, producing esters and glycerol [1].

The 3:1 molar ratio of alcohol/triglycerides is required for the complete transesterification. However, an excess of alcohol is usually added to displace the equilibrium of the reaction, ensuring the ester formation completely. Besides the molar ratio, there are other reaction variables such as temperature, type and quantity of catalyst and type of agitation, among others, that will affect the equilibrium and biodiesel production.

The conventional biodiesel production method uses mechanical agitation and high temperatures to facilitate mass transfer between the immiscible reagents (triglycerides and alcohol). Alternative methods were developed with the aim of increasing ester conversion with the decreasing of the reaction time [2].

The use of ultrasound in biodiesel production has gained emphasis over the years [3–6], since ultrasound can promote homogenization between the reagents through acoustic cavitation. Acoustic cavitation is the growth and violent collapse of cavitation bubbles, which, when exploded, generate an increase in temperature in the reaction medium. This phenomenon is able to increase the speed of the reaction, reduce the amount of catalyst and reduce the reaction time from hours to minutes [7]. In most of the cases, the reactions use simple ultrasonic baths or ultrasonic probes operating in the frequency range between 20 and 50 kHz and high output power (typically over 200 W). New developments introduced biodiesel as an important tool in biodiesel production, using more economical equipment and demonstrating satisfactory conversion values using powers as low as 50 W or even lower [8].

Not just as a way to accelerate the transesterification, the ultrasound is being studied as a tool to monitor the biodiesel reaction [9]. The use of low-power ultrasound to determine the end of the reaction in an inline method cannot just save time and energy, but also it can potentially avoid waste.

As a method for material characterization and analysis, ultrasound has been used for several decades in several applications. However, ultrasonic analytical methods for biodiesel production are quite recent. The aim of this chapter is to demonstrate advances of using ultrasonic techniques for the production and the characterization of biodiesel, as well as an appraisal of the current technology status, and to provide insights into future developments.

2. What is ultrasound?

2.1. Ultrasound basic concepts

According to IEC 60050-802:2011 [10], ultrasound is defined as “acoustic oscillation whose frequency is above the high-frequency limit of audible sound (about 20 kHz)” and has no difference from sound concerning its physical properties, except in that humans cannot hear it. In large spectrum, ultrasound devices operate with frequencies from 20 kHz up to several gigahertz. The most relevant physical properties are summarized hereafter.

Propagation direction. Considering ultrasonic waves propagating through matter, energy is transferred from one location to another, but this energy is not associated with mass transfer. Based on the relation between the wave propagation direction and the motion direction of the particles constituting the medium, the waves can be divided in two propagation types: longitudinal and transverse. In the longitudinal propagation, the direction of displacement for the medium's particles is parallel to the direction of wave propagation (**Figure 1**, top). For the transverse propagation, the direction of displacement for the medium's particles is perpendicular to the direction of wave propagation (**Figure 1**, bottom). Despite that this basic division is frequently used in ultrasound, it is important to have in mind that there are also wave types for which the direction of motion for the medium's particles is not fixed relative to the wave propagation direction. In surface waves, for example, the angle between the two directions changes continuously [11].

Wave front geometry. Another important classification is based on the wave front geometry. Using this approach, waves can be divided into planar, in which the wave front is located on a plane that propagates in space and spherical ones that propagates symmetrically around a reference point (**Figure 2**). However, in practice, intermediate type of waves can be found over the ultrasonic beam transmitted. Considering a disc-shaped transducer, planar wave characteristics are observed near the transducer particularly around its central region. However, as far as the propagation is from the transducer, the wave will have more and more spherical wave characteristics. Similarly, as the ratio between the transducer diameter and the wavelength is decreased, the same behavior is observed [11]. The general case is defined by Huygens' principle, in which

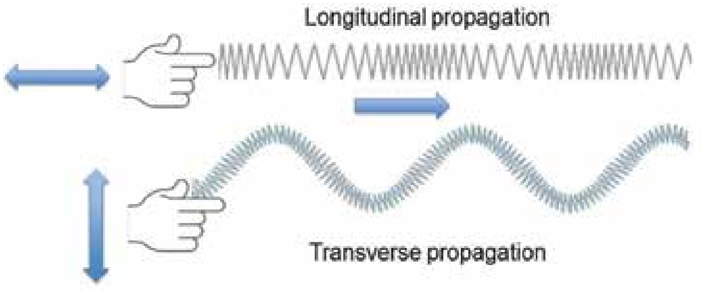

Figure 1. Example of longitudinal (top) and transverse (bottom) propagation.

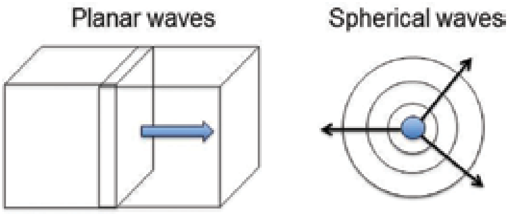

Figure 2. Diagram representing planar (left) and spherical (right) waves.

any wave source (or wave front) can be considered as an infinite collection of spherical wave sources (**Figure 3**).

Diffraction. It is a phenomenon by which a sound wave is changed in direction by an obstacle or other heterogeneity in the medium. This phenomenon is enhanced for wavelengths that are relatively long relative to the geometry of the obstacle [11]. The diffraction phenomenon is illustrated in **Figure 3**.

Interference. An important phenomenon occurs when two waves encounter each other in a propagation medium. It is called interference. The interference can be constructive, when the amplitudes of two waves enhance each other, or destructive, and their amplitudes attenuate each other. After passing through each other, if nonlinear effects are negligible (see "Nonlinear Propagation" section), the two waves proceed as though nothing has happened. Summarizing, within interference zone the result amplitude is the sum of all the interacting wave amplitudes, which is defined as the "superposition principle" [11].

Characteristic impedance of a medium. Product of the equilibrium density (ρ) and speed of sound (v) in a medium, as represented in (1). It can be understood as a measure of the impediment caused by a medium to the movement induced by a pressure applied to it. It is noteworthy that for a plane acoustic wave propagating in a non-dissipative medium, the specific acoustic impedance (at a specified surface, quotient of sound pressure (P) by volume velocity (U) through the surface) relative to this wave is equal to the characteristic impedance of the medium [11]:

$$Z = v \cdot \rho = \frac{P}{U} \tag{1}$$

Reflection and transmission. Given an incident wave at the interface between two media with different acoustic impedances, part of its energy is reflected, and part is transmitted to the adjacent medium, with or without a change in direction. The proportions of reflected (E_R) and transmitted (E_T) energies, relative to energy of the incident wave (E_I), can be estimated from the reflection (R) and transmission (T) coefficients. Eqs. (2) and (3) define these coefficients

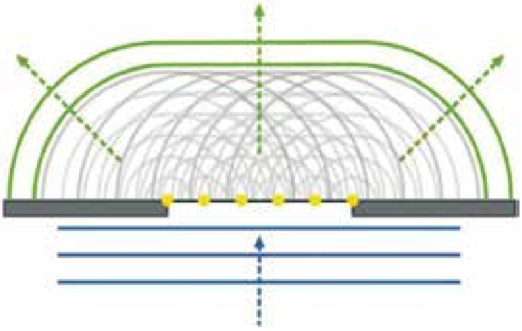

Figure 3. Schematic demonstration of Huygens' principle (left). Demonstration of the diffraction phenomenon for a planar wave propagating from the bottom toward the top and passing through a slot (right).

when the incidence at the interface of the media is perpendicular to the direction of wave propagation [11]:

$$R = \frac{I_R}{I_I} = \frac{(Z_2 - Z_1)^2}{(Z_2 + Z_1)^2} \tag{2}$$

$$T = \frac{I_T}{I_I} = \frac{(4 \cdot Z_2 \cdot Z_1)}{(Z_2 + Z_1)^2} \tag{3}$$

Propagation velocity. The propagation velocity of the wave in a medium (v) is dependent on the density and modulus of elasticity of the medium and can also be represented by the product of the ultrasonic frequency by wavelength as presented in (4):

$$v = \left(\frac{K}{\rho}\right)^{\frac{1}{2}} = f \times \lambda \tag{4}$$

in which f is the frequency of the ultrasound, λ is the wavelength, K is the modulus of elasticity (rigidity) and ρ is the density of the propagation medium [11]. Propagation velocity is named as speed of sound as well. Depending on some medium and the sound characteristics, phase velocity and group velocity are quantities more usable to physically describe the waveform displacement per unit of time.

Attenuation. In a planar wave propagating in a free field, the main causes of attenuation (loss of energy due to the distance traveled by the wave in a medium) of the ultrasound are scattering and absorption (mechanical energy conversion into thermal energy). Therefore, the attenuation of the signal is influenced by the characteristics of the medium [11].

2.2. Linear propagation

One of the most evident features in the shape of the ultrasonic beam generated by a piston, circular or not, is caused by the so-called edge effect [12]. This effect generates constructive and destructive interferences in a region known as near field, being observed in continuous waves. These interferences are not so evident in short-duration pulses [13, 14]. The edge effect is originated by the diffraction of the wave caused by the transducer because it has a finite aperture in relation to ultrasound wavelength.

Each element of the transducer surface can be considered an infinitely smaller point source and as such can generate spherical acoustic waves that create field interferences. In **Figure 4**, point A is distant from the transducer surface by a distance r, and it is apart from the symmetry axis by a distance r′. The lines d1 and d2 represent the distances from point A to the nearest and the farthest edges, respectively. Analytical expressions for pressure at A are available in the literature [14] and are relatively simple to derive because of the axial symmetry of a piston-like circular transducer. An even greater and possible simplification is the case where d1 = d2, i.e. the point A is on the symmetry axis of the transducer [15]. For this particular situation, Eq. 8.31b of Ref. [16], reproduced in (5), expresses the amplitude of the acoustic pressure as a

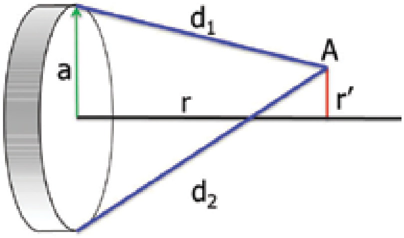

Figure 4. Representation of a point **A** positioned in the acoustic field generated by a flat piston with radius **a**.

function of the distance to the center of the piston, being valid for continuous waves or long tone bursts.

$$p(r) = 2\rho_0 c_0 U_0 \left| sen\left\{\frac{1}{2}kr\left[\sqrt{1+\left(\frac{a}{r}\right)^2}-1\right]\right\}\right| \tag{5}$$

In Eq. (5), $p(r)$ is the pressure amplitude along the symmetry axis as function of the distance; r, ρ_0 and c_0 denote the density and the phase velocity of the medium, respectively; U_0 is the transducer's surface velocity in the direction perpendicular to its face; and $k = \frac{2\pi}{\lambda}$ is the circular wavenumber ($\lambda = \frac{c_0}{f_0}$ and f_0 is the frequency). **Figure 2** shows the normalized amplitude $\frac{p(r)}{2\rho_0 c_0 U_0}$ plotted as a function of the normalized distance $\frac{r}{a}$ for the case in which $\frac{a}{\lambda} = 4$. The distance r_{Max}, described in (6), is the position of the last maximum in the increasing direction of r. It is considered the point of separation between the near field and the distant (or remote or far) field, from which the pressure amplitude decays with increasing r. In the example of **Figure 5**, $r_{Max} \cong 4a$:

$$r_{Max} = \frac{a^2}{\lambda} - \frac{\lambda}{4} \tag{6}$$

Another important position in the symmetry axis of a piston-like circular transducer is the last minimum, which Eq. (7) defines

$$r_{Min} = \frac{a^2 - \lambda^2}{2 \cdot \lambda} \tag{7}$$

According to [16], if $r > 6.41\frac{a}{\lambda}$, then (1) can be approximated to the far field equation $p(r) = \frac{k\rho_0 c_0 U_0}{2r}$, ensuring an error of less than 1% with that approximation. In general, measurements are taken in the far field, except when the effects of the near field are of interest in the measurement.

2.3. Nonlinear propagation

The theory adopted in the formulation of Eqs. (5) and (7) considers only the linear terms of the wave equation, so it is only an approximation of reality. The nonlinear effects of the

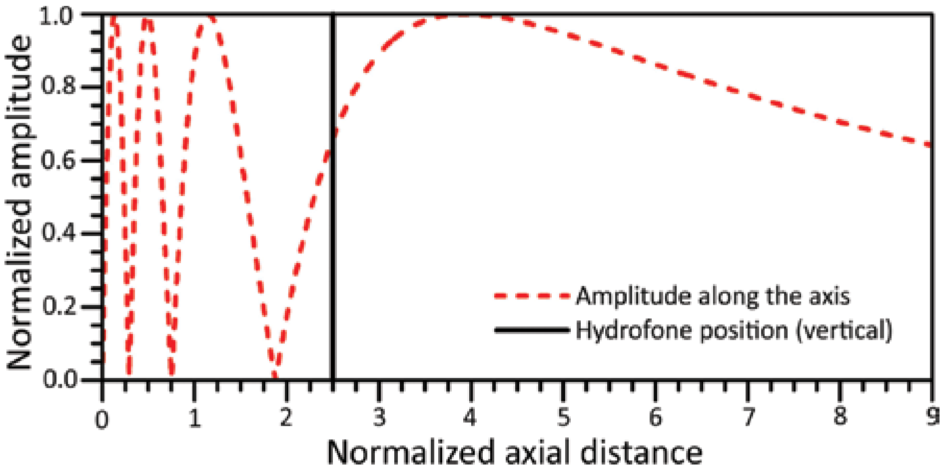

Figure 5. Pressure amplitude generated on the axis of symmetry of a plane circular piston-like transducer for $\frac{a}{\lambda} = 4$. The continuous vertical line simulates the position of a hydrophone in the field generated by the piston. In the example, the hydrophone is positioned at $r = 2.5a$, given a normalized pressure of 0.663.

propagation of the ultrasonic wave in fluid media cannot be arbitrarily neglected, under penalty of the theoretical model to present great discrepancies in relation to the realized measurements [17, 18], particularly in the ultrasonic fields generated by focused transducers [17, 19, 20]. Nonlinear effects can be observed even for small amplitudes [21, 22], from the propagation of only a few wavelengths [23, 24], in both water and other liquids [25, 26]. Essentially, the nonlinear propagation of the mono-frequency ultrasonic wave makes the power of the spectral component of the fundamental frequency to be gradually transferred to the higher harmonics, transforming an originally sine wave into a distorted or shock wave [27]. Despite that the shock wave profile is often compared to a sawtooth wave [22], in fact the negative peak of the wave is always smaller than the positive peak [17, 28], and the upward region of the wave has a curved and non-rectilinear profile (see **Figure 6**). The theory presented in [28] was used in the simulation of a distorted sine wave (burst) caused by the nonlinear propagation in water. The values of the relations between the harmonics, shown in the bottom graph of the figure, agree with [22] for a harmonic distortion parameter $\sigma \cong 5.7$, i.e. the wave of shock is completely developed—see Eq. (8). **Figure 7** shows the evolution of the composition of the harmonics as a function of the propagation distance.

Nonlinearity can be mathematically described by considering the higher-order terms in the resolution of the wave equation in which the wave propagation velocity becomes dependent on the velocity of the particle. During the compression (positive wave peak) the propagation velocity is higher than during rarefaction, and the waveform became distorted [22]. The shape of the beam is also changed, becoming more directional whilst the harmonics are being generated [29].

An effect resulting from the transfer of energy to high frequencies, particularly evident in organic medium such as fuel and biofuel, is the increase of absorption, since this effect is

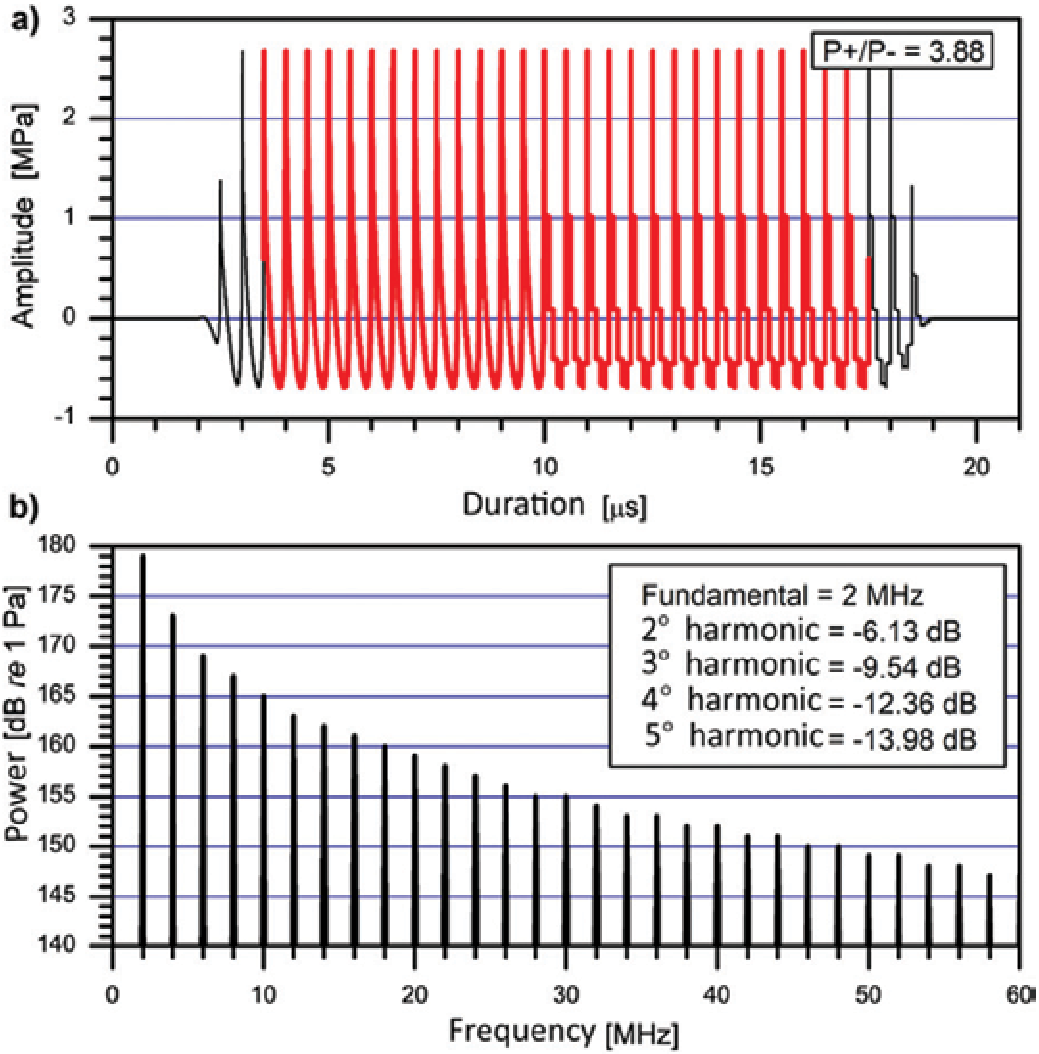

Figure 6. Example of a sine wave distorted by nonlinear propagation. (a) Graph of the wave in the time domain, showing the ratio between the positive and negative peaks (P+/P-). (b) Graph in the frequency domain, showing the ratio between the powers of the harmonics 2–5 in relation to the fundamental, in dB, which is related to the degree of wave distortion. For the example of the figure, $\sigma \cong 5.7$.

directly proportional to the frequency. In other words, the higher the energy at high frequencies, the greater the attenuation caused by propagation at these frequencies.

Although the waveform distortion mechanism is physically complex, involving the generation of harmonics and diffraction, dissipation and dispersion phenomena during the propagation of the acoustic wave in the fluid medium [28], mathematical models are available and are able to portray fairly accurately experimental results [30–33]. Of course, appropriate equipment allows reliable measurements capable of corroborating theoretical models [34], which was

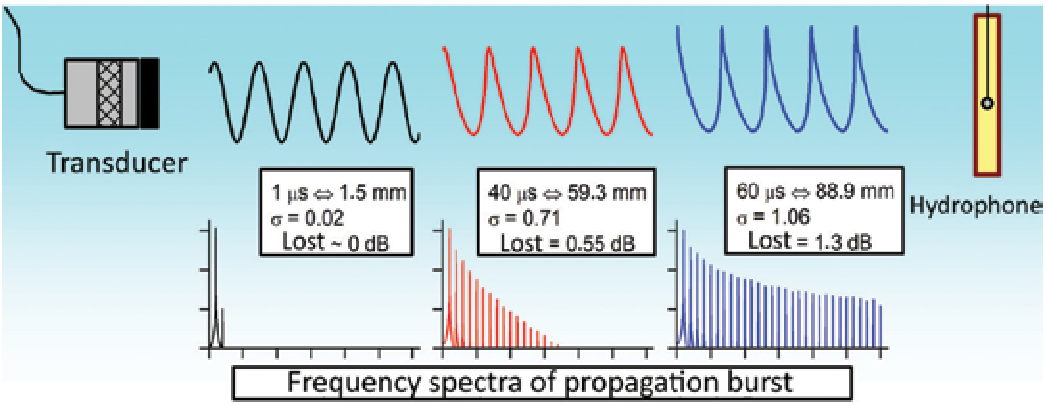

Figure 7. Sine wave distortion as a function of propagation distance.

more difficult to obtain in the past [35]. The theoretical model on which most of experimental applications are based today is described by Blackstock [30], which can be found in formulations of easy computational implementation [17, 22, 28].

A parameter used to describe the nonlinear deformation stage of the ultrasonic wave is called the degree of harmonic distortion σ, which for plane waves is defined as

$$\sigma = 2\pi\beta \frac{P_0 f_0 \Delta t}{\rho_0 c_0^2} \tag{8}$$

In Eq. (8), β is a dimensionless parameter dependent on the propagation medium (for water at 20°C, $\beta = 3.5$, according to [36]), P_0 is the effective pressure amplitude in the face of the generating transducer, Δt is the elapsed time since the waveform starts its propagation away from the transducer, and the other parameters are the same described previously.

2.4. Ultrasound industrial applications

Ultrasound is used in many different fields, and different devices have been constructed to specific applications. The most common uses include detecting objects and measuring distances; ultrasound imaging is used in medicine for diagnostic and in non-destructive testing of products, materials and structures to detect invisible flaws for raw eyes. Industrial applications of ultrasound include cleaning, mixing and accelerating chemical processes.

According to [37], sonicate is "to disrupt (something) by exposure to high-frequency sound waves", and sonication is "the act of applying sound energy to agitate particles in a sample, for various purposes". Hence, ultrasonication is a process in which ultrasonic frequencies are usually used to produce alternating low- and high-pressure waves in liquids, leading to the formation and violent collapse of small vacuum bubbles. This phenomenon is called cavitation and causes high-speed foist liquid jets and strong hydrodynamic shear forces. Ultrasonication proffers great potential in the processing of liquids, improving the mixing and chemical reactions in various industrial applications.

Industrial processes like the disintegration of cells or the mixing of reactants as well as the deagglomeration and milling of micrometer and nanometer-size materials are examples of ultrasonication application. Besides, chemical reactions benefit from the free radicals created by the cavitation, as well as from the energy input and the material transfer through boundary layers. For many processes, this sonochemical effect leads to a substantial reduction in the reaction time, like in the transesterification of oil into biodiesel.

In general, ultrasonic concepts of industrial processes are initially tested on laboratory scale to prove feasibility and establish the required operation ultrasonic parameters. The next step is to transfer the validated concept to a pilot scale for optimization and finally to an industrial scale. During the scale-up, it is important to guarantee that all exposure conditions (e.g. ultrasonic amplitude, working frequency, cavitation intensity, ultrasound exposure time, etc.) remain the same, in order to assure the final product quality, whilst the productivity is increased by a "scale-up factor".

2.5. Ultrasound parameter measurement

Considering some industrial applications, high ultrasonic power is required for many processes. On the other hand, when ultrasound is used to analyze the quality of chemical inputs [38] or the behavior of chemical reactions, low-power ultrasound is used to avoid any alteration in the chemical product or any interference in the chemical reaction.

In this direction, ultrasound parameters shall be calibrated to guarantee the adequate use of ultrasound at each specific industrial application. Herein, some parameters will be highlighted and how they are measured, as the output power and the working frequency, which are related to the device that generates the ultrasonic waves, and the propagation velocity and the attenuation, which are intrinsically correlated to the properties of the medium in which the ultrasonic waves are traveling.

According to IEC 61161 [39], output ultrasonic power (O_P) is defined as the "time-average ultrasonic power emitted by an ultrasonic transducer into an approximately free field under specified conditions in a specified medium, preferably water". The output power is expressed in watt (W). In general, ultrasonic power is measured in water, based on the measurement of the ultrasonic radiation force (F), which is the time-average force (expressed in N) acting on a target in an ultrasonic field and caused by the ultrasonic field. This force is typically measured using the radiation force balance that consists of a reflecting or absorbing target connected to a gravimetric microbalance. The ultrasonic beam is directed vertically upwards or downwards on the target, and the gravimetric balance measures the radiation force exerted by the ultrasonic beam. The radiation force component on the absorbing target in the propagation direction of the incident wave is related to the acoustic output power of the ultrasonic transducer as presented in (9):

$$O_P = v \cdot F \tag{9}$$

The ultrasonic power shall be determined from the difference between the force measured with and without ultrasonic radiation. The great advantage of radiation force measurements is that a value for the total radiated power is obtained without the need to integrate field data over the cross section of the radiated ultrasound beam.

The working frequency of an ultrasonic transducer is defined as the frequency of an ultrasonic signal based on the observation of the output of a hydrophone placed in an ultrasonic field at the position corresponding to the spatial-peak temporal-peak ultrasonic pressure [40]. The hydrophone is a transducer made from either polyvinylidene fluoride (PVDF) or piezoceramic (PZT) that produces electrical signals in response to surface input of ultrasonic signals [41]. Those signals are often measured using an oscilloscope, and the signal is analyzed using either the zero-crossing technique or a spectral analysis method [40].

The ultrasonic properties of materials within the megahertz frequency range are determined using techniques commonly referred to as the through-transmission substitution technique [42, 43] and as pulse-echo technique [44]. Using those techniques, it is possible to measure speed of sound and attenuation coefficient of the material under text. In general lines, the time of flight (related to the speed of sound) and the amplitude (related to attenuation) of the ultrasonic signal are measured in a reference medium, normally water. In the sequence, the time of flight and the amplitude are measured over the material under test. As the speed of sound and attenuation coefficient in the water are well known, and accurately determined based on measured temperature, the properties of the material under test are determined relative to water [45].

In more details, calculation of speed of sound is carried out by measuring the arrival time of the ultrasonic pulse both with (t_s) and without (t_0) the test sample in the ultrasonic beam. The difference in these times ($t = t_s - t_0$) is the time-shift caused by the different speed of sound in the material (v_s), which can be derived as [45]

$$v_s = \frac{l \cdot v_w}{v_w \cdot t + l} \tag{10}$$

in which v_w is the speed of sound in water at the temperature of interest and l is the sample thickness.

The ultrasonic transmission loss (TL) can be determined by measuring the frequency-dependent (f) change in amplitude of the electrical waveform through water ($V_0(f)$) and with the test sample in the ultrasonic beam ($V_s(f)$), which shall be positioned and aligned within the beam:

$$TL(dB) = -20 \cdot \log_{10} \frac{V_0(f)}{V_s(f)} \tag{11}$$

The attenuation coefficient of the test sample is obtained by dividing the TL by the sample thickness, after appropriately correcting for attenuation in water path and reflection of the incident wave at the interface between the water and the sample.

3. The past

It is known that biodiesel is typically obtained by the transesterification of the triglycerides of oils and fats with an alcohol in the presence of an acid or alkaline catalyst [46]. This reaction is traditionally performed using mechanical stirring, but this process is limited by mass transfer between the different reactants. This limitation is normally overcome by increase stirring, temperature and reaction time to aid in solubility between the reactants.

Originally, the ultrasound was used in transesterification reactions to homogenize the two immiscible phases (triglyceride and alcohol). This homogenization is caused by acoustic cavitation. This phenomenon releases large amounts of energy resulting in very high temperatures and pressures [47].

In addition, there is another application which consists of the use of non-destructive ultrasound for characterization and analysis of materials. Ultrasound has been used for this purpose for several decades in various industrial applications, including chemistry reactions. However, in the past, methods were not addressed for the characterization and analysis of materials focused in the production of biodiesel. There is a study [46] that uses ultrasound to characterize the by-product (glycerol) formed in the transesterification reaction. The objective was not the ester formation, but the analyses of glycerol deposition instead.

That said, a systematic review of the use of ultrasound in biodiesel production will be presented in this section. Taking into account the importance of technology, the review will include a discussion about the notorious advantages of the technique, interaction with other methods and method limitations.

3.1. Ultrasound-assisted biodiesel production

According to [47], in 1927, Alfred L. Loomis was the first chemist to recognize the effect of intense sound waves propagating through the liquid, more known as sonochemical effect. Despite the discovery, research focused on the area started from 1980. In this context, since 2003, ultrasound has been a favorable tool in biodiesel production, due to the ability to eliminate the mass transfer resistance and for being an efficient and low-cost method.

WO2007/077302A1 [48] is the first patent that encompasses an ultrasound method and the production of biodiesel. This invention relates to equipment and process for producing biodiesel where ultrasound is used to destruct heated fat. The preheated fat is cracked in several tanks that are connected to each other in series or in parallel. The ultrasound device is situated inside the tank and uses ultrasonic frequency between 15 and 55 kHz.

Subsequently, two more patents were deposited. KR20100110678 [49] describes a reactor for biodiesel production, where the ultrasonic horn is exposed in the inside of the reactor. The reaction is performed under pressure from 100 to 350 bar, temperature between 35 and 60°C and ultrasonic power from 60 to 1.500 W. This invention aims to synthesize biodiesel with high reaction speed and high yield. The other invention US2012279111 [50] is a continuous process for producing biodiesel fuel. In this process, the reagents are fed into an ultrasonic cavitation reactor. After 5–30 s, the flow leaves the reactor and goes to an agitated-tank-type reactor. The mixture remains for about 1 h, which is the time needed to yield the final conversion of triglycerides of about 96%. The mechanical stirring is responsible for most of the reaction, and ultrasonic cavitation only assists the homogenization of the reagents.

Ultrasound methods for biodiesel production have developed continuously. **Table 1** compiles several papers published in the last decade, whether by irradiation ultrasonic indirect (bath) or direct (probe and transducer), in the presence of acid or basic catalysts, using the most diverse raw materials.

The main perspective in the past was the use of equipment available in any chemical laboratory, with ultrasonic waves of low frequency (up to 500 kHz) and high power [51].

The ultrasonic probe is a usual commercialized equipment that has high power output capability as it concentrates energy delivering. In this type of equipment, there is a distance (about 5 cm) between the transducer (responsible for irradiation) and the tip of the horn. The ultrasonic energy is provided to the liquid through the horn immersed in it, as shown in **Figure 8**.

Many studies using this equipment for producing biodiesel are found in the literature [3–6]. In the study by Lifka et al. [3], an ultrasonic processor (24 kHz; 200 W) known as ultrasonic probe was used in the transesterification reaction of canola oil with ethanol. After 30 min of reaction, a conversion of 87% was obtained to a molar ratio of 6:1 and 0.5–1% of the sodium hydroxide. A study of the energy balance was carried out comparing the three methods of agitation: magnetic, mechanical and by ultrasound. It was concluded that using ultrasound obtains lower energy costs. Georgogianni et al. [4] also performed biodiesel production with ultrasonic probe at low frequency (24 kHz; 200 W). They used sunflower oil and methanol at a molar ratio alcohol/oil of 7:1 and 2% sodium hydroxide. In 20 min of reaction, it reached 95% yield. In the presence of ethanol, using the same reaction parameters, the ultrasound led to high ester

Feedstock	Alcohol type; molar ratio	Catalyst type; (%)	Frequency; power	Time(min); conversion (%)	Refs.
Canola oil	Methanol 6:1	NaOH; 0.5	20 kHz; 200 W	30 min; 87	[3]
Sunflower oil	Methanol 7:1	NaOH; 2	24 kHz; 200 W	20 min; 95	[4]
Coconut oil	Ethanol 6:1	KOH; 0.75	24 kHz; 200 W	7 min; 98	[5]
Canola oil	Methanol 5:1	KOH; 0.7	20 kHz; 2000 W	50 min; 99	[6]
Synthetic oil	Methanol 6:1	NaOH; 0.5	40 kHz; 840 W	20 min; 98	[52]
Soybean oil	Ethanol 10:1	NaOH; 0.3	40 kHz;	30 min; 91.8	[53]
Oleic acid	Ethanol 3:1	H_2SO_4; 5	40 kHz; 700 W	120 min; 90	[54]
Fish oil	Methanol 9:1	H_2SO_4; 2	40 kHz; 60 W	90 min; 98.2	[55]
Waste cooking oil	Methanol 6:1	KOH; 1	20 kHz; 200 W	40 min; 89	[56]
Cottonseed oil	Methanol 6:1	KOH; 1	40 kHz;	5 min; 96.0	[57]
Palm acid	Methanol 7:1	H_2SO_4; 5	22 kHz; 120 W	200 min; >90	[58]
Waste cooking oil	Methanol 9:1	H_2SO_4; 3	40 kHz; 200 W	60 min; 99.9	[59]
Jatropha oil	Methanol 7:1	H_2SO_4; 4	210 W	60 min; 96.4	[60]

Table 1. Compilation of studies with typical parameters in ultrasound-assisted transesterifications.

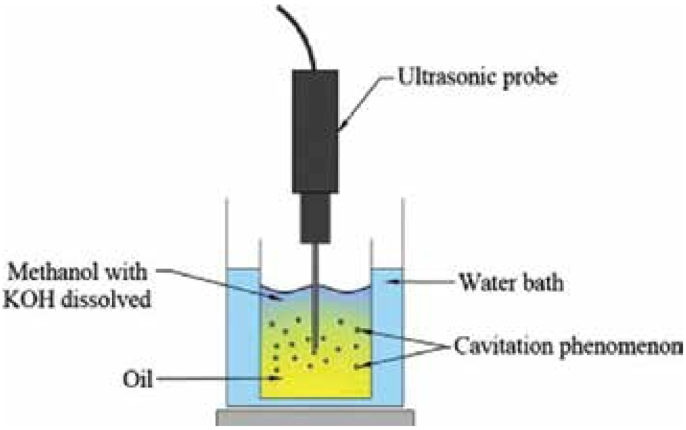

Figure 8. Schematic representation of the reaction using ultrasonic probe. Adapted from Sáez-Bastante et al. [7].

yields, about 98%. In only 40 min of reaction while using mechanical stirring it gave lower yields, about 88%, even after 4 h of reaction time.

Kumar et al. [5] used the same equipment as described in [3] in the transesterification of coconut oil to produce ethyl ester. A 98% conversion of the ethyl ester was obtained in 7 min of reaction at a molar ratio of 6:1. In these studies the ultrasonic probe was used as an alternative to the usual production process and resulted in high conversions. Thanh et al. [6] developed a pilot scale plant for biodiesel production from canola oil catalyzed by hydroxide potassium. An ultrasonic probe was used at low frequency (20 kHz). After 50 min of reaction, a maximum conversion of more than 99% was obtained with a methanol-to-oil molar ratio of 5:1, 0.7% catalyst concentration. The authors conclude that optimization of ultrasonic power and mode of delivery (pulsed ultrasound) can be carried out to minimize energy consumption while attaining high conversions.

Although it has been widely used, the ultrasonic probe has some disadvantages as it easily corrodes the horn tip [51] and presents low cavitation efficiency. In addition, the acoustic intensity is distributed in a concentrated and non-homogeneous fashion.

Another equipment commonly used in the production of biodiesel mainly because of its low cost and for being an equipment of easy acquisition is the ultrasonic bath. In this equipment, the ultrasonic transducers are positioned in the bottom or lateral position of the bath, and a reactor is fixed to the bottom, as shown in **Figure 9**.

There are several studies that performed transesterification reactions in ultrasonic baths. In these studies, the conversion results were greater than 90% [52–55]. Stavarache et al. [52] produced biodiesel using an ultrasonic bath with frequency of 40 kHz. The authors compared the profile of methyl esters of different vegetable oils produced under ultrasonic irradiation with conventional heating. The profile of methyl esters in the presence of potassium hydroxide was quite similar for both procedures. In the case of sodium hydroxide, the reaction with using ultrasound gave better results. In this study, the highest conversion obtained was 98% after 20 min of reaction at an alcohol-to-oil molar ratio of 6:1.

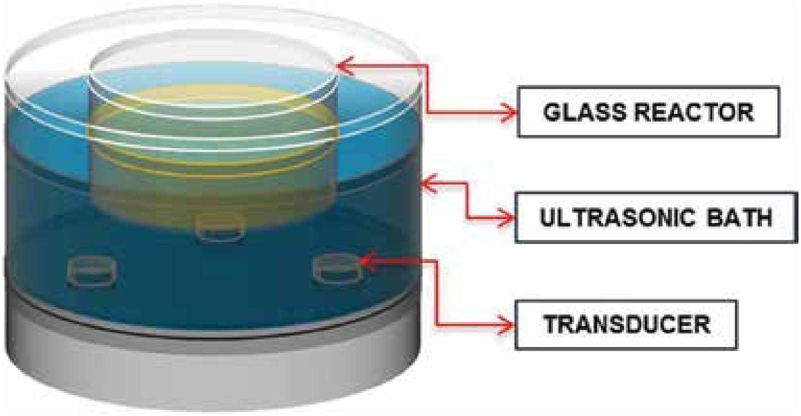

Figure 9. Schematic representation of the reaction using ultrasonic bath.

Rodrigues et al. [53] also produced biodiesel in an ultrasonic bath with low-frequency waves (40 kHz), using soybean oil as raw material and ethanol. The author reports that after 30 min of reaction, the conversion (91.8%) was greater than the conversion obtained using the conventional process. Studies from other research groups too have confirmed the high conversion by using the ultrasonic bath. In study of Hanh et al. [54], the reaction was carried out in an ultrasonic bath operating at 40 kHz and 700 W. The conversion obtained was 90% after 120 min of reaction, using oleic acid and ethanol at an alcohol-to-oil molar ratio of 3:1. Santos et al. [55] also used ultrasonic bath, operating at 40 kHz and 60 W. The biodiesel was produced from reaction fish oil with methanol by an ultrasound-assisted method. The reaction was carried out with molar ratio alcohol/oil of 9:1 and a catalyst concentration of 2.0%. A higher methyl ester yield was achieved as compared to mechanical stirring. The yield was equal to 98.2% in 90 min of reaction.

It may be noted that using an ultrasonic bath, it is possible to achieve high conversions. The ultrasonic bath was designed for cleaning and degassing and does not allow directional irradiation in the reaction medium. Therefore, a possible explanation for their performance is that these reactions are always conducted with external heating between 40 and 70°C, and heating facilitates transesterification of triglycerides. Despite the favorable results, this equipment has as disadvantage the low cavitation efficiency and distribution of the dispersed and non-homogeneous acoustic intensity and usually requires mechanical agitation [61].

In 2009, the use of ultrasonic transducer directly applied in the reaction media begins to be proposed. Different than the use of ultrasonic probe, in this application there is no separation between the transducer and the liquid surface; thus, the volume of wave propagation is more confined (see **Figure 10**).

Hingu et al. [56] synthesized biodiesel from waste cooking oil using a low-frequency ultrasonic reactor at 20 kHz with power of 200 W. The optimum conditions for the process have been molar ratio of alcohol to oil of 6:1, catalyst concentration of 1% and temperature of 45°C. The

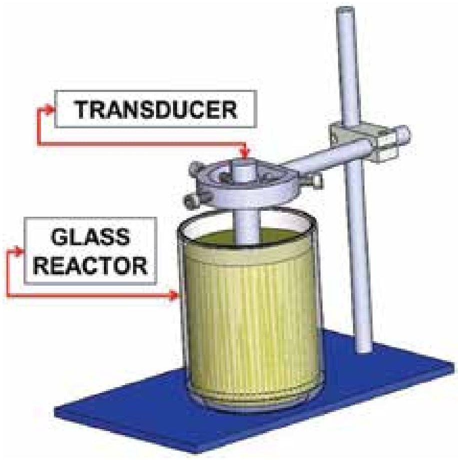

Figure 10. Schematic representation of the reaction using ultrasonic transducer.

power effect was studied, and the obtained conversion was around 66% at a power of 150 W. However, when the power was increased to 200 W, extent of conversion also increased to about 89%. On the other hand, an increase in the power dissipation from 200 to 250 W resulted in lower conversions. It was concluded that this can be attributed to the fact that at higher power levels, usually cushioning effect is observed which results in to decrease the transfer of energy into the system.

Fan et al. [57] used a transducer powered by a function generator to perform the transesterification of crude cottonseed oil with methanol in molar ratio of 6:1 in the presence of base catalyst. The reaction was conducted with low-frequency ultrasonic irradiation at room temperature. After 60 min of reaction, using the 40-kHz frequency waveform, a yield of approximately 90% yield was obtained. Four different frequencies were investigated: 400 Hz, 4 kHz, 40 kHz and 400 kHz. Significant difference in biodiesel yield among different frequencies was not observed. This suggests that there were no remarkable differences in the formation of the cavitation bubbles at the examined frequencies.

In the past, the use of ultrasound has proved to be an efficient technique to produce biodiesel. However, several ultrasonic parameters such as power, frequency and mode of operation can optimize the efficiency of this reaction. In this context, the development of new methods and equipment for ultrasound application must occur to make biodiesel production increasingly competitive.

4. The present

For the last 7 years, several studies showed the effective system optimization regarding the use of high-power and low-frequency (typically up to 50 kHz) ultrasound in the biodiesel production [7, 62–66]. These studies investigate the best procedure or configuration to achieve a better yield. This improvement made this technique to be one of the most studied for the biodiesel production.

Although the use of ultrasound to improve the biofuel production has been used for decades, the literature about low-power ultrasound (less than 50 W), for this purpose, is rare.

When the question is "can we make better for the environment?" or "can we think in a greener procedure?", the use of high-power ultrasound for biodiesel production, even as it already demands less energy than the usual method, makes us reflect about the real energy necessary to produce a biofuel with quality. Within this approach, the Laboratory of Ultrasound of the Brazilian National Metrology Institute (Inmetro) has been developing different ways to produce biodiesel. The first results published about this study [8] used an ultrasonic transducer with 9 W to produce soybean biodiesel with methanol and potassium hydroxide as a catalyst. Despite that the results were considered good (conversion around 95%), the method used to analyze the conversion in that paper is not so well described in the literature regarding the reproducibility. In this way, the researches continued regarding the use of a lower-power and high-frequency ultrasound in the biofuel field production. Promising results have been obtained with the same equipment used in [8] (see **Figure 11**).

The optimization of the parameters and experimental setup were not the only changes in the study as shown in **Figure 11**. The monitoring of the conversion using the nuclear magnetic resonance of hydrogen (^{1}H NMR) gives more reliability to this study. The output power was calibrated according to the international standard [39], and 9.06 W was the effective acoustic power. The 85% of conversion supports the idea that reducing the delivered ultrasound energy is possible to produce biodiesel with a good conversion rate. Furthermore, it shows that the increase of the alcohol/oil ratio to 8:1 decrease the necessary time to achieve the maximum conversion rate.

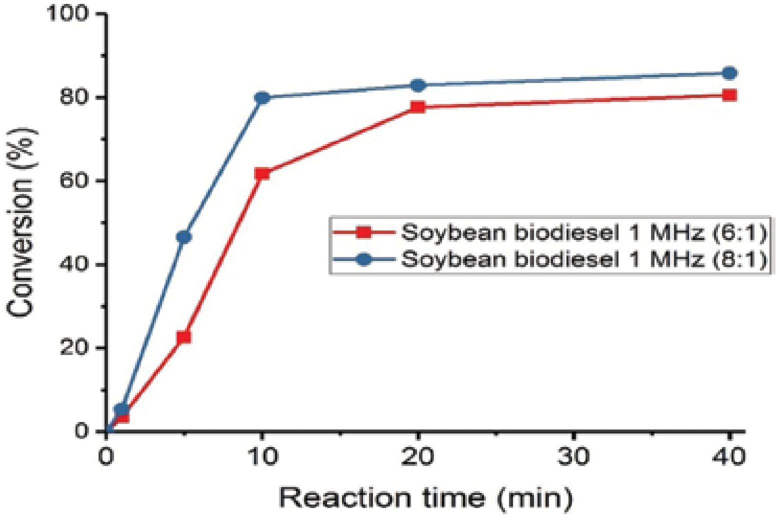

Figure 11. Soybean biodiesel by ultrasound using the 1 MHz transducer using an alcohol/oil ratio of 6:1 and 8:1.

The reactions described in **Figure 11** achieve 43°C without necessity of a heating system. This leads an energy saving, when you think that the most expensive part of the reaction is the heating. These first results aim not just the optimization of the ultrasound use in the transesterification but the current concerns about energy wasting.

However, the use of ultrasound to produce biofuels is not the only application of this versatile technique. The use of very low-power and high-frequency ultrasound to monitor the liquid properties has been used in several fields for many years [46, 67–72]. One of the first studies was in 1995, when Sheen et al. [73] showed a non-invasive and inline system capable to measure the density and viscosity of Newtonian liquids using a 1 MHz transducer. The inline applicability of the ultrasound techniques boosted the development of these techniques in the biofuel field. In the last 6 years, studies to detect the adulteration in biofuels [74, 75], to quantify oil and grease contents in biofuel wastewater [76] and to monitor the biodiesel reactions [77] were carried out with good results. The ethanol adulteration analyzed by Figueiredo et al. [75] introduced the idea of the importance of the metrology in the biofuel system. Not just the possibility of the use of ultrasound was proved to be simple and accurate but its feasibility as an auxiliary tool that can be applied in the line process.

In this way, the constant search for the improvement in ultrasound measurements is developing the real possibility of an ultimate ultrasound system to monitor not just the biodiesel production but its quality as well.

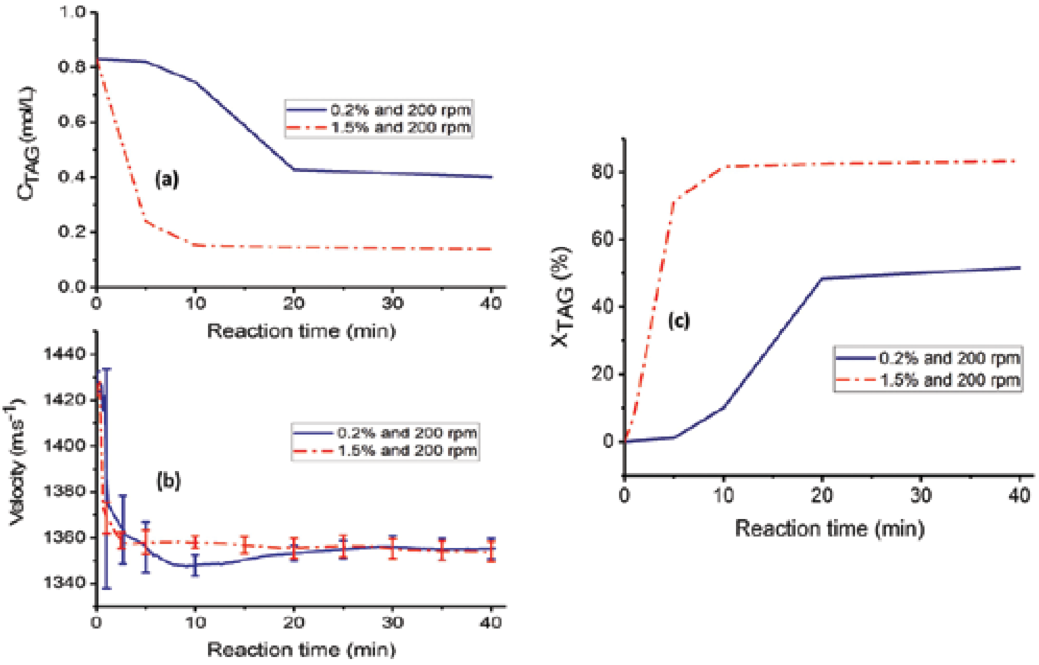

Figure 12. Variation of (a) TAG concentration, (b) propagation velocity and (c) TAG conversion for the reactions with 200 rpm of rotation. Reprinted from Baêsso et al. [9].

Considering the present worldwide biodiesel consumption, which increases every year, a new method for monitoring the production, helping to avoiding the waste of reagents, energy and time, is extremely necessary. The expensive and offline available methods can lead to accurate values but just in the end of each batch. This means that if something goes wrong during the process, the results would be noticed just after the end of the production. Thus, a low-cost and accurate technique, suitable to the process line, has been studied recently as a technological alternative way in the biodiesel industry.

Baesso et al. [9] disclose in their study that ultrasound can notice changes in the medium during transesterification reaction but can also monitor the kinetics behind the biodiesel production. That study analyzed four different reactions to produce biodiesel from commercial soybean oil. Methanol was the alcohol used, and potassium hydroxide was the catalyst. The changing of the catalyst concentration (0.2 or 1.5%) and the mechanical stirring (200 or 520 rpm) allowed the analyses of ultrasound capability to detect the real impact of changing these parameters. The study compared and related the oil consumption (CTAG), the biodiesel conversion rate (XTAG) and the propagation velocity. Both CTAG and XTAG were monitored by ^{1}H NMR, as an offline method. **Figures 12** and **13** show some results published in [9].

From the both figures reprinted from [9], it is possible to notice that ultrasound follows the results obtained by the ^{1}H NMR technique but in an inline mode. Baesso et al. [9] proved that for the four analyzed reactions, the ultrasound was capable to distinguish the end of

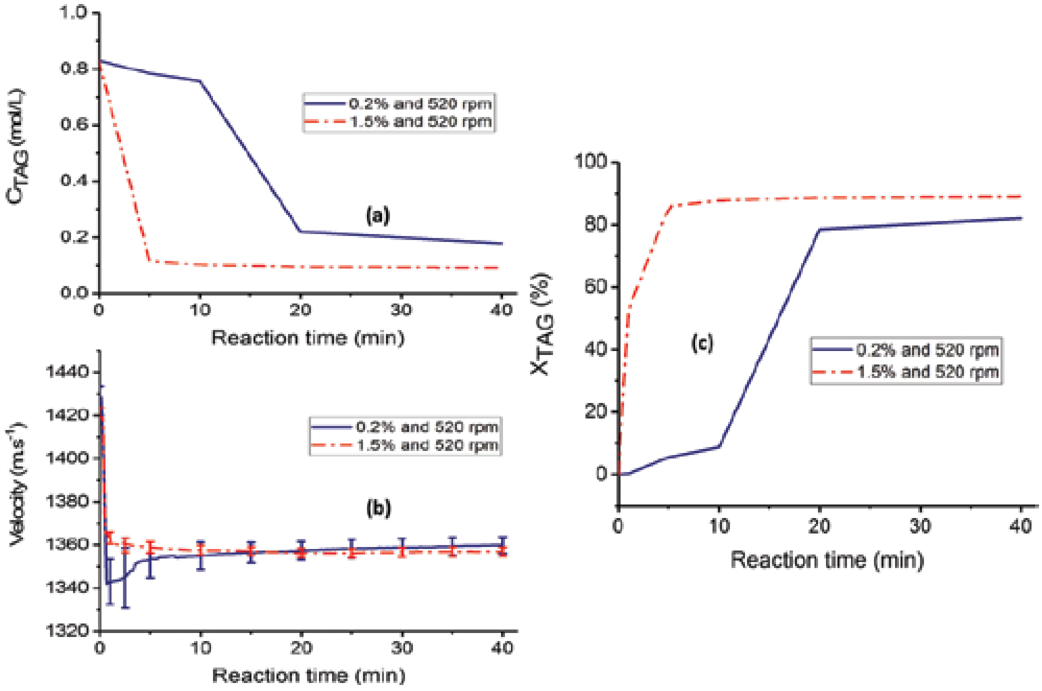

Figure 13. Variation of (a) TAG concentration, (b) propagation velocity and (c) TAG conversion for the reactions with 520 rpm of rotation. Reprinted from Baêsso et al. [9].

each one without any sample pretreatment. The use of the ultrasound in this study would allow the industry save not just energy with the reducing time but with the expensive techniques to analyze the final product. Not just the idea of using this kind of technology in biodiesel industry is remarkable, but the use of the metrology gives more reliability for the current technologies that aim the biofuel production optimization.

5. The future

Disclosing the future is not often considered science. Nevertheless, some clues can be gathered in the well-established state of the technique to point out some possible tracks to be followed. With respect to the use of ultrasound in biodiesel production and analysis, the future seems to be related to the use of broadband, frequency-modulated waveforms. Deconvolution techniques, both in time or frequency domains, are ready enough to be used in biodiesel analysis and production. Some recent achievement will be discussed in this section, and a sort of future prediction will be essayed.

Quantitative ultrasound (QUS) is a measurement approach for quantifying ultrasonic parameters of a medium. In general, the ultrasonic quantities are derived from two basic measuring quantities: time of flight and amplitude. Those quantities vary as function of frequency and physical-chemical properties of the interrogated medium, including density, temperature, viscosity, the presence of scatters, discontinuities and other interleaved structures or intercurrent phenomena. The aforementioned quantities are extracted from a time- or frequency-domain ultrasonic signal.

For inspection in liquid media, the most important aspects are the ultrasonic phase velocity and the scattering pattern [42, 43, 45]. The behavior of those derived quantities as function of frequency is deeply related to density and viscosity. Many studies have been demonstrating the relationship between QUS and fuel [9, 75, 76, 78]. Another approach to the use of ultrasound in the industry of fuel and biofuel is its use for production [1, 8, 54, 63, 64]. Ultrasound has been demonstrated to be useful to cell culture treatment [79], as well. In all cases, a proper evaluation of ultrasonic parameters or transducer characteristics plays an important role, and some basic metrological procedures shall be followed, including uncertainty determination [80–83].

Ultrasound propagation has intrinsic capability of generating nonlinear distortion, depending of some factors such as frequency, power and propagation distance [17, 23, 30]. It could even be of great interest as a disaster for ultrasound analysis. Fortunately, there is relatively simple way to deal with nonlinear distorted fields, which is the use of compensated frequency-modulated signals to identify systems and perform ultrasound measurements [84, 85]. The method described in those papers can be generalized for virtually any system to be measured, for instance, fuel and biofuel, including contaminants. The basis consists in constructing a waveform in the time domain from information previously known or experimentally obtained about the system frequency response. **Figure 14** was extracted and adapted from [84] and summarizes the signal construction method.

The system frequency response (FR) shall be previously determined or arbitrarily defined. After that, it is band-limited and pseudo-inverted, defining a bandwidth for the final signal. The group

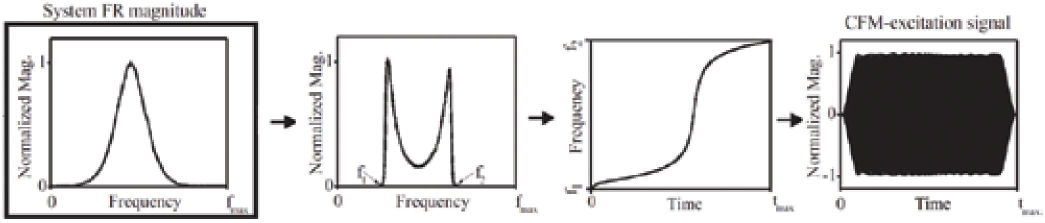

Figure 14. CFM construction forms a predetermined system frequency response. Adapted from Costa-Felix et al. [84].

delay is mathematically constructed based on the pseudo-inverted frequency spectrum, and the complex frequency spectrum is determined on sequence. Finally, the time-domain signal is constructed using the inverse Fourier transformation. Details of the processing can be found in the literature. The important concept here is that the system identification method developed as that has the intrinsic characteristic of putting apart any distortion caused by the system, including that one caused by nonlinear propagation. The distortion can even be evaluated separately, being the harmonics characterized or quantified individually. Such process has a completely unexploited capability to be used in fuel and biofuel analysis. It is our bet for the future of ultrasound methods on fuel identification, quantification and quality control.

6. Final remarks

Throughout this chapter, the past, the present and the future of biodiesel production and analyses using ultrasound methods were presented and discussed. The chapter was written aiming to let the not insider reader to be able to conquest the basis of ultrasound and biodiesel technical relationship.

The past was a remarkable assortment of attempts to make use of generic ultrasound systems to accelerate biodiesel production. The present brings several dedicated instruments, measurement systems and fabrications tools specially designed for the use of ultrasound in fuel and biofuel. In the future, who knows? The trend seems to be related to the use of digital signal processing for specially designed applications, using, for instance, online real-time signal design based on transfer function and system identification for manufacturing optimization. That is our best bet.

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Chapter 8

Kinetics of Transesterification Processes for Biodiesel Production

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Additional information is available at the end of the chapter

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Abstract

Biodiesel is a renewable fuel mainly produced by transesterification of oils and fats that can be used as a transportation fuel, solvent and for energy generation with the potential to reduce the emissions of CO_2, SO_2, CO and HC, compared to fossil fuels. In this work, the kinetic behavior of triglycerides by different transesterification technologies is investigated through a critical review of the kinetic models reported in the study with the aim to establish a trend of the reaction mechanisms and the main variable effects and to further optimize the chemical process. The study of the transesterification reaction kinetics is performed for every type of transesterification, that is, homogeneous, heterogeneous, enzymatic and supercritical. The kinetic models are thus reviewed by describing the way they have evolved and how they can be used for process simulation and optimization. This chapter is divided in a study of the state of the art, an analysis and synthesis of research results, and an application for further optimization of the biodiesel production process.

Keywords: biodiesel, kinetics, transesterification, optimization, modeling

1. Introduction

Biodiesel is a renewable fuel of key importance to meet environmental and economic sustainability. It is produced by transesterification of vegetable oils or animal fats with an alcohol, such as methanol or ethanol, on an alkaline, acid or enzyme catalyst, and it is composed of a mixture with at least 96 wt% of fatty acid methyl or ethyl esters (FAME or FAEE).

A high percentage of the current investigations in the domain of biodiesel production is oriented toward the design of suitable solid catalysts, either with acid or with alkaline properties. Likewise, much emphasis is being placed on research on free or supported enzyme catalysts. Other transesterification methods that are under development include the application of supercritical conditions without the use of catalysts and the use of radiofrequency or ultrasonic assistance.

The development and optimization of biodiesel production processes involve much experimental work, as well as the application of kinetic models that try to describe the process in a more comprehensive and realistic way. Some of the variables that are commonly studied in the development of kinetic models are the reaction temperature, the feedstock composition, including different contents of free fatty acids (FFAs), the alcohol-to-oil molar ratio, the mixing speed and the reaction time. The internal and external mass transfer limitations when using solid catalysts have also been studied.

This chapter deals with the main challenges in the development and application of kinetic models for the transesterification reaction, as well as representative results of current developments in this area.

2. The importance of kinetic modeling for process optimization

The development of kinetic models of chemical transformation processes for the production of higher added-value products is a powerful tool for reactor design. The kinetic model is also necessary for the optimization of the complete process, including the separation and heating steps. Thus, the kinetic model must be incorporated into the reactor model and then applied in the process simulation.

Regarding chemical or biochemical transformations in reactors or bioreactors, the kinetic models are of great help in the selection of the most favorable reaction conditions (e.g. temperature, pressure, mixing rate) to maximize the formation of desired products with the least investment of material and the use of economic resources. This also applies to the different biodiesel production processes, including homogeneous, heterogeneous, enzyme catalysis, and so on, which will be addressed in the next sections.

A well-planned experimental study and the subsequent development of a kinetic model are considered one of the most crucial steps in the chemical process development for industrial applications.

Kinetic models may offer different levels of detail and predictive capabilities, as they can take into account mass and heat transfer phenomena, as well as thermodynamic equilibrium. The level of theory for modeling the reactions can go from the use of quantum chemistry to the individual elementary steps up to a series of encompassed reaction steps between pseudo-components (lumped model). The catalyst deactivation, the presence of undesired side reactions, the consideration of inhibition processes and a detailed feedstock composition are among other factors that can be considered to derive more realistic kinetic models and with a higher predictive capacity. A more comprehensive model can give a more significant response and provide more detail on the composition and, therefore, on the quality of the products. Thus, a more robust model can be more useful; however, the number of kinetic parameters can increase significantly. The estimation of these parameters must be performed rigorously in order to generate reliable results.

On the other hand, modeling of chemical reactors is very useful for the simulation and control of the process involved. This requires a previous selection of the kinetic model to be applied. Reactor modeling is used to determine concentration, temperature and pressure profiles, generating valuable information for the scaling-up of the process. The reactor model may include more or less the detail of the variables of interest, being possible to determine temperature and concentration profiles at intraparticle conditions, as in the case of heterogeneous reactors.

The development of kinetic models of biodiesel production processes and their application to simulate and optimize these processes has been investigated and reported by a number of researchers. Portha et al. [1], for example, reduced the excess of ethanol used in the transesterification reaction of oils in a continuous process by using a two-stage continuous heterogeneous catalytic reactor. Their simulation results enabled them to determine that the overall performance of the system could be improved with the use of an inter-stage methanol addition as well as by changing the reaction temperature for the second reactor. In their experimentation with triolein as a model compound, the authors found converting the main part of triolein in the first reactor and converting diglyceride and monoglyceride in the second one to be useful. Their simulations also indicated that a higher temperature in the second reactor was advisable to enhance reaction rates at this stage. They also worked on the optimization of the inlet methanol-to-triolein molar ratio, finding that the use of a molar ratio larger than than 25:1 mol/mol had no further significant impact on the biodiesel yield. Furthermore, by introducing the kinetic model into a reactor model, the authors calculated internal concentration profiles and found that the internal diffusion of triglycerides (TG), diglycerides (DG) and monoglycerides (MG) was the limiting phenomena in the overall transformation.

A kinetic model can also be applied as a strategic tool for obtaining a better understanding of the rates of product formation and the inhibition patterns present in the transformation scheme [2]. A reaction scheme for the biodiesel production, for example, through enzymatic processes, can consider much more reaction steps and thus a higher number of reaction parameters. This certainly introduces an additional complication in the development of a kinetic model, but when this model is solved, it can be used to design a reactor based on enzyme catalysis and ultimately to optimize the process.

In the field of research and process development, the application of kinetic models that are able to accurately simulate the process at different reaction conditions is useful to provide the guidelines for further experimental work, helping in this way to discard potentially unproductive experimental trials. Models can also help to predict the effect of composition on the quality of the product. For example, a model could predict how the FFA or the water content in the feedstock can affect the reaction conversion and therefore the yield and quality of biodiesel.

3. Kinetic modeling for biodiesel production

There is a consensus on the reaction steps involved in the transesterification process of triglycerides, which are indicated in **Figure 1**. These are the three consecutive and reversible reactions.

In the first reaction, triglyceride (TG) molecule reacts with an alcohol molecule, typically methanol (M) to produce diglyceride (DG) and a fatty acid methyl ester (ME). Then, in the second reaction, diglyceride reacts with alcohol to form monoglyceride (MG) and another molecule of fatty acid ester. In the third reaction, monoglyceride (MG) reacts with alcohol to produce glycerol (G) and a third molecule of fatty acid ester.

When the concentration of FFA present in the oil requires a previous (or simultaneous) stage of esterification, the following reaction that forms one molecule of methyl ester and one molecule of water (W) is considered in the model:

$$\mathrm{FFA} + \mathrm{M} \leftrightarrow \mathrm{ME} + \mathrm{W} \tag{1}$$

The development of kinetic equations is performed from the reactions taken into account for each particular case. The final form of the kinetic expressions is affected by the nature of the reacting mixture, homogeneous or heterogeneous, the selected alcohol, the alcohol-to-oil molar ratio and the influence of mass transfer effects, among other factors. In the following subsections, representative kinetic models for each type of reaction are discussed.

3.1. Homogeneous transesterification

Most of the work reported on the kinetics of transesterification of oils and fats has been derived from experiments with homogeneous catalysts and mainly with alkaline catalysts.

Freedman et al. [3] carried out the homogeneous transesterification of soybean oil using butanol and methanol and both alkali and acid catalysts, finding that alkaline-catalyzed reactions proceed at considerably faster rates than acid-catalyzed transesterification. The kinetic coefficients reported at 60°C for the former were two to four orders of magnitude higher than the latter. For this reason and because alkaline catalysts are less corrosive to industrial equipment than acid catalysts, most commercial biodiesel processes are conducted with alkaline catalysts. Sodium alkoxides are among the alkaline catalysts that have been used extensively for this reaction [4]. Freedman et al. [3] also found that the reaction with butanol follows a second-order reaction. These authors performed alkaline- and acid-catalyzed experiments

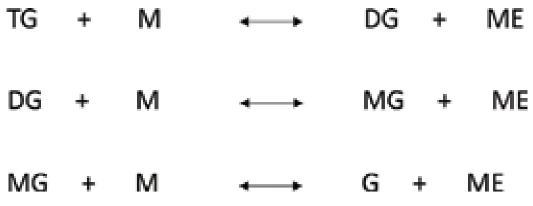

Figure 1. Consecutive reversible reaction steps considered in the formation of methyl esters from triglycerides.

using a larger excess of alcohol. From their results with a butanol-to-soybean oil molar ratio of 30:1 mol/mol, they found that the forward reaction followed pseudo-first-order kinetics for both alkaline and acid catalysts, as expected. The kinetic coefficients for the first reaction shown in **Figure 1** are higher than those for the second and third reactions. This is valid for the forward and reverse reactions and is a general result reported by different authors for alkaline-catalyzed transesterification [5]. In the case of acid-catalyzed tests, the rate coefficients for the first reaction were lower than those for the second and third reactions for both forward and reverse reactions. This has also been reported by other authors [6]. The activation energies for all the alkaline- and acid-catalyzed transesterifications using both butanol and ethanol ranged from 8000 to 20,000 cal/mol. These results are also in agreement with the activation energies reported by other researchers [5, 6].

Other kinetic models like the one proposed by Gonzalez-Brambila et al. [7] consider the effects of mass transfer phenomena on the transesterification of soybean oil with methanol and NaOH in a batch reactor, using the experimental data from the study [8] and by proposing a mass transfer-kinetic dynamic model. Two liquid phases were considered: a non-polar TG-rich phase and a polar methanol-rich phase, and the reaction was considered to take place only in the interphase of the drops. Besides the six kinetic coefficients derived from **Figure 1**, the mass transfer coefficient between drops and alcohol phase was evaluated. In this way, the model can not only describe the evolution on time of TG, DG, MG, glycerine, methanol and ester composition but also estimate the reduction of drops' radii during the reaction, which are relevant data considering that reaction takes place on the drops' surface.

3.2. Heterogeneous transesterification

The use of heterogeneous catalysts presents several advantages over the use of homogeneous catalysts, among which the ones that have been most emphasized include the elimination of the washing section and huge amounts of waste water, reusable catalyst and easier disposal of the spent one, high purity of glycerol and the end product [9]. Hence, several conventional solid bases and acids (with and without promoters/dopants) have been investigated with this purpose. These included different solid acid catalysts such as sulphated zirconia [10], zeolites [11], heteropolyacids [12], ion-exchange resins [13] and sulphonated carbons [14]. Moreover, it has been reported that working under optimal conditions, heterogeneous transesterification can approximate the activity obtained with homogeneous catalysts. For example, Kim et al. [15] used the heterogeneous catalyst $Na/NaOH/\gamma\text{-}Al_2O_3$, reaching conversions of 95%, with a methanol-to-oil molar ratio of 9:1 mol/mol at an atmospheric pressure. These results are comparable to those obtained with the conventional homogeneous catalyst (NaOH).

Like homogeneous acid catalysis, when the oil to be fed has a concentration of FFA greater than 3 wt%, an acid solid catalyst that tolerates the presence of FFA and possess activity for both esterification and transesterification to convert FFA and oil to biodiesel should be used.

Normally, the first option to carry out the scaling-up of a continuous heterogeneous transesterification process is the use of a fixed bed reactor (FBR), due to the simplicity of its design and the ease of its operation. However, the effect of the diffusive resistances must be considered in order to obtain a reactor design that meets the expected conversion levels.

The transesterification reactions of oils in a fixed bed reactor (FBR) present different mass transport processes that affect the rate of production of biodiesel. The reaction system has two liquid (L) phases and one solid (S) phase represented by the catalyst. One of the liquid phases is rich in oil, while the other is rich in methanol, or any other alcohol. In this way, the external diffusive resistances associated with the transport of methanol and triglyceride toward the surface of the catalyst must be considered and the intraparticle diffusive resistances as well. The modeling of these complex processes involves the calculation of mass transfer coefficients of the components involved in the chemical reactions. Moreover, as reaction proceeds, the solubility of methanol in the oil-rich phase is increased due to a higher presence of esters, which act as co-solvents for methanol. The formation of monoglycerides and diglycerides increases the solubility of methanol in the oil-rich phase. As this solubility increases, the diffusive resistances at the L-L interface decrease [8], accelerating the transport of the reactants and therefore increasing the reaction rates. A similar effect is observed in the case of feedstock with a high FFA content, giving rise to a greater solubility and ease of transportation of the reactants in the L-L interface and thus allowing higher rates of biodiesel formation. This was confirmed by the results of Bhoi et al. [16], who reported that the rates observed for pure TG were significantly lower than those for a mixture of TG and FFA. They also estimated that for a mixture containing 20 wt% FFA, the rise in solubility was of the order of 1.35–1.5 times the solubility in pure TG. Similar results have also been reported by Singh et al. [17].

The application of a model that considers the mentioned effects in the three consecutive reversible reaction steps shown in **Figure 1** is not an easy task, since it requires data on liquid-liquid distribution for reactants and products and the relative proportion of each phase at different reaction conversions.

Bhoi et al. [16] developed a model that incorporates the effect of mass transfer resistances at both L-L and L-S interfaces for the transesterification reaction and simulated an FBR. Experimental data were obtained from two reactors, a spinning basket reactor (SBR) and an FBR and using a catalyst in pellets of a 6-mm diameter and an 8–10-mm length. Higher reaction rates in the reactor free of external diffusive resistances, that is, the SBR, were observed, concluding that the FBR is strongly hampered by external mass transfer resistances. The estimated kinetic parameters with the SBR were observed to be affected by internal diffusive resistances, which were corroborated by an estimated value of the activation energy of 25 kJ/mol, corresponding to the first reaction (forward) shown in **Figure 1**. Although this reaction was only considered in their kinetics for lower conversions, they were able to estimate the L-L and the L-S mass transfer coefficients. The latter was found to be four to eight times higher. Thus, they concluded that resistance in the L-L interface determined the overall rate of the process.

Bhoi et al. [1] developed a model for an FBR with axial dispersion considering mass transfer limitations in the catalyst as well as dynamic aspects. The reactor was considered to operate isothermally considering that transesterification reactions are almost athermic. The reaction stage consisted of two FBR connected in series and at 50 bar and 175°C. The simulations yielded a conversion of triolein (model feedstock) of 87% with a methanol:triolein ratio of 36:1 mol/mol, over a solid alkaline catalyst. It was found that the kinetic system behaves according to a second-order rate law. Adsorption terms were not included in the developed kinetic expressions. Similar to what has been reported for homogeneous-catalyzed transesterification of triglycerides, the calculation of the kinetic coefficients for the three reactions shown in

Figure 1 indicated that the first reaction was the fastest, while the second and third reactions were about one order of magnitude lower.

In an experimental study that considered the adsorption process, Dossin et al. [18] evaluated the intrinsic kinetics of the transesterification of ethyl acetate with methanol over an MgO catalyst. Among the evaluated models, the one that best fitted the experimental data corresponded to an Eley-Rideal (ER) type model, with the adsorption of methanol as the rate-limiting step.

3.3. Other transesterification methods

Other promising transesterification methods for producing biodiesel that are gaining more relevance as research progresses are enzyme catalysis and supercritical methanol.

Among the main advantages of using enzymes (free or immobilized) is that they can process variable and low-quality feedstocks, as they are less sensitive to high FFA and water content. Then, enzymes can process FFA and TG in a single reaction step. Moreover, when using enzymes, there is no need for a subsequent washing step. On the other hand, lipases have the disadvantage of being sensitive to high concentrations of methanol, and their implementation is currently more expensive compared with other methods. The mechanism widely accepted for describing enzymatic transesterification corresponds to a double-displacement type or a ping-pong mechanism [19]. This reaction scheme presents a great complexity to be modeled, since the number of kinetic coefficients involved is high, and their experimental determination is a great challenge. Due to this complexity, simplified models are used, which generally do not describe the formation and transformation of di- and monoglycerides, as well as the influence of temperature on the enzyme deactivation and the conversion limits derived from equilibrium. The complexity of the process can further increase if the presence of multiple phases is taken into account when immobilized enzymes are employed. Moreover, stearic effects may have an important impact due to the large size of the glyceride molecules. To promote the fitting of experimental data to kinetic models of the process, simplified models such as the Michaelis-Menten type are used [20], although their predictive capacity is limited generally. Kinetic studies on the enzymatic production of biodiesel have been performed mainly with immobilized lipases, and most of these simplified models consider only irreversible reactions. Firdaus et al. [2] applied a simplification of the ping-pong model that resulted in the evaluation of about 30 rates coefficients, including those corresponding to the reversible steps. This model was later applied to describe the transformation of oil with a liquid lipase from *Thermomyces lanuginosus* in a 24-h reaction at 35°C. The authors analysed, among other aspects, the effect of water and FFA content and reported that the biodiesel obtained nearly complies with the quality standards.

Catalytic and non-catalytic transesterification using an alcohol at supercritical conditions is another method under intensive investigation. This process has a high potential for both the transesterification of TG and for the esterification of FFA. Conversions reported are commonly greater than 90%, and reaction times are as short as 10 min or less [21]. The high temperatures and pressures required for the application of this technique represent, however, a limitation for its development and application, mainly due to the high energy costs of the process. In recent years, there have been an increasing number of reports in which this process is applied, either with the use of a catalyst or without it. In a recent work [22], the application of simplified kinetic models that describe only the formation of esters and disappearance of triglycerides as a function of conversion has been performed.

4. Analysis of general aspects affecting the kinetics of transesterification

4.1. Homogeneous catalysis

Homogeneous catalysis is commonly used during transesterification reaction, and alkaline and acid catalysts are used. The most active catalysts have been reported to be alkaline ones [23].

4.1.1. Reaction mechanisms

Two mechanisms are involved in transesterification reaction depending on whether acid or basic catalysts are used.

4.1.1.1. Basic catalysis

In the case of alkaline catalysts, the reaction proceeds very fast, hydroxides, alkoxides, and sodium and potassium carbonate being the most commonly used catalysts (**Figure 2**). When an alkali is used, the first step is the formation of an alkoxide, which is a strong nucleophile that attacks the electrophilic carbon in a carbonyl group of the triglyceride. This attack turns the carbonyl into a tetrahedral intermediate as shown in the second step. Then, the tetrahedral carbon is separated from the intermediate to form an alkyl ester (third step). Deprotonation of catalyst regenerates the alkali, whereas the proton is attached to a diglyceride anion as shown (fourth step). Catalyst can react with another alcohol molecule and the mechanism is repeated until the catalyst reacts once again with an alcohol molecule to produce glycerol and alkyl esters [24].

4.1.1.2. Acid catalysis

When sulphuric or sulphonic acid is used, a very high yield of alkyl esters is obtained. In this case, the reaction mechanism is acid catalyzed. Early research [3] has reported that transesterification of soybean oil with methanol reached almost 100% after 50 h of reaction at 65°C using 1 mol% of sulphuric acid with an alcohol-to-oil molar ratio of 30:1 mol/mol, whereas using ethanol and 1-butanol as alcohols took 18 and 3 h, respectively; however, reaction temperature was higher (78 and 117°C, respectively). Inconvenience such as glycerol recovery due to alcohol in excess is to be expected by which the oil-to-alcohol molar ratio needs to be optimized [24].

Figure 3 shows a schematic reaction mechanism when an acid is used as catalyst, which is valid not only for a monoglyceride but also for di- and triglycerides. Protonation of the carbonyl group is the first stage (I). A carbocation (II) is then formed and undergoes a nucleophilic attack. Alcohol is attached to the tetrahedral intermediate (III), and a new ester (IV) is obtained by glycerol elimination and catalyst regeneration. The carbocation formed in step II is highly reactive by which water must be avoided during reaction because this molecule can act as a nucleophile and form carboxylic acids, which is a competitive reaction [24].

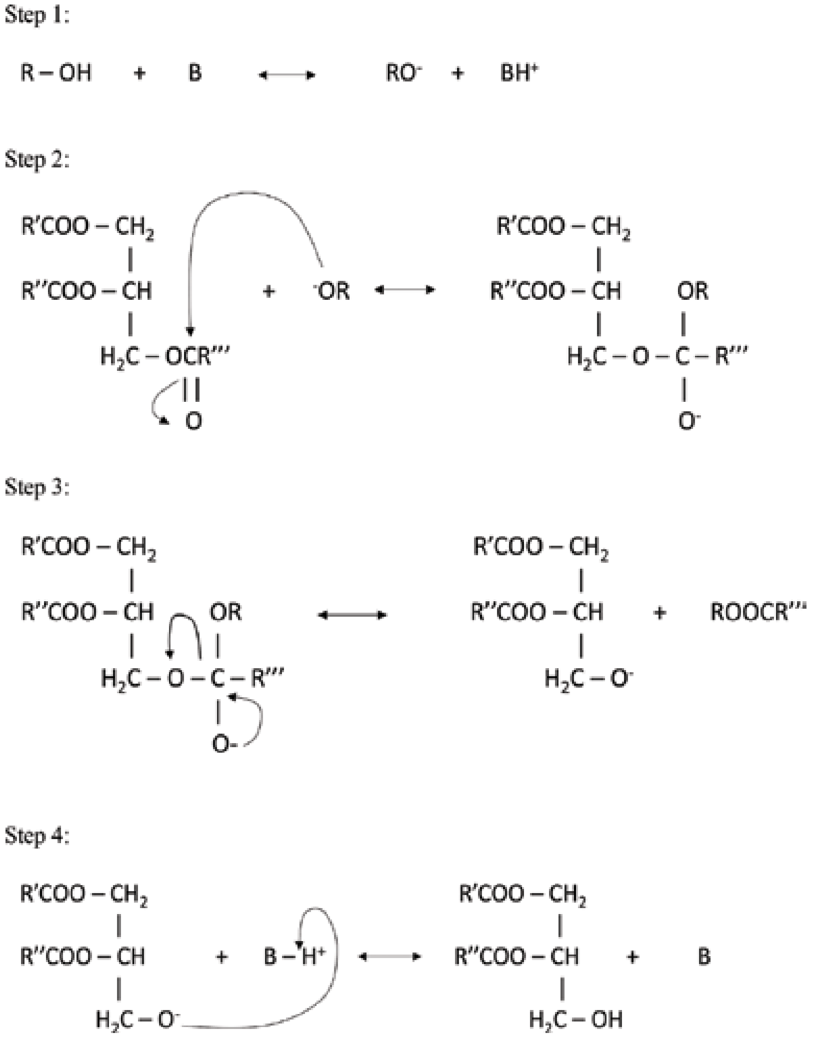

Figure 2. Alkali-catalyzed reaction mechanism.

To select the most suitable transesterification reaction pathway, either alkaline or acid, it is necessary to determine firstly the FFA content. This value must be lower than 3 wt% to proceed by the alkaline-catalyzed route without the significant formation of soap. This can lead to an emulsion that makes difficult the biodiesel and glycerol phases separation. Thus, oils with a high FFA content require a two-step process to be converted into biodiesel: (1) the FFAs are converted to fatty acid methyl esters as a pre-treatment with acid and (2) transesterification with basic catalyst is carried out [4, 25]. In this way, both the acid- and alkaline-catalyzed processes are efficiently used.

4.1.2. Mass transfer limitations and reactors for transesterification

Since alcohol and triglycerides are immiscible at room temperature, stirring needs to be carried out to enhance the contact between phases so that a perfect mixing is achieved, avoiding

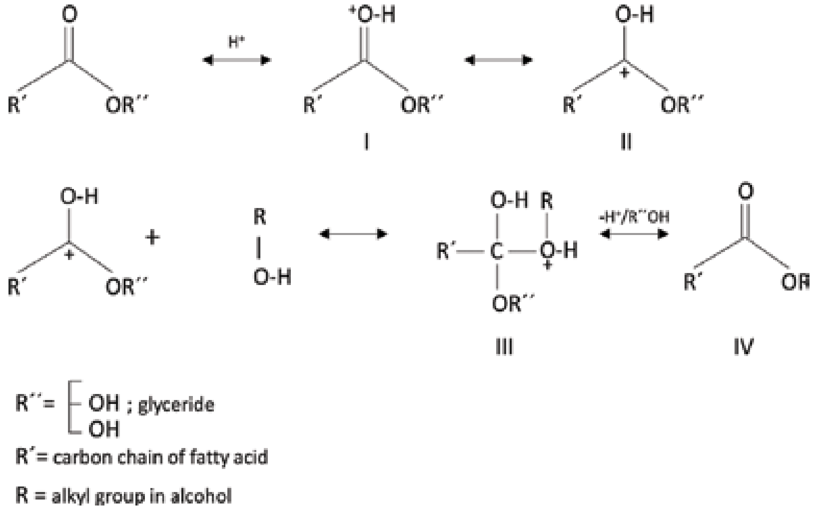

Figure 3. Acid-catalyzed reaction mechanism.

mass transfer limitations and performing the reaction under an intrinsic kinetics. This is not so easy to achieve.

Mass transfer limitation studies have been reported and modeled in detail in a continuous tubular reactor at different reaction conditions [26, 27]. According to the authors, there are two steps that need to be addressed: (1) the reaction mixture passes through the mass transfer-determining region (heterogeneous system where methanol is the dispersed phase and the oil is the continuous phase) to (2) the kinetic-determining region (pseudo-homogeneous system in a single phase).

When using methanol, an emulsion is very quickly formed which is then broken down into two phases, that is, an upper phase constituted by methyl esters and a lower one formed by glycerol. When NaOH is used as catalyst, for example, it dissolves into the alcohol and then triglycerides diffuse through this mixture, and so the reaction is initially mass transfer controlled [4].

Transesterification by supercritical conditions is another reported process to reduce the mass transfer limitations. Several reports have discussed different supercritical conditions to carry out transesterification [28–45] ranging in the case of temperature from 270 to 350°C and pressure from 10 to 45 MPa to ensure only one reacting phase, which eliminate the mass transfer limitations; however, an increase in operation cost is to be expected, while high temperature and pressure could enhance the degradation of fatty acids or FAME, which is known to occur above 250°C. Reaction time has also been reported to vary from 4 to 110 min. The alcohol-to-oil molar ratio is also quite high at these conditions, that is, from 20 to 40. At supercritical conditions, alcohol acts as an acid catalyst [29] and FFA and water present in the feed do not affect the transesterification conversion [46].

To further minimize the mass transfer limitations, reactors that enhance the contact between phases can be used. One of these reactors is the so-called oscillatory baffled reactor (OBR) composed of a tube containing equally spaced orifice plate baffles in which the oscillatory flow forms vortices, improving radial mixing and plug flow behavior [47]. Optimal baffle spacing has been previously calculated, and it was found that mass transfer rate depends on this spacing along with oscillation frequency and amplitude [48]. A better contact between phases is obtained with the use of static mixers consisting of motionless elements inside a pipe or a column to create radial mixing between immiscible liquids [49, 50]. A micro-channel reactor also improves the mass and heat transfer because of its high surface area/volume ratio which enhances the yield of methyl esters (above 90% in short reaction time) as reported elsewhere [51]. Cavitation-based reactors use acoustic energy to collapse cavities that increase local temperature and pressure. Cavitation intensifies the mass transfer rate creating local turbulence and reaching a high yield of FAME at room conditions [52]. Other studies have reported a FAME yield higher than 95% at 35°C, with an ultrasound frequency of 40 kHz at 1200 W of power using 1 wt% of KOH as catalyst, a methanol-to-oil molar ratio of 6:1 mol/mol, for 25 min [53].

4.1.3. *Effect of catalyst concentration*

As mentioned earlier, if FFA or water content is high, then acid-catalyzed transesterification is preferred. In this case, sulphuric, phosphoric, hydrochloric, or sulphonic acids are the most used catalysts. A comparison among HCl and H_2SO_4 as catalyst was made elsewhere and the latter behaved better at 2.25 M [54]. Sulphuric acid at 0.87 M was used during transesterification of Hevea br*a*siliensis at ca. 56°C and 240 min of reaction time [55].

Alkaline catalysts such as sodium alkoxide are very active in short reaction times at low catalyst amount but anhydrous conditions are required. Instead, KOH and NaOH can be used in typical concentrations from 0.4 to 2% w/w of oil [4]. Earlier studies have reported that potassium carbonate (2–3%) as catalyst yielded a high content of methyl esters with minimal soap formation [56]. Encinar et al. [23] used KOH at 0.7% w/w of oil and obtained around 98% of methyl esters. The higher the catalyst concentration, the higher the reaction rate. However, catalyst in excess will turn the separation of products very difficult by which the amount of catalyst must be optimized.

4.1.4. *Effect of mixing speed*

When the methanol and sodium hydroxide solution are immiscible, mixing is necessary to promote the reaction [57]. The initial agitation improves the contact among phases and reduces the mass transfer limitations. Once reaction advances, methyl esters formed act as solvent for reactants and mixing needs to be continued for promoting the reaction rate. Mixing speed was studied by Encinar et al. [23] varying from 500 to 1100 rpm. The optimal mixing speed was stated at 700 rpm, and only a slight increase on the yield of methyl esters was observed above 95%.

4.1.5. *Effect of solvent/co-solvent*

Oil concentration in alcohol is low, particularly when methanol is used once transesterification reaction begins. As oil concentration increases in alcohol, the reaction rate is also increased and triglycerides are converted into diglycerides, which subsequently can react in the alcohol phase rather than being dispersed into the oil phase. As reaction progresses, a glycerol layer is separated. To reduce the mass transfer limitations, the use of nonreactive co-solvents to form a single phase is recommended [58]. Co-solvents such as tetrahydrofuran (THF), dimethyl ether and methyl tert-butyl ether (MTBE) have been reported to improve miscibility among alcohol and oil. Previous reports [58] have stated that THF and MTBE behave as good co-solvents, THF being better than MTBE. Using a ratio of 1.25 vol/vol of methanol and keeping the methanol-to-oil molar ratio in 6:1 mol/mol at 23°C, the yield of methyl esters was 95% at 20 min. Other authors have studied the influence of methanol/co-solvent molar ratio in the range of 1:0.5–1:2 mol/mol and different co-solvents such as acetone, diethyl ether, dibutyl ether, methyl tert-butyl ether, diisopropyl ether and tetrahydrofuran [23]. Diethyl ether was the preferred co-solvent in a methanol/co-solvent molar ratio of 1:1 mol/mol.

Acetone was used as co-solvent at 25 wt% using KOH as catalyst at 1 wt% and 4.5:1 mol/mol as methanol-to-oil molar ratio, and a yield of 98% of methyl esters was obtained at room temperature after 30 min [59]. Acetone at 20 wt% as co-solvent has also been reported elsewhere [60]. Other authors used dichlorobenzene and acetone at 10% (vol/vol) in methanol as co-solvents and reducing the reaction time by 60% [61]. THF was used as co-solvent in a methanol/co-solvent molar ratio of 1:1 mol/mol and 0.5 wt% of catalyst along with a methanol-to-oil molar ratio of 4:1 mol/mol, and a yield of 98% of methyl esters was obtained after 10 min at 40°C and 200 rpm [62].

When selecting a suitable co-solvent, one has to take into account that at the end of reaction, it will be removed and if possible it will be reused. Thus, its boiling point needs to be maintained low.

4.1.6. Effect of temperature

Temperature influences on kinetics and equilibrium of reaction. It diminishes the viscosity of products and improves the mass transfer. At high temperature values, saponification is enhanced, lowering the yield of methyl esters. If methanol is used, the reaction temperature is commonly set at a value lower than its boiling point [63]. The effect of temperature on FAME yield has been studied from 20 to 40°C. If co-solvent is used, then temperature will be lower than its boiling point to avoid vaporization. The authors found that the yield of methyl esters at 30°C was optimal [23]. Some authors have reported temperature values ranging from 50 to 60°C [64]. The use of novel reactors as mentioned earlier is intended to reduce the reaction temperature at near room temperature.

4.1.7. Effect of methanol-to-oil molar ratio

Stoichiometrically, three moles of methanol are required by one mole of triglycerides. Since transesterification is a reversible reaction, the addition of methanol in excess displaces the equilibrium toward products in such a way that triglycerides will be converted into methyl esters, by which commonly methanol-to-triglycerides molar ratio is set to 6:1 mol/mol or higher. Nevertheless, methanol in excess increases the cost of biodiesel production, and therefore its recovery is one of the options used to improve the economy of the process. Some reports have studied the effect of methanol-to-oil molar ratio on FAME yield and have found an increase in the yield of methyl esters from 86 to 95% when increasing the molar ratio from 6:1 to 10:1 mol/mol [65]. When using waste cooking oil as feedstock, a higher methanol-to-oil molar ratio of 16:1 mol/mol decreased the yield of FAME, probably because of a reduced catalyst concentration in the reacting mixture. Thus, the optimal molar ratio was 10:1 mol/mol

[65]. In other cases, the optimal alcohol-to-oil molar ratio has been reported to be 9:1 mol/mol that yielded ~94% of methyl esters [23]. This molar ratio is also reported in previous reports [66]; however, depending on the type and quality of the oil, the methanol-to-oil molar ratio must be optimized in each case as in catalyst concentration.

4.1.8. *Effect of reaction time*

The conversion of triglycerides increases as the reaction time gets longer. In the case of alkaline catalysts, the reaction time is lower than 90 min to reach a maximum yield of methyl esters. As the alcohol and oil mixing starts, their immiscibility slows down the reaction within the first minutes; however, when reactants are well mixed, the reaction proceeds fast [63]. When acid catalysts are used, the reaction time is commonly increased up to several hours as reported before where sulphuric acid in the presence of soybean oil and methanol took 50 h to reach almost 100% of yield of methyl esters [3]. As in the case of methanol-to-oil molar ratio and temperature, the optimal values need to be found for each case depending on the catalyst type and the oil to be used.

4.2. Heterogeneous catalysis

The transesterification of triglycerides by heterogeneous catalysis is an alternative way to produce a biofuel that could help to reduce CO_2 emissions at reduced production costs, becoming thus competitive with petroleum-based diesel fuel [67–69]. There are still many areas of opportunity to improve the economy of the process. Heterogeneous transesterification has been shown to reduce the separation operations, the generation of waste and the use of large quantities of water [70]. One of the most difficult challenges is to find a catalyst with comparable activity to that of homogeneous catalysis, that is, at the same pressure and temperature and in which leaching is not present [71].

4.2.1. *Kinetics*

The kinetics of the transesterification reaction of oils and fats by heterogeneous catalysis is not so well understood as it is for homogeneous catalysis [72]. Most research works on heterogeneous catalysis have been focused on the synthesis and application of catalysts, and only a few deal with kinetic modeling. Among these, the efforts have been put on the use of small solid particles to obtain reaction conditions under an intrinsic kinetics and in which the phenomena of both intraparticle and external mass transfer are negligible.

Thus, most heterogeneous vegetable oil transesterifications have found to follow a pseudo-first-order rate law. For example, Kaur and Ali [73], in their study with 15-Zr/CaO-700 catalyzed methanolysis and ethanolysis of Jatropha curcas L. oil, found that both reactions followed a pseudo-first-order rate law. The negligibility of the transport influences was demonstrated by the Koros-Nowak test. Lukić et al. [74] also found at optimal conditions for the transesterification of sunflower oil a first-order reversible rate law using a ZnO-alumina/silica-supported catalyst and by evaluating both the effects of the calcination temperature and the effects of various supports. A number of kinetic modeling works of heterogeneous transesterification are presented in **Table 1**.

Oil source and catalyst	**Reaction conditions**	**Kinetic model: rate constant (*k*) and activation energy (E_a)**	**Ref.**
Soybean oil Catalyst: Amberlyst A26-OH basic ion-exchange resin	Molar ratio 10:1, methanol:oil with 5% oleic acid and without acid Agitation speed: 550 rpm Temperature: 50°C	Kinetic model: Eley-Rideal $k = 7.48x10^{-4}$ h^{-1} without FFA $k = 1.94$ h^{-1} with FFA	[72]
Jatropha Curcas L. oil Catalyst: Zr/CaO	Agitation speed: 500 rpm Methanolysis Molar ratio 15:1 methanol:oil Temperature: 65°C Ethanolysis Molar ratio 21:1 ethanol:oil Temperature: 75° C	Kinetic model: Pseudo-first order $E_a = 29.8$ KJ mol^{-1}; $k = 0.062$ min^{-1} $E_a = 42.5$ KJ mol^{-1}; $k = 0.0123$ min^{-1}	[73]
Sunflower oil Catalyst: ZnO/alumina-silica, 2 wt %	Molar ratio 30:1 methanol:oil Temperature: 200°C Pressure: 37 bar Reaction time: 4 h Catalyst ZnO Al/Si ratio 3/1 Calcination 600 °C, 12 h Catalyst ZnO Al/Si ratio 3/1 Calcination 300 °C, 12 h Catalyst ZnO Al/Si ratio 1/0 Calcination 600°C, 12 h Catalyst ZnO Al/Si ratio 1/0 Calcination 300 °C, 12 h	Kinetic model: First-order, *k* model irreversible (for catalyst with lower activity) k_1, k_{-1} model reversible $k = 0.0138$ min^{-1}; $k_1 = 0.0190$ min^{-1} $k_{-1} = 0.00140$ min^{-1} $k = 0.0027$ min^{-1}; $k_1 = 0.0054$ min^{-1} $k_{-1} = 0.00170$ min^{-1} $k = 0.0036$ min^{-1}; $k_1 = 0.0059$ min^{-1} $k_{-1} = 0.00082$ min^{-1} $k = 0.0064$ min^{-1}; $k_1 = 0.0068$ min^{-1} $k_{-1} = 0.00014$ min^{-1}	[74]
Sunflower oil CaO, 1 wt % $Ca(OH)_2$, 1 wt % CaO·ZnO, 2wt %	Temperature: 60 °C Agitation speed: 900 rpm Molar ratio 6:1, methanol:oil Agitation speed: 900 rpm Molar ratio 6:1, methanol:oil Agitation speed: 300 rpm Molar ratio 10:1, methanol:oil	Kinetic model: Miladinovic model, *k* is an apparent reaction rate constant and *K* is a model parameter defining the TG affinity for the catalyst active sites. $k = 0.063$ $dm^6mol^{-2}min^{-1}$; $K = 1.63$mol dm^{-3} $k = 0.025$ $dm^6mol^{-2}min^{-1}$; $K = 0.539$mol dm^{-3} $k = 0.043$ $dm^6mol^{-2}min^{-1}$; $K = 3.414$mol dm^{-3}	[75]
Sunflower oil Catalyst: $Ca(OH)_2$, 1-10 wt % based on oil weight	Molar ratio 6:1 methanol:oil Reaction time: 5 h Temperature: 60 °C Agitation speed: 900 rpm	Kinetic model: Pseudo-first order. $k = 0.07(1-\exp(- C_{cat}/2.86)$; min^{-1} Where C_{cat} is the catalyst amount (in wt% based on the oil weight)	[77]

Oil source and catalyst	Reaction conditions	Kinetic model: rate constant (k) and activation energy (E_a)	Ref.
Sunflower oil Catalyst: CaO, 1, 2.5 and 10 wt %	Molar ratio 6:1 methanol:oil Temperature: 60 °C Agitation speed: 900 rpm	Kinetic model: Pseudo-first order reaction $k = 0.07$ min^{-1}	[78]
Canola oil Catalyst: Mg-Co-Al-La HDL, 2 wt%	Molar ratio 16:1 ethanol: oil Reaction time: 5 h Temperature: 413-473 K	Kinetic model: First order E_a: 60.5 KJ/mol	[79]
Sunflower and waste cooking oil Catalyst: CaO·ZnO 2 wt %	Molar ratio 10:1 methanol:oil Agitation speed: 300 rpm Temperatures range: 60-96 °C With sunflower oil Temperatures:	Kinetic model: Pseudo-first order Constant k and triglycerides (TG) mass transfer coefficient k_{mtTG}	[80]
	60 °C	$k = 0.043$ min^{-1}; $(k_{\mathrm{mt,TG}})_0 = 0.00021$ min^{-1} $(k_{\mathrm{mt,TG}})_{\mathrm{AVE}} = 0.012$ min^{-1}	
	70 °C	$k = 0.051$ min^{-1}; $(k_{\mathrm{mt,TG}})_0 = 0.00244$ min^{-1} $(k_{\mathrm{mt,TG}})_{\mathrm{AVE}} = 0.151$ min^{-1}	
	84 °C	$k = 0.083$ min^{-1}; $(k_{\mathrm{mt,TG}})_0 = 0.00285$ min^{-1} $(k_{\mathrm{mt,TG}})_{\mathrm{AVE}} = 0.244$ min^{-1}	
	96 °C	$k = 0.120$ min^{-1}; $(k_{\mathrm{mt,TG}})_0 = 0.140$ min^{-1} $(k_{\mathrm{mt,TG}})_{\mathrm{AVE}} = 0.170$ min^{-1}	
	With waste cooking oil		
	60 °C	$k = 0.120$ min^{-1}; $(k_{\mathrm{mt,TG}})_0 = 0.0038$ min^{-1} $(k_{\mathrm{mt,TG}})_{\mathrm{AVE}} = 0.311$ min^{-1}	
	84 °C	$k = 0.140$ min^{-1}; $(k_{\mathrm{mt,TG}})_0 = 0.0033$ min^{-1} $(\mathrm{k}_{\mathrm{mt,TG}})_{\mathrm{AVE}} = 0.493$ min^{-1}	
	96 °C	$k = 0.170$ min^{-1}; $(k_{\mathrm{mt,TG}})_0 = 0.0038$ min^{-1} $(k_{\mathrm{mt,TG}})_{\mathrm{AVE}} = 1.664$ min^{-1}	
Waste cooking oil Catalysts: Heteropoly acid, 10 wt %	Molar ratio 70:1 methanol:oil Agitation speed: 300 rpm Reaction time: 14 h Temperatures:	Kinetic model: First order $E_a = 53.99$ KJ/mol	[81]
	50 °C	$k = 0.059$ min^{-1}	
	55 °C	$k = 0.067$ min^{-1}	
	60 °C	$k = 0.091$ min^{-1}	
	65 °C	$k = 0.144$ min^{-1}	
	70 °C	$k = 0.1062$ min^{-1}	

Oil source and catalyst	Reaction conditions	Kinetic model: rate constant (*k*) and activation energy (E_a)	Ref.
Sunflower oil Catalyst: CaO, 1 wt %	Molar ratio 6:1 methanol:oil Agitation speed: 200 rpm Pressure: 1-15 bars Temperature: 60-120 °C	Kinetic model: Pseudo-first order with significant diffusion restrictions at 80 °C k [=] (10^{-3} min^{-1})	[9]
	Reaction time: 1.5 h	k(60°C) = 2.67, k(80°C) = 73.71, k(100°C) = 175.4, k(120°C) = 220.86	
	Reaction time: 2.5 h	k(60°C) = 3.08, k(80°C) = 88.09, k(100°C) = 140.77, k(120°C) = 131.96	
	Reaction time: 3.5 h	k(60°C) = 3.26, k(80°C) = 81.81, k(100°C) = 100.41, k(120°C) = 94.25	
	Reaction time: 4.5 h	k(60°C) = 5.32, k(80°C) = 77.68, k(100°C) = 76.94, k(120°C) = 72.79	
	Reaction time: 5.5 h	k(60°C) = 8.3, k(80°C) = 65.63, k(100°C) = 61, k(120°C) = 59.22	

Table 1. A review of kinetic models and reaction conditions of heterogeneous transesterification of vegetable oils.

4.2.2. Reaction mechanisms

The heterogeneous catalysis of vegetable oils takes place in a number of steps and in a three-phase system consisting of a solid (heterogeneous catalyst) and two immiscible liquid phases (oil and alcohol, usually methanol or ethanol). To determine the rate-limiting step, a comparison of rates of the different elementary steps should be performed. This has been tried by several researchers by using either the Eley-Rideal (ER) or the Langmuir-Hinshelwood-Hougen-Watson (LHHW) methods.

Jamal et al. [72] have used both ER and LHHW in the transesterification of soybean oil on an Amberlyst A26-OH basic ion-exchange resin and in the presence and absence of free fatty acids. They proposed a four-step mechanism: (1) methanol adsorption by ion exchange on basic resin surface; (2) fatty acid (oleic acid) adsorption by ion exchange on basic resin surface; (3) hydrolysis of tri-, di- and monoglycerides from soybean oil; and (4) transesterification of glycerides (tri-, di- and mono-) with basic resin surface-bound methoxide. By considering the first step as the rate-limiting step, they showed that the ER model describes better the surface interactions occurring on the resin.

Some other authors have developed kinetic models based on first-order rate law. The following three cases show how sunflower methanolysis kinetics has been modeled within two stages, the first one being the initial TG mass transfer limitations and the second one the chemically controlled region.

Tasić et al. [75] have developed a reaction model for the methanolysis of sunflower oil on three calcium-based catalysts: CaO, $Ca(OH)_2$ and CaO·ZnO, by using the chemical kinetics reported by Miladinović et al. [76], in which it is assumed that the methoxide ions are first adsorbed on the active centers and then they react with the liquid phase TG that are close to the active centers. The mass transfer limitations of the methanol adsorption were found to be negligible.

Miladinović et al. [76] also used a first-order reaction rate with respect to TG and FAMEs, respectively. Tasić et al. [75] also showed that the TG mass transfer limitation depends on the methanol-to-oil dispersion. When it is not fine enough, the available active surface is small. To reduce that effect, that is, to increase the TG-methanol miscibility, a co-solvent can be added. However, these authors found that FAME can act as a co-solvent, and therefore as it is formed, the interfacial area gets larger, and hence the transfer limitations become smaller.

Stamenković et al. [77], studied the kinetics of the methanolysis of sunflower seed oil at 60°C, using a methanol-to-oil molar ratio of 6:1 mol/mol and different amounts of $Ca(OH)_2$ catalyst. They proposed a pseudo-first-order reaction kinetic model and related the TG mass transfer limitations to the limited available surface area that resulted from the high adsorbed methanol concentration in the first stage of the reaction. Mass transfer limitations were also important when small amounts of catalyst were used (1–2.5 wt%, oil based). When the catalyst was used in amounts greater than 10 wt%, the significant agglomeration of catalyst particles occasioned the limitation of TG mass transfer.

4.2.3. Effect of particle size

Practically, the entire active surface of the porous granules is internal, and the reaction that takes place inside the pellet consumes reactants and induces internal gradients of concentration and temperature which may be of sufficient magnitude to cause a significant variation of the reaction rate. Thus, the size of the particles of the catalyst affects the mass transfer at both intraparticle and at the interface. A suitable size of particle can be found experimentally so that a reaction rate and the final conversion degree do not depend on it, which is fundamental in kinetic studies to obtain the intrinsic kinetics.

There are few studies on particle size in the production of biodiesel by heterogeneous catalysis. Veljković et al. [78] in their study on sunflower methanolysis with CaO showed that the intraparticle diffusion of reactants from the surface to the active sites was the rate-controlling step; however, when they used catalyst particles in between 3 and 15 μm, they found no influence of the average particle size on the reaction rate and the final conversion, which indicated that the resistance due to intraparticle mass transfer was negligible in this size range.

Li et al. [79] in their study on ethanolysis of canola oil using a lactate dehydrogenase (LDH) oxide catalyst (Mg_2CoAl) compared the reaction rates for two different particle sizes, one being greater than 1 mm and another being less than 100 μm, both at the same conditions. In both cases, a reduction in the conversion was found, indicating that there is a resistance to internal mass transfer and therefore an intraparticle diffusion control. However, for both cases, the rates were very similar in between 30 and 90 min, but with a delay of about 15 min for the larger particles. They concluded that the conversion rate was kinetically controlled rather than intraparticle diffusion.

4.2.4. Effect of stirring speed

The stirring speed plays an important role in the evaluation of the limitations of external mass transfer, so to corroborate if there are external mass transfer limitations from the reactants to the particle surface, a study of the reaction rate is usually carried out at different agitation speeds. Veljković et al. [78] carried out studies at agitation speeds of 700 and 900 rpm for a methanolysis reaction with 1 wt% catalyst and speeds of 900–1250 rpm with a 10 wt% catalyst, and by using the correlation of Dossin et al. [18], they found that the minimum stirring speed to carry out a perfect mixture and a complete suspension of catalyst particles was 430 rpm for the former and 740 rpm for the latter. They found that agitation speeds of 1250 rpm introduced air inside the reactant mixture. The experimental conditions and values of the kinetic constants are summarized in **Table 1** [78].

4.2.5. Effect of temperature

The effect of temperature on the reaction rate plays also a very important role since the rate constants are temperature-dependent. The temperature can influence transport phenomena in heterogeneous catalysis; Lukić et al. [80], for example, conducted the transesterification of sunflower and waste cooking oil using methanol at temperatures in a range between 60 and 96°C. As catalyst, they used CaOZnO with a methanol-to-oil molar ratio of 10:1 mol/mol. They showed that at relatively low temperatures of 60–70°C and at the start of the reaction for the production of esters, there is a resistance to the mass transfer, but with an increase in the production of methyl esters, the resistance to mass transfer reduced, so that the initial TG mass transfer limits the rate process, and eventually as biodiesel concentration increases, the chemical reaction is the rate-limiting step. For temperatures higher than 84 and 96°C, the resistance to mass transfer is almost negligible, and thus the conversion rate is controlled by the chemical reaction. The reaction rate was expressed by a pseudo-first-order model and corresponding values of the mass transfer coefficients.

In another study [81], a heteropoly acid catalyst was used to carry out the transesterification reaction of waste cooking oil with methanol temperatures in the range of 50–70°C to determine how temperature influences the conversion of TG. The conversion degree had a considerable increase when the temperature increased from 50 to 65°C, in the range of 40% (from 20 to 60%) at 50°C and 57.6% (from 31 to 88.6%) at 65°C. However, above 65°C, the conversion rate decreased, which was claimed to be due to the chemical reactions that occur during the cooking process, as these reactions can generate undesirable components such as free fatty acids that cause a decrease in the conversion of TG and therefore the production of biodiesel.

4.2.6. Effect of alcohol-to-oil molar ratio

Methanol is mostly used for transesterification of vegetable oils, mainly to avoid the formation of a stable emulsion between biodiesel and glycerol. In practice, it is better to perform a study at different molar ratios for each specific case of conditions and catalysts. Vujicic et al. [9], for example, used CaO as catalyst to transesterify sunflower oil. An excess of alcohol was observed to influence the reaction kinetics, and the overall reaction rate was found to follow strictly a fourth-order kinetics, since each TG molecule should be converted into glycerol by consecutive reactions, first becoming diglyceride, then monoglyceride and finally glycerol, but when carrying out the reaction with a large alcohol excess, the kinetics was observed to follow a pseudo-first order (**Table 1**).

4.2.7. Effect of reaction time

Reaction time is very significant in the production of biodiesel by heterogeneous catalysis, since to obtain the same yields as those in homogeneous catalysis sometimes need up to more than five times the time that is carried by homogeneous catalysis. In the abovementioned work carried out by Vujicic et al. [9], the achieved activities at reaction temperatures of 80 and 100°C were significantly affected by the reaction run, and high steady-state conversions were reached after 5.5 and 2.5 h, respectively.

5. Simulation and optimization of biodiesel production

5.1. Simulation of transesterification process

The economic evaluation of biodiesel production is based on general mass and energy balances that can be obtained from process simulation [82]. Among the most common process simulators used for the simulation of biodiesel production are Aspen Plus®, Aspen HYSIS, PRO/II, SuperPro Designer, and VMGsim. These programs can be used to design and optimize a large-scale biodiesel production. **Table 2** shows relevant data for different simulation studies. Complimentary numbers can be found elsewhere [83–85].

The typical process simulation procedure involves definition of the components, selection of the thermodynamic model, property estimation, drawing of the flowsheet, definition of chemistry and kinetic models, and the input of units and operation conditions.

Most simulators do not contain all the components present in the transesterification reaction, so that their properties cannot be estimated. Thus, triolein ($C_{57}H_{104}O_6$) is regularly used as a model compound of TG, mainly because it accounts for 40–75 wt% in most used oils for biodiesel production, such as olive, canola, palm and jatropha oils [83, 86], and hence biodiesel is represented by methyl oleate ($C_{19}H_{36}O_2$). When the oil contains FFA that requires an esterification pre-treatment process, oleic acid ($C_{18}H_{34}O_2$) is used as a model compound.

The most recent version of Aspen Plus® (ver. 10) includes most of the TG and methyl esters present in the transesterification reaction, including (tri)ricinoleine, which is the main component in castor oil. The properties of these components are estimated in the simulators. However, some important properties estimated for these components, for example, normal boiling points and vapor pressures, are somehow inconsistent with experimental data and databases, and therefore some researchers choose to update their values from either experimental data [87, 88], contribution methods [89] or from properties databanks such as NIST [83].

The Non-Random Two Liquid (NRTL) or the Universal Quasi Chemical (UNIQUAC) models are the preferred thermodynamic models, mainly because of the presence of highly polar compounds, such as methanol and glycerol. In Aspen Plus, however, the binary NRTL coefficients usually need to be estimated, which is commonly carried out by the UNIFAC LLE model for liquid-liquid equilibrium and Peng-Robinson or SRK equations of state for vapor. The performance of NRTL has been shown to be better than UNIQUAC [90]. These mod-

Materials		Reactor models		Operation mode	Thermodynamic model	Program	Production size	Reference
Feedstock (Model compound)	Catalyst	Transesterification	Esterification				Tonnes/year	
Rapeseed (triolein)	MgO	Eley-Rideal Pseudo second-order reversible	none	Bach and continuous (slurry)	UNIFAC	Aspen Plus	100000	[94]
Rapeseed (triolein)	KOH/Enzyme	Yield model (96 %)	None	Continuous (CSTR)	Dortmund UNIFAC	Aspen Plus	8000	[84]
Seven kinds of vegetable oils	NaOH	Second order reversible	None	Batch	Dortmund UNIFAC	Aspen Plus	9125	[83]
Cottonseed (pseudo-components)	NaOH	Second order irreversible	None	Continuous/Batch	Dortmund UNIFAC	Aspen HYSYS	562 (feed)	[95]
Soybean (triolein)	Nb_2O_5	Pseudo homogeneous (hydrolysis) reversible	Pseudo homogeneous	Continuous (Pack bed reactor/RDC)	Dortmund UNIFAC	Non-commercial computational code	2134	[96]
Soybean (triolein)	$Mg(OCH_3)_2$ (heterogeneous)	Second order reversible	None	Continuous (CSTR/RD)	Dortmund UNIFAC	Aspen Plus	7542	[97]
Palm (triolein)	KOH or NaOH	Second-order reversible	Second-order reversible	Continuous (CSTR)	UNIFAC and NRTL	Aspen Plus	100000	[98]
Soybean (trilinolein)	$NaOCH_3$	Conversion reactor (99%)	None	Continuous	NRTL UNIQUAC	Aspen Plus	150000	[99]
Jatropha (triolein)	NaOH	Conversion rector (98.86%)	None	Continuous (CSTR)	NRTL UNIFAC	Aspen HYSYS	8000	[100]
Waste cooking oil	Tungsten on alumina supported (WAI)	Conversion reactor (96.54%)	Conversion reactor (92.34%)	Membrane reactor	NRTL	Aspen HYSYS	N/A	[101]

Table 2. Key features of some simulation studies for biodiesel production.

els present different characteristics that make them complimentary [91], and the use of both (UNIQUAC as referenced model) can achieve more reliable simulations.

The Dortmund UNIFAC excess free energy model has also been used for the estimation of activity coefficients [84], as it has been found to provide good fit between estimated and measured methanol-biodiesel and methanol-glycerol vapor-liquid equilibrium data [92]. In this study performed by Kuramochi et al. [92], the Dortmund-UNIFAC was found to represent the best way to model the liquid-vapor equilibrium in the biodiesel process, while UNIFAC-LLE was found to be the best method to model the liquid–liquid equilibrium with methanol, methyl oleate and glycerin mixture and methanol water system. The COSMO-SAC model, included in Aspen Plus, has also been used for VLE calculations in the esterification reactor [93]. The advantages of this method compared to NRTL are that its predictions are based on quantum chemistry, and the parameters required for its use are of molecular and electronic nature, and therefore they will not be affected by temperature changes along the process [93].

The selection of a kinetic model for both the transesterification and esterification reactions is very important for determining the product yield and performance of the equipment. Despite the multiple kinetic models found in the study, as shown in Section 3, a number of simulation studies do not include a detailed kinetic model to simulate the reactors. Instead, the simulation is performed by using a stoichiometric or an equilibrium reactor and using a specific value for the conversion or yield. Different studies for base-catalyzed reaction use a conversion value in between 95 and 99%. Some authors [100] argue that the various kinetics and mechanisms are not clear enough to design methods to follow and hence they prefer to simulate the reactors as conversion reactors.

Similarly, since many kinetic models for transesterification reaction have been obtained for the entire mixture of TG and FFA, the use of triolein in the simulation does not entirely represent the observed kinetic behavior in the reactor. In addition, most kinetic models found in the study have only been derived for one TG as a pseudocomponent. A detailed kinetic, and hence a more realistic simulation, should include triolein, tripalmitin, trilinolein and tristearin, as they account for more than 90 wt% of jatropha, palm, soybean, rapeseed and sunflower oils [84, 102].

Lee et al. [103] have developed a kinetic model based on three TGs, that is, for each component, kinetics parameters have been estimated. This model was used by Garcia et al. [90], who simulated the biodiesel production by considering a feedstock containing four TGs.

Most simulation studies found in literature have been performed at a large-scale process; however, there seems to be a lack of data about industrial performances that are not totally realistic. A more comprehensive and close comparison between real plant operation and process simulation could help to reduce this gap.

5.2. Process optimization for biodiesel production

Optimization is one of the most quantitative tools in the industrial decision-making process [91]. The purpose of biodiesel production optimization is to find the value of the variables involved in the process that maximizes the profit, minimizes the cost of the process or maximizes the yield of biodiesel, so that the process becomes competitive in the fuel market. The optimization of biodiesel process should start from the optimization of the reaction conditions at a laboratory scale. This is usually performed by running a design of experiments and optimizing the conditions by the use of the surface response methodology (SRM). The model can later be validated at bench or pilot plant scale. Thus, the model can be used in the simulation process as a yield model.

The use of a simulator can also be useful to add different factors that are not present at a laboratory scale, as well as to optimize the operation of the different equipment in the industrial plants by performing a sensitivity analysis. Several optimization studies have been reported in literature, mainly to perform an economic analysis [84, 88], to determine the optimal conditions to maximize the conversion of vegetable oils [104], to perform sensitivity analyst of design parameters and operating conditions to optimize the operation of each step [96], to study the excess methanol recovery in continuous production [105] and to evaluate new process intensification technologies [106], among others.

6. Conclusions

The goal in the development of heterogeneous catalysis seems to be the development of catalysts with high activity at low temperatures and pressures, being selective, being stable and should not be deactivated by water or leached. The kinetic modeling of the transesterification reaction should include more TG components; this, however, requires a more detailed characterization of both the feedstock and reaction products. These detailed kinetic models should also allow the simulation of TG mixtures or feedstocks such as waste cooking oil. By doing so, a more realistic simulation and optimization of the process could be obtained. As chemical process simulators have been incorporating most of the components in the biodiesel process, it is expected that the estimation of the properties becomes more reliable in these programs and provide more realistic simulated results. There is, however, a need for information on industrial data for the different biodiesel technologies, so that the biodiesel simulation studies can be compared and be validated with industrial data.

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Study About Nitrogen Oxide Emissions and Fuel Consumption in Diesel Engines Fueled with B20

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Additional information is available at the end of the chapter

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Abstract

The use of biodiesel is one of the alternatives to reduce oil dependence in the transport sector and to reduce greenhouse gas emissions. One of the most common engines in Europe was subjected to some tests, aiming to discover the efficiency effects and the emission characteristics when consuming a fuel containing 20% of biodiesel and 80% of diesel (B20), and comparing the results with the use of 100% diesel (B0). Using an engine test bench, several working points of the engine were chosen considering different engine rotation from idle speed to 3500 rpm and from residual torque to 120 Nm, covering the great majority of the normal running operation of this kind of engines when installed in light vehicles. The results revealed a non-proportional effect for fuel consumption for different engine regimes where the energetic differences were, in some operation regimes, totally compensated with efficiency increase. The NOx emission analysis allows to admit that the use of biodiesel in the fuel leads to a consequence on emissions increase that is not always obvious, since in some regimes that increase is noticeable, but for other regimes a slight decrease or no significant change was detected.

Keywords: biodiesel, alternative fuel, energy, greenhouse gases, sustainability, NOx emissions

1. Introduction

The use of oil as a source of energy was a key factor in the development of industry, economy and world's society. Actually, society is strongly addicted to this energetic source, revealing an enormous inability to free itself from this submission. The world is also subjugated to the

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incessant desire to consume more energy, becoming increasingly degraded, subordinating all other aspects to be consumed almost exclusively in the control of privileged access to oil.

In 2009, the European Commission unveiled its intentions of promoting the use of renewable energy sources. In the so-called Energy Policy Objectives, this commission defined sustainability criteria for the use of biofuels, making it mandatory for each of the member states of the European Community to define concrete objectives in such a way that, in general, it could be possible, to reach a quota up to 20% of the European Union's final energy consumption from renewable energy sources by the year 2020. In order to achieve this goal, each Member State should promote and encourage energy efficiency and energy savings [1].

In order to reduce energy dependency on oil and CO_2 emissions, some measures have already been taken by the European Community [1] by setting targets for 10% of the energy used in the transport sector by 2020 to be obtained from biofuels. In the European Union, between 2005 and 2010, consumption of biofuels increased from 1.03 to 4.42% of total fuel consumption by the transport sector, but remained below the target set for 2010, with 5.75%. In parallel, there was a reduction in CO_2 emissions from transport of 16.4 megatonnes (Mt) in 2008 and 26.6 Mt in 2009, with a total of 920.74 Mt of CO_2 emissions [2].

The bet on biofuels is increasing and is an obvious alternative to the automotive sector, given the enormous amount of energy used by road vehicles, adding to the difficulty of finding alternative solutions to oil guaranteeing the essential energy mobility for this sector. In fact, the biggest problems in implementing solutions with lower environmental impact reside in the processes of distribution and storage of energy, making it accessible and allowing autonomy and reliability close to the existing solution. The European Community has determined the need to increase the production of commercially viable biofuels which are CO_2-efficient and compatible with combustion engines for motor vehicles [1] and also intends to ensure the development of biofuels from sources other than food sources [3]. From the European point of view, the use of biofuels increases security of energy supply, reduces greenhouse gas emissions and increases the yield and employability of agricultural activity [4].

The most widely used biofuel in Europe is biodiesel, an ester produced from vegetable or animal oils, through a transesterification process. This renewable energy source accounted for 82% of total biofuels produced in Europe (27 members) in 2003 [4] and in 2007 a share of 84.7% of all biofuels consumed [5]. The European Union is the largest producer and consumer of biodiesel, with a production of 9164 million liters of biodiesel in 2008, about half of the world's biodiesel production [6]. The world average of biodiesel production in the years 2013–2015 was 31.1 billion liters, and it is expected to reach 37.9 billion liters by 2020 [7]. The consumption of vegetable oils to produce biodiesel has been increasing in the World, mainly due to its renewable nature and to the fact that it is less polluting when compared to petroleum-based diesel. Biodiesel is a renewable fuel which can alternatively be used in internal combustion engines of compression ignition, without having to make any changes, substituting part or all of the fuel of fossil origin. The efficient use of biodiesel in the transport sector brings some important environmental, economic and social benefits, resulting in job creation, reduction of pollutant emissions, reduction of the country's dependence on petroleum and reduction of CO_2 emissions levels for the transport sector. The International Energy Agency believes that in 2050 it will be possible for biofuels to account for 27% of the total amount of fuels in the transport sector, which would reduce CO_2 emissions per year by 2.1 gigatonnes (Gt) if a sustainable system was considered [8].

Considering the use of biodiesel, savings in terms of CO_2 emissions can range from 36 to 83% when compared to conventional diesel [9]. However, for this fuel to be economically profitable, it will be necessary to use subsidies to balance the difference in the price of production and to account for the savings effects per tonne of CO_2 not emitted.

2. Literature review

Given the lower amount of available energy per unit mass of biodiesel compared to diesel, to provide the same amount of energy required by the engine, it would be expected an increase in fuel consumption when biodiesel was used. However, biodiesel affects engine combustion and the consequent emissions [10] existing several conditions that contribute to this behavior. These conditions are higher density of biodiesel, because fuel supply control is made on a volume basis; the existence of oxygen in biodiesel that can affect the thermal yield and other properties such as viscosity; the cetane number among others that affects how the fuel mixes in the heated air inside the cylinder and influences the way energy is released. It is still necessary to consider the cumulative effect of these parameters with the different interactions promoted by the use of diverse blends of biodiesel in diesel.

Analyzing what is reported by various researchers, there is often an association between increased fuel consumption caused by the lower calorific value of biodiesel [11]. In concrete terms, the heat-based calorific value of biodiesel is 10–14% lower than that of diesel [12] [13]. In this way, it will be expected that the mass consumption of fuel will increase in the same proportion. However, as already mentioned, the fuel supply to the engine is made on a volumetric basis, so given the density differences, where biodiesel is denser between 3 and 4% [13], it would be expected that specific fuel consumption (g/kWh) would increase by 10–14% and the volume (l/km) should increase by 5–10%. In the case of using a B20 blend, with 20% biodiesel and 80% of fossil diesel, it means that the difference in terms of amount of energy in that blend only implies a reduction of 2–3%.

Graboski and McCormick [14] explicitly state that regardless of whether the consumption of biodiesel is pure or mixed with diesel, a proportional fuel economy is revealed in the difference between the calorific value and there is no improvement or degradation of energy efficiency. In fact, the question is whether the use of biodiesel will promote an increase in energy efficiency. Deviations in this efficiency relative to diesel can be justified when considering other properties such as viscosity and density that promote changes in the type and shape of the spray and which affect the way the fuel is mixed in the air [15, 16] or when assessing the impact of the existence of oxygen on the molecular structure with biodiesel that modifies the way how combustion reaction is performed [15, 17–22]. It is explicitly referred by Demirbas [22] that despite the lower calorific value of biodiesel the oxygen content in this fuel promotes more complete combustion due to improved homogeneity in the local fuel mixture in the air.

Most of the authors report that the consumption of biodiesel in substitution of diesel fuel induces an increase in NOx emissions [11]. As possible causes for the variation in NOx emissions due to the use of biodiesel, pointed out by Graboski and McCormick [14], are the increase of the flame temperature and the decrease of the radiate effect that promotes the increase of the temperature in the combustion chamber, since the heat transfer by radiation is carried out by particles. Since biodiesel has reduced particle emissions, it decreases this ability to radiate heat, resulting in higher temperatures and consequently higher NOx emissions. In fact, the increase in the in-cylinder temperature is the most relevant parameter that causes an increase in NOx emissions [23].

The engine regime and the way how fuel flow interacts in the injection process for each regime shows to some significant differences with respect to the energy efficiency of the combustion process for the different fuels [24–33]. It is expressed by several authors that the use of 20% biodiesel in a mixture with 80% of fossil diesel (B20) corresponds to the optimum mixture where the maximum value of thermal efficiency is revealed and logically a minimum value of specific consumption is expected [11–13, 31, 33]. The study performed by Suresh et al. revealed that the engine presents different heat release rate behaviors with partial load and full load for diesel when compared with B10, B20 and B30, where B20 presents the most significant results [34]. Also the goals imposed by the European Union point out that in the near future the amount of biodiesel incorporated in the commercial diesel is close to 20%. This lead to the analysis that was done in the present work considering the realization of tests with a B20 blend covering all the operation regime of the engine, finding how this fuel affects engine in terms of energetic efficiency and in terms of NOx emissions, that is the most controversial emission for diesel engines, after the introduction of diesel particles filters (DPF).

3. Experimental methodology

Tests were completed using an engine test bench, equipped with a Schenk hydraulic dynamometer with a capacity to test engines up to 230 kW at a maximum engine rotation of 13,000 rpm and a torque limit of 600 Nm. It also has an AVL gravimetric fuel consumption measurement system and a Horiba gas analyzer. The schematic of the experimental setup is represented in **Figure 1**.

A data acquisition system collects the engine data, the equipment measurements (fuel consumption, exhaust emissions, temperature and pressure sensors). The acquisition system is integrated with a control system that defines the parameters specified by the test cycle imposed, without the intervention of the technician, which allows a better accuracy and reliability of the obtained results [20].

The engine used for these tests was a VW 1.9 TDI with four cylinders in line and 1896cm^3, developing a maximum power of 66 kW, with EuroII exhaust emission technology. This engine equipped a large part of the VW group of vehicles with great success, such as the VW Passat, VW Golf, Audi A3, A4 and Seat Ibiza. The main characteristics of the engine are presented in **Table 1**, including that it is a direct injection supercharged engine with EGR. This engine is known to have high reliability, allowing having a maximum torque a relative low engine rotation (202 Nm at 1900 rpm).

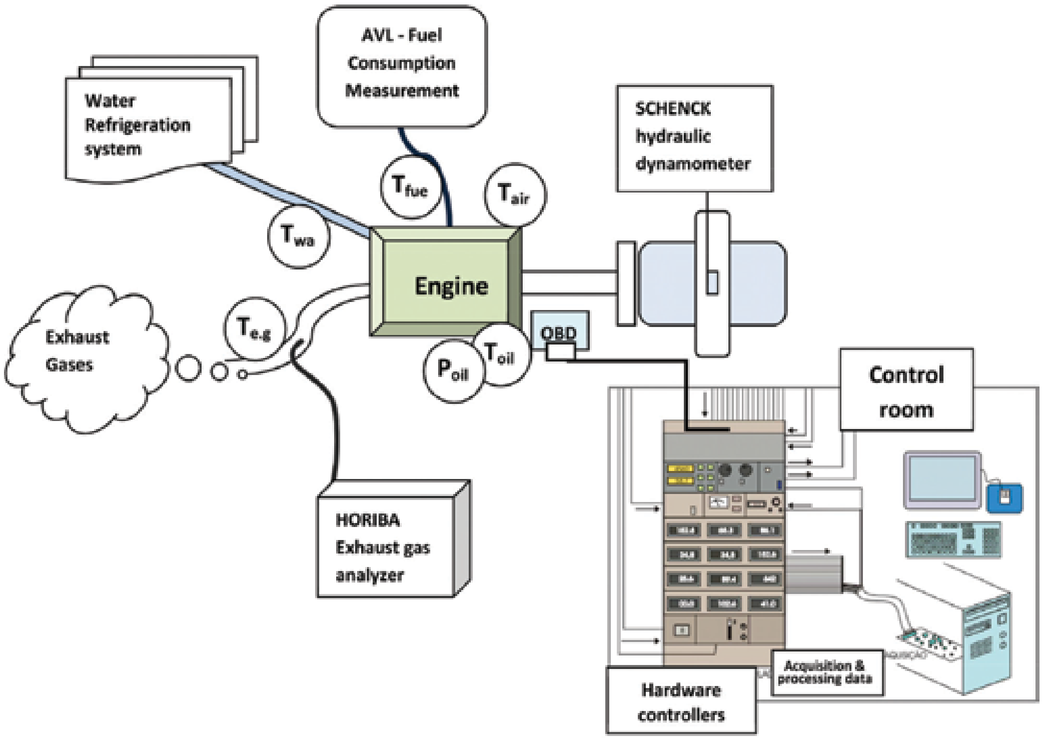

Figure 1. Engine test bench.

Tests were made using two different biodiesel blends (B0 and B20). The properties of the fuels, biodiesel and commercial diesel, are presented in **Table 2**. B0 is fully constituted by a petroleum-based fuel, and the B20 was made by mixing this base fuel with biodiesel constituting a blend in proportion 80 diesel – 20 biodiesel. This B20 blend was selected considering that the amount of petroleum diesel incorporated in diesel is of 5–7%, so it seems important to better characterize the expected blends in the next few years, considering that the use of 20% biodiesel will be a highly plausible scenario.

Since all engines are produced assuming that they will consume petroleum diesel fuel, it is important to define a specific methodology for this kind of studies, including the way how different fuels affect engine efficiency and performance. It is expected that the use of biodiesel, with different properties that interact differently with injection system and combustion process, will certainly produce effects on emissions and consumption [10]. Furthermore, there is a certain inadequacy of the regulated cycles for engine homologation to reflect the proper effects of changing from petroleum diesel to biodiesel in a certain proportion.

In the first evaluations of the engine's operation, it was verified that there were some problems that conditioned the test's performance. The original idea was to carry out a detailed analysis of the entire motor parameter map. In this way, a series of tests were carried out in stabilized regimes to obtain the consumption and emissions of exhaust gases relative to the engine

Engine	VW 1.9 TDI
Engine code	1Z/AHU
Type	4 cylinders in line, 8 valv.
Swapped volume	1896 cm^3
Compression ratio	19.5:1
Ignition system	Rotate pump with direct injection electronic controlled
Supercharged	Yes, with intercooler
Exhaust emissions technology	Yes (Euro II)
Power máx.	66 kW (89cv) @ 4000 rpm
Torque máx.	202 Nm @ 1900 rpm

Table 1. Main characteristics of the engine used in the bench tests.

Parameter/Unit	**Biodiesel (BD) (Soybean 86.5% + Palm 13.5%)**		**Fossil diesel (FD)**
	Results	**Method**	**Results**
Density at 15°C (kg/m^3)	**882**	EN ISO 3675	**840**
Ester Content [% (m/m)]	**97.7**	EN ISO 14103	—
Kinematic Viscosity at 40°C [mm^2/s]	**4.15**	EN ISO 3104	**2.43**
Flash Point (°C)	**>120**	EN ISO 3679	**>55**
Water Content (mg/kg)	**216.8**	EN ISO 12937	—
Iodine Value (g iodine/100 g)	**117**	EN ISO 14111	—
Sulfated ash content [% (m/m)]	**<0.02**	ASTM D 874	—
Cetane number	**51**	EN ISO 5165	**>51**
Higher heating value (HHV) [kJ/kg]	**39,909**	ASTM D 240	**45,620**
Oxidation stability, 110°C (hours)	**6.3**	EN 14112	—

Table 2. Biodiesel and fossil diesel properties.

operation from idle to 4000 rpm in successive increments of 500 rpm, and from 0% load up to 80% load, in increments of 20%.

However, it was found that in certain schemes engine operation became quite unstable due to several occurrences: the opening and closing of the exhaust gas recirculation "EGR" valve; the functioning of the turbocharger and the waste gate valve which adjusts its operating pressure, and the excessive heating of the engine in higher load conditions. Thus, after a few attempts to establish a procedure that would allow reliable data to be obtained and at the same time guarantee the operability and reliability of the engine without damaging it, a 30-point table was chosen, shown in **Figure 2**. This distribution covers the major part of the engine operating regime when in normal operation to drive a light vehicle.

The sequence of the tests was as follows: after ensuring the stabilized normal operating conditions of the engine on the test bench, the speed of rotation is set at 1250 rpm, with the brake torque at its minimum value, corresponding to the residual torque which is the sum of the energy losses due to friction and to the inertia that must be overcome in order to keep the engine at the desired speed.

After reaching a stable operation, reading and acquiring the information about the performance of the motor at this operating point, the torque value is increased to 40 Nm, for the same rotation, waiting for the stabilization of the operation of the various parameters to make the data acquisition. This process is repeated in successive steps for various values of resistant torque until reaching the value of 120 Nm. At this point and after data collection, the rotation is increased to 2000 rpm. Following the stabilization at this rotation value, the cycle already performed is repeated, but successively decreasing the torque value by 20 Nm, with the corresponding lowering of the throttle position.

The process is repeated by maintaining the descending torque sequence until the throttle reaches the minimum position. When this operating point is properly characterized, the whole process will be repeated with the increase of rotation to 2500 rpm, followed by the addition in terms of torque to the value 120 Nm, doing the same in the downward direction, with successive increments of 500 rpm, repeating this sequence until the rotation reaches 3500 rpm. In the most demanding conditions, such as rotations above 3000 and 3500 rpm with torque

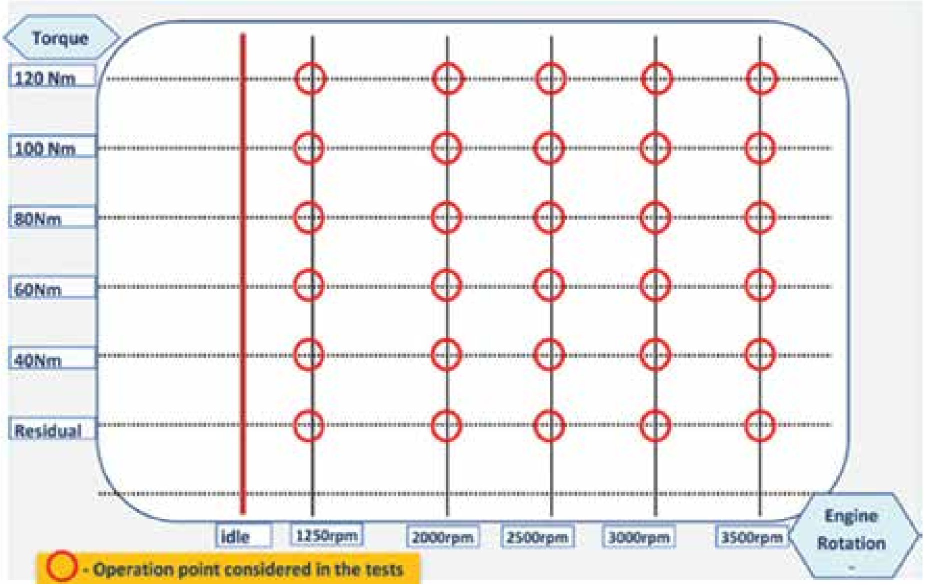

Figure 2. Operation points chosen for the tests.

values above 80 Nm, it was found necessary to interrupt the sequential process to allow engine cooling. Thus, when the engine oil temperature was no longer stable, the cycle was interrupted so that some of the accumulated energy could be dissipated and the established process could continue.

4. Results

Each of the cycles defined in the methodology was repeated two times, according to a certain sequence that would allow analyzing possible degradations in the operation and in the performance of the motor. As such, two measurements were performed with B0, followed by three measurements with B20 and a new measurement with B0. The results obtained are the average of the three measurements whenever they do not differ by more than the standard deviation of the three measurements made. When this happens, the value that shows higher deviations from the average value is not considered, resulting in the final value considered from the average of the two values that meet the defined criteria.

Of all the information collected a large part served as a way of controlling the process in order to guarantee the comparability of the results and to verify the occurrence of some situations, as was verified for the control of the exhaust gas circulation and the turbocharger, for example.

The data presented are related to the two most relevant aspects of this work, fuel consumption and NOx emissions, which are more controversial about how the use of biodiesel affects the engine. The emissions of CO and HC are not the most problematic emissions for this type of motor and, considering the low resolution of the equipment in the measurement of CO, it was decided to devote more attention to the emissions of NOx, having not considered the emissions of CO and HC, although the data on these combustion products were collected.

4.1. Fuel consumption

The results presented relate to the consumption on a mass basis, through the result of the specific consumption (g/kWh), taking into account that the measurement was carried out according to a gravimetric process to avoid problems with fuel density. Considering the importance of the efficiency process in the evaluation of the engines, the results in terms of energy conversion efficiency (ECE) are also presented, using the different energy values available in each of the fuels. This will allow evaluating the way how the engine can avail this energy at useful power from different available energy levels.

The energy conversion efficiency (ECE) is a very useful concept to compare different fuels since it allows having quantification about the way how the available energy in the fuel can be converted into work. This parameter can be determined with the mathematic expression (1) where: “sfc” (g/kWh) is the specific fuel consumption obtained through the gravimetric measurement of the fuel consumed in each operation point divided by the developed engine power at that same point; “PCS” is the higher heating value (HHV) of the fuel that characterizes the amount of energy that fuel releases in an ideal combustion and that can be obtained in an laboratorial experience.

$$ECE = \frac{1}{\frac{sfc}{3600*1000}*HHV}*100 \tag{1}$$

The graphical presentation of the results is based on the representation of the consumption values measured with the two types of fuel in the narrow bars, read on the vertical axis on the left and correspondent representation of the relative difference in the wide bars read on the vertical axis on the right. The value of the relative difference is calculated with reference to the case of consumption for B0. Thus, if the bar is above the red dashed line it translates into an increase of consumption, efficiency or emissions for biodiesel; if, on the other hand, the bar is below the red line it represents a decrease of the parameters in question.

The analysis of the results obtained with this engine reveals that the mass fuel consumption shown graphically in **Figure 3a** and **b** does not exhibit a behavior proportional to the introduction of biodiesel and the corresponding slight decrease in energy associated with the use of this type of fuel. It is apparent that in certain regimes, usually associated with high torque values, specific consumption increases when using B20; however, the variations are very slight for torque values of 40 and 60 Nm. In this situation there is some variation in terms of specific fuel consumption, with a slight increase for low rotation (1250 rpm), as opposed to the slight reduction corresponding to 2000 rpm, with an increase of more than 5% to 40 Nm at 2500 rpm and a reduction of about 5% to 60 Nm. An abnormally high amount of consumption occurs at 3000 rpm with residual torque when using B20, however, given that this situation is quite unlikely to occur under normal vehicle use and that the engine has a somewhat unstable behavior at this rate, because of the rather oscillating operation of the turbocharger, a more in-depth study of this situation was not considered relevant.

Overall, it cannot be stated in full that the use of biodiesel in a blend containing 20% biodiesel and 80% diesel results in a direct increase in specific fuel consumption, but there is a tendency for that increase to occur when the engine is subjected to high torque demanding situations in high revs (3000 and 3500 rpm) and very low rotation (1250 rpm).

If the evaluation of the results obtained account for the higher fuel density promoted by the incorporation of biodiesel, comparing the consumptions on a volumetric basis, it is possible to emphasize what was already pointed out in the mass analysis, that is, only in the situation of torque of 40 Nm at 2500 rpm and 60 Nm at 1250 rpm there is an increase in consumption, except for cases of higher torque (100 and 120 Nm). It may even be considered that in volumetric terms, the use of B20 promotes very few changes in the total fuel consumption. In the most normal conditions of engine operation when under normal road conditions, which correspond to low torque values and low and medium engine rotation, it may be possible to observe an overall slight reduction in volumetric fuel consumption.

The analysis of the energy conversion efficiency (ECE) results, shown in **Figure 4**, accentuates what has already been verified in the evaluation of consumption results, that is, for loads up to 80 Nm there is a similar efficiency of conversion of the existing energy in the B20 relative to the

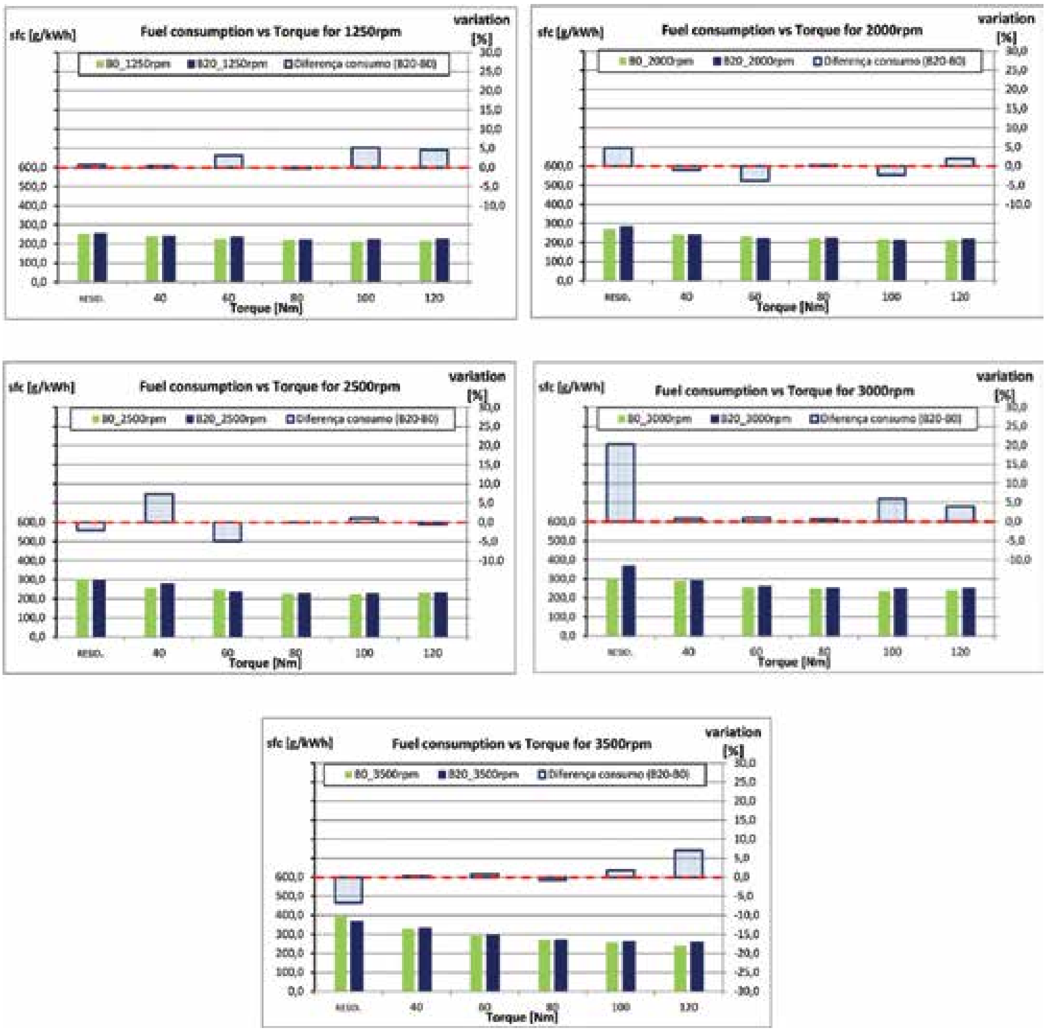

Figure 3. Results for specific fuel consumption (g/kWh) with B0 and B20.

B0. Although only slight, it is an aspect that needs to be analyzed in detail in order to enhance this energy gain. Considering that the maximum torque for this engine is obtained with 1900 rpm, it is interesting to observe that the results for 2000 rpm with biodiesel reveal an overall increase of ECE for all load conditions evaluated.

As indicated above, somewhat different values occur in terms of magnitude in cases of high rotation (3000 and 3500 rpm) under residual torque conditions, where the minimum required effort is to overcome the mechanical losses. In these circumstances which are very rare to occur in actual circulation, the engine exhibits an unstable behavior, in which the turbocharger exhibits some sudden deviations and the consumption is relatively low, allowing that small variations, due to the behavior of the engine in terms of control, become most noticeably in global terms.

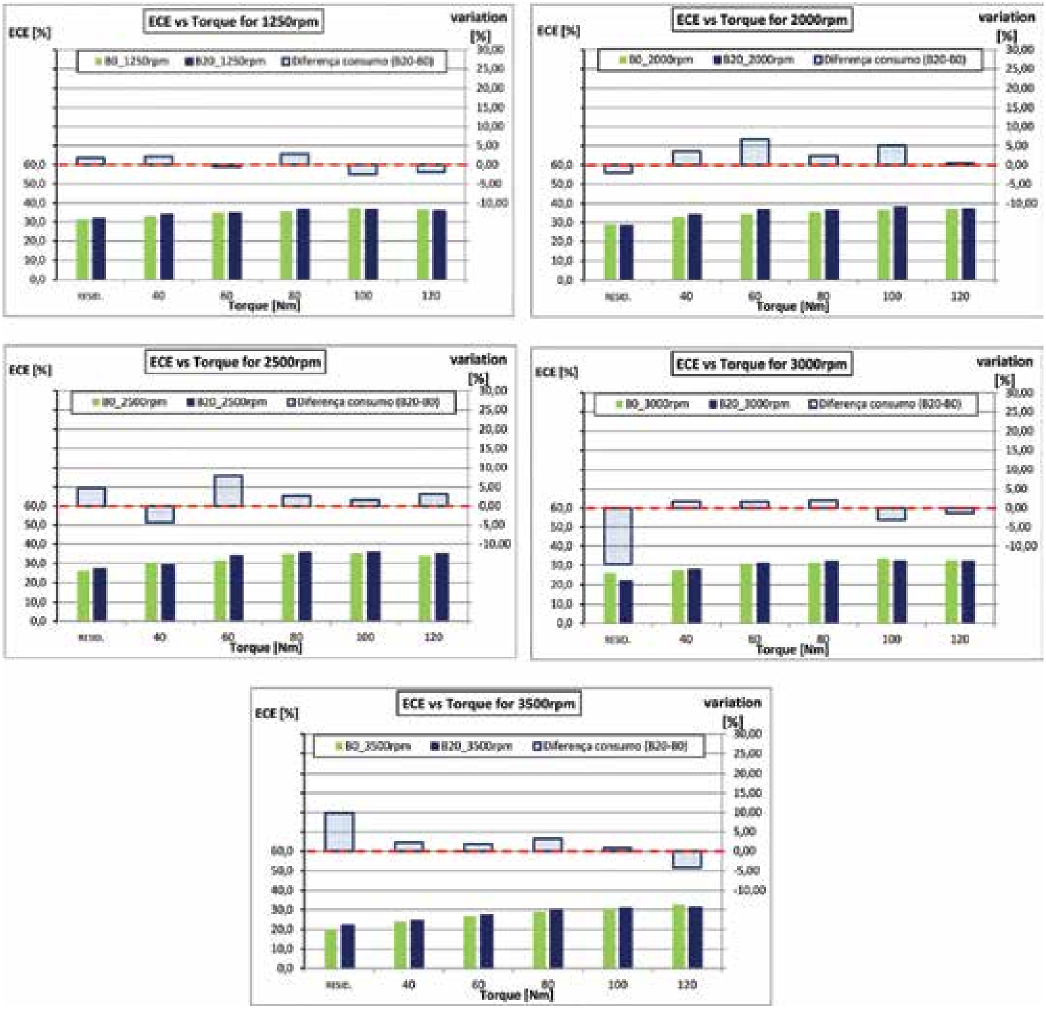

Figure 4. Results for energetic conversion efficiency (ECE) (%) with B0 and B20.

In the remaining points analyzed and considering the normal operating conditions of the engine, when installed in a vehicle subject to actual driving on the road, it can be stated that there are serious indications of the possibility of slight increases in engine efficiency when supplied with B20 compared to the consumption of B0, mainly when low and medium operating regimes are required, corresponding to the urban and extra-urban circuit operation. In a more demanding operating regime, such as high-slope or high-speed road traffic, where the required engine operation is supported at higher torque values, the use of B0 indicates a slight advantage over the B20 in energetic terms.

Analysis of fuel or energy consumption results reinforces the need to evaluate the behavior of the vehicle in real road situations so that it will become possible to see how this behavior will affect fuel consumption. An assessment can be made of these results and try to fit the type of behavior expected on the road for a light vehicle and realize the perspectives for overall results of consumption. In this way, it is possible to verify that the specific mass consumption presents small oscillations that were already expected, given the little significant difference in calorific value of the two evaluated fuels (B0 and B20). However, the differences became more significant only in the relative circumstances of higher rotation and high load, which may correspond to the typical high-speed freeway circulation, which implies a high engine speed and also high loads since the aerodynamic drag force becomes very relevant. For the other situations, corresponding to urban and extra-urban traffic, characterized by low and medium speeds and low and medium loads, the differences in consumption are minor, revealing a tendency to small decrease in fuel consumption when fueling the engine with B20, especially if a consumption analysis is made on a volumetric basis.

4.2. NOx emissions

As mentioned above, the study on the impact on NOx emissions by the use of B20 compared to the use of B0 was established. The results below are the reflection of this study allowing evaluating the influence that the B20 consumption has on the NOx emissions when compared to the consumption of diesel, for the various selected engine operating regimes. In order to make the analyzed results more comparable, the value of the NOx volumetric percentage present in the exhaust gas was divided by the power obtained corresponding to each selected engine operating point, and the results of **Figure 5** in (ppm/kWh) corresponding to specific NOx emissions.

The analysis of the specific NOx emission results presented in the graphs of **Figure 5** reveals an interesting behavior and probably explains what has been the major focus of controversy regarding the use of biodiesel.

In fact, depending on the engine operating regime, there is typically an increase or a decrease in NOx emissions due to the use of biodiesel. The analysis of the graphs related to the representation of the NOx emission results allows to conclude that: when the engine operates at low RPM and high RPM, the use of biodiesel leads to a decrease in emissions; however, for average engine rotation regime (2000 and 2500 rpm), the use of B20 conducts into an increase in specific NOx emissions. It appears that there is not a discernible direct relation between the load and the differences in NOx emissions related to the two fuels considered, except in the case of the tests carried out at 2500 rpm where, as the load increases, there is an increase in NOx emissions caused by the use of B20.

The relative effect of NOx emissions may be associated with increased energy conversion efficiency, which will enhance an increase in the combustion temperature responsible for the eventual formation of NOx compounds via the thermal process (Zeldovich formation process). Nevertheless, the increase in energy conversion efficiency is not the only responsible for the fluctuations in NOx emissions.

In fact, the presence of oxygen in the fuel allows the combustion process to be carried out differently from the two fuels, creating a different evolution of the heat release to take place, which could enhance or reduce NOx formation. These differences are surely also justified by the formation of the fuel spray, driven by the different properties introduced with biodiesel and the different levels of saturation of the molecules that constitute it.

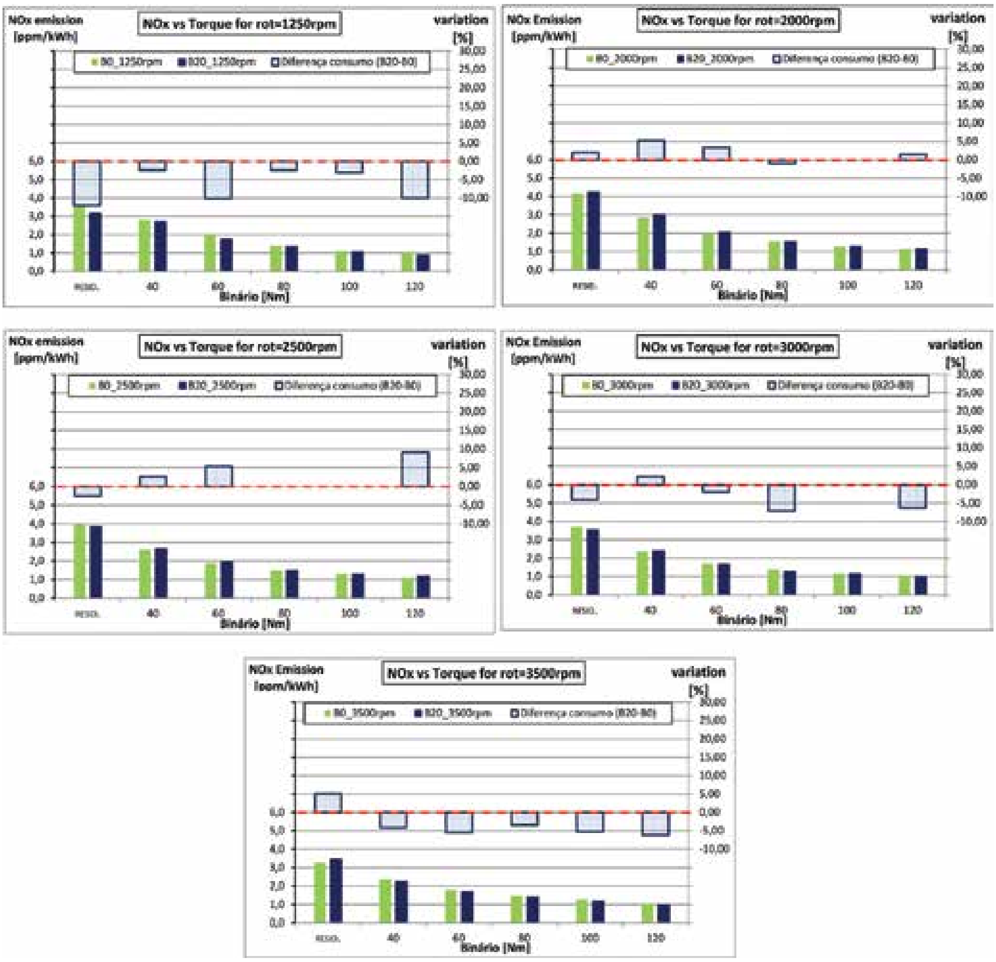

Figure 5. Results for specific NOx emission [ppm/kWh] with B0 and B20.

What is clear from the present study is that it is not possible to directly express an increase or decrease in NOx emissions caused by the use of biodiesel, without it being possible to characterize the way in which the vehicle equipped with a given engine operates under normal operating conditions. However, variations in NOx are not significant either in terms of increase or decrease and, given that the results were obtained without the exhaust gas passing through any treatment system, it can be concluded that any negative connotation on the use of biodiesel associated with NOx emissions, considering that the small variations in the use of B20, whether positive or negative, are always below 10% and will therefore be practically canceled out by the use of an efficient exhaust treatment system.

The present work on NOx emissions allows clarifying the existing doubts on this subject with the existence of disparate results from different studies, evaluating the behavior of the engines at a given rotation or a given torque. In reality, only through a study like the one carried out in the present study, considering a large number of points of operation, it is possible to draw a real range of results that allow to cross with the typical characterization of an engine when installed in a vehicle, leading to authentic values of NOx emissions emitted by that engine into the atmosphere when fueled by biodiesel or other fuel.

Comparing the results obtained with those of other researchers it is clear that only in similar situations, where a very wide set of engine operating points was considered, it was possible to register positive and negative oscillations in NOx emission values due to the use of [15, 35, 36]. Most of the works report an increase in NOx emissions, but it also becomes obvious that this situation reflects the testing in a narrow range of the normally operating engine.

As indicated by Yanowitz and McCormick [37] when averaging NOx emissions, masks the complex variability that occurs with the emission of these substances when using biodiesel in the engines, it is also important to remember what is reported by Hribernik and Kegl [38] confirming that the influence of biodiesel on combustion and emissions in an engine cannot be generalized, since they are engine-specific parameters. In fact, the engine type, circuit typology and driving mode completely change the way the engine operates when fueled with fuels containing biodiesel in different proportions. The different fuels offer different properties, namely in the presence of oxygen, density and viscosity, volatility, energy content and degree of saturation, being these factors responsible for the occurrence of different behaviors in the process of fuel injection. It is also important to note that the results obtained with single-cylinder engines, light-duty engines and engines of heavy vehicles lead to different conclusions, so it is necessary that the analyzes should also be different. This complexity is confirmed by the analysis performed on the results obtained by the present work, which helps to understand that the conclusions obtained by the work of other researchers in this area are, once again, emphasizing the need to evaluate the behavior of vehicles in circulation on the road, complementing those results with those obtained in the laboratory tests.

5. Conclusions

The energy dependence of the transport sector is evident, being effectively minimized by the use of biodiesel. It may be argued that this energetic option will only be transitional and that in the near future some other solution will emerge with other potentialities, given that despite the decrease of greenhouse gas emissions impacts, this decrease is not as relevant as desired. However, in the current circumstances, this is effectively a real solution and already with some evidence given, arising with the ability to replace part of the diesel fuel consumed in the world.

The present work is a concrete evaluation of the effects that the use of biodiesel in substitution of diesel would bring in terms of fuel consumption and greenhouse gas emissions. It can be concluded that there is no significant impact due to the use of biodiesel, especially when considering the use of incorporations of up to 20% biodiesel in diesel. Contrary to what is stated in several publications, it is not absolutely clear that the use of biodiesel, because it has lower energy content per liter of fuel, translates this characteristic directly into an increase in consumption. There is a reason to believe that in certain situations there is an increase in energy efficiency, and it is possible that, even with the use of a fuel with less energy results greater energy availability. It is also clear, through the results obtained, that due to the behavior of engines when subjected to different types of requirement, corresponding to different types of route, a distinct evaluation in terms of consumption and NOx emissions occurs when the engine is supplied with a mixture of biodiesel in diesel.

It should be noted that currently engines are designed to use diesel, not considering the use of biodiesel at the outset. A step has already been taken by the European Union to ensure the mandatory incorporation of biodiesel into diesel and to ensure that the biodiesel used effectively corresponds to a reduction in greenhouse gas emissions. By guaranteeing the use of a sustained form of production of this energy source, it will also be important that the development of engines corresponds to the preferential use of a given amount of biodiesel incorporated in the diesel fuel, so that it can derive the maximum yield.

Still, in relation to the obtaining results, as already recognized by the European community itself, it is not enough to have characterized a certain cycle of tests for approval of engines and use it in characterizing the behavior of these engines when fueled by fuels from different sources. It will be necessary to integrate the use of in-service vehicle tests under real traffic, road and environmental conditions, allowing for a more faithful and less standardized characterization in order to provide a more adequate response to the actual conditions in which the vehicles will be used.

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Chapter 10

Cultivation Systems of Microalgae for the Production of Biofuels

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Additional information is available at the end of the chapter

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Abstract

As reported in the study, the high-oil/ha-year productivity of microalgae has raised a lot of interest in their use as a source of raw materials for biofuels. However, the high costs of production and maintenance of closed culture systems (photobioreactor type) and the problems of contamination that lead to lower productivity of open systems (of the "open-pond" type) have become important limitations in evaluating the sustainability of producing biofuels from microalgae.In the view of the favorable prospects of employing microalgae as an economically viable source of raw materials for the production of biofuels, this chapter outlines the different ways microalgae are cultivated, the required nutritional conditions and the main procedures used for increasing their scale. Additionally, those more commonly used on a large scale are described and their advantages and disadvantages are pointed out. This analysis results in a proposal of a new type of photobioreactor, of the cylindrical container type, constructed of polyethylene, a non-transparent material that is cheaper and more durable than the ones that are commonly used (polycarbonate, glass or polymethyl methacrylate (PMMA)). Internal illumination of the photobioreactor is provided by a beam from plastic optical fibers that receive sunlight focused at the extremity of the beam.

Keywords: cultivation systems, microalgae, biofuels, photobioreactor

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1. Introduction

The progressive exhaustion of fossil-based fuels, the uncertainity in their respective prices and the growing control of their emissions in large cities have led to the generation of energy from renewable sources that reduce the dependence on petroleum and the problems associated with environmental pollution. In Brazil, 45% of the energy and 18% of the fuels are renewable while in the rest of the world 86% is produced from non-sustainable sources. A world leader in the use of biofuels, Brazil, has reached a position that is sought by many countries that try to develop renewable sources of energy as strategic alternatives to petroleum. Bioethanol is used as an automotive fuel since the early twentieth century and all new cars are "flex-fuel" (they run on either ethanol or a combination of around 25% of anhydrous ethanol in gasoline). In the case of biodiesel, it has been added to diesel fuel since 2005, starting with 2% in 2005 and reaching 8% in March 2017 [1].

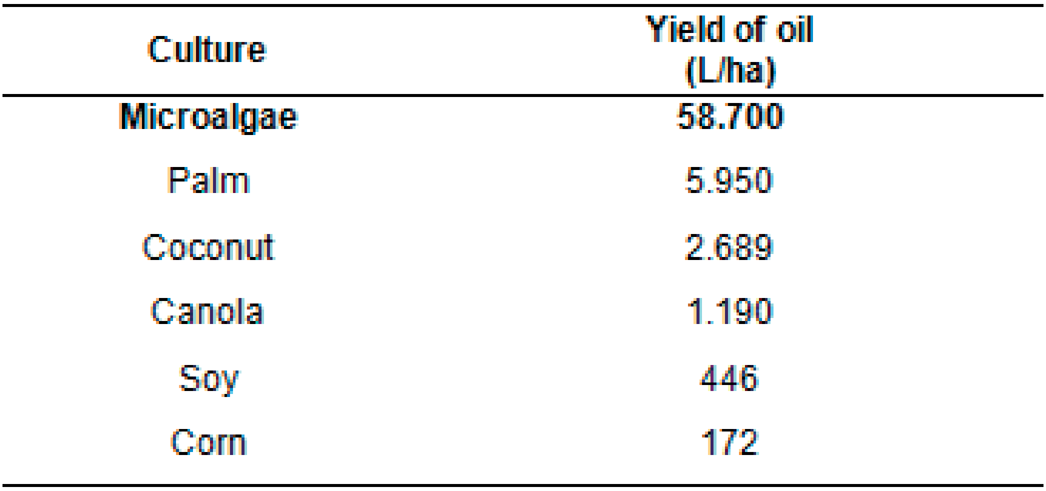
From this experience, it was possible to determine that 80% of the final cost of the production of biodiesel can be attributed to raw materials. In general, the investigation of alternative and economically viable sources has been the main goal of research on the subject. Thus, ideal sources of biofuels are determined mainly by their availability and costs.

Biofuels can be produced from many different sources. For biodiesel, for example, the most common are soy, palm, sunflower and cotton and among other sources of vegetable oils, animal fats and residues from food preparation. However these sources are not limited to conventional raw materials, they also apply to microalgae. Recent studies have confirmed that the conditions in which they grow, their high productivity in terms of oil/ha/year, viability of genetic manipulation of metabolic pathways, multiplication of yields of biomass in short periods of time and the possibility of controlling these conditions give microalgae a very large advantage in the evaluation of alternative sources of biofuels. Here, we emphasize the cultivation systems that are employed in the production of biomass from microalgae [2, 3].

2. Microalgae in the production of biofuels

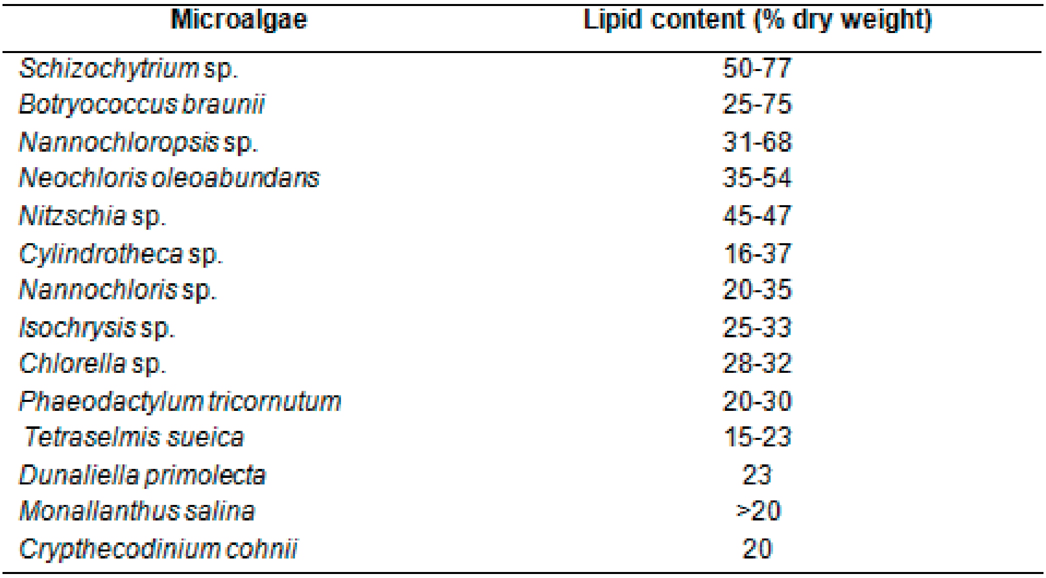
Oils found in microalgae have physic-chemical characteristics similar to those of vegetable oils [4, 5] and thus are considered potential raw materials for the production of biofuels. In conventional production systems, microalgae have a higher productivity of oil by hectare than palm, the commercial source of oil with the highest productivity (**Table 1**). Recent reports confirm that microalgae are capable of meeting global demands for combustible oils [6, 7].

.Microalgae can be considered a very good alternative source of lipids since they have content between 15 and 75% of their dry weight depending on the type and conditions under which they are cultivated (**Table 2**) [3]. In some cases, when this content reaches 75% of their weight relative to the dry mass, a reduction in cellular growth occurs as is the case of *Botryococcusbraunii*, for example. For other microalgae, with levels of oils between 20 and 50%, such as *Chlorella* sp., *Dunaliella* sp., *Isochrysis* sp., *Nannochloris* sp., *Nannochloropsis* sp. and *Tetraselmis* sp., higher growths are reported [8].



Culture	Yield of oil (L/ha)
Microalgae	**58.700**
Palm	5.950
Coconut	2.689
Canola	1.190
Soy	446
Corn	172

Table 1. Yields in oil/ha from selected sources of biomass.



Microalgae	Lipid content (% dry weight)
Schizochytrium sp.	50-77
Botryococcus braunii	25-75
Nannochloropsis sp.	31-68
Neochloris oleoabundans	35-54
Nitzschia sp.	45-47
Cylindrotheca sp.	16-37
Nannochloris sp.	20-35
Isochrysis sp.	25-33
Chlorella sp.	28-32
Phaeodactylum tricornutum	20-30
Tetraselmis sueica	15-23
Dunaliella primolecta	23
Monallanthus salina	>20
Crypthecodinium cohnii	20

Table 2. Lipid content of selected microalgae.

3. Cultivation of microalgae

The growth characteristics and composition of microalgae are significantly dependent on the type of cultivation—phototrophic, heterotrophic, mixotrophic and photoheterotrophic being the principal types used [9, 10]. Phototrophic cultures occur when the microalgae use light, for example sunlight, as a source of energy, and CO_2 as a source of inorganic carbon, to produce chemical energy by photosynthesis [11].

This type of cultivation has an environmental advantage. Since atmospheric carbon dioxide, the principal contribution to the greenhouse effect, may be used in the production of microalgal biomass for biofuels, it results in a favorable energy balance. Mainly because of this, the phototrophic cultivation is most commonly used for the growth of microalgae [12].

Mata et al. [8] report that the lipid content of microalgae can vary from 5 to 60%, depending on the specie, when cultivated phototropically. However, light intensity and the insufficient supply of CO_2 are always problematic questions for this type of cultivation. In open cultivation systems the limitation is mostly relative to the photoperiod. Besides, the irregular distribution of light intensity affects the productivity in terms of biomass. Final concentrations of biomass of over 2 $g.L^{-1}$ of Na are rarely reported in the study [13, 14].

Some authors suggest that supplementation with CO_2 could increase productivities of biomass and lipids, since its concentration in the atmosphere is low [15, 16]. However, it is important to construct systems that prevent the loss of excess CO_2. Still, it must be taken into consideration that the accumulation of oxygen, formed in the process of photosynthesis, increases the production of O_2 that acts as an inhibitor of hydrogenases, the enzymes responsible for the production of hydrogen necessary for the production of lipids. With this, the increase in CO_2 could result in a reduction in the production of lipids [17].

Some species of microalgae can not only grow under phototrophic conditions but can also use organic carbon in the absence of light. In this case, in which algae use organic carbon both as a source of energy and carbon, the cultivation is referred to as heterotrophic [18, 19].

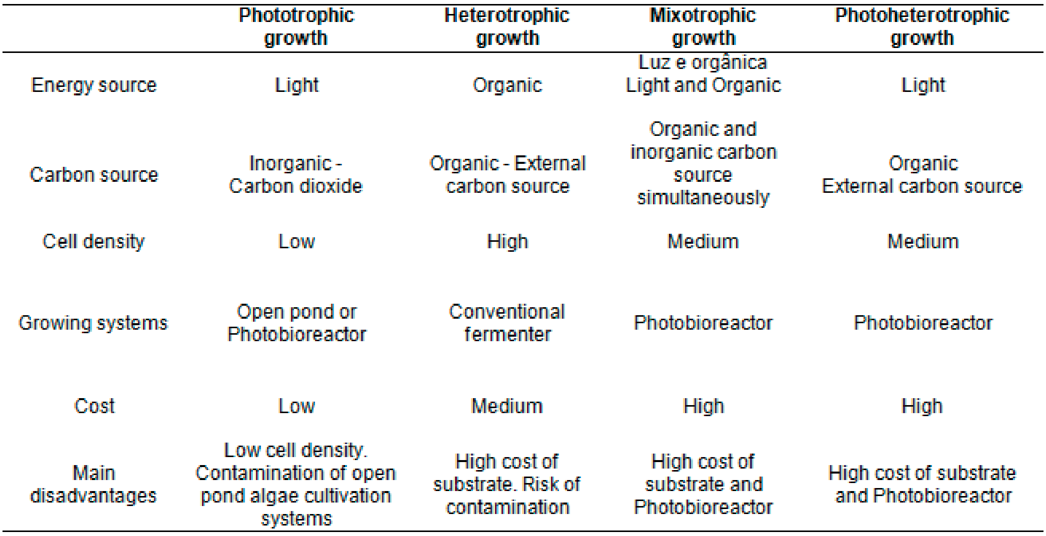
Heterotrophic cultivation avoids problems associated with the limitation of light and has led to relevant results in the production of microalgal biomass, the yields being significantly superior to those from phototrophic cultivation [11].

Xu et al. [20] observed an increase of 40% in the lipid content when they altered the type of culture from phototrophic to heterotrophic for *Chlorella protothecoides.*

The choice of heterotrophic metabolism is questioned in the sense that it is necessary to add a source of organic carbon and may lead to high costs if it must be purchased, making the production of biofuels from microalgae unviable [21, 22].

In mixotrophic cultivation, the microalgae are submitted to photosynthesis and uses organic and inorganic (CO_2) compounds as a source of carbon for growth. Thus, microalgae are capable of living under both phototrophic as well as heterotrophic conditions As they use organic compounds, microalgae release CO_2 via respiration, being absorbed and utilized under phototrophic cultivation [8].

In photoheterotrophic cultivation, microalgae require light when they use organic compounds as a source of carbon. The principle difference between the mixotrophic and photoheterotrophic is that, for the former, only light is used as a source of energy. Besides, in photoheterotrophic systems, light and other organic sources are necessary at the same time. Although the production of some metabolites regulated by the intensity of light could be increased in



	Phototrophic growth	Heterotrophic growth	Mixotrophic growth	Photoheterotrophic growth
Energy source	Light	Organic	Luz e orgânica Light and Organic	Light
Carbon source	Inorganic - Carbon dioxide	Organic - External carbon source	Organic and inorganic carbon source simultaneously	Organic External carbon source
Cell density	Low	High	Medium	Medium
Growing systems	Open pond or Photobioreactor	Conventional fermenter	Photobioreactor	Photobioreactor
Cost	Low	Medium	High	High
Main disadvantages	Low cell density. Contamination of open pond algae cultivation systems	High cost of substrate. Risk of contamination	High cost of substrate and Photobioreactor	High cost of substrate and Photobioreactor

Table 3. Cultivation methods.

photoheterotrophic cultivation, the application of this type of cultivation for production of biodiesel is very rare, as is the case with mixotrophic cultivation. Both types of cultivation are limited by the risk of contamination and the presence of light may require a special large-scale photobioreactor, resulting in high costs of operation [17].

Table 3 summarizes the main characteristics of each type of cultivation.

4. Nutritional conditions for the cultivation of microalgae

The production of lipids and the concentrations of different fatty acids in microalgae are also influenced by the composition of culture media. Frequently the increase in the accumulation of fatty acids is described as a consequence of the effects of the limitation of nutrients and the time of cultivation [8].

Under growth limiting conditions a drop in cellular division is verified in the photosynthetic rate of protein synthesis. The photosynthetic energy is deviated from the cellular division to the accumulation of carbohydrates and synthesis of lipids, also resulting in an increase in the synthesis of enzymes that are specific for the absorption of nutrients [23, 24].

On the other hand, Huerlimann et al. [18] verified an increase in the content of some lipid classes in the exponential phase of *Rhodomonas* sp. and *Isochrisys* sp. cultivated, in K^+ medium and under 250 μ moles photons.m^{-2}.s^{-1}. Usually, microalgae present a small production of lipids during the exponential phase, generally of polars polyunsaturates, with an increase in the synthesis when cultures reach the stationary phase of growth, the apolars predominating [25, 26].

In the composition of microalgae, besides carbon (C), at least 19 chemical elements are present. Some are necessary in concentrations in the order of milligrams per liter, such as H, N, O, P, S, K, Na, Ca and Mg. Others can be detected as trace elements or micronutrients and normally are required in concentrations of nanograms to micrograms per liter, such as Si, Fe, Mn, Mo, Cu, Co, Zn, B and Va. These micronutrients are incorporated in essential organic molecules as a variety of coenzymes (CoA, cobamamide, etc.) that participate in reactions that are primordial to the life of the cells [27].

The macronutrients form the structural constituents of biomolecules, in the cytoplasmic membranes of the intracellular medium, and still take part in the energetic and metabolic regulation processes. The absence or insufficiency of these micronutrients can cause damage affecting some of the vital functions of these microorganisms [28].

Among the most important nutrients are phosphorus (P) and nitrogen (N) that exist in the aquatic environment in diverse forms. They may be dissolved, as particulates or in biotic form. However, only the dissolved form is directly available for growth of microalgae. Several species still require minute quantities of organic compounds for their growth, as is the case with vitamins [28].

Phosphorus is an important limiting factor for the growth of microalgae, since it is essential for cellular processes such as the transfer of energy (ATP) and the biosynthesis of nucleic acids, phospholipids, DNA, and so on, influencing the composition of biomass. Inorganic orthophosphate (PO_4^{-3}) is the ionic form of phosphorus preferred by microalgae and its absorption depends on energy. Thus, this is the source of phosphorus most commonly used in culture media. Other sources of inorganic phosphorus exist that could be absorbed by microalgae, such as dyadic phosphate or dihydrogen phosphate ($H_2PO_4^-$) which are species obtained from orthophosphoric acid (H_3PO_4) [29].

Vitamins are essential organic compounds for the functioning of the metabolism and many can be found as cofactors of enzymes, carrying out the functions of coenzymes that have vital roles for the viability and growth as well as the accumulation of biomolecules in the cell. Among them, biotin stands out as the coenzyme that catalyzes activation and transfer of CO_2 reactions, cobalamine (B12), a coenzyme that catalyzes de-isomerization and transfer of methyl group reactions, and thymine (B1), the coenzyme that catalyzes activation and transfer of aldehyde reactions [30].

Some biotechnological processes with microalgae aim for high yields in biomass and, for this, must choose the adequate nutrients and physic-chemical parameters, taking into consideration the natural habitat of the species in order to determine the basic necessities for their growth. On the other hand, some biotechnological applications are directed to stress conditions to optimize the biosynthesis of specific bio-compounds, such as fatty acids. The most widely studied stress factors are the concentrations of certain nutrients, light intensity, temperature, salinity and pH. The limitation of nutrients in the cultures affects, in large proportions, the chemical composition of the algae, as well as their rate of growth [31].

In studies run with microalgae cultivated under low concentrations of nitrogen, Piorreck et al. [25] observed an increase in the lipid content of these microalgae without, however, altering the lipid and fatty acid profile. In *Chlorella,* cultures in which the cellular division ceased because of the lack of nitrogen in the culture medium, the lipid content of the cells increased from 28 to 70%, coinciding with a decrease in the protein content from 30 to 8% [32]. Most of the culture media used to facilitate accumulation of lipids in the microalgae are modified according to those that are known such as BG-11 [33] and BOLD 3 N [34].

5. Advantages of using microaIgae for biofuels

The cultivation of microalgae for the production of biofuels can be considered highly promising mainly because of the diverse advantages already mentioned in the study [2, 6, 35–39].

- They do not require arable land and can be cultivated in desert regions and on degraded soils since the demand for land is only utilized as a support for the cultivation system.
- The do not compete with agriculture.
- Even growing in aqueous media, they consume less water than terrestrial plants and, depending on the process utilized in concentration of biomass, the residual water may be reutilized in the process, reducing global consumption of fresh water.
- They are produced all year round and do not depend on seasons and crops.
- They have high productivity in biomass and rapidly accumulate lipids, between 15 and 50% in dry mass in many species.
- They can produce more than half the oxygen in nature.
- Their cultivation does not require the application of herbicides or pesticides.
- The nutrients for their cultivation can be obtained from residual waters and agroindustrial wastes.
- They efficiently fix atmospheric carbon, or even residues from industrial process, through photosynthesis (each ton of biomass produced consumes 1.7 tons of CO_2, 10–20 times more that is absorbed by cultures of oilseeds).
- They can produce a series of other valuable products besides lipids, such as proteins, carotenoids and carbohydrates that can be utilized as foods or fertilizers, fermented to produce ethanol or other products with high added value.

Besides the innumerous advantages previously cited, the production of oil from microalgae of approximately 60,000 liters/ha/year can surpass that of palm oil (5000 liters/ha/year) and of soya (450 liters/ha/year). More optimistic financial analyses affirm that oil from microalgae can be produced at a cost of US$ 0.50/L [2, 3].

6. Cultivation of microalgae on a lab scale

The cultivation of microalgae requires a climatized space, with stable temperature, so that the thermal amplitude allows the activities that are necessary to the cell. The atmosphere must have controlled access to reduce the heat exchange and contamination. As the temperature affects the metabolic rate of the organisms, it must be chosen according to species that is studied and what the cultivation is for. The constancy of the temperature and the low variability (< 0.5°C) provide stability and predictability to the cultivation. Tropical species can be cultivated under temperatures between 20 and 25°C, such as, for example, Spirulina, Scenedesmus, Ankistrodermus, Monoraphidium, Chlorella and Chlamydomonas, among others. Generally, the choice is for a temperature of 23°C that is tolerated, although it may not favor optimum growth. Light intensity, its duration and wavelength influence growth of phytoplankton. Incandescent lamps better simulate the amplitude of wavelengths between 350 and 700 nm, necessary for photosynthesis but could heat the cultivation. Fluorescent lamps do not heat up since the wavelengths in the red region are not emitted, but they could lead to unsatisfactory growth. Sunlight, not in excess, could stimulate growth. The efficiency of solar collectors in the production of microalgae also is being studied [40]. Lamps of 40 and 20 W are more frequently utilized, a distance of 25–30 cm from the cultivation is being recommended to minimize the heat. The adequate photoperiod is important, the use of 12:12 hours (dark light) for maintenance of cultivations and continuous light for 18:6 hours being common for commercial purposes [28, 41].

In the cultivation rooms the inoculums of microalgae are normally preserved in sterile glass tubes (**Figure 1A**) utilizing an incubator (**Figure 1B**). This preservation is conducted under controlled conditions (temperature between 20 and 25°C, light intensities of 40 μ moles.m^{-2}.s^{-1}, photoperiod of 12 h) and with manual agitation three times a week in order to not allow the cells to decant for too long.

6.1. Scaling up the cultivation of microalgae from the lab

The cultivation of microalgae from the lab is scaled up by successive transfers of algal cultures of systems of cultivation from smaller to larger followed by the addition of culture media. In most cases four transfers are made, namely culture from the preservation tube to the cultivation system of 250 mL; activation culture, from the activation culture to the system of 1 L, a pre-inoculum culture; from the pre-inoculum culture to a system of 20 L, to obtain the bottle cultivation; followed by the propagation from the bottle to various systems of 20 L, called propagation cultivations to obtain the volume of culture to be inoculated in the photo-bioreactors reaching, in this step, the cultivation of microalgae on a pilot scale (**Figure 2**). The four transfers, from the preservation step until the cultivation propagation, are run under sterile atmospheres and also utilize sterile materials.

The growth of cultures regarding microalgae, in each step of cultivation previously described, follows the growth phases given in **Figure 3**—*Lag or adaptation* (induction of growth), *Log* (exponential growth), *Transition* (reduction of growth), *stationary* and *decline/death*. The period of duration of each phase depends on the specie and the conditions of cultivation. For the construction of

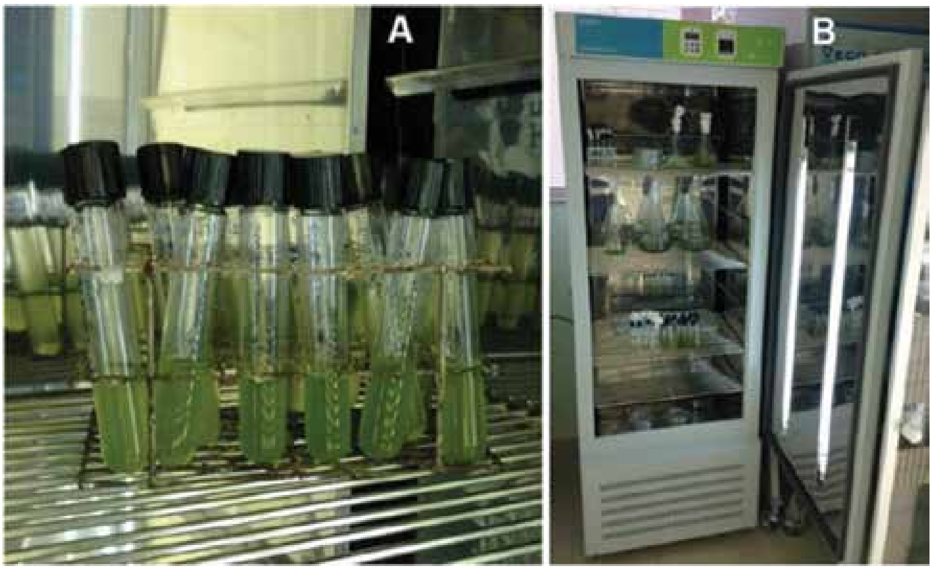


Figure 1. *Scenedesmus* sp. inoculum, conserved (A) and incubator (B).

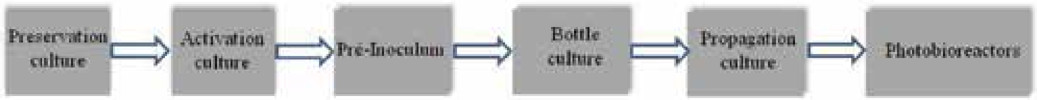


Figure 2. Flowchart of scale up for the cultivation of microalgae used by GreenTech.

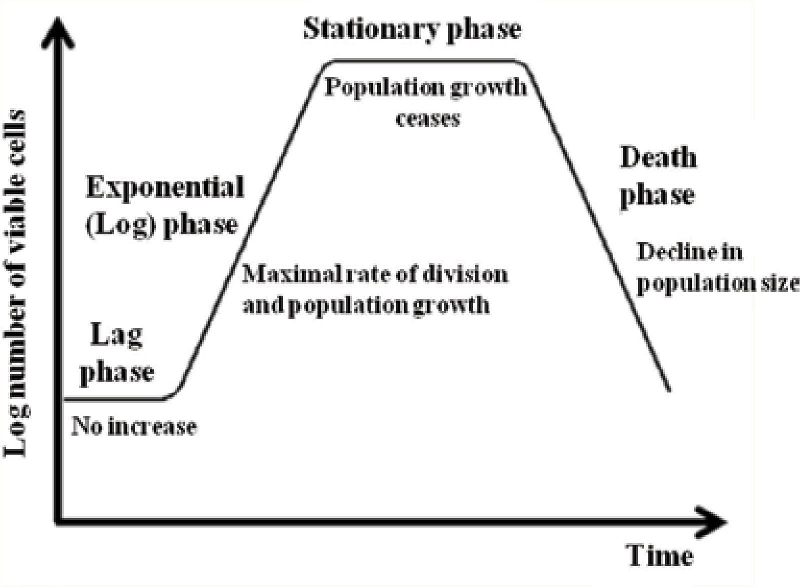


Figure 3. Microbial growth curve.

kinetic profiles of each culture, necessary to monitor the biomass produced, samples are collected every day, and their analyses of cell count, dry weight and turbidity are run.

7. Principal cultivation systems of microalgae on a large scale

The large-scale systems of cultivation of microalgae were developed during the first decades of the twentieth century. These organisms can be cultivated in diverse systems of production. The systems of cultivation on a large scale commonly employ types like "*open ponds*", generally called "*raceways*", where tanks of varied sizes are kept in the open air, exposed to natural conditions of illumination, temperature, evaporation and contamination. These tanks generally are shallow, constructed in concrete, fiberglass or polycarbonate, with an earth bottom or coated with plastic material, where the cultures are kept in constant circulation. The other well-known open system of cultivation is the cascade model or descending film, developed in the Czech Republic around the 1970s. Here, the culture is exposed to sunlight in a thin film, of about 1 cm, that promotes a cellular density of up to 10 g L^{-1}. This system has a circuit with a base originally in glass, which made it very expensive, but with the evolution of models, the use of cheaper materials, plastics, cement or metals made the costs decrease. The system has some advantages, namely a thin film of culture leading to a high concentration of cells, an efficient transfer of gas liquids favoring the exposure of the culture to sunlight even more, a low cost compared to other closed reactors and the necessity of less area for its installation, when compared to the *raceway*. Although it is a system with good productivity, the possibility of contamination remains analogous to systems of *raceways*. There are some variations of this system where the tray on which the culture is exposed to sunlight presents undulations, allowing cycles of light and dark, that result in an increase in lipid content of the cell, in spite of the decrease in productivity [42, 43].

An open photobioreactor of the descending film type was constructed in fiberglass at the Laboratory of GreenTechnologies, GreenTec/EQ/UFRJ, with the objective of producing biomass from microalgae to be utilized as a raw material in the development of technologies for the production of biofuels (**Figure 4**). Additionally, in this system of cultivation, it was possible to monitor the growth of lineages of microalgae that were cultivated and compare the results obtained from the growth of lineages in photobioreactors.

Today, 95% of the total production of microalgae is in open systems. The volume of around 20,000 tons of microalgae/year is considered incipient in terms of biofuels [44].

Other more sophisticated systems of cultivation of microalgae are the closed ones known as photobioreactors. These cultivators are usually constructed from transparent materials, glass or plastics, distributed in flat panels or in serpentines. There are diverse models of photobioreactors: bubble columns, windows, horizontal tubes, helicoidal, agitated tanks and so on [45]. In spite of the higher initial costs, photobioreactors have many advantages over open systems. In photobioreactors, it is possible to control the conditions of cultivation. This way the concentration of nutrients, temperature, light and pH can be adjusted to obtain higher yields of biomass in shorter times, reaching much higher productivities when compared to open systems.

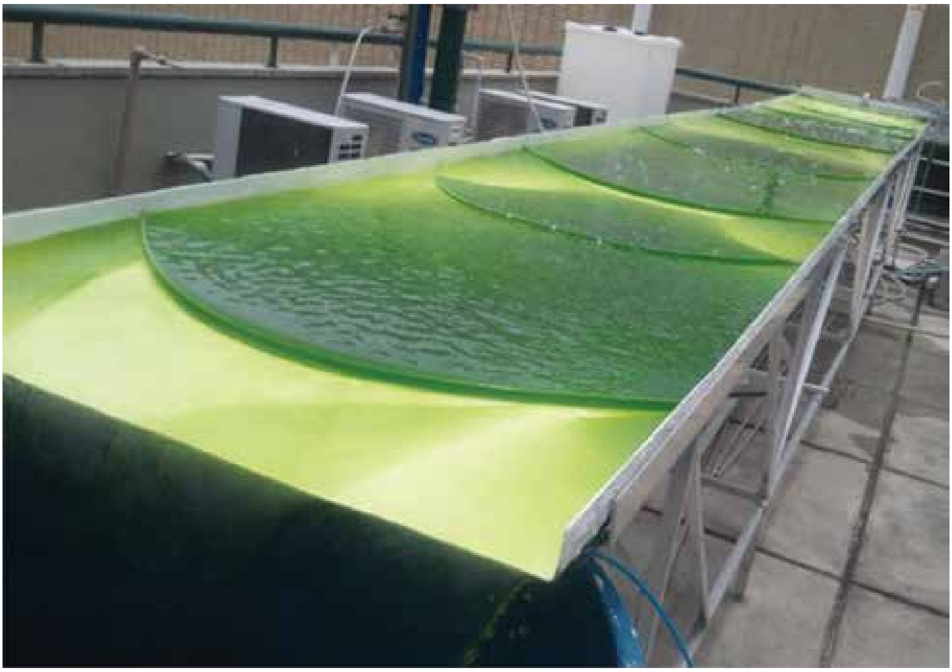


Figure 4. Thin-layer cascade cultivator installed at GreenTech.

In the GreenTec/EQ/UFRJ pilot unit 30, vertical photobioreactors of the window type are distributed in 3 series of 10 arranged in parallel as can be visualized in **Figure 5**. Each series of photobioreactors has a capacity of 1100 L of cultivation.

The series of photobioreactors of the pilot unit have the following characteristics:

- polycarbonate structure (5 mm thickness) that is 1.2 m wide, 0.8 m in height and 11 cm thickness, containing internal baffles, top lid, two lower outlets and a connections for hoses.
- three refrigeration systems composed of three iced-water generators with temperature controllers; tubes with isolation; three temperature sensors; and three stainless steel serpentines, submerged in the culture of the first photobioreactor in each series;
- an air injection system in each photobioreactor with stainless steel tubes, with outlets of bubbled air in the basal part of the reactor and valves to control the flow of air;
- a system to control the pH, composed of a control panel, three pH sensors and tubes connected to the CO_2 network through which cultures are injected when the pH limit is passed;
- recirculation of the cultivation system with tubes and pumps.

The recirculation of the culture along 10 photobioreactors of each series occurs through its passage from the first reactor to the second, from the second to the third and so successively, until reaching the tenth, from where it is pumped back to the first via tubes (**Figure 6**).

Figure 5. Photobioreactors at GreenTech.

The passage of the culture from one reactor to the other occurs by overflow through a small canal, situated between the reactors in the superior part. In each reactor, the culture follows a trajectory in a zigzag determined by the positioning of the internal baffles (**Figure 7**). The water utilized to make the cultures of microalgae developed in photobioreactors is treated through a hollow-fiber microfiltration system and activated pressurized charcoal that has a capacity of approximately 900 L/h.

In open systems, productions close to 180 tons per ha/year can be reached, competing naturally with the other microorganism in culture medium. The production in closed photobioreactors is more expressive, giving bigger volumes and, at times, over 1.500 tons/ha/year, since they can optimize the cultivation conditions, such as luminosity, temperature and pH that are favorable for the growth of populations of microalgae [40].

A study by Chisti [3] confirms the advantages of production of microalgae in photobioreactors in place of recirculation tanks. Taking as a basis the calculation of production of 100 tons of biomass for the two systems, with the same absorption of CO_2, the volumetric productivity

Figure 6. Recirculation of cultivation system along the ten photobioreactors at GreenTech.

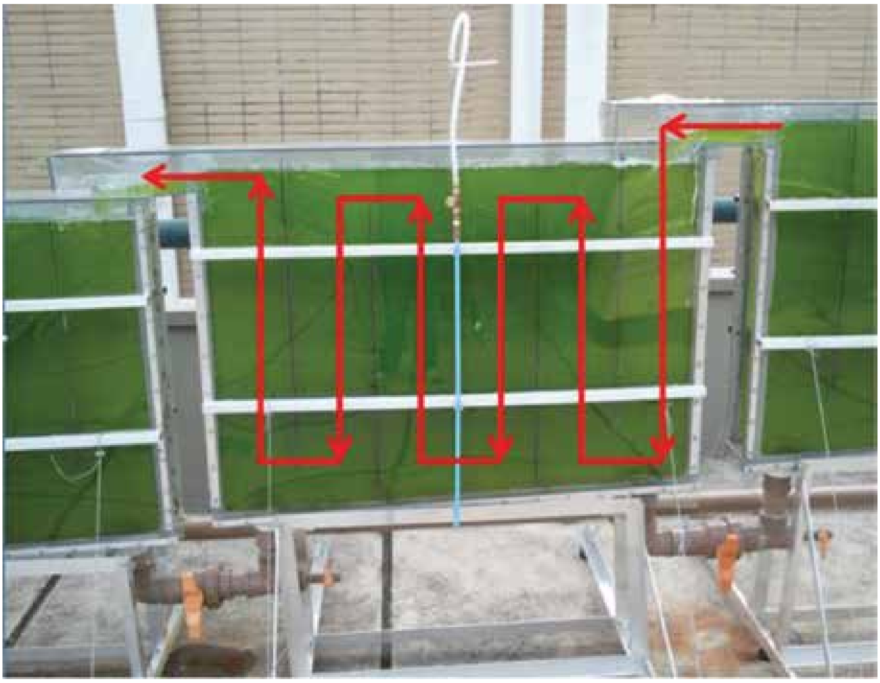


Figure 7. Trajectory of cultivation system in photobioreactors during recirculation.

of photobioreactors is 13 times larger than that of tanks. The area necessary also favors the photobioreactors, being approximately 30% inferior, assuming a similar productivity for the two systems of cultivation. The costs of separation are also an advantage of the photobioreactors, since the culture is 30 times more concentrated than in the recirculation tanks, and thus the separation of biomass from water is facilitated [46].

The estimated cost of production for each kilogram of biomass is, respectively, € 6.39 and € 3.80 for photobioreactors and recirculation tanks. These values do not take into account the costs of CO_2, which could be obtained at cost zero. If the annual capacity of production of biomass could go over 10,000 tons, the costs of production for each kilogram are reduced to US$ 4.11 and US$ 1.17, for photobioreactors and recirculation tanks, respectively, because of economies of scale [47].

However, photobioreactors have several disadvantages that need to be considered and validated, such as difficulties with amplification, deterioration of the transparent material utilized, high cost of construction (investments including 10 times that of an open tank) and damage to the cells because of shearing stress [8, 48].

Based on advantages and disadvantages of systems of closed cultivation (photobioreactors), at GreenTec/EQ/UFRJ, a new model of photobioreactor of the cylindrical container type, of a volume similar to that described previously but occupying a smaller area because of the relative depth, was developed. The internal illumination of the photobioreactor is made by a beam of optical plastic fibers that receive sunlight from lenses focused on the extremities of the beam. These lenses are mounted on a solar tracking system that permits a more efficient use of light.

The great differential of this system of illumination is that it is possible to use non-transparent materials in the construction of photobioreactors that are much cheaper and durable, such as polypropylene, without incurring in additional energy costs.

The proposed model will have the following advantages when compared to conventional photobioreactors: (a) systems with less entrance and exit of air, minimizing contamination; (b) occupies a small area; (c) uses materials that are not transparent, thus cheaper and more durable; (d) does not require the use of systems of heat exchangers to avoid the increase in temperature of the culture because of the use of isolation with polyurethane in the external part of the tank; (e) higher productivity of microalgae biomass relative to open systems; and (f) higher yields of lipids in the composition, fundamental aspects in the production of biodiesel.

In the pilot unit of GreenTec/EQ/UFRJ, a prototype of this new photobioreactor was mounted as can be visualized in **Figures 8** and **9** utilizing a polypropylene tank of 25 L capacity. An increase in the scale of this model is planned for a tank of similar characteristics and a volume of 1000 L.

After each cultivation is over, a culture of microalgae is directed to the concentration step. Diverse processes have been tested and continue being evaluated in this step, especially flocculation, microfiltration and centrifugation.

Two technologies flocculation followed by centrifugation and microfiltration followed by centrifugation are fundamentally utilized in the pilot unit of GreenTec/EQ/UFRJ. Biomass from microfiltration concentrated approximately 35 times is submitted to centrifugation at 10,000 rpm, 6°C, during 15 minutes, to obtain a cultivation concentrated over a 100 times (**Figure 10**).

Figure 8. Prototype: non-transparent photobioreactor with internal illumination by plastic optical fibers, coupled to solar tracking.

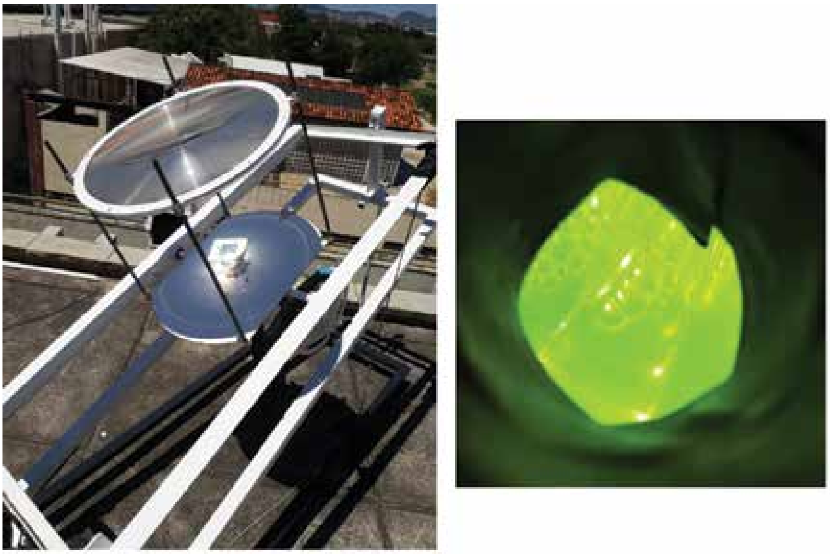


Figure 9. Components of the prototype.

Figure 10. Concentrated microalgal biomass.

Filtered and centrifuged residual water is treated in a system of microfiltration with activated carbon and reutilized in cultures of photobioreactors.

8. Main challenges in the production of biodiesel from microalgae

The principal challenge in the use of microalgae as raw material for biodiesel is the selection of promising species with triacylglyrides in optimum conditions of cultivation, adaptation and growth of cultures (inocula), systems on a large scale and overall reduction of production costs [26].

The production of microalgae biomass requires basic inputs such as energy, water, CO_2 and mineral nutrients. In order to assure the viability of the cultivation of microalgae on the necessary scale, industrial effluents are presently discarded into the environment and use CO_2 produced by several industries such as power plants cement factories and so on.

The refining of bio-oil extracted from microalgae is another of the current limitations in the production of international quality biodiesel. This fraction, in addition to being composed of triglycerides and fatty acids convertible into biodiesel, contains antioxidants and hydrocarbons that cannot be converted into biodiesel. The latter have polarity and degree of saturation similar to the compounds of interest for biodiesel, making it difficult to extract them.

It is also indispensible to invest in the development of processes that make full use of microalgae according to the biorefinery concept [49, 50].

However, in the last few years, the research related to this topic has been advanced, fundamentally in the cultivation stage, responsible for the higher costs of the productive process. With this objective, new and cheaper cultivation systems with higher productivity of biomass are being developed and proposed. In addition, studies are carried out to modify the composition of culture media, aiming at reducing the cost of the nutrients used as sources of nitrogen and phosphorus.

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Section 5

Biofuels, Alternative Fuels, Biorefineries

Potential of Biofuel Usage in Turkey's Energy Supply

Sirri Uyanik, Yavuz Sucu and Zeynep Zaimoglu

Additional information is available at the end of the chapter

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Abstract

Rapidly growing population and industrialization brought about the enormous need for energy, alongside the environmental problems. Since biofuel energy is inexhaustible, it is becoming increasingly important to address the energy problem. Today, it is possible to classify biomass energy into two classes: classical and modern. Classical biofuel utilization is the simple burning of wood obtained from tree cutting and animal wastes, where modern biofuel application consists of a variety of fuels produced from various sources. Turkey's potential for biofuels is estimated to be around 45 Mg. As a renewable energy, it's been under the Renewable Support Scheme by regulation for more than a decade now. By the end of 2016, installed biofuel electricity generation capacity had reached 468 MW with 2 billion kWh realized (~0.7% of national demand). The aim for 2023 is reaching at least 1000 MW (which will be around 1.3% by then). Many analysts believe that the potential for development is higher and realization therefore will surpass the official aims. Effective usage of biofuels for power generation may not be sizable but it's critical and will make multilayer contributions to energy supply and dependence as well as to meeting climate and sustainability targets of the country.

Keywords: energy policy, biofuel, agricultural and environmental interaction

1. Introduction

The civilization tendencies toward modernization mainly progress through industrialization of societies. Combining the economic results of modernization, which are mainly increased public welfare, eased access to consumption, alongside the growth in population, leads to enormous increase in energy demand, where the upward acceleration persists for decades [1].

Economic impacts	Sustainability
	Fuel diversity
	Increased number of rural manufacturing jobs
	Increased investments' innovation
	Agricultural development
	International competitiveness
	Reducing the dependency on imported petroleum
Environmental impacts	Greenhouse gas reductions
	Reducing of air pollution
	Biodegradability
	Higher combustion efficiency
	Improved land and water use
	Carbon sequestration
Energy security	Domestic targets
	Supply reliability
	Reducing use of fossil fuels
	Ready availability
	Domestic distribution
	Renewability

Table 1. Major benefits of biofuels [37].

In the current situation, the leading primary energy sources used are fossil-based sources, having a contribution around 85% globally, where the largest consumer is power industry, utilizing 42% of the total primary sources, followed by industry and transport [1–3]. Despite global consensus on the need to shift primary energy sources to renewables, the situation is not expected to change drastically. Future scenario studies show only a slight decrease, down to 75% in 2040, on fossil fuel dependence [4], even with implementing new policy measures promoting to wane fossil fuels. Given the abundance of coal, oil, and natural gas globally, with new extraction technologies, potential reserves, and unconventional reserve exploitation (e.g. for natural gas), it is highly possible the fossil sources will be available for a considerable period at low costs [5–7]. Although supply reserve and financial scenarios demonstrate that fossil resources will continue dominating in the future for a number of decades, it is widely accepted that the current position has drawbacks.

Besides, fossil fuel is not sustainable by definition and many countries have concerns over fossil fuel dependence mainly connected to four conditions: (1) depleting fossil fuel stock [8], (2) price volatility of fossil resources [9], (3) greenhouse gas emissions in the atmosphere [10], and (4) geopolitical supply security [6, 7]. Even though each of these conditions is enough to convince conversion to renewables, a dilemma arises for countries being forced to use fossil sources as a result of financial conditions accompanied by fossil-based technology infrastructure and hence the pace to migrate from fossils to renewables remains low.

It is more widely accepted that the thread of global climate change is increasing, which is addressed to the greenhouse emissions from fossil fuel utilization. Thus, global debates on migration from carbon emitting resources are held in order to find a common international understanding [11]. In conjunction with environmental consequences of fossil fuel mining, the associated climate change projections predict some serious threads [10], including several negative impacts on human health along with the Earth's ecology [12]. Therefore, in order to overcome two detrimental challenges, namely energy crisis and environmental pollution, new alternative energy sources are required, which are essentially renewable, sustainable, environment friendly, efficient, and economically viable [12–14]. Many power generation alternatives are put forward to replace fossil fuels; the primarily listed and tested ones are wind, solar (thermal and photovoltaic [PV]), nuclear, geothermal, tidal, fuel cells and biofuels [15]. Among these alternatives, each has advantages and drawbacks against fossil fuels, where biofuels are found favorable over petroleum fuels because (1) they can be easily extracted from the biomass, (2) they are sustainable due to their biodegradability, (3) their combustion is based on carbon dioxide cycle, and (4) they are more environment friendly [3]. Further benefits in integrating biofuels to the fuel mix are summarized in **Table 1**.

In this study, definitions, applicability, and potentials of biofuels as an alternative energy source are investigated, with their current and probable future positions in the Turkish energy mix.

2. Evolution of biofuels

Although in the common and popular context biofuel is used to define liquids, scientifically, the term "biofuel" refers to all fuels produced from biomass in forms of:

- solids (biochar),
- liquids (alcohols like bioethanol, biodiesel, vegetable oil, synthetic hydrocarbons, and their mixtures),
- and gases (biogas, syngas, and biohydrogen).

Biofuels are commonly classified as primary and secondary according to the form of utilization. Primary biofuels are organic materials directly used to extract energy. Primary biofuels include wood, wood chips, pellet, animal wastes, forest and crop residuals, landfill gas, and so on from which energy is extracted traditionally without a conversion process. Secondary biofuel refers to chemically converted fuels [16] in solid, liquid, or gaseous forms, derived from organic material. **Figure 1** illustrates the common classification of biofuels.

Primary biofuel has relatively low efficiency and has limited utilization possibilities in terms of energy conversion and transportability, compared to the so-called secondary biofuel technologies, which are also classified further into generations. The first-generation fuels are bioethanol/butanol chemically produced from rape seed, soya bean, sunflower, date palm,

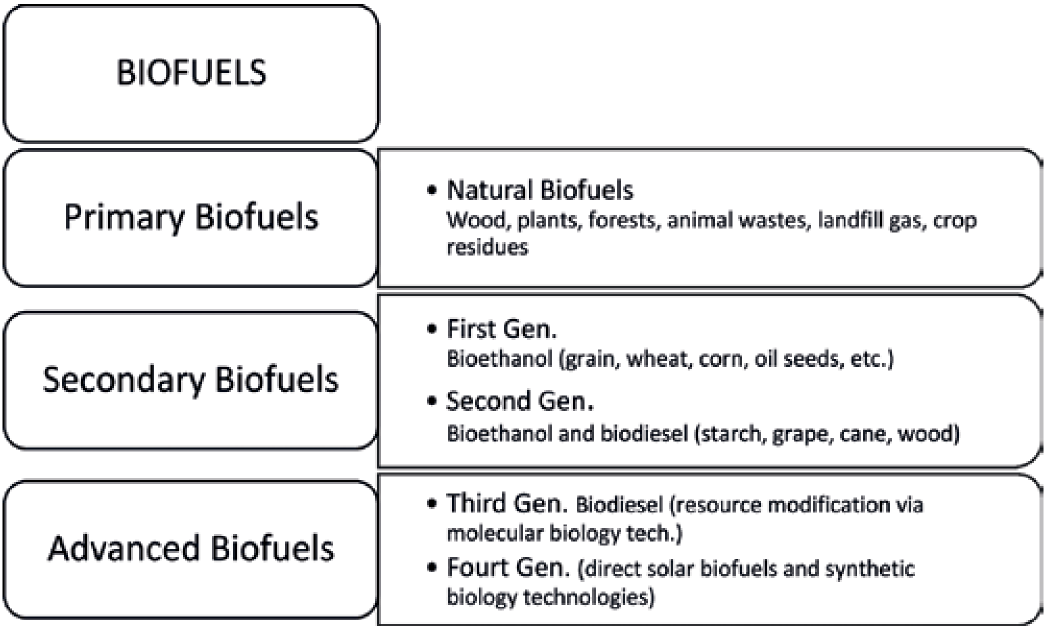

Figure 1. Classification and sources of biofuels [17].

coconut, and animal oils, fermented from the starch of wheat, barley, corn, potato, sugar cane, and sugar beet [17]. The first-generation biofuels are well defined and have reached commercials level, especially in the US, EU, and Brazil [18]. First-generation biofuel production systems require large-scale land acquisition and have some environmental and economic limitations. Since they are mainly derived from food and oil crops, they directly compete with food for crops and agricultural land [5, 19]. There are many studies not only reporting the competition between food and fuel for land use, but also defining the dependence between a remarkable increase in food prices, mainly corn and soybean, with increased oil prices [20].

In order to overcome the competition between fuel and food crops over the limited agricultural land, second-generation biofuels, produced from mainly agricultural wastes, are used. Second-generation biofuels can be defined as bioethanol/biofuel generation from jatropha, cassava, miscanthus and bioethanol, biobutanol, or syndiesel production from lignocellulosic materials such as straw, wood, agricultural wastes, and grass [21, 22]. They are derived from biomass sources mainly agricultural residue, forest harvesting residue, wood processing, and non-edible parts of food crops. Thus, second-generation biofuels are not directly competing with agricultural lands and have lower environmental footprint than the first generation [18]. Limitation of second generation comes from its lower conversion rates (see **Table 2**). At this moment, with current conversion rates the process is not economically feasible [19]. The low conversion rates also require the second-generation biofuels to occupy large amount of lands, particularly arable lands for energy crop cultivation [23].

The third-generation biofuels are differentiated from the second-generation biofuels to the point where the utilized resource is modified via molecular biology technologies. Because

Crop	Seed oil (% oil by wt)	Oil yield (L oil/ha yr)	Land area use (m^2 yr./kg biodiesel)
1st generation			
Corn	44	172	
Soybean	18	446–636	18
Safflower	20	779	
Camelia	42	915	12
Sunflower	40	952–1070	11
Peanut	70	1059	
Canola	41	974–1190	12
2nd generation			
Castor	48	1307–1413	9
Jatropha	20–60	1892	15
Polanga	65–75	2000	
Coconut	65–75	2689	
Oil palm	36	5366–5950	2
3rd generation			
Microalgae	30–70	58,700–136,900	0.1–0.2

Table 2. Comparison of various biofuel sources [18].

of familiarity in other applications, algae, commonly known as weeds, are referred within third-generation biofuel production, and for long years they are known as nutrient additive for animal feedstock. Due to the environmental concerns as well as the increase in oil prices, studies on biofuel sources have gained importance and algae have been considered as a promising sustainability and energy source. Because the first-generation biofuels are prone to creating environmental pollution during production process, whereas second-generation biofuels require expensive and complicated production technologies [5], far more innovative solutions—the fourth-generation biofuels or direct solar biofuels and synthetic biology technologies—are pertinently needed for replacement of all fossil fuels. Researchers are focused on third- and fourth-generation biofuels, collectively referred to as advanced biofuels, which are promising in terms of conversion rates as shown in **Table 2**.

Microalgae are a large and diverse group of simple, aquatic, and mostly microscopic unicellular organisms [24], which are capable of performing photosynthesis. These microalgae utilize light and produce biomass from CO_2, water, and nutrients.

While the percentages vary with the type, in general, nearly 15–77% of the microalgae cell is made up of oil. High oil content and growth efficiency compared to other plants make microalgae a promising and attractive source for biodiesel and biogas production. Generation of these fuels from microalgae would help to meet the increasing global demand in addition to contributing to the prevention of global warming by partially sequestering the excess amount of carbon dioxide via photosynthesis and converting it to new products. Due to rapid growth rate, contribution to reduce greenhouse gas and high oil generation capacity, microalgae are one of the most preferred third-generation biofuel sources. They can grow on areas unsuitable for agricultural purposes and on aquatic mediums and therefore do not compete with arable lands [25]. Besides, unlike the terrestrial plants, algae have reduced environmental risks on drinking water resources, and they are very efficient at removing nutrients like nitrogen and phosphorus from water. Many researchers consider microalgae as the unrivaled energy source and also emphasize the contribution to gaseous emissions. With very limited amount of water, microalgae can duplicate their population in 1 day by using solar energy. In fact, some types of algae require only few hours to reach such growth rates. This allows for production of millions of liters of biofuel per hectare per year, which is fairly high when compared with the palm oil (5950 L/ha) and makes algae one of the most desirable alternative sources of energy. Although not all types of algae are suitable for biodiesel production, some types are convenient for this purpose. The studies are concentrated particularly on fresh water algae (Chlorella) since it is easy to grow at laboratory conditions and is one of the best alternative algae for biodiesel production. The main processes to produce fuel from microalgae are listed in **Table 3**.

Studies on energy production including the use of a variety of algal species are generally lab-scaled, pilot, or small-scaled studies. Although these studies are successfully completed, desired efficiency is not achieved at large-scale production due to the failure in creating ideal conditions in full-scale systems.

2.1. Biofuel generation from microalgae

Microalgae can be found in natural water resources. More than 300,000 types of microalgae were determined. These organisms are very effective in converting the solar energy into biomass and contain more than 80% oil. Industrial life cycle and product line of algae are shown in **Figure 2**.

The growth phase requires setting up and operating a supporting medium in favor of algae. Under ideal conditions, in fact, it is hard to achieve in full-scale plants; they reproduce easily and grow very rapidly [27]. Ideal temperature range for the growth of microalgae is 20–30°C. They also require organic and inorganic elements (nitrogen, phosphorus, iron, and

Final product	Production process
Biodiesel	Extraction of oil from algae and transesterification
Ethanol	Fermentation
Methane	Anaerobic fermentation of algae
Heat and electricity	Direct combustion of algae or gasification of biomass

Table 3. Use of microalgae.

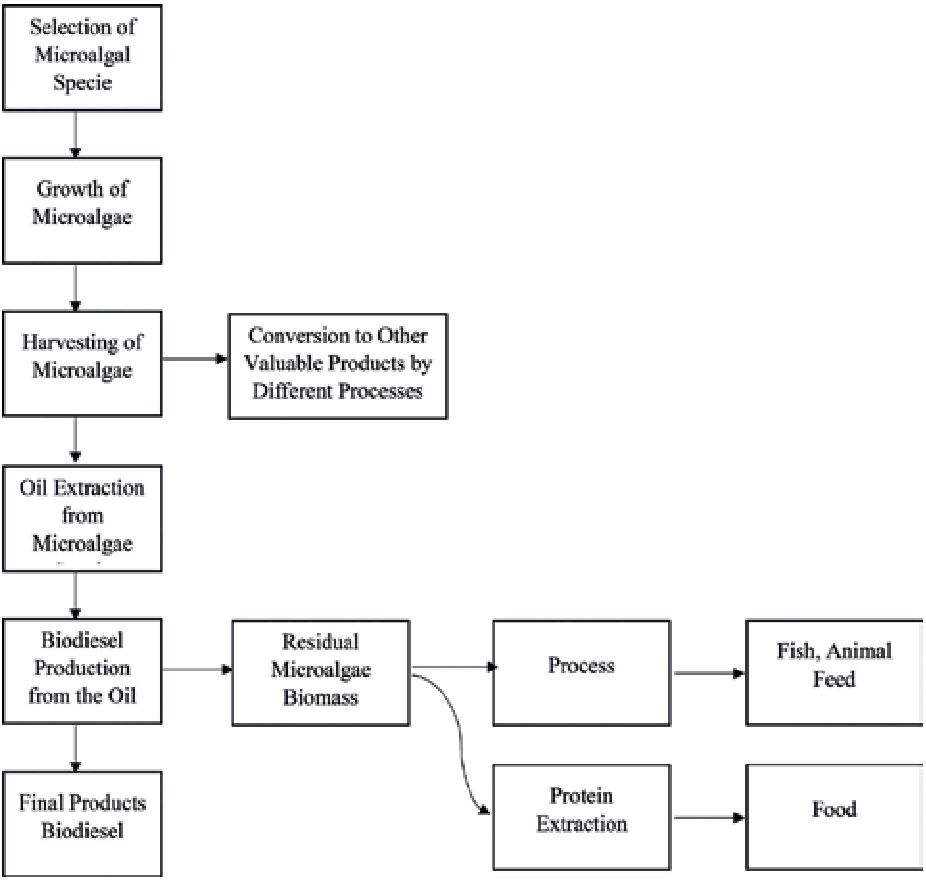

Figure 2. Industrial life cycle of microalgae [26].

silicon in some cases) to grow up. In addition to trace elements, they can reproduce at domestic wastewaters, animal wastes, industrial wastewaters, and some aquatic environments in the case of carbon deficiency [28]. There are two main methods used to cultivate microalgae, which are suspended cultures and immobilized cultures.

During the production of oil, they use sunlight and CO_2 more effectively than the oil plants. In addition, their growth rate is very fast. During the rapid growth period, doubling time of microalgae biomass is 3.5 h. For these reasons, larger quantities of microalgae can be produced at smaller areas with lower costs compared to the oil plants that are cultivated widely. The most popular algal species and microalgae are defined and their chemical compositions, properties, and cultivation techniques are mainly determined.

After the growth phase, algae should be harvested using various methods, which can be classified as chemical, mechanical, biological, and electrical methods. Among the processes of biofuel production from algae, one of the most costly steps is harvesting, summing up to

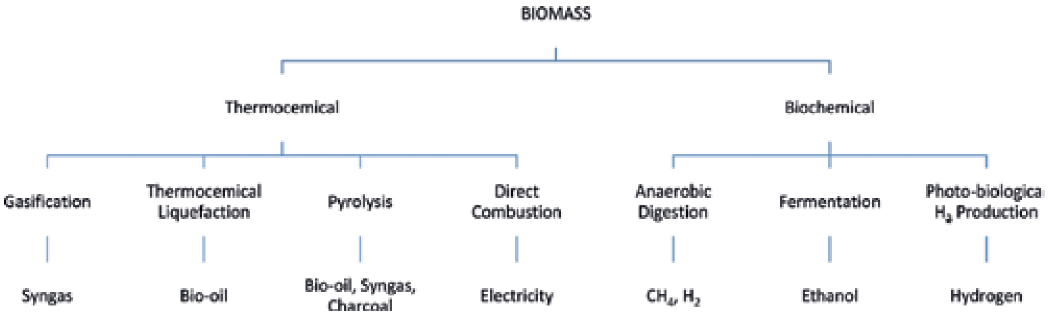

Figure 3. Conversion process alternatives and their end products [30].

20–30% of total production costs [29]. Harvesting is accomplished in two separate steps—bulk harvesting (using e.g. flocculation, floatation, and sedimentation) followed by concentrating the biomass (via centrifugation or filtration). Subsequently, the biomass should be prepared for conversion process, where dehydration is essential. Many dehydration methods, like sun drying, low-pressure shelf drying, spraying, drum drying, fluidized bed drying, and freeze drying, may be used. The trade-off is between choosing low-cost, time-consuming sun drying and high-energy-consuming efficient methods. Conversion process alternatives and their end products are given in **Figure 3**.

3. Renewable energy outlook

3.1. Global

In recent years, several developments and trends clearly demonstrate a tendency and increased attention on renewable energy. The continuing comparatively low global fossil fuel prices, dramatic price reductions of several renewable energy technologies (especially solar PV and wind power), increase in energy storage, and increased appetite toward renewable technology and facility investments can easily be interpreted in favor of renewables.

Although it varies by country widely, global primary energy demand has grown by an annual average of around 1.8% in the last 5 years (**Figure 4**). Growth in primary energy demand has occurred largely in developing countries, whereas in developed countries it has slowed or even declined [31].

Looking into carbon emissions, when it is combined with increased renewable use, it is not surprising to see that, from 2013 to 2016, for the third consecutive year, global energy-related carbon dioxide emissions from fossil fuels and industries were nearly stabilized. The average increase of carbon dioxide emissions was 2.2% annually, in the previous decade [31], which cannot be connected directly to the economic recession. The breakdown of global renewable energy shares is given in **Figure 5** and share of renewables by sector is given in **Figure 6**.

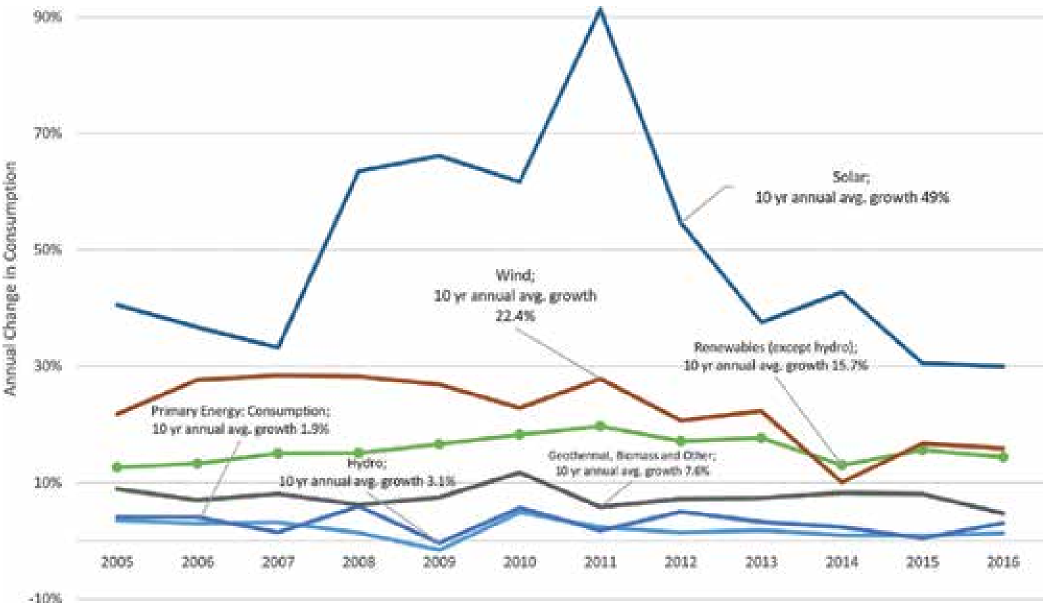

Figure 4. Growth in global renewable energy and total final energy consumption, 2005–2016 (data from [32]).

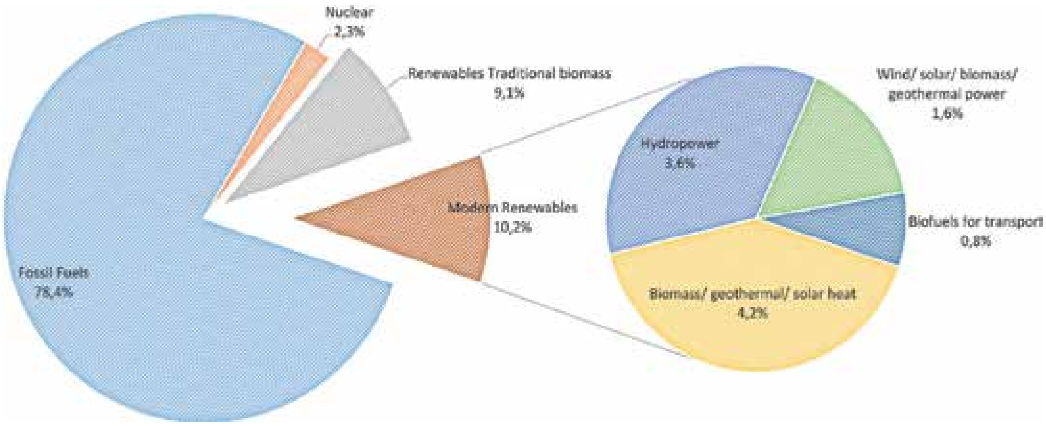

Figure 5. Global renewable energy share (data from [33]).

As it can be seen from **Figure 5**, biomass-originated fuels became the fourth largest energy resource after coal, oil, and natural gas. Currently nearly 10% of global primary energy is sequestrated from biomass used for heating, cooking, transportation, and electric power generation. The utilization pathways are diverse through traditional use of primary fuel and bio-based liquid fuels. Yet, for many countries setting targets on renewable energy, biomass is not the pointed focus, and the share in the energy mix is not expected to stack up in the future, as **Figure 6** implies.

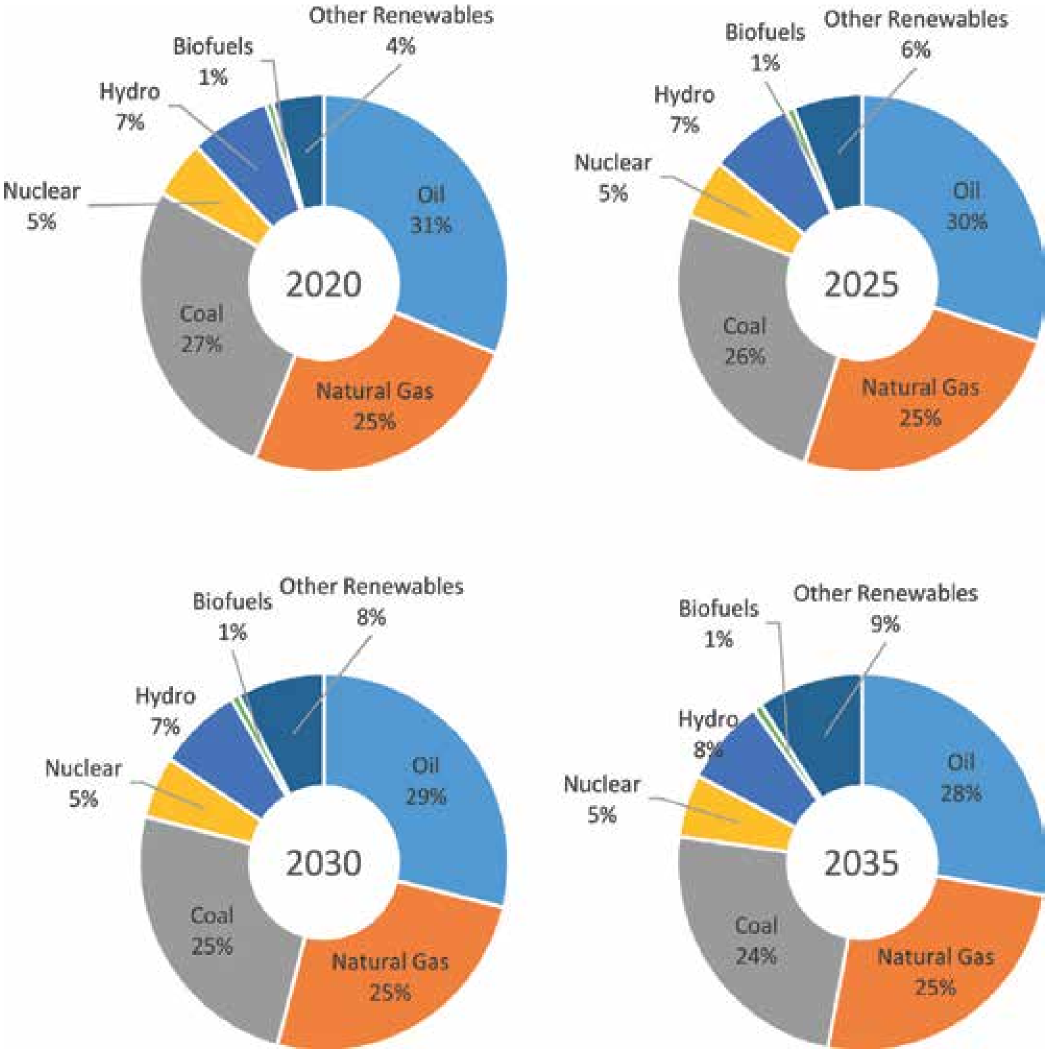

Figure 6. Projection of global primary energy consumption by fuel (MTOE) (data from [34]).

3.2. Biofuels in energy policy

Biofuels traditionally are attributed to transport because they are the only candidates used in vehicles, besides EV. Particularly, biofuels are options that do not require costly modifications to existing infrastructure and the vehicle fleet. Biofuel production is driven through blending mandates (e.g. Brazil and Indonesia, increasing their mandates in recent years), subsidies (e.g. the US), or a combination of both. In the EU, because of sustainability concerns, the trend is accelerating the transition to more advanced biofuels [35]. Currently, the EU set a 7% cap on conventional biofuels in final transport consumption while maintaining the 10% target for renewable sources in transport by 2020.

Even though biofuels have policy support for a number of years, the slow economic recovery and advances in conventional vehicle fuel economy have limited demand growth. There are also unsolved problems for biofuels to diffuse in the market, especially in distribution and lack of flex-fuel vehicles, as well as concerns on sustainability of first-generation biofuels. Nevertheless, developments like new biofuel plants and use of biofuels in commercial flights are still promising. Biojet fuels, with blends of up to 50% biofuel, have been used in more than 2500 commercial flights [36].

In addition to energy policies, biofuels are also connected to national economic policies, even to rural employment and rural development plans. Biofuel production line gets through agriculture, rural areas, producers and final consumers, creating multiple cross-industry effects. Thus subsidies towards biofuels are able to double their effects. Similar to any other renewable technology, biofuels have the ability to create new employment opportunities. Despite concerns on sustainability, some researchers argue that biofuels would perform better provided that barriers via regulations are removed and opened to the free market [37].

3.3. Turkey

Utilization of renewable energy, theoretically, backs up power generation by leading to three goals: (1) sustainable development, (2) decreasing energy import, thus relieving current account deficit, (3) and increasing energy security [38, 39]. Turkey has significant potential in terms of renewable energy. It is ranked 14th in the world with its geothermal energy capacity, 29th with its solar energy capacity and 16th with its wind energy capacity. For wind, the potential is estimated to be around 48 GW with a technically feasible capacity of 20–24 GW [40].

Historically, Turkish renewable energy generation was based on hydropower until privatization of the generation. From 2000s, renewable energy was put forward as one of the important issues on Turkey's energy agenda. Turkey's ambitious vision for 2023 envisages new and improved targets for the renewables, opening doors to other renewables other than hydropower [41]. Historical installed capacity of Turkey in terms of primary energy supply is given in **Figure 7**, and future projection of renewable capacity is given in **Figure 8**.

In addition to energy security and economical requirements, Turkey also connects the renewable source utilization targets into the low-carbon economy transition. Turkish Intended Nationally Determined Contributions (INDCs) [43] includes increasing solar energy capacity to 10 GW and wind capacity to 16 GW, until 2030. Looking back to 2008, where renewable capacity (excluding hydro) was 212 MW [44], Turkey has demonstrated a vast improvement within 9 years, carrying the capacity over 7800 MW, as of 2016. It is certain that if the increase is kept in the upwards direction, the 2030 targets seem highly probable.

The literature on the energy consumption-economic growth nexus has been widely researched (e.g. [45–47]); however, the renewable energy-based studies are still scarce [48]. It is well established that as a domestic natural resource, renewable energy source (RES) can make contributions to energy security. Some references [51] even proclaimed that RES could supply Turkey with full energy independence. It is clear that, even though it requires grid improvement and modular planning as well as grid operation, renewable energy supplies diversification into the grid, which in turn relieves energy dependence in the Turkish case.

Another focal point to be addressed is the dependency problem in terms of account deficit. **Figure 9** shows the imported energy bill of Turkey. It is notable that the decrease in the total

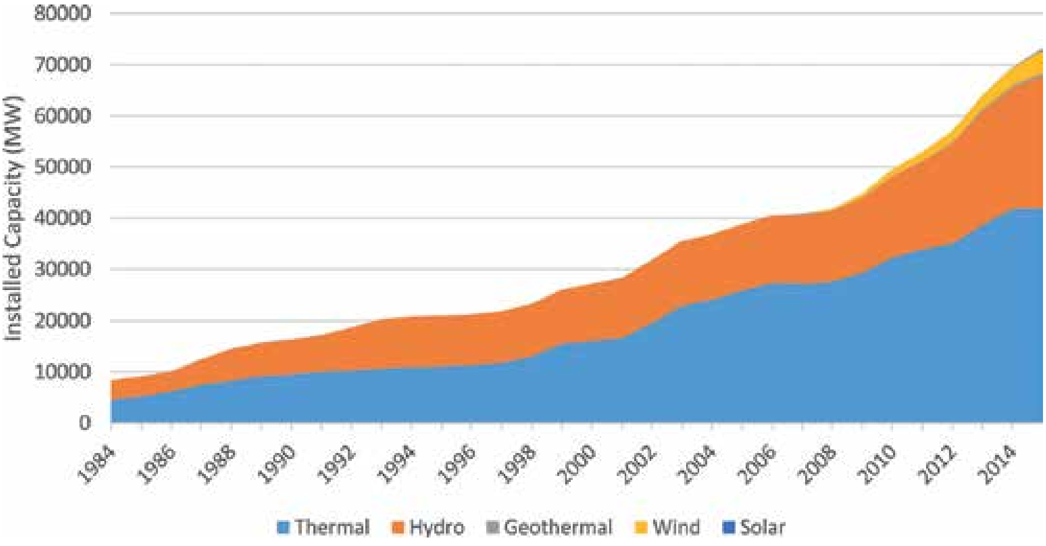

Figure 7. Development of installed capacity in Turkey (data collected from [42] and interpreted).

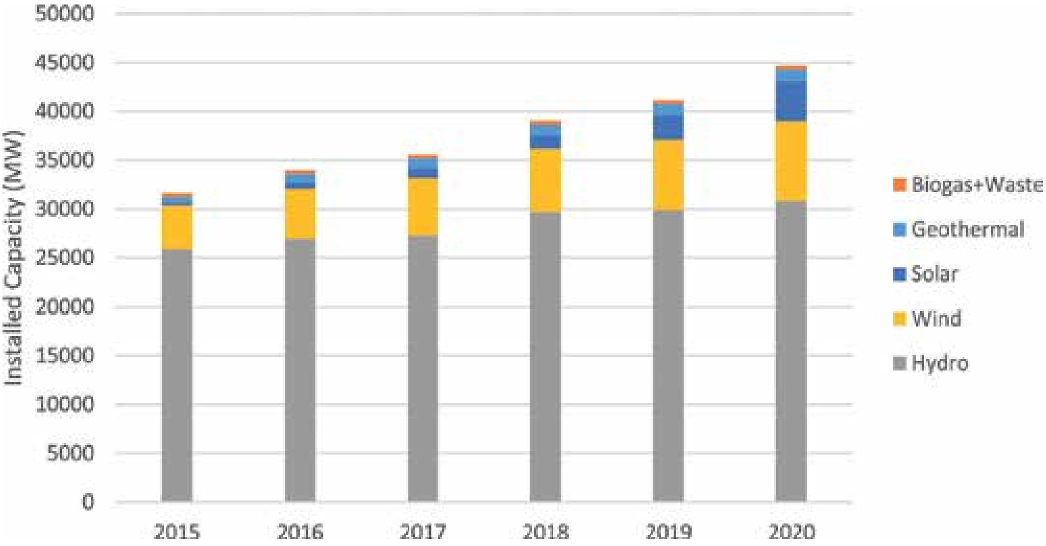

Figure 8. Installed renewable capacity projection in Turkey (data collected from [42] and interpreted).

import price results from the global energy sources (natural gas for the Turkish case), where imported energy sources have still been increasing and energy is the major expenditure in Turkey's national account.

3.4. Biofuel potential and utilization in Turkey

In line with the rapid growth (due to governmental support mechanism) of Renewable Energy Sources (RES) in power generation (see **Table 4**), the investment in biomass has also

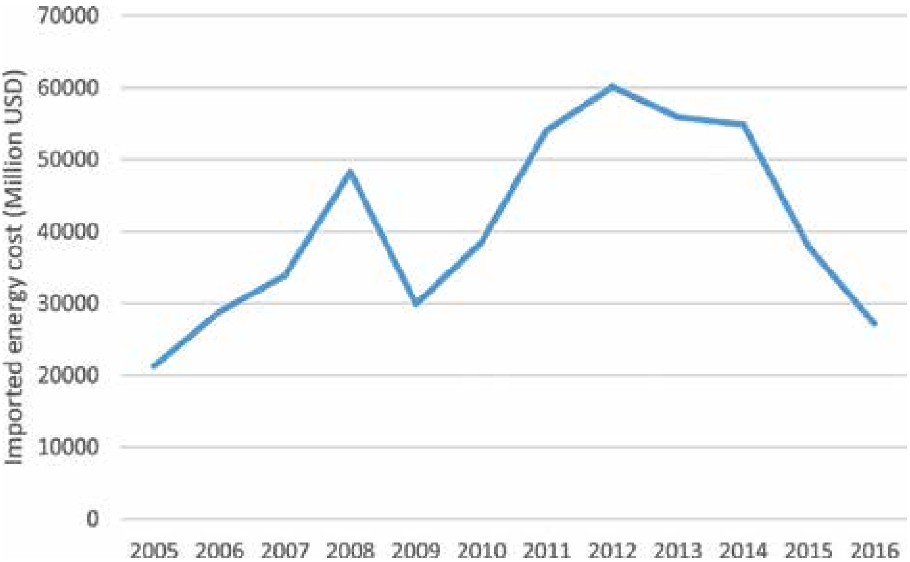

Figure 9. Imported energy cost of Turkey (TÜİK, 2017).

been increasing fast. While the installed capacity was only 43 MW in 2007, within 10 years, by the end of 2016, the installed capacity has reached 496 MW—that is more than a tenfold increase (**Figure 10**). The annual average growth rate is actually more than 30%.

As of today (end of 2016), there are more than 70 biomass/biogas power plants in diverse sizes (from less than 1 to 34 MW) (see **Table 5**). These plants were able to generate 2.372 GWh annually (which is 0.86% of total energy generated), with their 496 MW of installed capacity in total (0.63% of Turkey) (see **Figure 11**).

The ratio of generation to capacity shows that the capacity usage factor has been quite high in these plants, suggesting that they have functioned as reliable base-load plants as opposed to other intermittent (like wind and solar) RES, which are actually called variable renewable energy (VRE) and frequently referred to as one of the obstacles to full-fledged RES development.

Therefore, this is an important feature and an attractive point in relation to biomass-based power generation investment: base load, reliable, and stable power.

Although there is considerable potential (see **Figure 12**), other than traditional biomass and biogas, there is not yet any utilization of other types of biofuels in Turkey. Studies on microalgae are mainly conducted by the Faculties of Aquaculture at the larva bait production areas and at eutrophic marine and surface water sources. Although biomass production of algae has already been initiated at some universities, particularly at Aegean University, there are not enough studies and investigations focusing on energy generation from microalgae. Studies related with energy are concentrated on Izmir, Ankara, and Gebze. Studies on energy are generally lab-scaled, pilot, or small-scaled studies and completed successfully. However, desired efficiency is not achieved at large-scale production due to the failure in creating ideal conditions. General Directorate of Electricity Transmission Corporation states that the annual

Installed capacity	2008	2009	2010	2011	2012	2013	2014	2015	2016
Hard Coal + Imported Coal + Asphaltite	1,986	2,391	3,751	4,351	4,383	4,383	6,533	6,825	8,229
Lignite	8,205	8,199	8,199	8,199	8,193	8,223	8,281	8,696	9,127
Fuel Oil + Motorin + LPG + Nafta	1,819	1,699	1,593	1,300	1,286	616	595	523	445
Natural Gas	15,526	16,963	18,628	19,955	20,997	25,191	26,094	25,489	26,115
Biofuels	60	87	107	126	169	235	299	370	496
Hydro	13,829	14,553	15,831	17,137	19,609	22,289	23,643	25,868	26,681
Geothermal	30	77	94	114	162	311	405	624	821
Wind	364	792	1,320	1,729	2,261	2,760	3,630	4,503	5,751
Solar							40	249	833
Total	**41,817**	**44,761**	**49,524**	**52,911**	**57,059**	**64,008**	**69,520**	**73,147**	**78,497**

Table 4. Development of installed power generation capacity (MW)—Turkey (2008–2016).

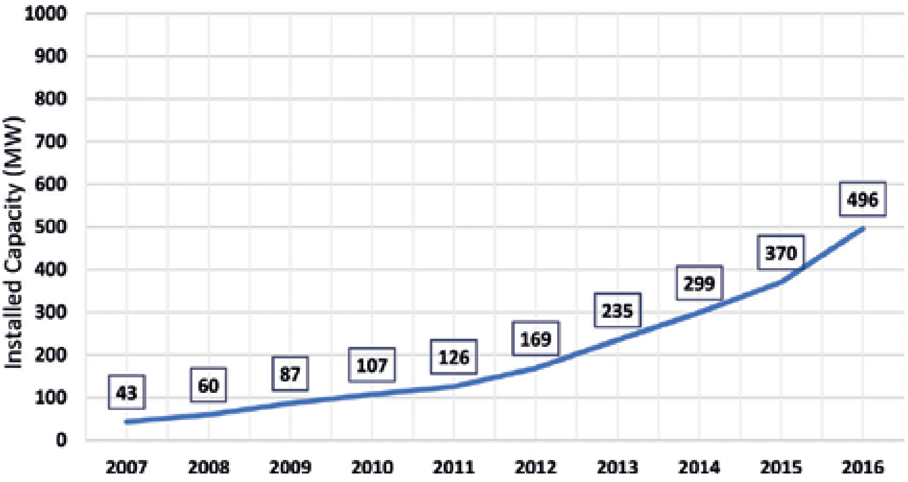

Figure 10. Development of biomass/biogas power generation capacity in Turkey (2007–2016).

sunshine average of Turkey is 2640 per hour; in other words, average amount of energy that can be generated is 3.6 kWh/m^2 in a day. Although, there are 50 licensed biofuel facilities in Turkey, having a total installed production capacity of 1.5 million Mg, only few of these are in production due to the misplanned raw material production or lack of feasibility. Algae are one of the main alternative fuel sources, and the weather condition of the country is suitable for algae production. In addition to this, all nutrient elements required for their growth are abundantly available. Alternative agricultural production is improving with the help of biofuel projects. Biofuels brought the agricultural activities back to the agenda and have opened new horizons for the countries by encouraging them to introduce new regulations.

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Power plant name	City	Company	Installed capacity
Odayeri Çöp Gazı Santrali	İstanbul	Ortadoğu Enerji	34.0 MW
Toros Tarım Samsun Atık Isı Santrali	Samsun	Toros Tarım	31.0 MW
Mutlular Biyokütle (Orman Atığı) Enerji Santrali	Balıkesir	Mutlular Enerji	30.0 MW
Mamak Çöplüğü Biyogaz Tesisi	Ankara	ITC Katı Atık Enerji	25.0 MW
Çadırtepe Biyokütle Sanrali	Ankara	ITC Katı Atık Enerji	23.0 MW
Sofulu Çöplüğü Biyogaz Santrali	Adana	ITC Katı Atık Enerji	16.0 MW
Akçansa Çimento Atık Isı Santrali	Çanakkale	Enerjisa Elektrik	15.0 MW
Kömürcüoda Çöplüğü Biyogaz Santrali	İstanbul	Ortadoğu Enerji	14.0 MW
Eti Alüminyum Atık Isı Elektrik Santrali	Konya	Cengiz Enerji	13.0 MW
Zeus Biyokütle Enerji Santrali	Kırklareli	Zeus Enerji	12.0 MW
Eti Maden Bandırma Atık Isı Santrali	Balıkesir	Eti Maden	12.0 MW
ITC-KA Sincan Biyokütle Gazlaştırma Tesisi	Ankara	ITC Katı Atık Enerji	11.0 MW
Bağfaş Gübre Fabrikası Biyogaz Santrali	Balıkesir	Bağfaş Gübre Fabrikası	9.9 MW
Hamitler Çöplüğü Biyogaz Santrali	Bursa	ITC Katı Atık Enerji	9.8 MW
Çimsa Atık Isı Santrali	Mersin	Enerjisa Elektrik	9.6 MW
Batıçim Atık Isı Santrali	İzmir	Batıçim Batı Anadolu	9.0 MW
Prokom Pirolitik Yağ ve Pirolitik Gaz Tesisi	Erzincan	Prokom Madencilik	7.0 MW
Aksaray OSB Gübre Gazı Elektrik Santrali	Aksaray	Sütaş Süt Enfaş Enerji	6.4 MW
Karacabey Biyogaz Tesisi	Bursa	Sütaş Süt Enfaş Enerji	6.4 MW
Şanlıurfa Biyokütle Enerji Santrali	Şanlıurfa	Full Force Enerji	6.2 MW
Eman Enerji Mersin Biyokütle Enerji Santrali	Mersin	Mersin Büyükşehir Belediyesi	6.0 MW
Avdan Biyogaz Tesisi	Samsun	Avdan Enerji	6.0 MW
Modern Biyokütle Enerji Santrali	Tekirdağ	Eren Enerji	6.0 MW
Trakya Yenişehir Cam Atık Isı Santrali	Bursa	Trakya Yenişehir Cam	6.0 MW
Kayseri Çöplüğü Biyogaz Elektrik Santrali	Kayseri	Her Enerji	5.8 MW
Konya Aslım Çöplüğü Elektrik Üretim Santrali	Konya	ITC Katı Atık Enerji	5.7 MW
Gaziantep Çöp Gazı	Gaziantep	CEV Enerji	5.7 MW
Batısöke Söke Çimento Atık Isı Elektrik Santrali	Aydın	Batısöke Söke Çimento	5.3 MW
Kocaeli Çöplüğü Biyogaz Santrali	Kocaeli	Ortadoğu Enerji	5.1 MW

Power plant name	City	Company	Installed capacity
Ovacık Biyogaz Enerji Santrali	Kırklareli	Işıt Biyokütle	4.8 MW
Tire Biyogaz Tesisi	İzmir	Sütaş Süt Enfaş Enerji	4.3 MW
Hatay Gökçegöz Çöp Santrali	Hatay	Atya Elektrik	4.2 MW
Hasdal	İstanbul	İstanbul Büyükşehir Belediyesi	4.0 MW
Afyon Biyogaz Enerji Santrali	Afyonkarahisar	Afyon Enerji	4.0 MW
Gönen Biyogaz Tesisi	Balıkesir	Gönen Yenilenebilir Enerji	3.6 MW
Belka Çöp Gazı Biyogaz	Ankara	Ankara Büyükşehir Belediyesi	3.2 MW
Atlas İnşaat Osmaniye Çöp Gazı Santrali	Osmaniye	Atlas İnşaat	3.1 MW
ITC-KA Elazığ Çöp Gazı Santrali	Elazığ	ITC-KA Enerji	2.8 MW
İskenderun Çöp Gazı Elektrik Üretim Tesisi	Hatay	Novtek Enerji	2.8 MW
Trabzon Rize Çöp Gazı Santrali	Trabzon	Mustafa Modoğlu Holding	2.8 MW
Sivas Biyokütle Elektrik Üretim Tesisi	Sivas	Novtek Enerji	2.8 MW
Konya Atıksu Biyogaz Santrali	Konya	Konya Büyükşehir Belediyesi	2.4 MW
Malatya BŞB Çöp Gazı Elektrik Üretim Santrali	Malatya	Malatya Büyükşehir Belediyesi	2.4 MW
Arel Enerji Biyokütle Tesisi	Afyonkarahisar	Arel Enerji	2.4 MW
Manavgat Çöp Gazı Santrali	Antalya	Arel Enerji	2.4 MW
Senkron Efeler Biyogaz Santrali	Aydın	Senkron Grup	2.4 MW
Mauri Maya Bandırma Biyogaz Santrali	Balıkesir	Mauri Maya	2.3 MW
Tokat Çöpgazı Elektrik Üretim Santrali	Tokat	Tokat Belediyesi	2.3 MW
Bandırma Edincik Biyogaz Santrali	Balıkesir	Telko Enerji	2.1 MW
Eses Enerji Biyogaz Santrali	Eskişehir	Eskişehir Büyükşehir Belediyesi	2.0 MW
Karaduvar Atıksu Arıtma Tesisi Biyogaz Santrali	Mersin	Mersin Büyükşehir Belediyesi	1.9 MW
Albe Biyogaz Santrali	Ankara	Era Grup	1.8 MW
GASKİ Atıksu Biyogaz Elektrik Santrali	Gaziantep	Gaziantep Büyükşehir Belediyesi	1.7 MW
Karma Gıda Biyogaz Santrali	Sakarya	Karma Gıda	1.5 MW
Polatlı Biyogaz Tesisi	Ankara	Polres Elektrik Üretim	1.5 MW
Aksaray Çöp Gazı Elektrik Santrali	Aksaray	ITC Katı Atık Enerji	1.4 MW
Karaman Biyogaz Tesisi	Karaman	Karaman Yenilenebilir Enerji	1.4 MW
Pamukova Katı Atık Biyogaz Santrali	Sakarya	Biosun Pamukova	1.4 MW

Power plant name	City	Company	Installed capacity
Eman Enerji Silifke Biyokütle Enerji Santrali	Mersin	Mersin Büyükşehir Belediyesi	1.2 MW
Uşak Çöpgazı enerji Santrali	Uşak	Uşak Belediyesi	1.2 MW
Amasya Çöp Gazı Elektrik Üretim Santrali	Amasya	Boğazköy Enerji Elektrik Üretim	1.2 MW
Ekim Grup Gübre Gazı	Konya	Ekim Grup Elektrik	1.2 MW
Malatya 1 Çöp Gaz Elektrik Üretim Tesisi	Malatya		1.2 MW
Bolu Çöplüğü Biyogaz Santrali	Bolu	CEV Enerji	1.1 MW
Kırıkkale Çöp Gazı Enerji Santrali	Kırıkkale	Mustafa Modoğlu Holding	1.0 MW
Sigma Suluova Biyogaz Tesisi	Amasya	Sigma Elektrik Üretim	1.0 MW
Kemerburgaz Çöplüğü Biyogaz Santrali	İstanbul	Ekolojik Enerji	1.0 MW
Hayat Biyokütle Elektrik Üretim Santrali	Kocaeli	Hayat Enerji	1.0 MW
Eman Enerji Karaman Biyokütle Enerji Santrali	Kahramanmaraş	Eman Enerji	1.0 MW
Adana Batı Atıksu Biyogaz Santrali	Adana	Adana Büyükşehir Belediyesi	0.8 MW
Adana Doğu Atıksu Biyogaz Santrali	Adana	Adana Büyükşehir Belediyesi	0.8 MW
Beypazarı Biyogaz Tesisi	Ankara	Derin Enerji Üretim	0.8 MW
Frito Lay Gıda Biyogaz Santrali	Kocaeli	Frito Lay Gıda	0.7 MW
Frito Lay Gıda Kojenerasyon Santrali	Mersin		0.7 MW
Kumkısık Çöplüğü Biyogaz Santrali	Denizli	Bereket Enerji	0.6 MW
Sezer Bio Enerji	Antalya	Kalemirler Enerji	0.5 MW
Denizli Atıksu Arıtma Tesisi Biyogaz Elektrik Üretim Santrali	Denizli	Denizli Büyükşehir Belediyesi	0.5 MW
Solaklar İzaydaş Çöp Gazı	Kocaeli	Kocaeli Büyükşehir Belediyesi	0.3 MW
Cargill Tarım Bursa Bioenerji Santrali	Bursa	Cargill Tarım	0.1 MW
		TOTAL	496.4 MW

Table 5. Biomass/biogas: full list of power plants in Turkey (2017).

3.5. The contribution of biomass in power generation to energy dependence, supply security, and national economy

It is well established that as a domestic natural resource, RES can make contributions to energy security. BNEF [49] and Hill [50] even proclaimed that RES could supply Turkey with full energy independence. It is clear thus that renewable energy supplies diversification into the grid which in turn relieves energy dependence in the Turkish case. One of the main promising

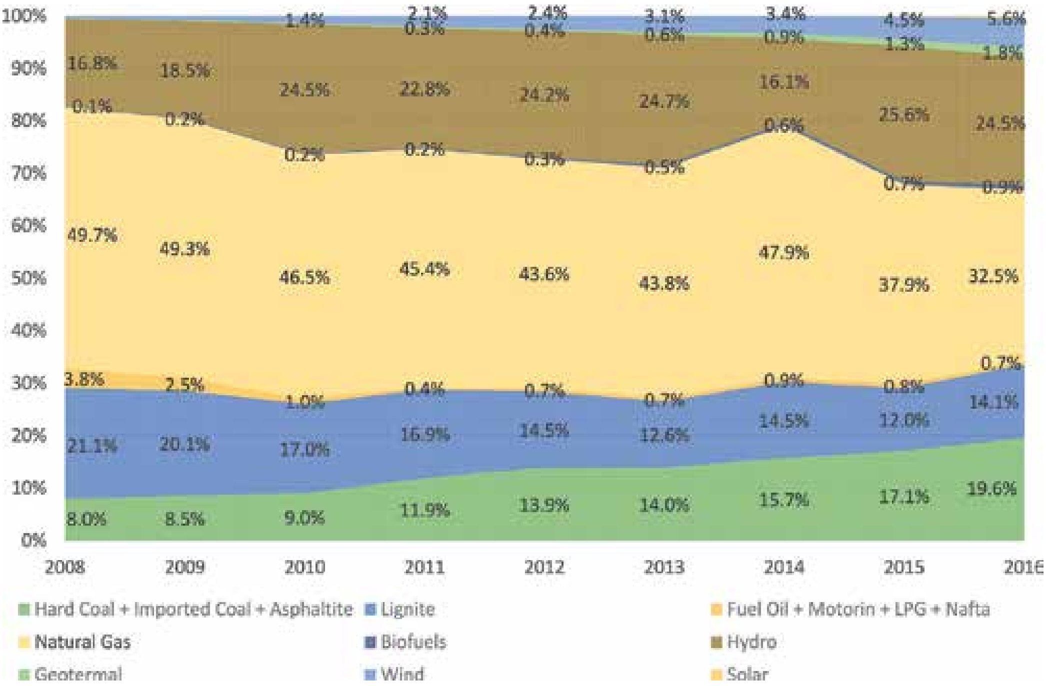
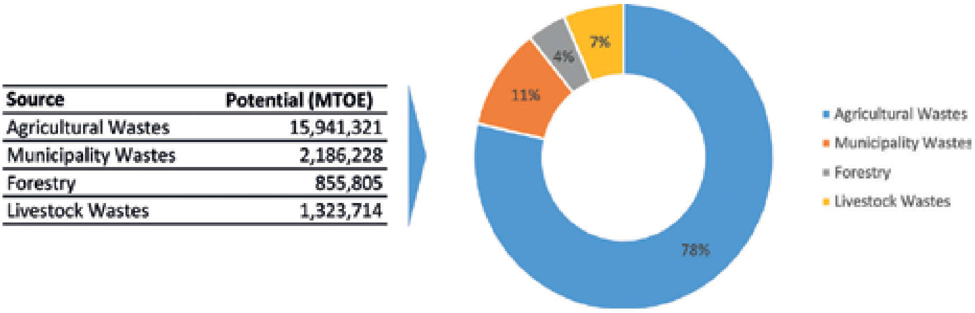


Figure 11. Development of power generation by sources (percentages) in Turkey (2008–2016).



Source	Potential (MTOE)
Agricultural Wastes	15,941,321
Municipality Wastes	2,186,228
Forestry	855,805
Livestock Wastes	1,323,714

Figure 12. Biomass potential of Turkey by fuel type.

sources within RES portfolio of Turkey is therefore biofuels (especially biomass and biogas, which could help substitute the import fossil fuels.

Another focal point to be addressed is therefore the dependency problem in terms of current account deficit. **Figure 9** shows the imported energy bill of Turkey. It is notable that the decrease in the total import price results basically from the decline in global energy prices (oil and gas), but still energy is the major item in Turkey's trade balance.

In the analysis below, in order to calculate the contribution of biomass to energy security as well as to the relief of current account deficit, we make a comparison in terms of how much of energy imports from fossil fuels (in our case we take gas, which is the most expensive and the most used power-generation fuel) was actually substituted for 2016.

The cost of imported natural gas in each MWh of electricity produced can be calculated as about 38 USD (with an assumption efficiency of average 55% of a combined cycle gas turbine (CCGT) plant current BOTAŞ wholesale gas price as 704 TL/1000 m^3 or ~195 USD/1000 m^3). For the year 2016, the monetary value of avoided (not imported or "substituted with biomass fuel") natural gas can be currently calculated as approximately 90 million USD: 38 USD × 2.372 GWh (which is the total generated from biomass only in 2016) = 90.136 T. USD.

In other words, an amount of around 456 million m^3 of natural gas (which is around 1% of the total gas import amount) has been avoided to be imported, only with the utilization biomass as a fuel of choice in power generation from the biomass power plants of a total installed capacity of 496 MW in the year 2016.

Taking the official aim of reaching 1 GW (1000 MW) installed capacity by 2023 (which is around 0.8% of total capacity then) into consideration and assuming the same efficiency and capacity usage factors as was realized in 2016, 4800 GWh of power is then calculated that can be generated (which could yield a generation percentage of around 1.1% in general totally). This amount is equivalent to approximately 920 million cubic meter of natural gas as a fuel source to be burnt for power generation, which could be avoided (not to be imported) with a monetary value of approximately 182 million USD.

In this way, the imported energy bill would have been cut by about 182 million USD by 2023. If we consider the fact that the total amount of imported natural gas was around 46 billion m^3 and out of this amount 17.5 billion m^3 was consumed for power generation with an import price tag of 3.5 billion USD (which had yielded 88.271 GWh of electricity), the import fuel-saved electricity from biomass (calculated to be 4.890 GWh) would therefore be equivalent to ~5.4% of total electricity obtained from natural gas per annum. Although the amount 182 million USD (which was achieved by burning biomass instead of gas) as savings in a gas-for-electricity portion of ~3.5 billion USD and around total gas import bill of 9 billion USD and of total 27 billion USD energy import bill or 32.6 billion current account deficit seems small (though only annual) and negligible, one should also consider the fact that biomass is actually one of the many domestic and environmentally friendly renewable energy sources (several of which, like wind, hydro, and solar, are much more contributive than biomass), which has enormous potential altogether to reduce significantly energy-dependence ratio and the total energy import bill of Turkey (and consequently current account deficit).

That is, the total value of RES potential for 2023 (the official government target year) is—with 38% of total generation—actually more than total for the "gas-for-electricity" amount (which is around 30%). In other words, with the total RES-generated electricity, which would have otherwise been generated from imported natural gas, more than 3.5 billion USD could be saved per annum by 2023. Thus, it can safely be said that together with other renewables, biomass has a role to play to reduce both energy-import dependence and import bill of Turkey in a better way.

4. Conclusions

It has been understood for some time now that the dependence of the world (especially in power generation) on fossil fuels is not sustainable. One of the identified solid alternatives therefore has been biofuels. As biofuels are regarded as carbon neutral (x ref), they are listed under the renewable category of energy sources and are thus "climate friendly," as opposed to fossil fuels; they are given priority and are supported globally by government policies, as is the case with generous subsidies (such as the highest off-take guarantees from biofuel power plants) in Turkey. The potential of biofuels (although not as huge as solar or wind) especially in power generation is considered to be significant due to the fact that it is not actually an intermittent source of power as is the case with other renewables such as wind- and solar- (as they are actually called "variable renewable energies") based generation. Thus, biofuels can easily substitute other fossil fuels as a reliable and base-load source of power generation with high availability, as opposed to the variability and intermittency of other sources. This has been actually demonstrated in Turkey in relation to the operational conditions (high availability and reliability) of existing biomass power plants.

Another result of this study in terms of the reasons for utilization of biomass/biogas resources is (in addition to all abovementioned environmental benefits)the contribution (so far small but promising for the future) of them reducing energy import dependence and energy import bill of Turkey. As analyzed in the relevant section, the development of biomass/biogas plants has been very rapid and the generation reached the equivalent of more than 5% of power generation from natural gas. Thus, the gas imports were reduced by this amount, or according to unit-based calculation, 1 MW of power generated by local/domestic and renewable biomass/biogas obviously meant "1 MW less of imported and fossil natural gas-based power". The total savings or avoided import value per year (for only the year 2016) is around 185 million USD. Considering the potential of biomass/biogas and the fast development in utilization of these resources lately, one could assume that this amount or value (also depending on the price of import gas) will increase and biomass will (along with other RES) play a meaningful role in terms of contributing to meeting national climate targets as well to reducing energy import bill of Turkey, thus enhancing energy security and independence of the country in the long run.

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Prospective Biodegradable Plastics from Biomass Conversion Processes

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Additional information is available at the end of the chapter

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Abstract

The biomass energy source has been a promising renewable alternative for fossil fuels and their inevitable environmental impacts on Earth's life, from which the greenhouse gas (GHG) emissions and the environment pollution followed by consequent ecosystem imbalance are major concerns. Biofuels and bioplastics are well-known examples of renewable products obtained from biomass that has shown increasing potential to succeed the conventional fuels and plastics. However, biofuels and especially bioplastics have faced their main hindrance in their uncompetitive costs. Furthermore, the "drop-in" plastics are the market leaders, which reduce the carbon footprint but continue to state the biodegradability concern attributed to most of plastic products, the packaging sector. This chapter outlines the common features and feedstocks of biofuels and bioplastics aiming to support their associated production set toward the bio-based and biodegradable poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs) as promising models with fast-growing production capacity forecasted for the next years and biodegradable solution for short-lived and disposable plastic materials.

Keywords: biofuel, bioplastic, biodegradable, PHA, PLA

1. Introduction

Nowadays, the world has faced the side effects from fossil fuel dependence such as environmental pollution, greenhouse gas (GHG) emissions, and ocean acidification. Besides the large utilization of oil, coal, and natural gas to generate energy, a variety of petrochemical derivatives have also accounted to the ecological imbalance worldwide. The petrochemical plastics are perfect examples of petroleum-based compounds, which imply a problematic ecological issue due to the high demand of their use for several applications, inappropriate discard, and environmental persistence [1, 2]. Conventional plastics take many decades to be decomposed in nature and produce toxins [3], particularly plastic additives (e.g., phthalates as plasticizers) and toxic monomer residues (e.g., vinyl chloride). Microplastics (particles less than 5 mm) in the oceans are seriously harmful to many aquatic organisms, and some of which inevitably end up in the human nutrition, the last consumer of this food chain [4].

As a result of the twentieth century development based on petroleum, coal, and natural gas exploitation, which were cheaply available, fossil fuels and their derivatives (e.g., fine chemicals, pharmaceuticals, detergents, plastics, fertilizers, lubricants, solvent, asphalt, and waxes) have become a major global threat directly linked to increasing levels of CO_2 in the atmosphere and consequent global warming. Since these fossil resources are not considered as sustainable and they are prejudicial from the ecological point of view [5], there have been rising concerns over their global impact, which has led to the development of technologies focused on the production of fuels and materials from renewable carbon sources, such as plant biomass [6]. Biomass has the potential to reduce GHG emissions by replacing fossil fuels. The combustion of biomass feedstock has been considered as carbon neutral or low-carbon fuel, since the plant crops assimilate carbon dioxide from the atmosphere during the growth. Accordingly, the so-called biofuels are a promising alternative to replace nonrenewable fuels [7, 8].

The main advantages of biofuels include their biodegradable and renewable properties; the generation of employment and technical development in rural areas; decentralized production from locally available domestic biomass; besides the combustion based on carbon dioxide cycle as mentioned above [8–10]. A global volume of more than 100 Bln L per year of conventional biofuels has been obtained, which is referred to as the first-generation biofuels including ethanol from sugar or starch crops and biodiesel from oils and fats. In addition, there have been many efforts focused on the second- and third-generation biofuels produced from a broad range of nonedible biomass feedstock [11].

Likewise, other chemicals and industrial products from fossil energy sources have been replaced by renewable ones. "Green" chemistry is a broad term referring to these compounds that support the sustainable development, from which the bioplastics can illustrate how the chemical industry is able to integrate sustainable innovation into a business model. On the other hand, the "green" chemistry companies must take into account efficient and less costly processes in order to make feasible their products commercialization [12]. Therefore, the economic viability of biofuel industry depends on facilities that integrate biomass conversion processes and equipment to produce value-added compounds, such as fuels, power, and chemicals. The larger the ability to derive value from biofuel, including byproducts and residues, the higher will be the feasibility of a bio-based industry from economic and environmental points of view [13].

A "green" biorefinery is a multifunctional and full-integrated system for biomass utilization. Besides the fuels obtained from "green" biomass, several products can be obtained from the "green" juice to the lignocellulosic materials, such as dyes, pigments, crude drugs, free amino acids, organic acids, enzymes, hormones, and minerals [5, 14]. Moreover, the biofuel byproducts have been a source of chemicals. Crude glycerol from transesterification of fats and oils, a byproduct of biodiesel industry, has been a promising feedstock to obtain a high diversity of products from microbial cultivation, which may be mentioned as 1,3-propanediol, dihydroxyacetone, succinic acid, propionic acid, ethanol, citric acid, biosurfactants, and bioplastics [15–24]. Lignocellulose hydrolysates are not only a source of the second-generation ethanol but also a feedstock of a multitude of chemicals such as xylose, mannose, galactose, acetic acid, ethylene, propylene, butadiene, xylitol, phenols, glucaric acid, glutamic acid, aspartic acid, syringols, eugenol, toluene, xylene, styrene, and others [14, 25–33].

Aside the environmental concern on fossil fuels being burnt into atmosphere, its plastic derivative is another critical issue, whose 60% of the total solid waste is discarded in landfills for 100 years of environmental persistence [1, 2]. Bioplastics from renewable energy sources that exhibit biodegradable characteristics are good candidates to replace short-lived and disposable plastic products, which accounts 50% of the total plastic production and so contributing for a significant diminishing of their long-term ecosystem intake and consequent harmful effects [4, 34, 35]. A biorefinery concept comprising biofuel and bioplastic production is an alternative solution to aggregate value to both industries and to improve the feasibility of a production set partially or totally disassociated from petrochemical compounds [23]. This chapter outlines a brief review on biofuels and bioplastics, and some of their interchangeable features in order to support a biorefinery model for bio-based and either biodegradable plastics belonging to biofuel production sets. Further, a special focus is dedicated to the production of poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs) from biofuel feedstocks and byproducts as promising bio-based and biodegradable plastics with fast-growing development foreseen for the next years.

2. Biofuels: an overview

Biofuel refers to solid, liquid, or gaseous fuel obtained from renewable feedstocks, from which bioethanol and biodiesel are the most produced transportation fuel as potential substitutes for gasoline and diesel fuel [9, 36, 37]. According to their production technology, biofuels are classified into the first-, second-, third-, and fourth-generation biofuels (**Figure 1**). The first-generation biofuels are produced from edible sources, such as grains, oil seeds, sugar and starch crops, and animal fats. Well-established examples of the first-generation biofuels are ethanol from sugarcane in Brazil, corn ethanol in the USA, biodiesel from rapeseed oil in Germany, and palm oil–based biodiesel in Malaysia. The second-generation biofuels are obtained from nonedible feedstock, such as lignocellulosic materials including cereal straw, forest and wood residues, sugarcane bagasse, short-rotation crops, and vegetative grasses [37].

The second-generation biofuels are an alternative to mitigate the main concern about the first-generation biofuels: food versus fuel. An additional advantage is the utilization of agricultural byproducts and municipal solid wastes and thus lowering costs and improving the urban waste management [37]. The former Directorate-General for Energy and Transport has proposed the third- and fourth-generation biofuels, which are classified as advanced biofuels. The third-generation biofuels are obtained using molecular biology techniques, such as low-lignin content trees and genetically modified microalgae. The fourth-generation biofuels are those that should provide carbon capture and storage (CCS) processes with improved

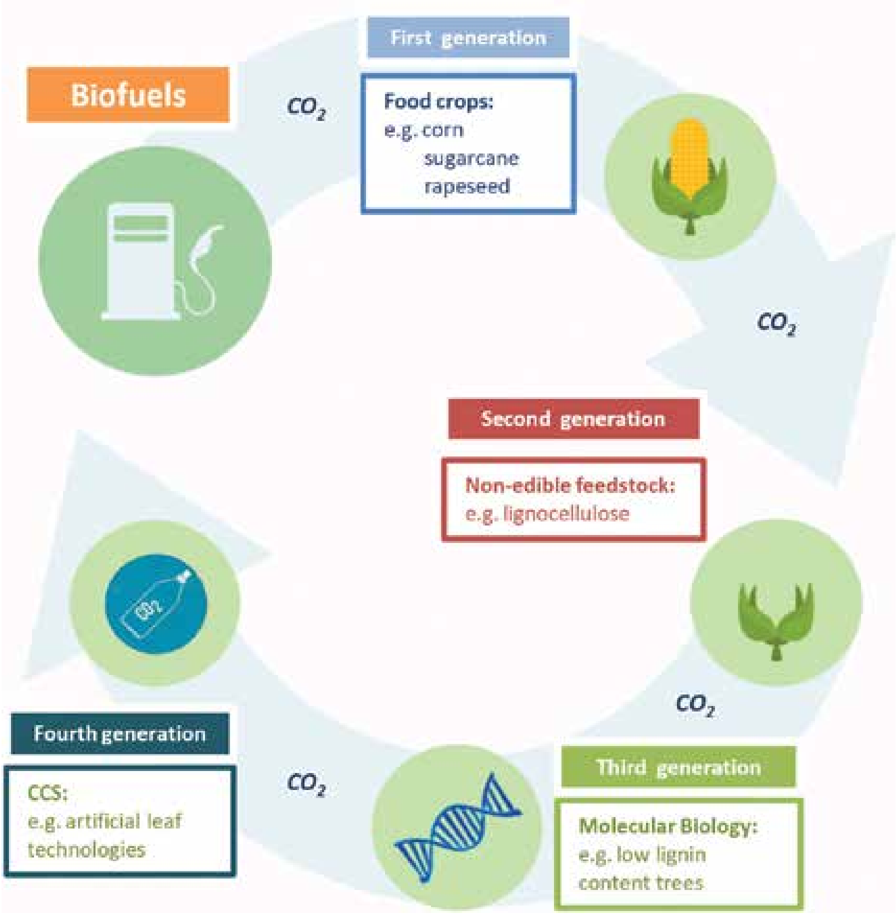

Figure 1. The first-, second-, third-, and fourth-generation biofuels.

CO_2 assimilation by genetically modified plants and CO_2 storage as geological formations by carbonation, crude oil, and gas headings [38].

The relative low increase in global oil production and rising prices of barrel between 2004 and 2009 were a boost to biofuel production [39]. Despite some previous experiences with biofuels such as in the 1970s with Brazilian National Alcohol Program [40] and in the 1990s with European biodiesel [41], only after 2003 major policy measures were legislated for promoting biofuel production in the EU and the USA followed by advancements in oil extraction technologies, which induced a global awareness about the requirement of alternative and ecological solutions regarding the depletion of petrochemical reserves and the environmental side effects from a century of its utilization. The International Energy Agency forecasts a percent global increase of transportation biofuels from 2% to up to 20% from 2012 to 2040, respectively [39, 42].

Nowadays, the USA, Brazil, and the EU have been the largest biofuel-producing countries whose the first-generation biofuels, bioethanol and biodiesel, are still the most well-established and current produced biofuels, which attend most of the commercial demand (**Figure 2**).

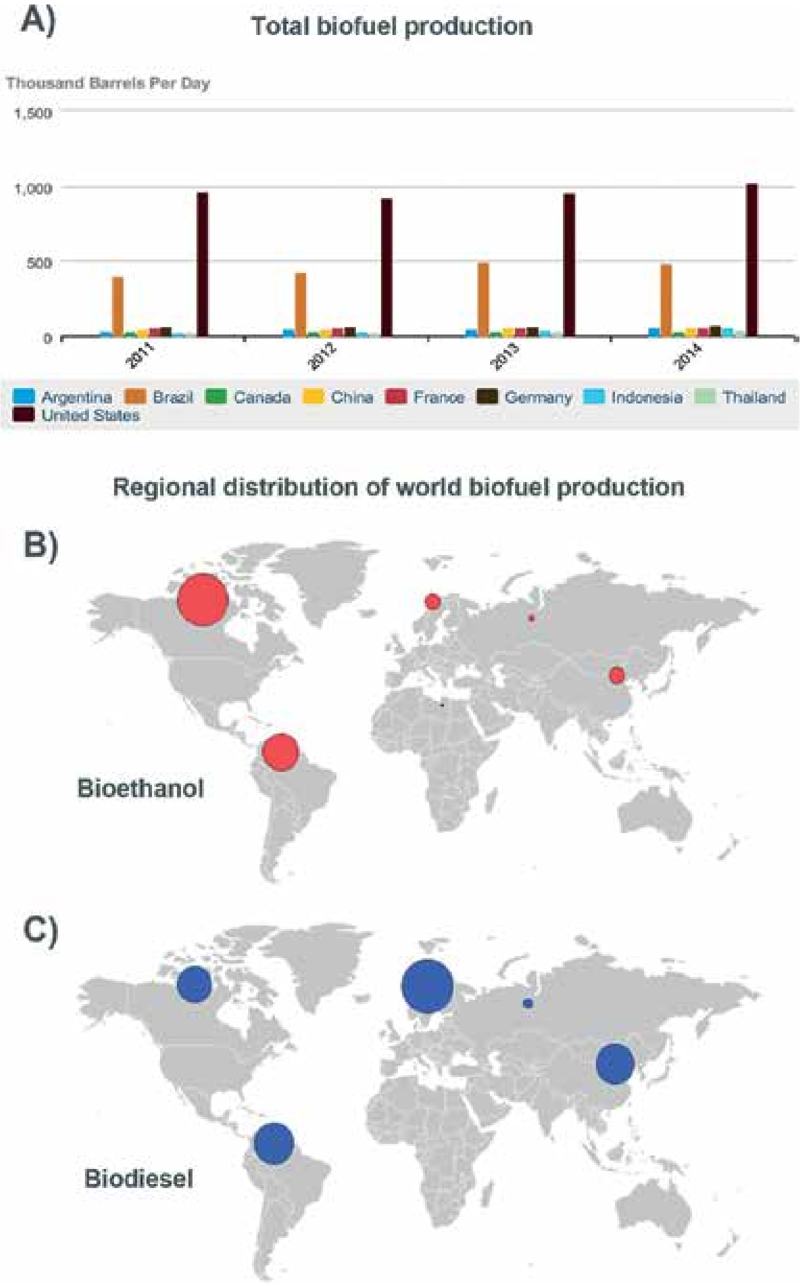

Figure 2. (A) Total biofuel production of main producing countries from 2011 to 2014. Regional distribution of world biofuel production in 2014: (B) bioethanol and (C) biodiesel [43].

However, there is still a big difference between the world ethanol and biodiesel production, while the first is predominant in the USA and Brazil accounting most of the biofuel production, the latter is mainly produced in the EU, which retains the largest biodiesel production [43, 44]. Bioethanol comprises more than 80% of liquid biofuels in the USA, Brazil, Canada, Australia, and China, while the European biodiesel accounts for more than 60% of total biofuel produced in these countries [39].

A sustainable alternative to petrochemical fuels and the environmental concern with such fuels have also drawn the attention of the international scientific community, which is reflected in the increasing number of biofuel-related publications. Approximately 50 additional papers were published every year regarding biofuels from 1990 to 2005. After 2005, this expanding rate increased to 550 biofuel-related papers. Most of publilshed papers on biofuels are still related to first-generation biofuels based on edible feedstocks, constituting 46% of biofuel publications from 1990 to 2014, while papers related to lignocellulosic biofuels total 40% of biofuel literature, from which remains 14% of published studies concerning algae third-generation biofuels [39].

Whereas bioethanol is the largest produced biofuel of the world, research studies on biodiesel production from vegetable oils constitute 60% of the literature on liquid biofuels. Jatropha and palm oil were the most widely studied feedstocks for biodiesel production followed by soybean and rapeseed oils. Among the most important lignocellulosic materials for the second-generation biofuel production are crop residues such as straw and bagasse; forest, municipal, and livestock wastes; and energy grasses. Finally, the algal feedstocks have received significant attention and have become one of the main biofuel categories. Therefore, the fast increase of biofuel-related publications can be considered as a direct result of research and development expenditure on biofuel science in the last years [39].

In 2015, several policies were finalized in favor of the biofuel market. In Brazil, the mandatory anhydrous ethanol blending ratio was increased from 25 to 27%. In the EU, the Renewable Energy Directive and the Fuel Quality Directive were reviewed in the transport sector by 2020, and the US Environmental Protection Agency proposed new mandates to increase the production levels of biofuels. Most of these political changes are driven by blending mandates and sustained fuel use to attend the demand of transportation sector. Future prospects report a modest expansion of the global ethanol production from 116 Bln L in 2015 to 128.4 Bln L by 2025, with half of this growth originating from Brazil, while a more prominent biodiesel production is expected for this period from 31 Bln L in 2015 to 41.4 Bln L by 2025 as a result of political incentives of the USA, Argentina, Brazil, Indonesia, and the EU [44].

Coarse grains and sugarcane are expected to remain the dominant feedstock for bioethanol production and vegetable oils to continue as the main biodiesel feedstock. Whereas the biodiesel production processes aiming at the utilization of nonagricultural biomass, waste oils, and animal fats are expected to develop in the EU and the USA, the second-generation ethanol from lignocellulosic materials is projected to share less than 1% of total ethanol production by 2025. According to these projections, biofuel production will consume 10.4% of coarse grains and 12% of vegetable oils. The ethanol industry will utilize 22% of global sugarcane crops to supply its production [44]. This prospect shows a continuous establishment of current technologies and evidences the need of developing competitive ones in order to make feasible the second-, third-, and fourth-generation biofuels, not only to spare petroleum reserves but also should replace this fossil fuel and, consequently, to diminish the environmental impacts attributed to its utilization with additional preservation of agricultural land intended for food crops.

Besides bioethanol and biodiesel fuels obtained from sugar fermentation and transesterification reaction of oils and fats, respectively, there are some alternatives consisting of liquid and gaseous biofuels, which are facing technological challenges of cost effectiveness and supporting structure for their economical viability. Pyrolysis is a high-temperature heating (300–900°C) of vegetative biomass in the absence of air resulting in three products: biochar, bio-oil, and syngas. Although this technique is relative old and was utilized in ancient China and by the indigenous Amazonians to generate biochar 100 years ago, the bio-oil is unstable, corrosive, and immiscible with hydrocarbon fuels and difficult to ignite, which needs a significant upgrading to be used as a petrol fuel alternative [41, 45, 46].

Some liquid biofuels such as butanol, liquefied biomass, syngas complexes, and sugar hydrocarbons have been developed to meet the existing fossil fuel specifications and hence to minimize the infrastructure and engine compatibility issues. They are the "drop-in" biofuels. Nevertheless, many efforts must continue to be made for the economical viability and the establishment of the "drop-in" biofuels as a renewable alternative in the future [41, 47]. Biogas is a gaseous alternative to natural gas from anaerobic digestion of organic wastes, which is constituted of methane, carbon dioxide, and a small percentage of sulfur hydroxide, water vapor, and hydrogen [41, 48]. Despite the minor biogas utilization in the energy sector, there is an impressive global potential for anaerobic digestion from agricultural and domestic wastes that could supply one quarter of the current natural gas and cover 6% of the global primary energy demand [41, 49].

Syngas is a gaseous fuel obtained from gasification or pyrolysis of vegetable sources and consists of carbon monoxide, hydrogen, carbon dioxide, and small percentages of methane, water vapor, sulfur hydroxide, carbon oxide sulfide, ammonia, and others. This product can be directly burned to generate electricity, or more commonly, it is purified for the synthesis of methanol, ethanol, methane, dimethyl ether, and other fuels. The hydrogen obtained from the syngas purification process can be used for electricity generation and as a vehicle fuel. The synthesis gas can also be processed to liquid hydrocarbons like diesel fuel via Fischer-Tropsch synthesis, which is an exothermal polymerization process converting H_2 and CO into hydrocarbons and water. The product distribution depends on different process parameters like temperature, pressure, and the catalyst material resulting in short- or long-chain hydrocarbons. However, the purification process of syngas is still rather costly and energy consuming [10, 41, 50].

3. Bioplastics: bio-based and/or biodegradable plastics

Plastics are organic polymers with high molecular weight, which are synthetically produced. The expression bioplastics have commonly been used to make a distinction from petrochemical polymers, which is partially misleading, since a polymer derived from biomass is not necessarily biocompatible, biodegradable, and ecologically friendly [4]. Bioplastics fulfill at least one of these two characteristics: biomass derivative or biodegradability. Thus, a bioplastic must be bio-based, biodegradable, or both (**Figure 3**). Bioplastics exhibit the same or similar properties as conventional plastics with additional environmental benefits such as reduced carbon footprint, organic recycling, or both [51]. This is a broad and logical bioplastic definition adopted by European Bioplastic Association [4, 51, 52].

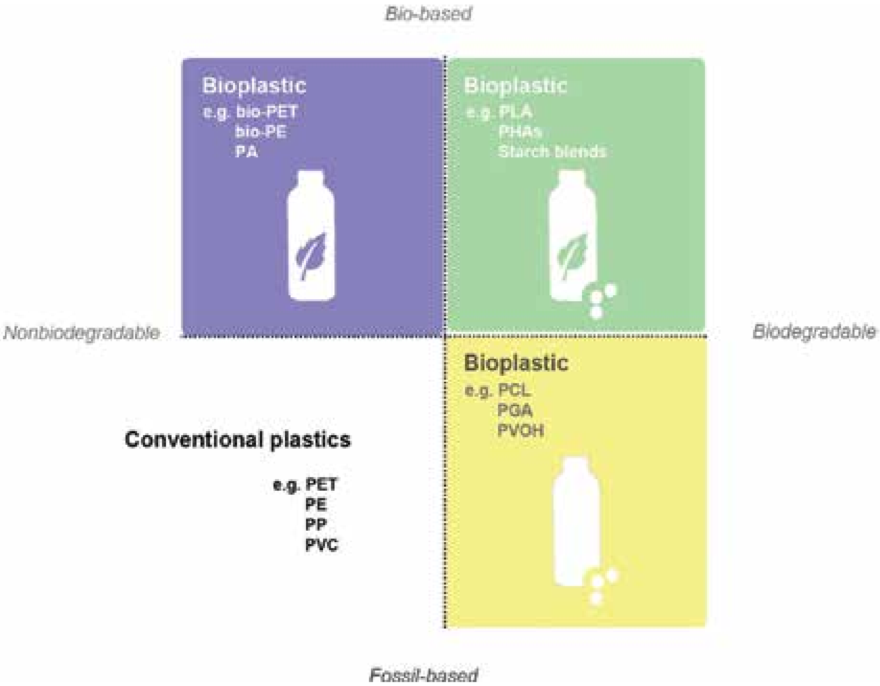

Figure 3. Bioplastics: bio-based and nonbiodegradable (blue); fossil-based and biodegradable (yellow); bio-based and biodegradable (green).

One of the bioplastic families is bio-based (or partially bio-based) and nonbiodegradable plastics, such as polyethylene (PE), polypropylene (PP), or polyethylene terephthalate (PET), also called as "drop-in" bioplastics, since they are the renewable alternative for petroleum-based plastics [53]. Polyvinyl chloride (PVC) is another commodity example of a nonbiodegradable, and in fact, one of the least environment-friendly synthetic plastics produced from renewable resources [4]. Bio-PE has been produced by Braskem (Brazil) on a large scale. A partially bio-based PET has been used for beverage bottles. Other examples of bio-based and nonbiodegradable plastics include polyamides (PA); polyesters such as polytrimethylene terephthalate (PTT), polybutylene terephthalate (PBT); polyurethanes (PUR); and polyepoxides. Important examples of bio-based and biodegradable plastics are thermoplastic starch blends (TPS), cellulose-acetate plastics (CA), poly(lactic acid) (PLA), and polyhydroxyalkanoates (PHAs). They are primarily used for short-lived applications, such as packaging and disposable products [53]. They are recognized as ecologically friendly, and some of them have been used for medical applications due to their lower or zero toxicity and high biocompatibility [54].

The third group constituted by non-bio-based and biodegradable polymers from fossil resources is a small group used in combination with other bioplastics, such as starch blends or applications, in which their biodegradable and mechanical properties [53] are desired. Examples of biodegradable petrochemical-based plastics are polycaprolactone (PCL), polyglycolide (PGA), and polyvinyl alcohol (PVOH) [4, 55]. Poly(butylene adipate-*co*-terephthalate) (PBAT) and polybutylene succinate (PBS) are bioplastics in class transition, since partially bio-based versions of these compounds are current being developed. PBAT is produced from 1,4-butanediol (1,4-BDO), terephthalate, and adipic acid. The bio-based adipic acid is not available yet for commercialization, and thus, PBAT can theoretically be up to 50% bio-based. Likewise, PBS is produced from 1,4-BDO and succinic acid, which can also theoretically be 100% bio-based [56]. Therefore, in a near future, PBAT and PBS are expected to be into the family of bio-based and biodegradable plastics.

4. Biofuels and bioplastics in a circular economy

Since most of conventional plastics and fuels are made from petrochemical compounds, in the opposite way, bioproducts derived from biomass such as biofuels and bioplastics share several favorable characteristics. All the advantages concerning the biofuel and bioplastic utilization can be addressed to a sustainable process, which has mainly driven by energy saving and reduction of GHG emissions [4]. According to the Intergovernmental Panel on Climate Change (IPCC), the CO_2 concentration of 450 ppm within the global atmosphere is the maximum limit to avoid a global warning increase of 2°C, which means a reduction of 50% of GHG emissions by 2050 [10, 57]. One alternative to reducing GHG emissions is the use of low carbon fuels [10] and bio-based plastics [4]. Since they are obtained from plant biomass, the released CO_2 can be at least minimized by plant CO_2 consumption during photosynthesis, reducing the carbon footprint in the global atmosphere [5].

The rural development with employment opportunities can be achieved from biomass utilization to produce bioproducts such as biofuels and biopolymers [4, 5, 10]. The job creation is a global priority, especially in developing countries with high unemployment levels [10]. Most of references regarding biofuels and bioplastics agree that these bioproducts reduce the oil dependence as a sustainable alternative from diversified feedstock [3–5, 9, 10]. Most of crude oil reserves are centralized and located within countries under political uncertainties [10]. Among the top 15 countries with the world's biggest crude oil reserves are Middle Eastern countries, Venezuela, Russia, Libya, Nigeria, Kazakhstan, China, and Brazil [58]. Therefore, biofuels and bioplastics exhibit an advantage regarding the security of energy supply supported by a local production from available domestic biomass [10].

The research reports and reviews have constantly warned about the depletion of fossil fuel reserves like petroleum, natural gas, and coal [9, 36]. On the other hand, 100 Bln tonnes of crude oil and natural gas have been discovered in the last 40 years; however, the consumption rate of these resources has also increased. The US alone consumes 25% of total oil supply, while having 1.6% of global oil reserves. According to some authors, at the current consumption rate of oil supplies, the fossil fuel reserves will be depleted within 40–70 years [1]. Regardless the period of time for oil reserves depletion, it is a true fact that they are finite, and despite the recent increase in their exploitation, the future of petrochemical sources remains uncertain [39].

The rising consumer consciousness and environmental awareness are the biggest drivers for biofuel and bioplastic production. The global society has become aware of environment concerns and has continuously improved its sustainability standards. Therefore, there is a global trend on using products from renewable sources even in the face of low oil prices [4, 10]. Several companies have followed this tendency and have associated their brand logos to renewable or biodegradable products as ecologically friendly companies with social and environment responsibility [4, 59]. Biodegradability and compostability are interesting properties of some products obtained from biomass, especially concerning short-lived or disposable plastic materials, which account 50% of the total plastic production [4, 34, 35]. In general, about 10% of municipal waste is consisted of plastics, primarily constituted of fossil-based PE, PET, PP, PS, and PVC [1]. Composting is other alternative solution for short-lived and disposable bioplastics, which can be disintegrated under microbial fermentation resulting in humus-rich soil. Therefore, composting is a good alternative for packaging materials, such as agricultural and horticulture films. Further, compostable plastics is an additional effort for waste stream management [51, 60].

5. Bioplastic market and future prospects

The bioplastic industry is a young and innovative sector [51]. The bio-based plastics share has increased from 1.4 to 2% of global polymer capacity, from 2011 to 2013 [56]. Thereafter, in recent years, this share has been stagnating, and the bioplastic growth rate has become the same of any plastic. While a prominent production capacity growth of 10% per year was observed from 2012 to 2014, this growth rate decelerated to 4% per year from 2015 onwards, which can be attributed to the lower oil prices, the unfavorable political support, a slower growth rate of the capacity utilization, and global debates about land and food crops use. However, the bio-based and biodegradable PHAs, the high-performance PA, and “drop-in” PET are exceptions that have shown fast increase rates of their production capacities [61].

In 2016, the bio-based plastic income was about $ 15 billion worldwide [61] with more than 43% of total bioplastic produced in Asia. The USA, Latin America, and Asia have implemented measures to attract investment and promote market development to achieve their production goal. The European bioplastic market is still restricted by a lack of economical and political incentives for scaling-up its production capacity. As one can see in **Figure 4**, the worldwide production capacity is forecasted to increase from 4.2 million tonnes in 2016 to 6.1 million tonnes by 2021 [51]. If the bio-based thermosets such as epoxies, ethylene propylene diene monomer rubber (EPDM) and CA were included in this forecast, the increase values of bioplastic production capacities can be extrapolated to 6.6–8.5 million tonnes for the same period [61].

Currently, the bioplastic market is dominated by bio-based and nonbiodegradable plastics with highlights of bio-based PUR and “drop-in” PET. “Drop-in” plastics exhibit the same properties and are identical to their petrochemical counterparts and thus do not demand further adaptation for processing. Some bioplastics have lower material performance and end up being utilized for blending with petrochemical polymers. Therefore, creating high-performance biopolymers at a competitive cost is still a key concern [12]. PUR market share is expected to remain stable, whereas PET share is forecasted to grow from 22.8% in 2016 to 28.2% by 2021 [61]. One of the big investors of bio-based PET has been The Coca-Cola Company with its Plant Bottle technology [59]. Bio-based PE is another “drop-in” bioplastic, which has been obtained from sugarcane-derived ethylene by Braskem Company in Brazil [4]. Among the bio-based and biodegradable polymers, Starch blends and CA markets are

Figure 4. Global production capacities of bioplastics by material type in 2016 (A) and expected for 2021 (B) [51, 61].

expected to continue steady, and PLA and PHA production capacities are expected to considerably grow in the next years [61].

There are infinite possible applications for bioplastics including textiles, construction and building, electrics and electronics, consumer goods, agriculture and horticultures, and automotive, although their largest application field is still the packaging, which shared almost 40% of the total bioplastic market in 2016. This percentage is expected to increase to 42% by 2021 (**Figure 5**). In the automotive industry, bioplastics make cars lighter to save fuel and, consecutively, make them to reduce their carbon exhaustion [51].

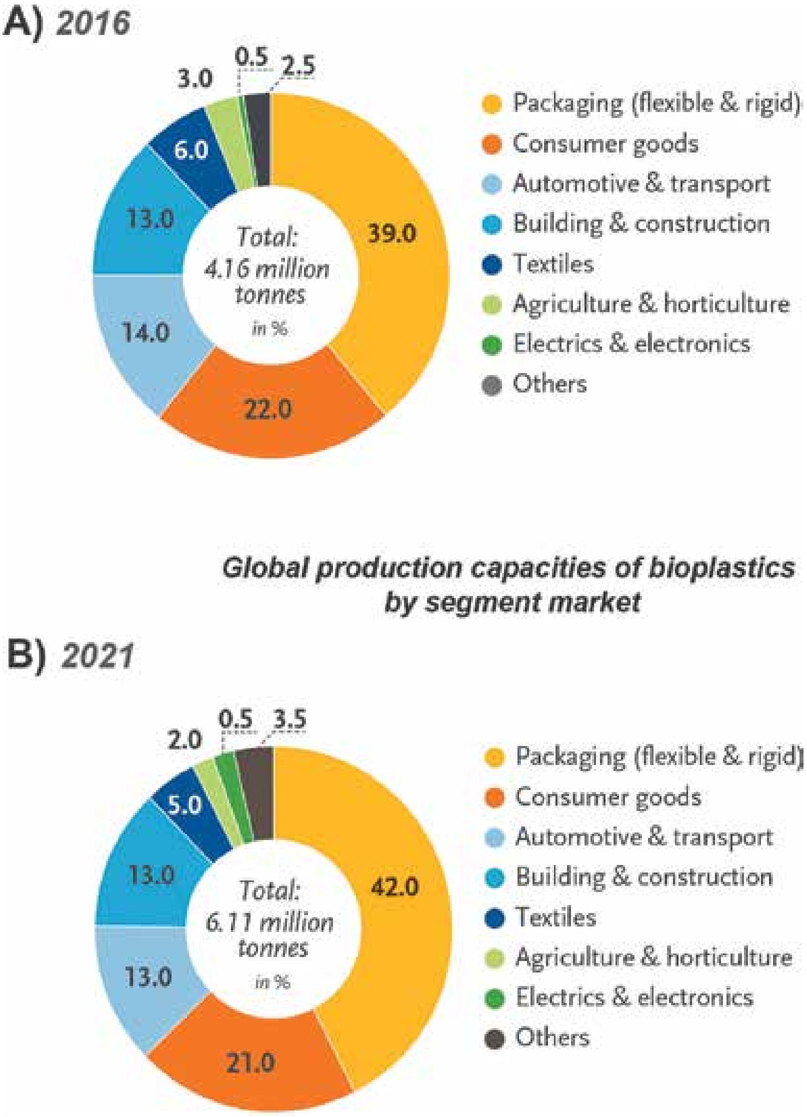

Figure 5. Global production capacities of bioplastics by market segment in 2016 (A) and expected for 2021 (B) [51, 61].

6. PLA and PHAs: promising bio-based and biodegradable plastics

Several companies have introduced starch and polyethylene blends as degradable materials for a number of short-lived applications, such as mulch films, beverage bottles, food containers, and plastic bags. Whereas starch component can be degraded, the polyethylene residues remain in the ecosystems. Therefore, many companies have failed associating plant-based blends with misleading biodegradable properties. Thenceforth, in order to restore the credibility of the bioplastic industry, the standard organizations have been concerned with distinguishing degradable, biodegradable, and compostable plastics [12]. Further, some countries such as Italy and France have started to devote strong political support for biodegradable plastics, especially for the packaging sector, which is the biggest in the plastic market. The packaging industry has been interested in biodegradable plastics for short-lived and disposable applications. In agriculture, most of applications are limited to biodegradable plastics. Although the biodegradable polymers are not market leaders, they are expected to grow strongly supported by environmental concerns [61].

Among the aliphatic biodegradable polymers, the main population of degrading microorganisms in different ecosystems has followed the order: PHAs = PCL > PBS > PLA [55]. PCL is fossil-based [4], and currently, PBS and PBAT are not fully bio-based. PBS is constituted of 1,4-BDO and succinic acid that are primarily fossil-based, although they could theoretically be obtained from microbial cultivation. Bio-based 1,4-BDO entered the market only in 2016. BioPBS is produced exclusively in Asia by Public Company Limited and Mitsubishi Chemical Corporation (PTT MCC Biochem) in Thailand [62]. Additional projects are not expected for the next years due to low oil prices. PLA has attracted a growing interest and nowadays accounts 20% of biodegradable plastic market [4]. The most dynamic development is forecasted for PHAs, whose production capacity is still small. However, the PHA market is foreseen to grow almost three fold by 2021 [61].

6.1. Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA), also called polylactide, refers to polymers based on lactic acid molecules, which is abbreviated as PLA. Therefore, the starting compound of PLA is lactic acid, a monomer that can be L(+) lactic acid or D(−) lactic acid due to the presence of a chiral carbon atom. The cyclization of two lactic acid molecules results in a dimer called lactide. Accordingly, there are two homochiral lactide L,L and D,D and a heterochiral meso-lactide L,D. *Lactococcus lactis* LL0018 and *Lactobacillus casei* produce L-lactic acid, while *Lactobacillus delbrueckii* LD0025 and *Sporolactobacillus inulinus* SI0073 produce D-lactic acid, with up to 99% purity. *Lactobacillus helveticus* LH0030 is able to produce a racemic lactic acid, containing almost an equal mixture of L-lactic acid and D-lactic acid. Thus, the final lactic acid content is directly dependent of the fermentation process. Thereafter, a major concern is the purification of culture broth in order to obtain pure lactic acid. The lactic acid polymerization methods provide high molar mass polymers with high chiral purity, which are primarily based on catalysts with Sn and Zn metal, resulting in polymers with molar masses up to 10^6 [63]. The most common route to obtain PLA is ring-opening polymerization of the intermediate dilactide. Direct condensation of lactic acid generally results in lower molecular mass [64].

The PLA currently available is based on linear macromolecules and presents low melting temperature. Consequently, more research must be developed aiming to improve the physical properties of such PLA [63]. PLA is a thermoplastic and is converted to a variety of products by injection molding, blow molding, foaming film extrusion, and fiber extrusion. The PLA applications include geotextile, agricultural film, packaging, 3D printing, absorbable sutures, and prosthetic devices [64]. The PLA is 100% bio-based and biodegradable under certain conditions. Nature Works is a leader company of PLA production. Among new bio-based polymers, PLA is the most well-established, and its market is expected to grow annually at a rate of 10% until 2021, with comparable prices to fossil-based plastics [61].

6.2. Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are microbial aliphatic polyesters synthesized as intracellular granules under nutrient imbalance and excess carbon source by several bacteria [65]. PHAs are a family of polymers constituted of monomers ranging from 3 to over 14 carbon atoms with more than 150 different monomer composition [3, 52]. PHAs have been classified into short-, medium-, and long-chain length PHAs (PHA_{SCL}, PHA_{MCL}, and PHA_{LCL}, respectively). PHA_{SCL} with monomers consisting of 3–5 carbon atoms exhibit thermoplastic properties, whereas PHA_{MCL} are constituted of monomers ranging from 5 to 14 carbon atoms, which are elastomeric materials. Poly(3-hydroxybutyrate) (PHB) is the most common and studied PHA. The PHA constituents are directly related to the carbon sources utilized for bacterial cultivations and the metabolic role of PHA synthases [3]. Such variety permits utilize PHAs in a large number of applications, such as packaging materials, biocompatible implants, and controlled drug delivery system [66].

PHAs are fully biodegradable and biocompatible and so are attractive for medical uses. They also meet the standard specification for marine degradability, which can be a biodegradable alternative for plastic wastes that end up within the ocean and are fragmented as microplastics. Furthermore, PHAs are compostable and at the same time exhibit good resistance to grease and oils besides boiling water [4]. Several companies are involved in the PHA market, although it is still small, mainly attributed to their relative high cost of production. However, PHA producers are optimistic, and several sugar companies are investing in PHAs, which are expected to triple their production capacity by 2021 [61].

7. Biofuel feedstocks for PLA and PHA production

The fermentation routes represent the most active areas of biopolymer production, which are generally performed at biorefineries based on particular agricultural feedstocks. A future trend is the utilization of multiple feedstocks according to the available resources and economic conditions, in order to increase the feasibility of bioplastic production [12]. This is also applicable to biofuels that are dependent on specific biomass sources, which are mostly terrestrial plants [9]. As aforementioned, PLA and PHAs are typically obtained from microbial cultivation and so can be adapted to multiple feedstocks. Particularly, PHA-producing bacteria are naturally very versatile and produce these biopolymers from many carbon sources. Next, it is shown some examples of PLA and PHA production from biofuel feedstocks and related byproducts, which may support a biorefinery model comprising biofuels and these bio-based and biodegradable plastics. Further, **Figure 6** presents a flow chart describing possible routes involving biofuels, PLA, and PHA bioplastics.

7.1. Starch

Starch is a mixture of glucans, and consequently, a source of glucose obtained from various plants [67]. Starch has widely been utilized for bioethanol production, especially in US, where it is mainly extracted from corn crops [11], and it is also a raw material for starch blends, an established sector of bioplastic market [61]. Only few lactic acid bacteria possess starch-degrading

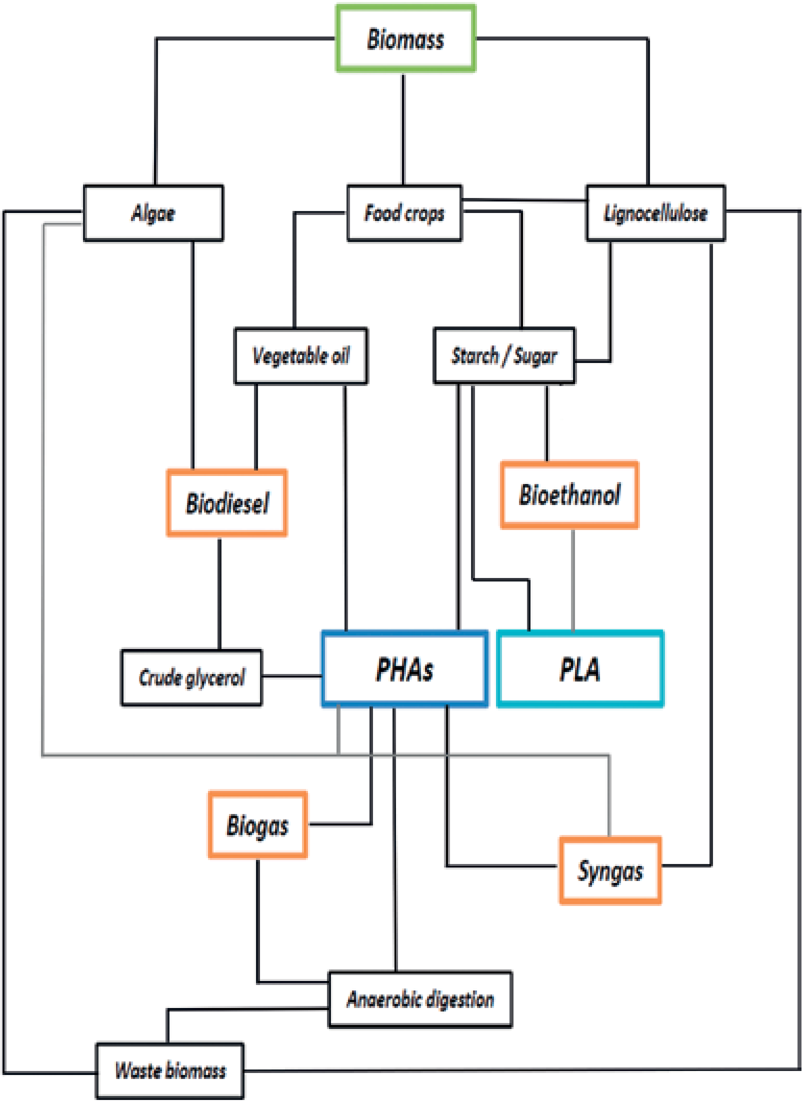

Figure 6. Common pathways for biofuels, PLA, and PHA production.

properties, and most of them exhibit low lactic acid production. However, many groups explore the acid or enzyme hydrolysis of starch compounds, such as wheat, corn, cassava, rice, potato, barley, rye, and sorghum, with subsequent use of sugars for lactic acid fermentation [67]. In the same way, starch has been a suitable carbon source for PHA production, including corn [68], potato [69], and cassava starch [70]. PHAs and PLAs have also been blended with starch materials, resulting in different physicochemical properties [4, 71].

7.2. Molasses

Molasses is a high sugar co-product generated from sugar manufacturing industries [72]. Sugarcane molasses have been utilized for ethanol production in Brazil, while beet molasses is more common in Southeastern Europe, North America, and Asia, where it is primarily used for sugar production [40]. *L. delbrueckii* has been generally a lactic acid–producing bacteria using this carbon source, whose most abundant sugar is sucrose [73]. PHB is the most common product from molasses, since the sucrose content can be converted to acetyl-CoA and after to 3-hydroxybutyryl-CoA, the building block utilized by PHA synthase for PHB polymerization [3]. *Azotobacter vinelandii* and *Bacillus megaterium* are examples of PHB-producing bacteria utilizing sugarcane molasses [74, 75]. PHA_{MCL} production has also been reported from *Pseudomonas corrugata* from soybean molasses [76].

7.3. Vegetable oil

Vegetable oils are feedstock for biofuels with biodiesel representing a well-known example, which is mostly obtained from soybean oil in US and Brazil and from rapeseed oil in Germany [37]. Intermediates from β-oxidation of alkanoic or fatty acids can provide hydroxyalkanoyl-CoA molecules for PHA_{MCL} production by several bacteria such as *Pseudomonas* strains [3].

Some authors have reported PHA_{MCL} production from waste cooking oil by *P. aeruginosa* [22]. *Aeromonas caviae* is also an additional example of bacterial strain that is able to synthesize the co-polymer poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) [P(3HB-*co*-3HHx)] from vegetable oil [77]. For the second-generation biofuel, nonedible oilseeds have been considered to avoid the debate food versus fuel, e.g., green seeds canola, high erucic mustard, Indian beech, etc., of which the most reported has been Jatropha [5]. Biosynthesis of co-polymers poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) [P(3HB-*co*-3 HV)] and P(3HB-*co*-3HHx) from Jatropha oil has also been observed [78].

7.4. Lignocellulosic materials

The postharvest processing of food crops, forest, and wood residues generates large amounts of lignocellulosic materials, which consist of cellulose, hemicellulose, and lignin. Cellulose is a crystalline glucose polymer, while hemicellulose is amorphous and exhibits xylose and arabinose sugars. Lignin is a large complex of aromatic compounds. Lignocellulose materials can be converted to sugars by acid or enzymatic hydrolysis, which can further be used for ethanol production [5]. The bioethanol production from sugarcane bagasse in Brazil is a well-known example of the second-generation biofuel from lignocellulosic materials [40]. The bioconversion of lignocellulosic biomass by lactic acid bacteria is still limited, and a pretreatment including hydrolysis is necessary to convert these materials to sugars for lactic acid fermentation. Recombinant strategies involving heterologous expression can be a solution for this problem. Some authors have reported that a simple consortium of recombinant *L. plantarum* strains was able to produce cellulase and xylanase and thus showing potential for biomass conversion [67, 79].

Saccharophagus degradans is a natural PHA-producing bacteria from tequila bagasse [80]. However, the main focus on PHA production from lignocellulosic materials has been based on this substrate conversion into monomer sugars, which are used for microbial cultivation [72]. Sugarcane bagasse was submitted to acid hydrolysis, and then, it was utilized for PHB and P(3HB-*co*-3 HV) production by *Burkholderia* sp. The co-polymer was obtained after addition of levunic acid to the medium, a 3HV precursor that can also be obtained from the hydrolysis of lignocellulosic compounds [81]. On the other hand, *Halomonas boliviensis* was able to assimilate the sugars from enzymatic hydrolysis of wheat bran, in which it was utilized a crude enzyme preparation from *Aspergillus oryzae* [82].

7.5. Crude glycerol

Nowadays, the crude glycerol is mainly obtained as a byproduct from the transesterification process of oils and fats for biodiesel production, which generates about 10% glycerol [83]. Since purified glycerol is a high-value chemical, alternative solutions are required to crude glycerol refining and one of the possible keys for this issue is the glycerol utilization in its crude form as carbon source in microbial cultivations, in order to obtain value-added chemicals such as bioplastics [84]. A glucose-affected mutant of *Cupriavidus necator*, former *Ralstonia eutropha* and a traditional PHA-producing strain, is able to accumulate PHB from crude glycerol [85]. Additionally, new wild bacterial strains have been isolated from the environment such as *Pandoraea* sp., which is able not only to produce PHAs from crude glycerol but also from sugarcane molasses and waste cooking oil, although the best polymer yields were obtained from crude glycerol [24].

7.6. Biogas and syngas

Biogas is a renewable gaseous fuel alternative to natural gas, which is generated from anaerobic digestion of organic wastes by numerous bacteria. The main component of biogas is methane [41]. Over 300 bacterial strains, including *Methylocystis paravus*, *Methylosinus sporium*, and *Methylocella tundra*, have shown the ability to synthesize PHB from methane [86]. Furthermore, the integration of PHA-rich biomass production into a municipal waste water treatment plant with sludge digestion has been proposed to support the biogas and PHA production [87]. Synthesis gas or syngas is another gaseous biofuel obtained from gasification or pyrolysis of biomass feedstock. Carbon monoxide, hydrogen, and carbon dioxide are the most abundant constituents of syngas [41]. The purple nonsulfur bacterium *Rhodospirillum rubrum* is able to utilize carbon monoxide and carbon dioxide and has also been a model organism for the synthesis of $\mathrm{PHA}_{\mathrm{SCL}}$ and $\mathrm{PHA}_{\mathrm{MCL}}$ from syngas [88].

7.7. Microalgae

Microalgae, such as blue-green algae, dinoflagellates, and bacillariophyta, can have from 8 to 31% of their dry weight constituted of lipids. They have been revealed as the best potential source for oil extraction compared to common biofuel crops [9]. Cyanobacteria are a good candidate for bioplastic production, which present the ability to grow in a variety of environments. Genetically engineered cyanobacteria were transformed with the genes encoding PHB synthesis, and their metabolisms have been extremely investigated aiming to establish new routes for PHA synthesis. Additionally, PLA/algae blends can be prepared and employed in bone and cartilage tissue engineering due to their biodegradability and biocompatibility [89]. Therefore, microalgae are new and promising branch not only for biofuels but also for bioplastics.

7.8. Simultaneous production of PLA and PHAs and their polymer blends

PHB production has been described in lactic acid bacteria for the genera *Lactobacillus*, *Lactococcus*, *Pediococcus*, and *Streptococcus*. *Cupriavidus necator*, *L. delbrueckii*, and *Propionibacterium* have been cultivated in a bacterial consortia, which resulted in a co-production of lactic acid and

PHAs. The implementation of co-cultures brings the advantage of increasing the range of substrates that can possibly be converted into accessible sugars by at least one of the members of microbial consortia [67]. Since PLA and PHA_{SCL} exhibit similar properties, PHA/PLA blend is one of the most studied blends. PHA_{SCL} generally presents higher melting temperatures than PLA, and thus, their utilization results in polymer blends with different properties. The poor processability of PHB is a drawback for its industrial applications, and the PHB/PLA blends represent a good alternative, which also brings improved properties to PLA. Additionally, PLA is cheaper than PHAs [90]. Therefore, the production of PHA/PLA blends is very advantageous for PHAs reducing their production cost [3, 63, 71].

7.9. PLA and PHA as sources for fuels

Hydroxyalkanoate methyl ester, a product from PHA esterification reaction with methanol, produces combustion heats similar to ethanol. The esterified PHA could be used as fuel additive for gasoline and diesel, with good properties of viscosity, flash point, and oxygen content. The implementation of PHAs as biofuels does not require highly purified PHAs, which can be obtained from activated sludge or waste water [91]. Lactic acid bacteria have been considered good candidates for biofuel production, such as ethanol and butanol. Other interesting compound that could be obtained from lactic acid bacteria is formate, which is a precursor substrate for hydrogen production by fermentation processes [67].

8. Challenges to be overcome by biofuels and bioplastics

Despite numerous advantages regarding the production of biofuels and bioplastics such as renewability and /or biodegradability, there are many concerns about bioproducts derived from biomass. Nowadays, the biggest economical challenges are still fossil fuel dependence and cost effectiveness. The oscillating oil prices and the current technology, the existing fuel supply, and infrastructure make conventional fossil sources and "drop-in" solutions the best economical choice for fuel and plastic markets [4, 41]. The concept of bioplastics as a "green" alternative for petrochemical plastics is a complex matter, and their environmental impact must be better evaluated. Composting and recycling properties are key concerns that should be taken into account for a case-by-case life cycle assessment [4].

Other environmental and economical concern on biofuels is the debate fuel versus food, which can also be applied to bioplastics. Currently, most of biofuels and bioplastics are made from agro-based resources and lignocellulosic materials [5, 51]. The food crops such as corn and sugarcane with high carbohydrates content are up to now the most efficient and profitable option for biofuel and bioplastic industries. Further, these plants are adapted to produce high yields resisting to pests and weather conditions [51]. The renewable energy has also been recovered from lignocellulosic materials as residues of food crops or short rotation of nonedible plants, organic wastes by anaerobic digestion, animal manures, algae biomass, and an endless variety of alternative biomass sources. However, these technologies for biofuel and bioplastic production are still in their infant stage, which needs many upgrades to become economically feasible in face of the conventional fuels and plastics [4, 41].

In 2014, the land area required to grow the total biomass ascribed to the global production capacities of bioplastics was approximately 680,000 ha. About 0.01% of the global agricultural area of 5 Bln ha would be enough to supply the current world's bioplastic production [51]. If it considered that the bioplastic industry is not yet well-established [4] summed to the land area demanded for biofuel production, the agricultural area utilized for a bio-industry can increase significantly, which necessarily leads to an over production of agricultural commodities [10]. Therefore, the increasing of the efficiency of feedstock and agricultural technology is mandatory to compensate the future increase of land use for biofuels and bioplastics [51]. On the other hand, only 1.25% of the entire land biomass is used for food crops, thus the expansion of agricultural lands is other possible solution to attend biofuel and bioplastic demands [5]. Accordingly, the sustainability initiatives should implement development schemes, which must be adapted to protect the land, communities and biodiversity [9]. Whereas bioenergy and biofuels have received political support during commercial production such as quotas, tax incentives, market introduction programs, the bio-based chemicals and plastics have suffered the effects of still weak policies and underinvestment by the private sector. Therefore, a strong political support from the whole society and government is imperative for the establishment of the bioplastic industry [61].

9. Conclusions

Biofuels and bioplastics are certainly a present and especially a future trend, whose promising perspectives have faced its main delay in the low crude oil prices and the lack of cost effective technologies. Bioethanol and biodiesel are expected to continue growing in the next year as well-established first-generation biofuels, according to the current political incentives for blending mandates. The lignocellulosic fuels are forecasted to still share a small percentage of bioethanol production, while biogas, syngas from biomass pyrolysis, algae-derived, and other advanced fuels are in their infant stage, which reflects the need of technological upgrades toward cost-effective processes. The bioplastic market has also found in the "drop-in" plastics an economically feasible alternative to associate the bio-based polymers with an ecologically friendly image, which is partially misleading, since bio-based plastics can help to reduce the carbon footprint, though the market leaders such as bio-PET, PE, and PUR are not biodegradable. Most of the plastic wastes are constituted of short term and disposable products; hence, the establishment of not only bio-based but also biodegradable plastic market is mandatory to minimize the strong persistence of conventional plastics in the environment and their inevitable damage to ecosystems. PLA is a bio-based and biodegradable plastic with a well-established and continuous growing market, while PHAs are the versatile alternative, which can be obtained from a variety of biomass sources and are expected to triple their production capacity for the next years. A biorefinery model comprising biofuels and bioplastics is one of the possible solutions to add value and support a bio-based industry, since both products have found common feedstocks into biomass. Despite the challenges faced by the bio-based industry, the environment concerns and the increasing global sense of social and environmental sustainability will continuously be the engine for biofuels and bioplastics.

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Syngas Production Using Natural Gas from the Environmental Point of View

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Additional information is available at the end of the chapter

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Abstract

The search for clean and low-cost fuels as alternative for petroleum is a popular research focus in the energy field. The demand of natural gas as an energy source has increased steadily. The high H:C ratio and the absence of heteroatoms make natural gas an attractive feedstock for synthetic fuels and chemicals that can replace those that are typically petroleum-derived. The search for efficient routes to convert methane to other higher added-value products is a challenge for the scientific community. In addition, new fields of oil and gas contain associated CO_2 (8–18%), and, in some specific fields, the associated gas encloses a higher CO_2 content (79%). In this context, the tri-reforming process combines two of the most problematic greenhouse gases (CH_4 and CO_2) to generate syngas for the synthesis of clean liquid fuels and valuable chemicals. Developments in tri-reforming processes, which include the new catalysts, are presented in this chapter.

Keywords: tri-reforming, syngas, catalysts, carbon dioxide, hydrogen production

1. Introduction

Significant efforts are being directed nowadays towards finding alternatives that could restrain the climate change. The consistent rise of CO_2 concentration in the atmosphere is known to be significantly detrimental to the environment. Thus, mitigating CO_2 is becoming an urgent need.

Current methods involving CO_2 mitigation can be broadly divided into two major categories, which involve (1) CO_2 capture and sequestration (CCS) and (2) CO_2 capture and utilization (CCU). Since the production of fuels/chemicals is an added feature along with mitigation in

CO_2 valorization-based methods, they could be economically favorable. An energy-intensive CO_2 capture step is a common drawback of most CO_2 valorization methods that aim to mitigate CO_2 from major CO_2 emission sources (such as industrial flue gases).

Different methane-rich gas streams can be found, both of natural and of anthropogenic origin. A decrease in fossil fuels and environmental concerns across the globe enforced researchers to work on energy resources like methane, which is the most abundant natural gas on earth [1].

Therefore, it is of utmost importance to seek for technologies that could convert two of the main product gases responsible for the greenhouse effect, methane and carbon dioxide, avoiding their massive release into the atmosphere.

Reforming of methane is one of the most important industrial processes, which convert natural gas into synthesis gas. Syngas is an intermediate feedstock for the production of hydrocarbons and hydrogen for fuel cells. Synthesis gas is produced from natural gas via catalytic processes based on dry reforming of methane (DRM), steam reforming of methane (SRM) and partial oxidation of methane (POM) [2]. In fact, the available natural gas can be exploited for the production of chemicals and fuels.

The reforming processes are classified based on the energetic demand of the process and the type of reforming agent. Steam reforming of methane (SRM) produces a high ratio of syngas ($H_2/CO = 3$), suitable for the production of ammonia. This process is endothermic and requires high investments. The partial oxidation of methane, an exothermic reaction, is an alternative process with reduced capital and operation costs. However, the partial oxidation of methane (POM) needs oxygen, and the cost of its production is about 50% of the investment of the whole process. There is a high risk of explosion at an elevated temperature [3]. On the other hand, the dry reforming of methane (DRM) is a valuable reaction for biogas utilization and transformation of greenhouse gases (CH_4 and CO_2) in high-valued products. DRM produces a low syngas ratio ($H_2/CO = 1$), which is suitable for the syntheses of oxygenates [4–6].

Tri-reforming of methane (TRM) is nowadays of great interest, because it combines the steam and dry reforming and partial oxidation of methane ($CH_4 + O_2 + CO_2 + H_2O$) processes; however, it holds the main advantages and disadvantages of all processes, to some extent [7].

It is well known that the major limitation of methane-reforming processes is the rapid deactivation of the catalyst, which has been commonly attributed to coke deposition and catalyst sintering.

The tri-reforming of methane may drastically reduce the carbon deposition. Furthermore, the presence of O_2 in the feed allows the generation of energy in situ, due to the exothermal oxidation of methane, which increases the energy efficiency of the process. Besides, the possibility of changing the reactants' compositions, allows for a versatile synthesis of gas composition, which can be suitable for different applications of synthesis gas [8, 9].

2. Tri-reforming process

Energy is the most important issue to modern economies, and it is predicted that a fast-rising energy demand will require US $45 trillion for new infrastructure investment by 2030.

In particular, natural gas processes increase the options for the production of high added-value chemicals and energy demand. The Fischer-Tropsch (FT) technology is the main technology for the production of liquid fuels, named GTL process, but this technology is yet very expensive, due to the high costs of syngas production using steam reforming of methane (SRM) [7]. The tri-reforming process (TRM), introduced by Song et al. [10], allows to use flue gas and methane to produce syngas, which can be converted to methanol and higher hydrocarbons. This new process is a synergic combination of the endothermic CO_2 and steam-reforming reactions with the exothermic oxidation of methane, as shown in Eqs. (1)–(4) [11], which are carried out in a single reactor.

$$H_2O + CH_4 \rightarrow CO + 3H_2; \Delta H^0_{298K} = 206.3 kJ.mol^{-1} \tag{1}$$

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2; \Delta H^0_{298K} = 247.3 kJ.mol^{-1} \tag{2}$$

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2; \Delta H^0_{298K} = -35.6 kJ.mol^{-1} \tag{3}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; \Delta H^0_{298K} = -880 kJ.mol^{-1} \tag{4}$$

In addition, during the tri-reforming process, methane cracking (Eq. (5)), CO disproportionation or Boudouard (Eq. (6)), water-gas shift (Eq. (7)) and complete oxidation of carbon reactions (Eq. (8)) occur simultaneously [12].

$$CH_4 \rightarrow C + 2H_2; \Delta H^0_{298K} = 75 kJ.mol^{-1} \tag{5}$$

$$2CO \rightarrow C + CO_2; \Delta H^0_{298K} = -172 kJ.mol^{-1} \tag{6}$$

$$CO + H_2O = CO_2 + H_2; \Delta H^0_{298K} = -41 kJ.mol^{-1} \tag{7}$$

$$C + O_2 = CO_2; \Delta H^0_{298K} = -393.7 kJ.mol^{-1} \tag{8}$$

The heat released during the POM reaction is used to supply the heat needed for the SRM and DRM reaction, and therefore the TRM reaction is energetically more efficient [13]. In addition, TRM offers several advantages for syngas production compared to the single reactions [14]. TRM does not require pure CO_2 supply in the reaction. This implies that the flue gas from the combustion processes of power plants or the coke oven gas (COG) from iron-making industries can be used directly as a CO_2 source for TRM process [15–17]. TRM can also be used to upgrade the syngas quality produced from biomass or coal gasification [18, 19]. The H_2/CO ratio in syngas produced from tri-reforming can be adjusted varying the amounts of reactants to satisfy the requirement for further processes, such as methanol and Fischer-Tropsch synthesis [20, 21]. In addition, integrating steam reforming and partial oxidation with CO_2 reforming could dramatically reduce or eliminate carbon formation on a reforming catalyst, thus increasing the catalyst life and process efficiency [14] due to the addition of O_2 in the feed, which also generates heat that increases the energy efficiency. Therefore, the tri-reforming has the advantage of using natural gas and flue gases from power plants. The syngas from tri-reforming is used for the production of chemicals (such as MeOH and dimethyl ether by oxo-synthesis), fuels (for the Fischer-Tropsch synthesis) and electricity in fuel cells, as shown in **Figure 1** [14].

Table 1 shows the advantages and disadvantages of tri-reforming compared to other reforming technologies [7, 18, 22].

However, due to the inherent problems of the reforming processes, there is a need to improve catalysts for optimizing the TRM process, improving the oxygen tolerance, resistance to coke formation and sintering of the metal-active sites at a high temperature.

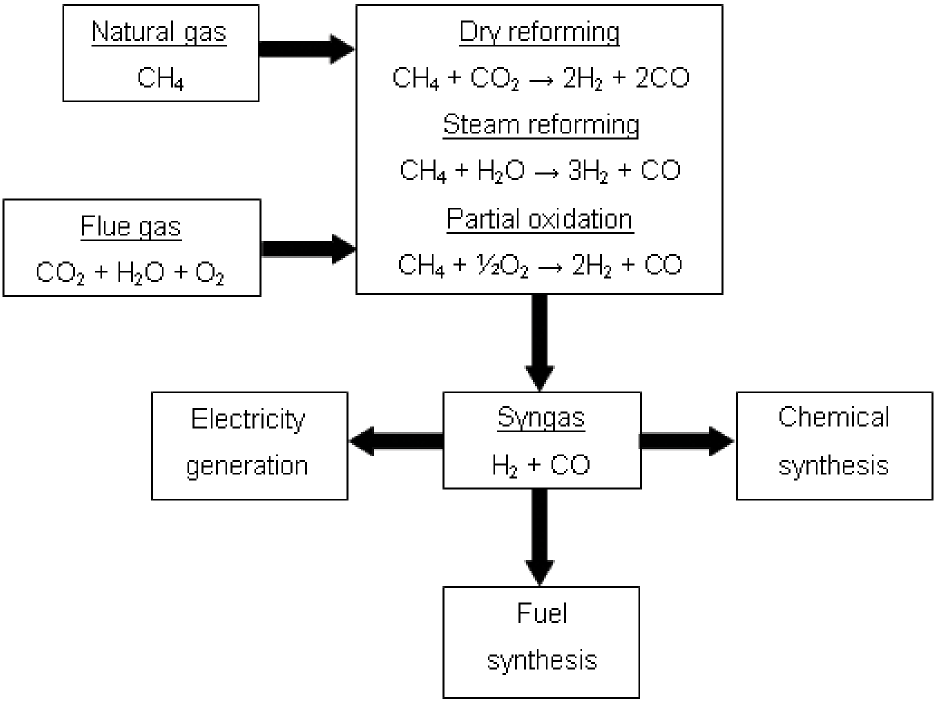

Figure 1. Tri-reforming of natural gas using flue gas from fossil fuel-based power plants.

Advantages	**Disadvantages**
Direct use of flue gases	Usually requires oxygen plant
High methane conversion	No existing industrial process
Elimination of CO_2 separation	No existing commercial catalysts
Different H_2/CO ratios	Would require high GHSV
Minimization of coke formation	Heat management
Use of waste H_2O/O_2	Mass management
Simplifying the processing system	

Table 1. Advantages and disadvantages of tri-reforming [7, 18, 22].

3. Catalysts for methane-reforming reactions

The drawback of methane-reforming processes is mainly the severe tendency to carbon formation that deactivates the catalysts [23–25]. Noble metal-based catalysts (Rh, Ru, Pt, Pd and Ir) presented a high activity and stability against coke formation [26, 27]. However, their costs are still highly prohibitive for feasible application in this process. In fact, nickel-based catalysts are more preferable in the CH_4 reforming, due to their availability and lower costs [28–30]. However, the stability of the nickel catalysts at elevated temperatures and the coke formation are the main obstacles for industrial applications [31, 32].

The addition of promoters to Ni-containing catalysts led to the reduction of coke deposition, better metal dispersion or smaller particle size, and the synergic effect between Ni and the promoter [33–36]. In fact, bimetallic catalyst exhibits a higher activity compared to noble metals but not totally eliminate the carbon deposition.

The metal dispersion influences the coke deposition, since this process is structure-sensitive. The build-up of carbon involves quite large active metal particles, which are usually formed at high reforming temperatures.

Alumina-based supports have been investigated mainly due to the high specific surface area, increasing the metal dispersion [37]. Nevertheless, the alumina supports easily deactivate due to the coke deposition and sintering. The formation of coke has been associated with the dehydration, cracking and polymerization reactions, occurring on the acid sites, while sintering is due to the transition of crystalline phase during reaction [37].

Additional improvement can be achieved using well-developed supports. An effort to overcome these problems is to search for basic additives or promoters, such as CeO_2, SiO_2, La_2O_3, BaO, CaO, SrO, MgO and ZrO_2 [37, 38].

Sintering of metal clusters can be prevented with supports having a strong interaction with the active component. In fact, ceria-based catalysts can minimize sintering and coke formation [39] compared to MgO, TiO_2, Al_2O_3, SiO_2 and ZrO_2 supports [40–46]. On the contrary, these supports facilitate sintering when submitted to higher temperatures. Moreover, ceria-based catalysts present good redox properties and high oxygen mobility, and as reported in the study, without noticeable oxygen mobility, the deactivation of the catalyst occurs very fast [47]. On the other hand, the thermal stability of pure ceria under the typical reforming conditions is quite poor.

3.1. Promising catalysts

Although tri-reforming has not yet been implemented commercially, similar to steam or to dry reforming, Ni catalysts supported on a wide range of different supported materials, such as Al_2O_3, ZrO_2, MgO, TiO_2, CeO_2, TiO_2, CeZrO and SiO_2, are the most popular catalysts for tri-reforming of methane [48].

Song et al. [14] suggested that the supports should have a high oxygen storage capacity that promotes CO_2 adsorption. They proposed a simplified mechanism for the CO_2 reforming reaction. The first step occurs with the activation of methane, followed by the surface reaction and the adsorbed surface CO_2 species or adsorbed oxygen atoms (Eq. (9)); CO_2 is more acidic, and basic supports may preferentially interact with CO_2. Therefore, the CO_2 adsorption at the surface facilitates the reaction with CH_4 producing CO and H_2. Moreover, supports with a high oxygen storage capacity may also facilitate the dissociative adsorption of CO_2 into CO and adsorbed oxygen, according to Eq. (9) [14]

$$CO_2 + \square = CO + O^{\square} \tag{9}$$

where $^{\square}$ denotes an active site.

Perovskite-type oxides have attracted significant interest as promising catalytic materials with applications in a wide range of reactions, including total oxidation and partial oxidation of hydrocarbons, carbon monoxide oxidation, alkenes hydrogenation, alkanes hydrogenolysis, alcohol synthesis, dry reforming and water-gas shift reaction [49–51]. The perovskites contain metallic and non-metallic elements, with a well-defined crystal structure. In general, the molecular formula is represented by ABO_3, where A refers to an alkali metal, an alkaline earth metal or a lanthanide and B to a transition metal. These solids exhibit interesting properties such as superconductivity, ferromagnetism, appreciable thermal stability and conductivity and finally a high catalytic activity. The intrinsic properties of each perovskite are dependent on the type of inserted element and principally on the preparation method. In fact, perovskites as catalysts showed a reductive capacity under appropriate conditions. The metal particles are highly dispersed in the oxide matrix (AO_X), inhibiting sintering of metal particles and carbon deposition. In fact, the high thermal stability makes the perovskites promising catalysts for the reforming of methane. Therefore, they are attractive alternatives to classic catalysts traditionally used in these reactions such as supported nickel and noble metals.

Various perovskites, including $LaFeO_3$, $LaNi_xFe_{1-x}O_3$, $LaNiO_3$ or $La_{1-x}Ce_xFe_{0.7}Ni_{0.3}O_3$, have been found to exhibit a high activity in the steam reforming of methane with a minimal coke deposition under low steam-to-carbon ratios [52–67]. However, the need for high-operating temperatures (e.g. $T \geq 600°C$) of methane-reforming reactions provokes irreversible structural changes, including structural collapse and dissolution of (reactive or inactive) metal particles from the perovskite lattice [57–60, 63, 64].

Choudhary et al. [63] verified that the oxygen from the $La_{1-x}Sr_xFeO_3$ perovskite-type oxides surface was responsible for the complete oxidation of CH_4–CO_2 and H_2O, while the bulk lattice oxygen was responsible for the deep reduction of Fe^{3+}–Fe^{2+}, and this was suitable for the partial oxidation of CH_4–H_2 and CO. The $La_{1-x}Sr_xFeO_3$ has had good repeatability in the catalytic performance, and no significant deactivation was observed over five redox cycles.

The $LaCrO_3$ and $LaFeO_3$ oxides doped with alkaline earth (AE = Ba, Ca, Mg and Sr) metals were prepared and studied on how the atomic oxygen influences the partial oxidation of methane to syngas [66]. A-site doping with AE metals generally increases the mobility of lattice oxygen ions and thus decreases the temperature for the hydrogen and CO production, when compared with the non-doped $LaCrO_3$ and $LaFeO_3$ oxides. There are minor structural changes during the partial oxidation of methane of $LaCrO_3$, which can be regenerated by oxidation at 950°C. However, the $LaFeO_3$ presented negligible structural modifications. The stability of the perovskites occurs during repeated reaction cycles of generation-regeneration.

The $LaFeO_3$, $La_{0.8}Sr_{0.2}FeO_3$ and $La_{0.8}Sr_{0.2}Fe_{0.9}Co_{0.1}O_3$ perovskite-type oxides were investigated in a continuous flow and sequential redox reaction [67] for the partial oxidation of methane in the absence of gaseous oxygen. The authors observed that methane reacted with sub-surface oxygen species of perovskite oxides in the absence of gaseous oxygen. The sequential redox reaction revealed that the structural stability is attributed to the continuous oxygen supply in the redox reaction, which evidences an excellent structural stability of the perovskite materials.

Other perovskites were employed for the DRM, SRM and POM reactions [68–72]. The effect of replacing cobalt by iron in $LaCo_{1-x}Fe_xO_3$ (x = 0.0, 0.5 and 1.0) perovskite-type oxides over its physical properties and catalytic performance in the partial oxidation of methane (POM) was investigated. The product distribution varying with space time and with perovskite-type catalyst employed is found to be remarkable. For lower W/F values, the major product was H_2 for the $LaCoO_3$ (55.8%) and $LaCo_{0.5}Fe_{0.5}O_3$ (59.2%), with similar ratios H_2/CO (1.8–1.9) and a low CO_2 formation [73].

We studied the combined dry and partial oxidation reaction on $LaCrO_3$ and perovskites, fed with $CH_4:CO_2:O_2$ = 1:1:0.5 and using a GSVH 60,000 h^{-1} at 700°C for 4 h. The conversions were 17% CH_4 and 94% O_2, respectively, and no conversion of CO_2. Results showed an increasing formation of CO_2 and a H_2/CO ratio equal to 2.7, which suggests that the partial and total oxidation of methane initially takes place, producing CO, CO_2 and H_2O, and subsequently the steam and dry reforming occur to produce syngas. In fact, the water-gas shift reaction also takes place due to the high H_2:CO ratio.

3.2. Effect of O_2 and H_2O concentration

Steam reforming of methane is the only large-scale industrial process currently available for the production of synthesis gas, producing high-purity hydrogen with a H_2/CO ratio equal to 3. The partial oxidation of methane produces synthesis gas with a H_2/CO ratio of 2, as required for methanol synthesis. However, the POM reaction is exothermic, and the control of the temperature of this process is difficult. Tri-reforming of methane is energetically favorable compared to the steam reforming of methane and partial oxidation of methane. The process is energetically thermal neutral. Compared to the SRM and POM reactions, the tri-reforming process has the advantage to produce different H_2/CO ratios.

Singha et al. [74] found the optimum feed ratio and the effect of O_2 and H_2O concentration (mole ratio) conditions for the reaction, by monitoring the feed mixture and keeping the methane to CO_2 mole ratio constant. The addition of oxygen in the feed helps to attain a thermal-neutral balance and compensate the heat necessary for the endothermic reactions occurring during the whole process [75]. A high oxygen concentration in the reaction feed inhibits the CO_2 reforming and lowers the CO_2 conversion [13] because the reaction between oxygen and methane is thermodynamically favored over the reaction between methane and CO_2. The higher concentration of oxygen in the feed allows a maximum methane consumption, and the available methane for the dry and steam reforming is very low [76]. **Table 2** shows the effect of O_2 concentration

Catalyst	GHSV (ml.g^{-1}. h^{-1})	Feed ratio, O_2:CO_2:H_2O:CH_4: He	CH_4 conv. (%)	CO_2 conv. (%)	H_2O conv. (%)	H_2/CO ratio
4.8NiZrO_2	80,000	0.75:1:2.1:5:18	60	50	55	2.3
		1:1:2.1:5:18	83	81	82	2.0
		1.25:1:2.1:5:18	90	38	89	3.0

Table 2. The effect of O_2 concentration (mole ratio) on the reactant conversions verified by reference [74].

over methane, CO_2 and H_2O conversions and H_2/CO ratios [74]. The effect of concentration of O_2 over the reactant conversion was mainly due to the heat generated by the partial oxidation and complete oxidation of methane and the enhanced coke removal process [76, 77]. Increasing O_2 concentration, the total oxidation of methane also increases, due to the exothermic reaction, and the amount of energy is released. The heat generated is useful for the steam- and dry-reforming reactions, which are endothermic, minimizing the required temperature to obtain a higher CH_4 conversion [78] and external energy. On the opposite, lower O_2 concentrations led to lower conversion; however, increasing the temperature, H_2O and CO_2 react with methane to produce synthesis gas [77]. The higher H_2/CO ratio was attributed to the steam reforming of methane, producing a H_2/CO ratio of 3, attributed to the water-gas shift reaction, which produces only hydrogen, without the production of CO [79]. On the other hand, with increasing temperature, one observes that the RWGS (reverse water-gas shift) reaction outweighs other reactions [77].

3.3. Effect of space velocity and methane/oxygen ratio

The effect of replacing cobalt by iron in $LaCo_{1-x}Fe_xO_3$ (x = 0.0, 0.5 and 1.0) perovskite-type oxides on its catalytic performance in the partial oxidation of methane (POM) process was investigated, varying the space velocity and methane/oxygen ratio. The inlet methane to oxygen proportion was fixed at 2:1. The methane conversion increased with the space time and the maximum conversion was 31% at 0.67 kg.s.mol^{-1} for the LF perovskite. In terms of product selectivity, the catalysts produced mainly H_2 and CO, CO_2, C_2H_4 and/or C_2H_6, as shown in **Table 3**. The product distribution varying with space time and perovskite type catalyst is found to be remarkable. The H_2 production decreased by about a half and the CO decreased four times for both LC and LCF catalysts. However, the CO_2 formation increased by a factor of about 10, and the H_2/CO ratio also increased by a factor of 2. Different was the product distribution of the LF perovskite presenting low H_2 and CO formations and a high production of CO_2, but a significant higher formation of C_2 hydrocarbons compared to the other samples as W/F increases [73].

Catalytic tests with the LF and LCF perovskites were also performed with a methane/oxygen ratio of 4 (W/F = 0.67 kg.s.mol^{-1}). **Table 4** shows that increasing the CH_4/O_2 ratio to 4, the methane conversion was halved, compared to the previous condition at a CH_4/O_2 ratio of 2 [73].

The formations of ethane and ethylene are attributed to secondary reactions. In particular, the oxidative coupling of methane reaction takes place, which increased the C_2H_4 and C_2H_6 to C_2H_4 at high temperatures ($2CH_4 + 1/2O_2 \rightarrow H_2O + 1/2C_2H_6$). Parallel reactions of oxidative or non-oxidative dehydrogenation of ethane would occur, converting also C_2H_6 to C_2H_4 and then

W/F (kg.s.mol^{-1})	Catalysts	X CH_4 (%)	H_2/CO	Selectivity (%)			
				H_2	CO	C2	CO_2
0.16	LC	13.7	1.8	55.8	31.5	5.50	7.10
	LF	19.2	1.6	46.0	28.0	4.10	22.0
	LCF	17.1	1.9	59.2	30.9	3.80	6.10
0.40	LC	22.0	2.8	22.2	7.90	1.50	68.4
	LF	28.1	2.2	16.6	7.50	3.10	72.8
	LCF	27.7	3.2	20.5	6.50	0.90	70.2
0.67	LC	28.6	3.5	25.7	7.30	0.70	66.3
	LF	31.0	3.2	8.30	2.60	5.30	83.8
	LCF	28.7	4.4	22.2	5.10	0.80	72.0

Table 3. Conversions and selectivity results over perovskites. Experimental conditions: P = 1 atm, inlet molar CH_4/O_2 ratio = 2/1, space time of reactants = 0.16, 0.40 and 0.67 kg s mol^{-1} and temperature of 700°C [73].

CH_4:O_2	Catalysts	X CH_4 (%)	H_2/CO	Selectivity (%)			
				H_2	CO	C2	CO_2
2	LF	31.0	3.2	8.30	2.60	5.30	83.8
	LCF	28.7	4.4	22.2	5.10	0.80	72.0
4	LF	15.5	0.0	0	2.70	10.5	86.8
	LCF	15.5	2.0	5.00	3.60	0.80	90.6

Table 4. Conversions and selectivities over LF and LCF perovskites. Experimental conditions: P = 1 atm, inlet molar CH_4/O_2 ratio = 2/1 and 4/1, space time of reactants = 0.67 kg s mol^{-1}, and temperature of 700°C [73].

ethane could be oxidized to CO_2. This last hypothesis is reinforced due to the increasing CO_2 concentration at higher temperatures, most likely due to the oxidation of part of C_2H_6 (which leads to H_2O and CO_2), according to the following reactions, suggesting different reaction paths: $C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O$ and $C_2H_6 \rightarrow C_2H_4 + H_2$.

4. Discussion

Different reactions may occur in the whole process; the formation of the desired product with maximum selectivity depends on the input feed mixture. Steam increases the methane reforming and the water-gas shift (Eq. (7)) (WGS) reaction. It also helps to reduce the carbon deposition, which occurs during the dry reforming of methane [75]. Therefore, the addition of H_2O is thermodynamically more favorable for the methane reforming than for the dry reforming [13]. For a lower H_2O concentration, the methane conversion was lower than the CO_2 conversion, which is assigned to the competition between H_2O and CO_2 molecules with methane. Increasing the H_2O concentration input, the CO_2 conversion decreases. Both WGS and steam reforming are equally important at a temperature below 650°C; however, with increasing temperature, the H_2O conversion increases. Above 650°C, the RWGS reaction prevailed, producing less H_2 and decreasing the H_2/CO ratio [77, 80].

The reaction mechanisms are yet unknown for oxide catalysts and in particular for perovskite structures, which apparently are the most promising catalysts for the tri-reforming, based on the combined SRM, DRM and POM reactions. One explanation is that these materials present defects which promote the modification of electronic effects. Indeed, electronic effects may arise in the presence of ions with different charges of those belonging to the ions of the network, or as a consequence of the transition energy levels of electrons normally filled (usually the valence band) to empty levels (the conduction band). In all cases, when an electron is missing, that is, when there is an electron deficiency, this is usually called electronic holes. In the absence of an electric field, the ionic networks of the oxide structures tend to be electronically neutral, which requires that charge defects are compensated by the presence of other filler defects in order to obtain the condition of electro-neutrality, making the structure more stable. This means that charge defects are always present as a combination of two or more types of failures [55].

A reaction mechanism on mixed oxides can be suggested, assuming that CH_4 is activated by the metal at the surface, forming carbon and H_2. The carbon atoms adsorbed at the surface can react directly with oxygen, forming CO and H_2. These intermediate species may react with the adsorbed CO_2 species or dissociated steam. Song et al. [14] claim that the different extent of interaction between CO_2 and catalysts could be responsible for this mechanism. They assumed that the interaction between CO_2 and the catalyst could change the CH_4 conversion rate, based on a simplified Langmuir-Hinshelwood (L-H) mechanism (Eqs. (10)–(12)).

$$CH_4 + \square \rightarrow CH_4^{\square} \tag{10}$$

$$CO_2 + \square \rightarrow CO_2^{\square} \tag{11}$$

$$CH_4^{\square} + CO_2^{\square} \rightarrow 2CO + H_2 + 2^{\square} \tag{12}$$

where $^{\square}$ are the metallic surface sites.

They observed that the reaction order of CH_4 on Ni/MgO is strongly compared to the adsorption of CO_2 over Ni/MgO/CeZrO which is close to zero. This suggests that the CH_4 conversion rate almost does not change with the partial pressure of CO_2. However, it was found that Ni/MgO/CeZrO has even more stronger interaction with CO_2 than Ni/MgO. In fact, the sites for a strong CO_2 adsorption over Ni/MgO/CeZrO are probably not the same as for CH_4 adsorption. It is important to note that the metal is itself believed to be able to activate CH_4, as suggested by Rostrup-Nielsen [47], while the types of supports, like MgO, facilitate the adsorption of CO_2. Hence, the locations of the interfaces between Ni and supports are fundamental, where the adsorption and reaction take place.

5. Conclusion

The energy crisis is a problem which will get exacerbated with depleting crude oil reserves around the world. There is an urgent need for alternative fuels around the world. The conversion of CO_2 to a high-valued product could provide the necessary economic incentive towards both CO_2 mitigation and fuel generation. The study reported new strategies of CO_2 valorization. The tri-reforming produces directly synthesis gas from flue gases using methane as a co-feed. The utilization of CO_2 without pre-separation from its sources saves energy, since a substantial energy input is required for CO_2 separation from its concentrated sources [81]. Tri-reforming of methane can be carried out by using CO_2, H_2O and O_2 as a co-feed with natural gas or methane, and flue gas can be a very good source of highly concentrated feed for the tri-reforming process. New catalysts have been suggested with suitable promoters, mixed oxides and different supports, resistant to coke formation and sintering of the metal-active sites and stable at an elevated temperature. Stable and active catalysts for industrial application are under development, and researches are expected to bridge the gaps in science and technology for the tri-reforming process, providing further improvements and economically feasible.

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This book offers the current state of knowledge in the field of biofuels, presented by selected research centers from around the world. Biogas from waste production process and areas of application of biomethane were characterized. Also, possibilities of applications of wastes from fruit bunch of oil palm tree and high biomass/bagasse from sorghum and Bermuda grass for second-generation bioethanol were presented. Processes and mechanisms of biodiesel production, including the review of catalytic transesterification process, and careful analysis of kinetics, including bioreactor system for algae breeding, were widely analyzed. Problem of emissivity of NOx from engines fueled by B20 fuel was characterized. The closing chapters deal with the assessment of the potential of biofuels in Turkey, the components of refinery systems for production of biodegradable plastics from biomass. Also, a chapter concerning the environmental conditions of synthesis gas production as a universal raw material for the production of alternative fuels was also added.

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