BIOFUEL EXTRACTION TECHNIQUES

Edited by
Lalit Prasad, Subhalaxmi Pradhan, and S.N. Naik

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Contents

Preface

Biofuels are viable alternatives to petroleum-based fuel because they are produced from organic materials such as plants and their wastes, agricultural crops, and their by-products. The development of cutting-edge technology has increased the need for energy significantly, which has resulted in an overreliance on fossil fuels. Renewable fuels are the subject of research because of their biodegradability, eco-friendliness, decrease in greenhouse gas (GHG) emissions, and favorable socioeconomic consequences to counteract imitations of fossil fuels.

Depending upon their physical state, biofuels can be classified into solid, liquid, or gas. Examples of solid biofuels are briquettes of biomass and briquetted biochar. Liquid biofuels include bioethanol and biodiesel, and gaseous biofuels include biogas and biomethane, among others. These are only a few examples.

Different extraction techniques are used for the production of biofuels from renewable feedstocks. Biodiesel is a promising biofuel which is produced by the transesterification of plant-based oils. Extraction of oil includes older traditional methods, solvent extraction, mechanical extraction, microwave-assisted, and ultrasonic-assisted methods. The solvent extraction method is more efficient and produces good quality oil. The limitation of this method is time-consuming and very tedious. Many innovative techniques are also used to overcome the limitations of conventional methods. Microwave-assisted and ultrasonic-assisted are some of the new techniques which include the pre-treatment of the raw material using either ultrasonic waves or radio waves which helps in increasing the efficiency of the extraction of oil and improves the final quality of the oil.

This new book covers the prospects and processing of feedstocks for biofuels, extraction techniques, catalysts and solvents used during production of biofuel, optimization of reaction techniques, carbon capturing during biofuel extraction, value addition to biofuel wastes, and their techno-economic and environmental acceptability. A total of 18 chapters are included in this book.

Chapter 1 is an introductory part which covers different plant seeds and their potential for biofuel production.

Chapters 2 and 3 cover the processing of feedstock in context of biodiesel production and extraction techniques for biodiesel production.

Chapters 4 and 5 include biomethane generation, stabilization of process parameters, upgradation systems for biogas and improving biomethane quality.

Chapters 6 and 7 cover renewable feedstocks for biofuels production and extraction techniques of gas to liquids (GtL) fuels respectively.

Chapters 8–10 incorporate bio-alcohol, bio-hydrogen extraction, purification, and analysis.

Chapters 11–13 include valorization of by-products produced during the extraction of biofuels, their purification, quality control, assurance, techno-economics and environmental sustainability.

Chapters 14 and 15 include the role of supercritical solvents and catalysts used during biofuel extraction and their efficiency.

Chapters 16 covers carbon capturing by microorganisms during the biofuel extraction process.

Chapters 17 and 18 include global aspects, new advancements of biofuel extractions and future trends.

It is expected that this book will spark the interest of numerous investigators in the academic universe towards biofuel research. It will provide new information about the recent advancements in the extraction techniques of biofuels, value addition to biofuel wastes and economic and environmental acceptability, sustainability and viability.

1

Plant Seed Oils and Their Potential for Biofuel Production in India

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Abstract
Many tree-borne oilseed plants are grown in India which produce non-food grade oil. Some of these have the potential to produce feedstock for biodiesel. Plants such as Pongamia and Jatropha are found throughout the country, whereas Mahua, Rubber, and Nahor are found in specific regions. The oilseeds are collected to a lesser extent by the local population for traditional uses as medicine, to fuel lamps, etc. and for the preparation of soap in industries. The National Mission on Biofuel has focused to grow Jatropha, whereas the existing tree born oilseeds are also potential sources for biodiesel feedstock. Non-edible oils with their potential as biodiesel feedstock in the country is discussed in this chapter. The oilseed plants less explored for biodiesel have also been discussed.

Keywords: Biodiesel, vegetable oil, non-edible oil, transesterification, methyl esters, jatropha, pongamia

1.1 Introduction

Presently, petroleum fractions are the preferred fuels for internal composition engines used for transport, as well as in the industrial and agricultural sectors. The global consumption of fossil based liquid fuels was above 100 million barrels per day during 2019 and forecasted to continue at the same rate during 2021 [1]. The contribution of CO_2 to the atmosphere is about

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3.1-3.2 times the consumption of fossil fuel. The exhaust emissions as a result of widespread use of fossil fuel are a global concern for the present time. The level of unburnt hydrocarbon and oxides of nitrogen, along with CO_2, are gradually increasing in the atmosphere. The research and development activities have been focused for the last few decades in search of alternative fuel from renewable sources for the nations to be self-reliant for energy sources and much effort is being done by countries with no oil reserves.

Biodiesel is the fatty acid methyl esters derived from renewable lipid feedstocks, such as vegetable oils, as an alternative to diesel fuel. The invention of diesel engines and compression ignition engines dates back to the 19^{th} century and the vegetable oils were used as fuel. The high viscosity and poor volatilities of vegetable oils, as well as the availability of middle distillate, i.e., diesel fuel, did not attract much interest for vegetable oil based fuel during those days.

The research and development activities on vegetable oil based biodiesel were initiated at the beginning of this century. The transesterification of vegetable oil reduces the viscosity by one-tenth, lower molecular weight of the triglyceride molecule by one-third, and improves the volatility along with the physical properties of the biodiesel. Worldwide biodiesel industries are set up and biodiesel blended diesel fuel is technically suitable for use in existing diesel engines with slight or no engine modifications. There is a scarcity of biodiesel feedstock for countries like India where the domestic demand of edible oil is met by import. The present article describes the potential non-food grade vegetable oil sources as feedstock for biodiesel in Indian context.

1.2 Background

India ranks third in terms of consumption of fossil fuels after China and the USA. Consumption grew by 2.3% in 2019 with a global share of 5.8%. Petroleum based fuel is the second largest energy source (239.1 million tons oil equivalent) after coal (452.2 million tons oil equivalent). The transportation fuel in India is mainly petroleum based diesel and the consumption is recorded at 83.5 million tons during 2018-19 [2].

The recent BS-VI in India, effective from 2020, is a stringent emission norm for diesel engines. The new pollution norm involves the reduction of NOx by 68% and particulate matter by 82-93% [3]. The fuel for diesel engines should burn clearly, which can be achieved by the inclusion of oxygenated fuel, i.e., biodiesel in petroleum based diesel fuel.

In the global context, the surplus of edible oils such as Rapeseed in Europe, Canola in Canada, Soybean in the USA, and Palm oil in Malaysia and Indonesia are the available feedstocks for biodiesel. In the Indian scenario, the requirement of edible oil is met by import. India imports Palm oil from Malaysia and Indonesia, and Soybean from Argentina and Brazil, and Sunflower from Ukraine and Russia. The import of vegetable oil was 150.02 lakh tons during 2017-18, which increased to 155.49 lakh tons during 2018-19 [4]. The import of edible oils for the last five years is shown in Table 1.1 [5]. The non-food vegetable oils may be a potential source of biodiesel feedstock.

There are over 300 different species of oilseed plants grown in India. Various tree borne oilseed derived oils are not suitable for human consumption due to the presence of toxic components, for example karanjin and pongamol in Pongamia oil, azadirachtin in neem oil, ricin in Castor oil, and phorbol esters in Jatropha oil. These tree-borne oilseeds require agricultural inputs in the initial period and rarely require any expense associated with its maintenance once fully grown. It can also be a cost-effective way to produce oilseed. The production for tree borne oilseed is about 3.0-3.5 million metric tons whereas 0.5-0.6 million tons of seed are collected [6]. The potential non-edible oilseed plants are Jatropha (*Jatropha curcas*), Karanja (*Pongamia pinnata*), Mahua (*Madhuca indica*), Nahor (*Mesua ferrea*), Rubber (*Hevea brasiliensis*), Castor (*Castor communis*), Neem (*Azadirachta indica*), Sal (*Shorea robusta*), Undi (*Calophyllum inophyllum*), Simarouba (*Simarouba glauca*), etc. Oil derived from tree born oilseed plants such as Neem, Castor, and Sal find specific applications. Neem oil containing azadirachtin is a natural pesticide and emulsifier in the agricultural sectors. The Castor oil with ricinoleic acid in the triglyceride has

Table 1.1 Import of major edible oil by India (in Lakh Tons) [s].

Year	Palm oil		Soybean		Sunflower	
	Crude	**Refined**	**Crude**	**Refined**	**Crude**	**Refined**
2015-16	71.1	25.7	39.6	0.0	14.9	0.0
2016-17	53.6	29.4	34.6	0.0	17.3	0.0
2017-18	67.5	27.7	31.5	0.0	22.5	0.0
2018-19	64.2	25.2	31.7	0.3	25.8	2.0
2019-2020 (April-Sept)	30.2	19.0	16.8	0.2	10.8	0.0

high viscosity and finds commercial application as a precursor for polyurethane, lubricant, binder, etc. Fat derived from the Sal tree is used as cocoa butter substitute for manufacturing of chocolates. With these exceptions, the rest of the oilseeds may be feedstock for biodiesel.

Various missions at national and state levels were made to promote the cultivation of oilseed crops. Pongamia and Jatropha were selected as suitable oilseed plants for plantation in the waste and degraded lands, avenue plantations, and perimeter fencing. Massive plantation of Jatropha has been carried out in the Chhattisgarh state and similarly, Pongamia in the Karnataka state of India. These are in addition to the existing potential of oilseed in the country.

1.3 Non-Edible Oil as Feedstock for Biodiesel

The biodiesel derived from vegetable oil should have properties as per EN 14214:2012 A1:2014 or IS 15607:2016 specifications. Properties such as iodine value, linolenic acid methyl ester, and oxidation stability are dependent upon the qualities of the feedstock. The physico-chemical properties of oils are listed in Table 1.2 [7, 8] and their fatty acid compositions in Table 1.3 [7, 9–12]. The saponification value (SV) and the iodine value (IV) are indicative of structures such as chain length of fatty acid and degree of unsaturation of fatty acids in the triglyceride. The cetane index (CI) is related to the saponification value and iodine value as per Equation (1.1) and the cetane number (CN) is related to the cetane index as per Equation (1.2) [9]. The MW_{oil} (weight average molecular weight of the oil) is calculated from the saponification value as per Equation (1.3) and the requirement of methanol for transesterification is calculated based on the MW_{oil}.

$$CI = 46.3 + \frac{5458}{SV} - 0.225 \times IV \tag{1.1}$$

$$CN = CI - 1.5\ to + 2.6 \tag{1.2}$$

$$MW_{oil} = \frac{56100}{SV} \tag{1.3}$$

Table 1.2 Physico-chemical characterisation of potential non-edible oils for biodiesel feedstock.

Sl. no.	Oil	Physical appearance at room temperature	Acid value	Iodine value	Saponification value	Unsaponifiable matter (%)
1.	Jatropha	Yellowish clear liquid	5-8	93-107	188-196	0.4-1.1
2.	Pongamia	Dark yellow to orange clear liquid	1-11	85-90	185-195	3.0
3.	Mahua	Pale yellow with semi solid fat	Up to 20	58-70	187-196	1-3
4.	Nahor	Dark brown or red viscous liquid	100	87	193-209	2.9
5.	Rubber	Dark brown liquid	84	131-148	190-195	1.83

Table 1.3 Fatty acid composition of potential non-edible oils for biodiesel feedstock.

Fatty acids	Percent fatty acid composition of oils				
	Jatropha	Pongamia	Mahua	Nahor	Rubber seed
Myristic acid ($C_{14:0}$)	-	-	0.13	2.72	-
Palmitic acid ($C_{16:0}$)	13.4	11.65	19.6	9.76	9.3
Palmitoleic acid ($C_{16:1}$)	0.3	-	-	-	-
Stearic acid ($C_{18:0}$)	5.8	7.50	25.9	13.45	8.4
Oleic acid ($C_{18:1}$)	40.9	51.59	37.3	58.12	25.4
Linoleic acid ($C_{18:2}$)	39.6	16.64	15.8	12.64	41.1
Linolenic acid ($C_{18:3}$)	-	-	-	-	15.3
Arachidic acid ($C_{20:0}$)	-	1.35	0.21	3.14	-
Eicosenoic acid ($C_{20:1}$)	-	-	0.15	-	-
Behenic acid ($C_{22:0}$)	-	4.45	-	-	-
Lignoceric acid ($C_{24:0}$)	-	1.09	-	-	-

The non-edible oils have been reported to have unsaponifiable matters and the lipid associates, as shown in Table 1.2, are required to remove these either by pretreatment or post-transesterification process.

The industrial scale of biodiesel production units set up worldwide employs homogeneous catalysts (methoxides or hydroxides of sodium or potassium) for transesterification, which is an efficient and cost-effective method for production of biodiesel in order to meet the fuel qualities as per biodiesel specifications. Among the homogeneous alkali catalytic process, sodium methoxide and potassium methoxide result in higher selectivity of the product with rare formation of byproducts [13]. The methoxide catalyzed transesterification of vegetable oils requires a low reaction temperature, about 60–65°C at atmospheric pressure, and the reaction is completed in a short reaction time. The methoxide catalyzed process results in complete conversion of the triglyceride oil in order to ascertain that produced biodiesel attains methyl ester content > 96.5% and the free glycerol and total glycerol within the limits specified by EN 14214 and IS 15607 biodiesel specifications. The catalytically active species is the methoxide ion, which is generated by dissolution of hydroxides in methanol [9]. The biodiesel feedstock, i.e., vegetable oil for the methoxide catalyzed transesterification mush, have free fatty acid less than 0.1%, moisture less than 0.1%, and phosphorus content less than 10 ppm as per the requirements specified by biodiesel manufacturers such as Lurgi and Desmet Ballestra [9]. The phosphorus content in biodiesel is permissible up to 4 ppm, as per revised specifications, and the pretreated oil should have the phosphorous content accordingly. The required specification of feedstocks may be achieved by pretreatment of the crude vegetable oil. The feedstock of the above mentioned specification, methanol, and catalyst sodium methoxide solution are allowed to act as the reaction vessel for transesterification. The required molar ration of methanol to triglyceride is 3:1, whereas 100% excess methanol is used during the process in order to ascertain the completion of reaction and the excess alcohol is recovered for further use. The completion of reaction is necessary to have methyl ester content above 96.5% and the triglycerides and partial glycerides within the maximum specified limit. The transesterification vessels are designed so that the reaction is accomplished in two or three steps. The glycerol formed in between the steps is removed and as a result, the reaction proceeds towards completion in a short time. The transesterification products are allowed to stand so that glycerol is separated due to high polarity and density and the biodiesel layer containing excel methanol and the residual catalyst is further washed and dried. The B-20 blend of biodiesel and diesel with a volume ratio of 20:80 is being used in the unmodified diesel engines and the targets are made to use B20 fuel as per the National Mission of Biofuels.

1.3.1 Jatropha

Jatropha (*Jatropha curcas*) is a shrub native to the tropical areas of Mexico and Central America and is presently being naturalized in the different parts of the globe as a potential plant to produce biodiesel feedstock. Jatropha is a small tree that starts flowering after one year and the economic yield starts after the third year of plantation. The plant starts flowering (Figure 1.1a) during summer and monsoon and male and female flowers are produced on the same inflorescence. The green fruits ripen, changing to yellow and are dried to black, contain three seeds, and its shape resembles castor seeds (Figures 1.1b and 1.1c). As an initiative for biodiesel in India, Jatropha plantation was carried out in an area of about 0.5 million hectares of low-quality wasteland [14]. Commercial scale plantations of Jatropha were carried out in low-quality and degraded land in the state of Chhattisgarh and the produced oil is being utilized as feedstock for biodiesel. The oil content in the Jatropha seed varies from 24 to 40%. The major fatty acids are palmitic acid, stearic acid, oleic acid, and linolenic acid, with the last two accounting for more than 80% w/w. The physico-chemical qualities of Jatropha oil are listed in Table 1.2 and the fatty acid composition is shown in Table 1.3. The Jatropha oil contains phorbol esters generally known for tumor promoting activities, making the oil toxic.

The preparation of biodiesel involves pretreatment to remove the fatty acids. The homogeneous alkali-transesterification of pretreated Jatropha oil is conducted where the hydroxide or methoxide of sodium or potassium is used as catalyst. The post transesterification process involves the separation of excess methanol, catalyst, glycerol, and moisture to get the biodiesel. The fuel qualities of Jatropha based biodiesel have been reported to be as per IS 15607 specifications. The high cetane number, favorable fatty acid composition, and fuel qualities as per specifications make the Jatropha a potential candidate for biodiesel feedstock and therefore, massive cultivation has been initiated in the country. The vulnerable qualities of biodiesel are the oxidative stability and the acid value. Processes have been developed to prepare biodiesel with low acid value [15] and enhanced oxidative stability by suitable additives.

In India, the government initiated the National Mission on Biofuels in 2003 and selected Jatropha as a potential biofuel crop since the plant has a low gestation period, hardy nature, is resistant to draught and flood, is not browsed by cattle, and requires a small plant to collect seeds. It has been observed that Jatropha cultivation lead to improved soil fertility, contributed to the reduction of soil erosion, helped in the rehabilitation of lands through greening, and created jobs for the local population in the rural areas.