Sustainable Materials and Technology

Anish Khan
Abdullah Asiri
Showkat Bhawani *Editors*

Waste to Biofuel Technology

Future Energy

Springer

Sustainable Materials and Technology

Series Editors

Mohammad Jawaid, Chemical and Petroleum Engineering, United Arab Emirates University, Al Ain, United Arab Emirates

Anish Khan, Centre of Excellence for Advanced Materials, King Abdulaziz University, Jeddah, Saudi Arabia

Sustainable Materials and Technology (SMT) book series publishes research monographs (both edited and authored volumes) showcasing the latest developments in the field and comprehensively covering topics such as:

- Recycling of waste into useful material and their energy applications
- Catalytic action of Nano oxides for efficient carbon reforming process
- Sustainable technologies for plastic transformation
- Bifunctional nanoparticles for sustainable water splitting applications
- Sustainable dying and printing
- New materials from waste
- Sustainable Manure Management and Technology: Potentials, Uses and limitations
- Sustainable Mechanical Engineering Approach
- Sustainable biochemistry for the improvement of health
- Sustainable development of Mechanical recycling of automotive components
- Sustainable-waste recycling and conversion in useful materials for different applications
- Sustainable development of inexpensive Nano-photo catalysts
- Sustainable development of recycling of discarded lithium ion batteries
- Modern sustainable cement and concrete
- Sustainable adsorbent for hazardous removal
- Sustainable superior electromagnetic shielding materials
- Excellent sustainable nanostructured materials for energy storage device
- Sustainable development of heavy metal detoxification from water
- Carbon dioxide utilization for sustainable energy
- Sustainable development in green syntheses of materials
- Environment friendly and sustainable cloth for garments application
- Sustainable design and application of eco-materials
- Nanoparticles for sustainable environment applications
- Sustainable remediation of industrial contaminated water towards potential industrial applications
- Biomaterials for sustainable bioremediations

Anish Khan · Abdullah Asiri · Showkat Bhawani
Editors

Waste to Biofuel Technology

Future Energy

Springer

Editors
Anish Khan
Center of Excellence for Advanced Materials Research
King Abdulaziz University
Jeddah, Saudi Arabia

Abdullah Asiri
Chemistry Department, Faculty of Science
King Abdulaziz University
Jeddah, Saudi Arabia

Showkat Bhawani
Faculty of Resource Science and Technology
Universiti Malaysia Sarawak
Kota Samarahan, Malaysia

ISSN 2731-0426 ISSN 2731-0434 (electronic)
Sustainable Materials and Technology
ISBN 978-981-97-4560-9 ISBN 978-981-97-4561-6 (eBook)
https://doi.org/10.1007/978-981-97-4561-6

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Contents

Valorization of Palm Biomass Wastes for Biodiesel Production

João H. C. Wancura, Maicon S. N. dos Santos, Carolina E. D. Oro, J. Vladimir de Oliveira, and Marcus V. Tres

Abstract The intensive and exacerbated use of fossil fuels has alarmed the global industrial system and has led to the adoption of sustainable alternatives aimed at minimizing the serious environmental impacts caused by the exploitation of these resources. One of the primordial scientific topics in recent years is the investigation for potential safe alternative fuels as a path to substitute the current energy exploitation. Appropriately, the use of plant biomass as potential agents in the synthesis of biofuels has been a highly viable and sustainable alternative, mainly from an environmental and economic outlook. Therefore, the palm oil and palm oil-based industries have been identified as prominent sources of bioenergy through the conversion of palm biomass into products with high added value. Consequently, the diversity of palm biomasses has indicated encouraging potentiality for application in a large-scale biofuel production chain, such as mesocarp fibers, trunk, frond, and kernel feedstocks. Accordingly, this study described the main application of palm biomass for biodiesel production. Contextually, the chapter presented valuable information on the main technological strategies applied for biodiesel preparation, such as pyrolysis, transesterification, and enzymatic and supercritical techniques. Additionally, the study comprehended important natural sources widely explored as potential products for biodiesel synthesis, highlighting the current scientific research on oil

J. H. C. Wancura
Laboratory of Biomass and Biofuels (L2B), Federal University of Santa Maria (UFSM), Santa Maria, RS, Brazil

M. S. N. dos Santos · M. V. Tres (✉)
Laboratory of Agroindustrial Processes Engineering (LAPE), Federal University of Santa Maria (UFSM), Cachoeira Do Sul, RS, Brazil
e-mail: marcus.tres@ufsm.br

C. E. D. Oro
Department of Food Engineering, Regional Integrated University of Upper Uruguai and Missions (URI), Erechim, RS, Brazil

J. V. de Oliveira
Department of Chemical and Food Engineering, Federal University of Santa Catarina (UFSC), Florianópolis, SC, Brazil
e-mail: jose.vladimir@ufsc.br

A. Khan et al. (eds.), *Waste to Biofuel Technology*, Sustainable Materials and Technology, https://doi.org/10.1007/978-981-97-4561-6_1

palm biomass. Moreover, the main characteristics of these biomasses as an encouraging feedstock option for biodiesel preparation were provided. Finally, conclusions and relevant future perspectives on the advancement of the oil palm feedstocks for biodiesel preparation and production were determined.

Keywords Bio-oil · Bioenergy · Antioxidants · Biorefinery approach · Oil palm biomasses · Plant wastes · Potential feedstocks · Sustainable agriculture · Transesterification · Vegetable add-value by-products

1 Introduction

Biodiesel (fatty acid methyl esters—FAME) is a renewable, non-toxic, and biodegradable biofuel usually obtained through a reaction involving oleaginous sources and short-chain alcohol with (or not) a catalyst [1]. This biofuel is considered an environmentally friendly energy source since it can offer a reduction in the amounts of direct and indirect greenhouse gases (like particulate matter, sulfur, hydrocarbonss and mainly carbon dioxide, and monoxide), protecting the environment [2]. Biodiesel also can be employed in diesel engines with minimal or no mechanical modification, being typically mixed with petrodiesel in volumetric proportions stipulated in government policies according to the country.

The main route to biodiesel production on industrial demands is through a homogeneous alkaline transesterification reaction, where at 64 °C, with 0.5 wt% of sodium methoxide, oil to methanol molar ratio of 1.0:6.0 and 1.0 h reaction, it is possible to achieve biodiesel yields above 97% [3, 4]. Within this perspective, diverse technological methods, catalyzed by different chemical compounds (heterogeneous alkaline and,homogeneous and heterogeneous acid) or enzymatic have been considered the target of several studies published recently for biofuel preparation [5, 6].

Distinct oils (or lipids) from either plant or animal can become a raw material for biodiesel synthesis. Typically, potential feedstocks used for biodiesel preparation are soybean, rapeseed, and palm oil, depending on the region where the determined oleaginous source has a predominance of cultivation [7]. These feedstocks can be categorized as the first, second, third, and fourth generation. First-generation raw materials are principally extracted from edible crops or biomass (palm, soybean oil, rapeseed, and sunflower, for example). Second-generation raw materials for biodiesel production originated from non-edible sources, such as WCO, grease, animal fat, and non-edible plant oils. Third-generation feedstocks originated from algal biomass. Feedstock destined for biodiesel of fourth-generation can be synthesized through one or a junction of three resources: specific photosynthetic microorganisms; a combination of photovoltaics production and microbial fuel; and (or) production of the artificial cell [7, 8].

Among the different biodiesels, those synthetized by palm residues have demonstrated themselves as the most dominant biofuel by virtue of the largest impact worldwide (35%), lowest cost (660 USD·ton^{-1}), higher oil content (5,000 kg oil·ha^{-1}), and yield of production (4.2 Mton·ha^{-1}) since it needs less sunlight to yield one unit of oil per hectare [9]. Moreover, the cultivation of palm trees can give fruit from fourth-year forward and can be reaped until 50 years [10]. The worldwide market of palm oil is developing gradually and it is projected to achieve a value market of US$ 92.8 billion in 2021 [9]. According to Ong et al. [11], in 2050, it is projected that the demand for palm oil will reach a massive amount of 240 Mton.

The application of edible oils, such as palm oil, for biodiesel synthesis, could result in growing food prices considering the increased demand for fuels and food products [12]. In terms of production costs, it is important to cite that the employment of edible oils as suitable raw material can represent 70 to 80% of the total, influencing the feasibility of determining projects [13]. Moreover, although non-edible oils such as WCO can directly be converted to biodiesel, these raw materials are not sufficiently available for large production and also can have their performance affected in cold weather [14]. In this scenario, the operation with alternative raw materials for biodiesel preparation is an interesting way to circumvent this type of situation.

Among the numerous unusual raw materials investigated for biodiesel preparation, palm wastes biomass has been the focus of different research recently [15–17). This situation may be associated with the current evolution of the palm oil industry and an expectation to result in a substantial increase in the quantities of solid biomass wastes [12]. Generally, one hundred tons of fresh palm bunches produce fifty tons of biowastes, particularly empty fruit bunches [18]. Nevertheless, is important to highlight that oil palm tree biomass comprises not only empty fruit bunch but also trunks, oil palm fronds, palm shell kernel, and mesocarp fiber, all with the potential for oil extraction (see Fig. 1). Therefore, with a promising demand for palm oil, it is projected that a generation of oil palm by-products will grow with the increase of this demand. These factors represent an excellent opportunity for eco-friendly biodiesel production employing oil palm biowastes as added-value raw material.

Furthermore, it is appropriate to establish a quantitative aspect of scientific studies on the applications of palm oil and palm raw materials as valuable resources for biodiesel production, particularly in the industrial context. From an academic/scientific background, the application of feedstocks for biofuel production has been largely identified as an advanced and highly sustainable alternative. Accordingly, the growth of scientific publications recently reported on the application of oil palm feedstocks is interesting and a pertinent factor to be discussed in this chapter. In this context, advanced research was performed on the scientific-based Web of Science® platform. To perform a particular investigation of the scientific articles published in the exploration of the topic of this study, the following keywords were assumed: *Oil palm biodiesel biomasses*; *oil palm kernel/oil palm mesocarp/oil palm trunk/oil palm frond* (Fig. 2).

The scientific investigation on the employment of oil palm feedstocks as potential sources for biodiesel synthesis indicated an expressive growth in the productive scenario in the last 10 years. Data acquired by the Web of Science® platform showed a large increase in addressing kernel, mesocarp, trunk, and frond biomass since 2011. 140 manuscripts were published in 2011 combining the different oil palm feedstocks. In 2020, 311 studies were counted. This growth was mainly driven

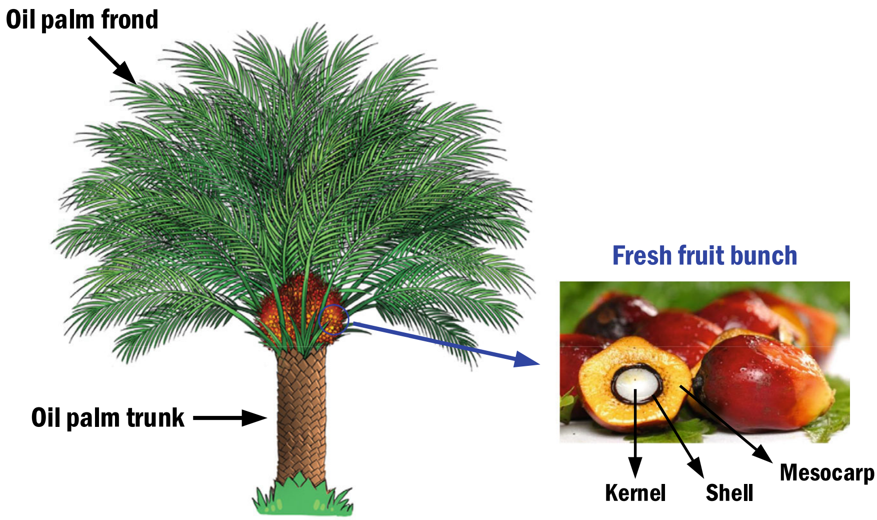

Fig. 1 Wastes generated from a palm trees

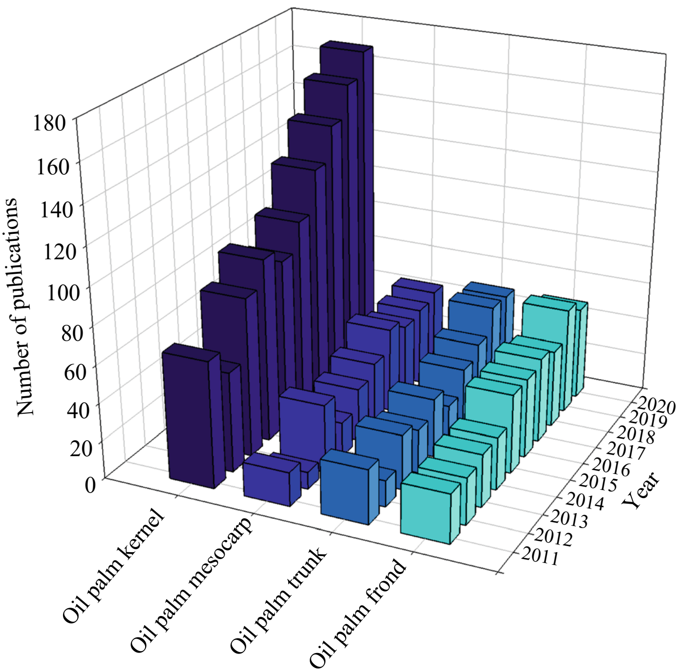

Fig. 2 Research on the dimension and frequency of publication of scientific articles on the application of oil palm feedstocks for biofuel production arranged by year from 2011 to 2020 according to the Web of Science® scientific-based platform with the following keywords: *Oil palm biodiesel biomasses*; *oil palm kernel/oil palm mesocarp/oil palm trunk/oil palm frond*

by the exploitation of the oil palm kernel resource. A range of technological strategies and the potentialization of the activity of this material in the biodiesel synthesis stages have been adopted recently. This panorama is strongly demonstrated by the resistant advance of the number of studies that investigate this biomass in biodiesel production processes. In 2011, 67 studies were published in scientific journals. In 2020, there were 169 manuscripts. Appropriately, the verified scenario expresses the importance of the magnitude of the pillars of economic, social, and environmental sustainability in the biodiesel production chain and reports the utilization of oil palm feedstocks as promising and competitive resources that have been largely potentialized for application in a global perspective.

Appropriately, the motivation of this chapter was to perform a comprehensive approach to value the palm oil biomass as feedstock to be applied to biodiesel production. For this proposal, the main technologies and wastes applied to biodiesel preparation, a discussion of the main studies published in recent years where palm oil biomass wastes to synthesize biodiesel was employed, as well as future perspectives related to the topic are discussed.

2 Technologies Applied to Biodiesel Preparation

Biodiesel can be obtained from vegetable oils or animal fat through the process of transesterification, thermal cracking (pyrolysis), or supercritical technique with or without the use of different catalysts, including homogeneous or heterogeneous chemical catalysts and enzymes [19]. Some details of the main technologies applied for the production of biodiesel are presented below.

2.1 Pyrolysis

Pyrolysis or thermal cracking is a process that causes the breakdown of molecules by heating at high temperatures in the absence of air or oxygen at temperatures above 450 °C. The final product consists of a mixture of chemical compounds with properties very similar to those of petroleum diesel. Pyrolysis processes employ esters of an alkyl chain attached to the ester group. In these processes, the main changes in the reaction are the number of double bonds and carbon atoms. This process can employ catalysts to break chemical bonds and generate smaller molecules [20–22]. The fuel obtained by cracking oils and fats is not considered biodiesel under international nomenclature. For this reason, it is called by the terms ecodiesel, cracked biodiesel, and bio-oil [23, 24].

Two distinct and successive steps occur in the thermal cracking process. First, the formation of carboxylic acids occurs by breaking carbon and oxygen bonds between the glyceride part and the rest of the triglyceride carbon chain. Then, the carboxylic acids formed in the initial step are deoxygenated through the routes of decarboxylation and decarbonylation [25].

In order to eliminate oxygenated products, some catalysts can be used to change the selectivity of pyrolysis products. The most used catalysts are aluminum oxide, silicon oxides, molybdenum oxides, nickel supported on alumina, acidic zeolites, phosphoric acid supported on silica, alumina doped with metallic oxides (tin and zinc), and several others based on silica [19, 23, 26]. Alumina, on the other hand, as it is not very selective, reduces the final acidity of the products and should be used in secondary cracking. Furthermore, pyrolysis is widely used in biomass to produce a combination of gases, biochar, and bio-oil [27, 28].

2.2 Transesterification

2.2.1 Alkaline Route

The most used technological route for the production of biodiesel in the world is the technological route of methyl transesterification, in which vegetable oils and/or animal fat are mixed with methanol and associated with a basic catalyst, biodiesel is produced. The alkaline route generates large amounts of glycerin, which must be separated from the final product. However, the purification steps of the final products (biodiesel and glycerin) in this process require the recovery or neutralization of the catalyst and the removal of the saponification products that are generated in the reaction. Another drawback of base-catalyzed transesterification is water intolerance. The negative effect occurs because water consumes the catalyst and reduces its efficiency in the process [29].

The use of catalysts in the alkaline route, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH), presents a fast reaction rate reaction. Biodiesel obtained by the alkaline route can be generated by homogeneous and heterogeneous processes. The transesterification of vegetable oils and/or animal fats in a homogeneous alkaline medium is still the most used method for the production of biodiesel [29]. However, some reaction inconveniences should be highlighted in the homogeneous reaction, such as the difficulty in separating the final product, large volumes of effluents, and the impossibility of reusing catalysts [19]. As for the process with the application of enzymatic catalysts, the use of heterogeneous catalysts overcomes these inconveniences. The interest is in obtaining a stable catalyst, with ease of separation from the reaction medium and that presents the possibility of being used in different operational recycles [30, 31], and the so-called heterogeneous reaction is performed. However, the heterogeneous process has a slow conversion rate compared to the homogeneous catalyst [12].

In this reaction route, special attention to the raw material and the catalyst must be given. The use of used vegetable oils, as in the case of household or restaurant frying oil residue, can form soap when reacting with the catalyst. Furthermore, the yield of biodiesel is decreased due to the presence of contaminants such as free fatty acids and water in this used oil [19]. In this case, the use of other catalysts is recommended, such as CaO [19].

2.2.2 Acid Technique

Transesterification can also be carried out in an acid medium. One of the advantages over the use of alkaline catalysts is that the amount of free fatty acids in the medium is not relevant, as they can be esterified in the same reaction vessel. Therefore, it is possible to use raw materials with lower added value in the process. However, acidic transesterification requires more energetic conditions compared to the alkaline process. In acidic esterification, usually sulfuric and sulfonic acids are used [32, 33].

2.3 Enzymatic Technique

The enzymatic synthesis of biodiesel presents some advantageous characteristics in relation to other production processes. Enzymatic synthesis employs mild temperature conditions, there is no generation of effluents, and there is no saponification due to the competence of enzymes in converting reagents into products. For this type of enzymatic reaction, lipases are used in their free or immobilized form [6, 34]. Lipases (EC 3.1.1.3) are classified as hydrolases and act on ester bonds present in acylglycerols, releasing fatty acids and glycerol, being a special class of esterases [35].

Lipases can be used in the reaction in their free or immobilized form. The immobilized form allows the separation and reuse of the immobilized in successive cycles. Therefore, it is necessary to choose a support that presents low cost and quick synthesis for the process to be viable [36, 37]. Wancura et al. [38] used the commercial Callera™ Trans L free lipase in the hydrolysis-esterification reaction to produce biodiesel with soybean oil and methanol and achieved a yield of 96.9% in 24 h. Furthermore, Wancura et al. [34] showed that it is possible to achieve a yield of 97.1% in 8 h through a two-step hydroesterification reaction system using NS40116 lipase. The result presented by the authors shows that the use of lipase in its liquid form presents a high biodiesel conversion rate.

The enzymatic process is considered a “green” process and has many advantages; however, it has lower reaction rates compared to the alkaline process. Another point worth mentioning is the high cost of enzymes, which can affect the price of the process [38].