Biodiesel Production from Seeds Oil of *Melia azedarach* L. by Using Bronsted Acidic Ionic Liquid as Catalyst

By

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It is to certify that the research work presented in this thesis, entitled **"Biodiesel Production from Seeds Oil of *Melia azedarach* L. by Using Bronsted Acidic Ionic Liquid as Catalyst"** was conducted by **Iqra Safdar (Reg. No. 02312111011**) under the supervision of **Dr. Mazhar Iqbal**. No part of this thesis has been submitted else for any other degree. This thesis is submitted to the **Department of Environmental Sciences,** in the partial fulfillment of the requirements for the degree of **Master of Philosophy** in the field of **Environmental Science**, Department of Environmental Sciences, Quaid-i-Azam University Islamabad, Pakistan.

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Ameen

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ABBREVIATIONS	PHRASE
CO	Carbon Dioxide
SOx	Sulphur Dioxide
NOx	Nitrogen Dioxide
ASTM	American Society for Testing and Materials.
FTIR	Fourier Transform Infrared Spectroscopy
(GC-MS)	(Gas Chromatography Mass Spectroscopy
EO	Extracted Oil.
IL	Ionic Liquid
CB	KOH Catalyzed Biodiesel
KOH	Potassium Hydroxide
ILB	Ionic Liquid Catalyzed Biodiesel
AV	Acid Value
PV	Peroxide Value

ABSTRACT

World demand for energy and concerns about the environment have sparked interest in renewable fuels such as biodiesel. This work describes the extraction and trans-esterification of biodiesel from Melia azedarach L. seeds utilizing KOH and 1-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulphate, a Bronsted acidic ionic liquid (IL), as catalysts. The effects of reaction parameters such as oil to methanol ratio, time, temperature, and catalyst dose were optimized to improve the biodiesel yield. Results showed that IL catalyzed biodiesel had 100% yield under optimized conditions of 120 minutes, 80 °C, 1% (*w/w*) catalyst dose, and 1:9 oil to methanol ratio. On the other hand, KOH catalyzed biodiesel had 97% yield under optimized conditions of 90 minutes, 100 °C, 1% (*w/w*) catalyst dose, and 1:6 oil to methanol ratio. Both biodiesels met the ASTM standards for biodiesel with respect to acid value, saponification value, peroxide value, iodine value, density, high heat values, cetane numbers, flash points, and pour points. Linoleic acid (79.69%) was discovered to be prominent in Melia azedarach L. oil after fatty acid characterization by GC-MS. Further FTIR analysis showed that the functional groups were successfully implemented in the IL as well as biodiesel. The study concludes that *Melia azedarach* L. seeds can be used to produce biodiesel at low cost, and IL catalyzed biodiesel results in higher quality biodiesel than KOH. The research has practical consequences for the quest for alternate and renewable energy sources, and it may help to reduce the harmful environmental effects of fossil fuels.

CHAPTER 1

INTRODUCTION

The global population continues to grow at an unprecedented rate, resulting in a sharp increase in energy demand. According to Kiakalaieh *et al.* (2013), global energy demand is expected to rise by 53% by 2030 compared to 2001. As of 2021, the US EIA (Energy Information Administration) recorded a total global consumption of petroleum and other fuel sources at 97.4 million barrels per day (b d^{-1}). The EIA also predicts a rise in the usage of these resources, with estimates of 99.4 and 101.5 million b d^{-1} for the years 2022 and 2023, respectively. However, in 2021, a 5.8% increase in primary energy demand was noted, with 82% of fossil fuels being used to meet this demand, resulting in an increase in carbon dioxide emissions of 5.7-5.9% compared to 2019 CO_2 emission data, which is a total of 38,976.6 million tons per year. This rise in demand, consumption, and industrial processes are the primary cause of these increased emissions. Figure 1.1 illustrates the world consumption of oil in different years (Statistical Review of World Energy 2022). The largest fuel-consuming countries are the OECD (Organization for Economic Cooperation and Development) participating countries, with the transportation sector being the most oil-intensive sector in the OECD. In 2020, automobile consumption accounted for 48.6% of all oil burned in the OECD, while the petrochemical industry, which produces plastics, resins, and other petroleum goods, accounted for 16.2% of the total (Figure 1.2).

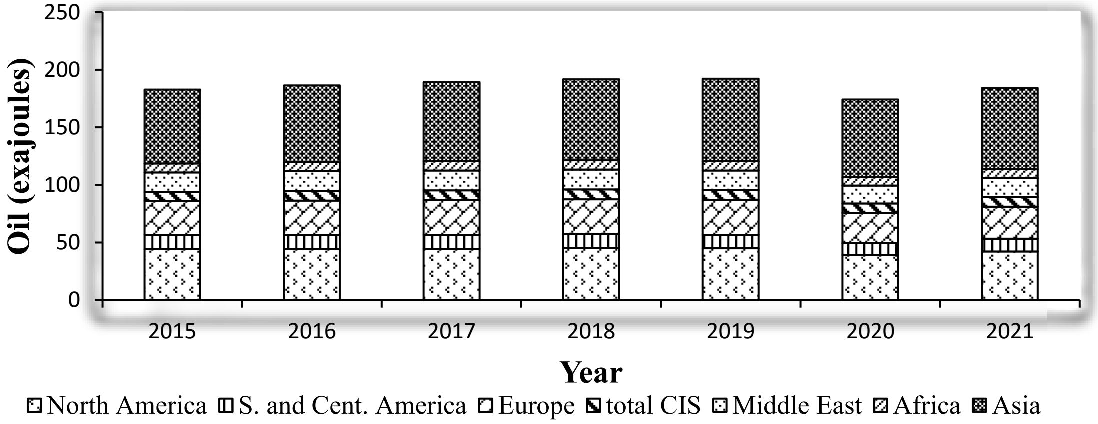


Figure 1.1. World oil consumption from 2015 – 2021 in exajoules (Statistical Review of World Energy 2022.

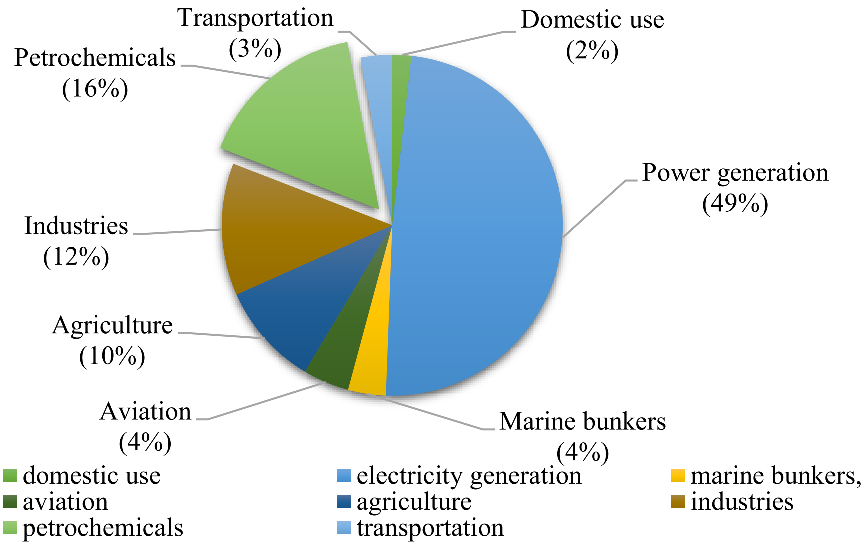


Figure 1.2. Oil Demand Division in The OECD By Sector In 2020 (Statista 2022).

The need for sustainable and environmentally friendly alternative fuels has become increasingly important due to the dwindling supply of fossil fuels and rising oil prices. Rudolf Diesel's invention of the vegetable oil-fueled engine in the 1900s was a first step towards this goal, but direct use of oil is not practical. The development of biodiesel, which started in the 1980s due to increasing interest in alternative energy sources for reducing greenhouse gas emissions and mitigating the depletion of fossil fuel stocks, has gained attention as a promising alternative to reduce dependence on fossil fuels. The American Society for Testing and Materials (ASTM) defines biodiesel as mono alkyl esters derived from lipid raw materials such as plant-based oils or fats from animals (Damanik *et al*., 2018). Its eco-friendly aspects make it an attractive alternative energy source.

1.1. Biodiesel

Biodiesel has gained significant attention in recent years due to its potential as an eco-friendly alternative to traditional fossil fuels. It is produced from various types of biomasses, including plant, algal, and animal waste, with triglycerides being the primary components of animal fats and vegetable oil. Transesterification, a chemical process that converts oil or fatty acids with alcohol in the presence of a catalyst, is used to manufacture biodiesel from biomass. Biodiesel has been found to emit lower levels of CO, greenhouse gases, and particulate matter compared to commercial diesel and can enhance the biodegradability of pollutant or oil-contaminated sites. Biodiesel's emergence as one of the most preferred biofuels is due to its biodegradability, non-toxicity, and low pollutant emissions. However, biodiesel production still has significant limitations, including high capital costs, limited availability of non-edible oils, and high costs associated with raw materials such as palm oil, castor oil, canola oil, and coconut oil. These limitations have implications for food security and fuel shortages. Figure 1.3 outlines the overall process of biodiesel production. Several studies have indicated that biodiesel is a sustainable and environmentally friendly alternative to traditional fossil fuels (Nabi *et al*., 2017; Pikula *et al*., 2019; Kim *et al*., 2018; Panahi *et al*., 2019; Mikulcic *et al*., 2020; Ng *et al*., 2015).

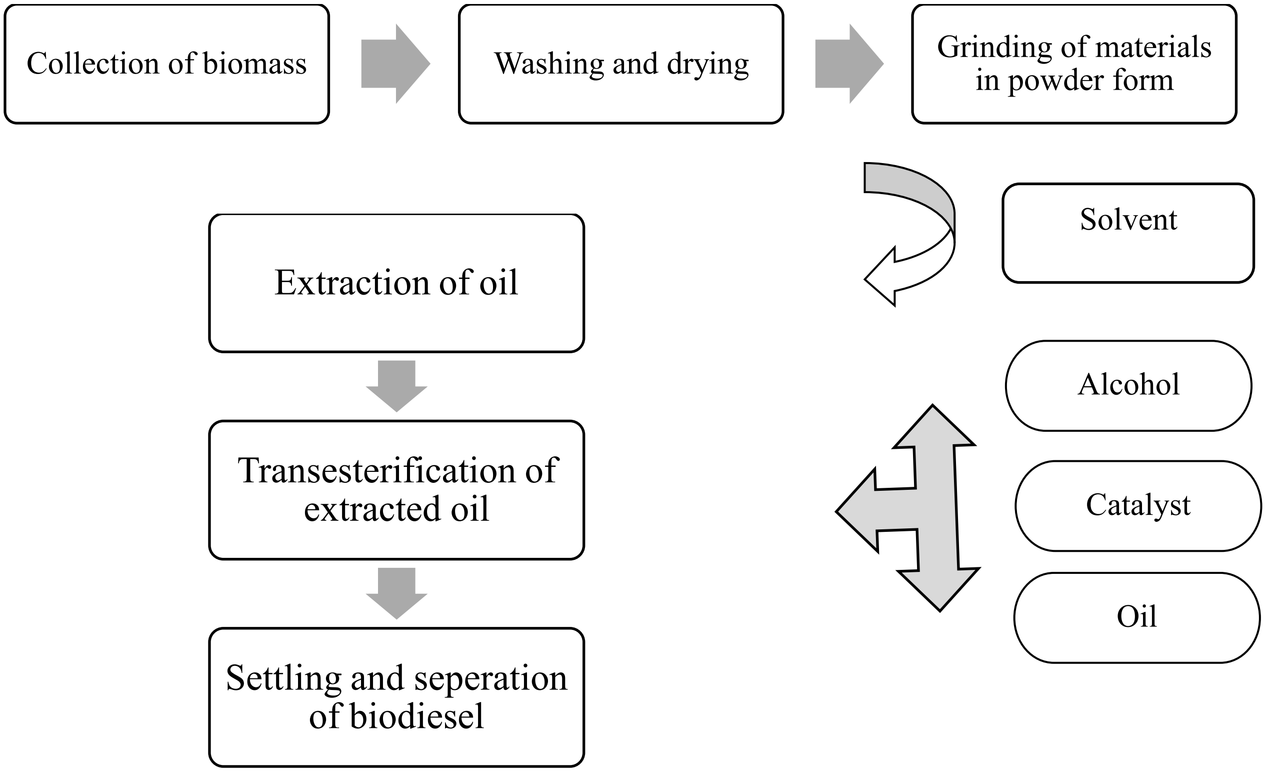


Figure 1.3. Step by step process of biodiesel production.

1.2. Feedstock Selection

The production of biodiesel requires the selection of a suitable biomass source, which is largely influenced by the feedstock's fatty acid content (Sitepu *et al*., 2020; Anwar *et al*., 2019). The properties and yield of biodiesel are directly influenced by the type of feedstock used (Singh *et al*., 2019; Ong *et al*., 2020). Based on the source of feedstock, biodiesel is categorized into four generations (Alalwan *et al*., 2019):

1. Edible plant or oil,

2. Non-edible plant source, animal fat, and waste cooking oil,
3. Algae.
4. Genetically modified organisms.

1.2.1. First Generation Feedstock

The first-generation biodiesel, which used consumable plant sources for oil production, was initially popular due to the easy availability of oil and simple production methods (Avhad *et al.*, 2015). However, almost 90% of biofuel feedstock is edible oil, which leads to instability, land requirement, deforestation, biodiversity loss, environmental problems, and high costs (Kim *et al.*, 2018; Singh *et al.*, 2020). Table 1 shows research studies on the use of first-generation feedstocks for biodiesel synthesis.

1.2.2. Second-Generation Feedstock

Biodiesel manufacturing from non-edible feedstocks has grown popular and is an increasingly attractive alternative to mitigate the problems associated with first-generation feedstocks. The use of waste cooking oil (WCO), animal fat, and various non-edible seeds and plants with high-fat content has shown promise as second-generation feedstocks for biodiesel production. Utilizing these feedstocks not only reduces the impact on food shortages but also addresses environmental concerns while being cost-effective (Foteinis *et al.*, 2020). However, the high free fatty acid (FFA) content in WCO poses a challenge to the yield of biodiesel. WCO can be categorized into two groups based on their FFA value:

- FFA < 15%, known as yellow oil.
- FFA > 15%, known as brown oil.

Yellow grease is highly utilized for biodiesel production and can be easily filtered out (Outili *et al.*, 2020). In this context, research studies have investigated the use of non-edible seeds and plants for biodiesel synthesis, including orange seeds, vegetables, and fruit peels (Dhanasekarana, 2016). Such studies have evaluated various properties of the produced biodiesel, including viscosity, density, and flashpoint. Advanced research studies are also available in the literature, as shown in Table 1.1.

1.2.3. Third Generation Feedstock

Third generation feedstock for biodiesel production has gained significant attention due to its numerous benefits, especially algae-based oil. Algae can be grown naturally or artificially in an environment that fulfills their basic needs, as a result, they are a viable non-consumable oil source for biodiesel manufacturing. (Al-Ameri *et al*., 2019). The oil content of algae ranges from 40-80%, making it a better choice than other feedstocks (Song *et al*., 2015). Algae species such as *Chlorella vulgaris*, cyanobacteria, and *Chlorella minutissima* have been extensively studied (Moravvej *et al*., 2019). Moreover, algae-based biomass sources are advantageous because they can easily grow in water and produce a higher biomass content per unit area than other plant sources (Sharma *et al*., 2020).

Lipid extraction is a critical phase in biodiesel production, with various parameters affecting the yield, including oil and alcohol molar ratio, catalyst dosage, reaction temperature, and retention time. Bharathi raja *et al.,* 2019, reported an 87.5% yield of biodiesel using Nano *Chloropsis oculata* algae under optimum conditions of 60 °C temperature, 4-hr reaction time, 5:1 oil and methanol ratio and 3.5% catalyst concentration. Advanced research studies on algae-based biodiesel production are available in the literature, (Table 1.1).

Choosing the right microalgae species for biodiesel production requires considering factors such as fast expansion rate, high content of FFA or oil, environmental sensitivity, immunity to different microalgae species, pathogenic illnesses, carbon dioxide level sensitivity, and oxygenation (Tan *et al*., 2018; Maghraby *et al*., 2015; Zhao *et al*., 2019; Struckas *et al*., 2017).

1.2.4. The Fourth-Generation Feedstock

The fourth-generation feedstock now has a path thanks to the recent advancements in synthetic biology. Using a biological system that was specifically built using solar energy, a renewable and affordable biodiesel feedstock could be created (Single *et al*., 2020). If the species isolated from nature are unsuitable for commercial use, employing metabolic and genetic engineering to improve the features of oil-producing bacteria might be a viable option for biodiesel production. (Abdullah *et al*., 2019).

In recent studies modified algae species was studied for biodiesel purpose. The major goals of microalgal modification are increased lipid and carbohydrate metabolism, enhanced cell disintegration, flocculation, hydrogen generation, greater nutrient usage efficiency, higher stress tolerance, and improved photosynthesis (Bharadwaj *et al*., 2020). Furthermore, by triggering autolysis and product secretion systems, genetic engineering can help in the production of oil from algal biomass.

Even though the fourth generation of biodiesel is still in the initial stages of research, it may eventually overcome the drawbacks of the prior three generations and substitute fossil fuels in the most efficient manner (Aro *et al*., 2016).

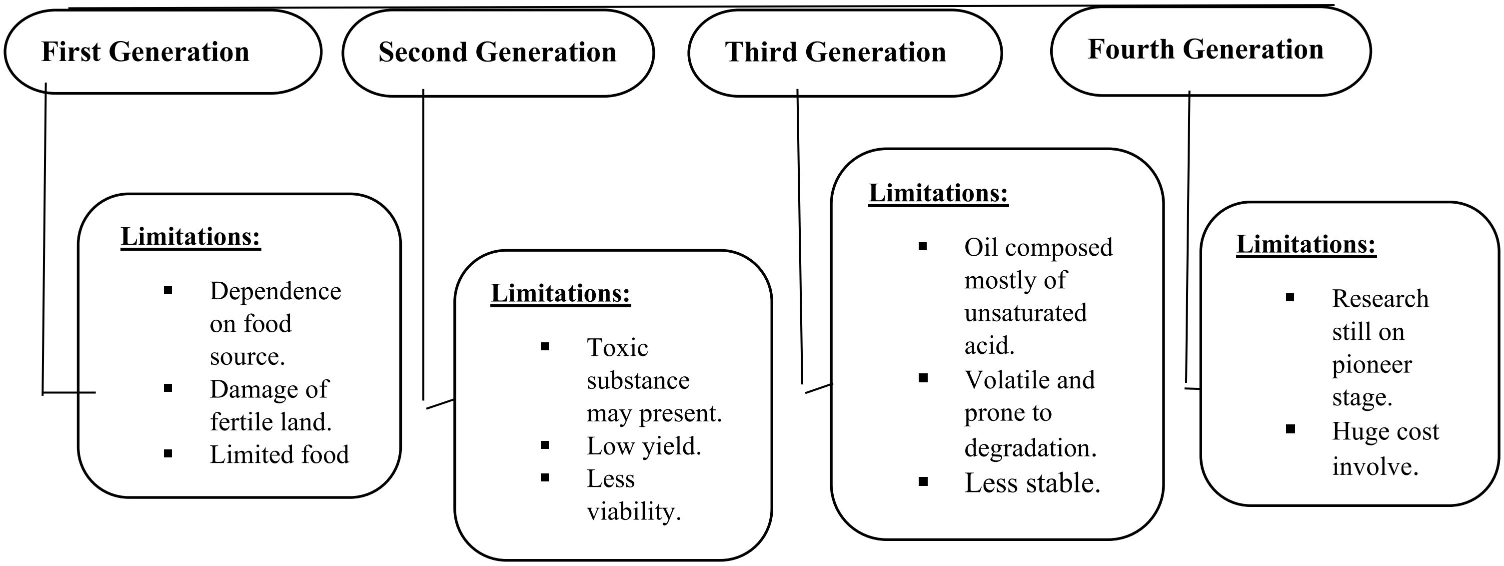


Figure 1.4. Limitations of generations of feedstock for biodiesel (Singh *et al*., 2020).

Table 1.1.

Synthesis of biodiesel from non-edible oil.

Feedstock		**FFA (%)**	**Catalyst used**	**CD % (w/w)**	**M:O**	**T (°C)**	**Rp**	**Yield (%)**	**Reference**
Waste Cooking oil	Waste cooking oil (cafeteria)	2.38	fused crab shell and plantain peels	5	13.03:1	60	149.94	93	(Amenaghawon *et al*., 2022)
	Waste cooking oil (fast food restaurant)	-	$LaPO_4$ supported nickel foam	2.5	5:1	90	120	91	(Rezania *et al*., 2021)
	Waste cottonseed cooking oil		KOH	0.50	6:1	50	10	98	(Oza *et al*., 2021)
	Waste cooking sunflower oil	-	CaO	1.5	6:1	60	60	93	(Topare *et al*., 2021)
	Waste cooking oil (restaurant)	-	KOH/Clinoptilolite	8.1	1:2.24	65	13.4	97.45	(Mohadesi *et al*., 2019)
Seeds	*Styrax officinalis* L. oil	1.94	NaOH	0.6	6:1	60	60	89.23	(Yesilyurt *et al*., 2020)
	Euonymus maackii Seed oil	-	phosphotungstic acid	2	10:1	60	40	94.74	(Liu *et al*., 2019)
	Croton macrostachyus seed			1	6:1	50		96	(Aga *et al*., 2019)
	Elaeagnus angustifolia. L seed	-	KOH	1	9:1	60	60	95	(Kamran *et al*., 2020)
	Annona squamosa seed oil		H_2SO_4	3.5	9:1	60	60	88	(Parthiban *et al*., 2021)
Algae	Microalgae	-	SO_4 2−/Fe_3O_4-Al_2O_3	8	9:1	120	240	87.6	(Safakish *et al.,* 2020)
	Dry algae	-	NaOH, H_2SO_4	3.361	8:1	50	60.4	87.42	(Chamola *et al*., 2020)
	Algae oil, sunflower oil	1	NaOH	1.392	6:1	50	130	95	(Khan *et al*., 2020)
	Microalgae *Spirulina sp*	0.05	KOH	1	5:1	60	120	85.28	(Pradana *et al.,* 2020)
	Dried microalgae (95% *Chlorella vulgaris*)	-	NaOH	2	12:1	60	30	88	(Cercado *et al.,* 2018)
Sludge	Tannery sludge	-	H_2SO_4	3	25:1	60	720	89.7	(Kumar *et al.,* 2020)
	Water treatment sludge	-	H_2SO_4	5	15:1	100	130	97	(Junior *et al*., 2020)
	Activated sludge of milk processing plant	-	NaOH	0.8	6:1	55	40	97.4	(Balasubramanian., 2018)
	Sludge of edible oil industry	-	Cupriferous mineral nano catalyst	5	9:1	75	180	94	(Ngoie *et al*., 2020)
	Sludge palm oil	-	Biocatalyst	2	3:1	40	240	91.30	(Muanruksa *et al.,* 2020)

CD = FFA = Free Fatty Acid, CD = Catalyst Dosage, M:O = Methanol ratio oil, T = Temperature, Rp = Reaction period.

1.3. Oil Extraction Methods

Oil extraction is a crucial step in the production of edible oils and biofuels. The extraction procedure is critical in assessing purity, efficiency, and effectiveness of the oil produced. According to Tahir *et al*. (2019), the extraction procedure has a considerable impact on the oil's quality. There are three main types of extraction methods used in the industry, namely mechanical, solvent, and enzyme extraction. Advanced methods may involve a combination of these methods. However, large-scale solvent extraction is the preferred method, as stated by Rutz *et al*. (2008).

1.3.1. Mechanical Extraction

Mechanical extraction is the most used method, and it involves the use of screw or ram press machines powered either by human or motor energy. To achieve the best oil production, the design of the press is crucial, as highlighted by Atabani *et al*. (2012). Additionally, pre-treatment of oilseeds is necessary to tenderize them and improve oil output, which is achieved through techniques such as roasting or steam heating, as mentioned by Ahmad *et al*. (2015). However, repeatedly passing the oilseed or oil fruit through the mechanical press can also increase oil production, with both advantages and disadvantages (Table 1.2).

1.3.2. Solvent Extraction

The method of extracting a solid's component using a liquid solvent is known as solvent extraction. Solvents come in two different varieties: polar and non-polar. Alcohol, acetone, and isopropanol are a some of the examples of polar solvents. Non-polar solvents include toluene, chloroform, hexane, and n-pentane. Hexane performs best among these solvents in terms of oil production. There are some advance solvent extraction methods which are describe as:

1.3.2.1. Accelerated Solvent Extraction

The novel extraction technique known as ASE can be employed in place of more traditional extraction procedures like sonification and Soxhlet extraction this new extraction method aimed to shorten the extraction process and utilize less organic solvent by applying high pressure and high temperature above boiling point. Increased temperature can result in high oil yield because it loosens the biomass's cell walls and increases the solubility of lipid in solvent (Karim *et al.,* 2020).

Using the ASE approach with n-hexane as the solvent, Paul Hellier *et al.* (2018) stated that they were able to extract oil from used coffee sample with 64% oil yield at 70 °C (n- hexane boiling point) before raising the temperature to 145 °C, where they obtained an 85% oil yield. That explains how temperature may boost oil production up to a particular degree. to get the maximum yield.

1.3.3. Microwave Assisted Extraction (MAE)

Microwave heating immediately transforms electrical energy into heat. This concept enabled microwave-assisted oil extraction by focusing thermal energy on the seed and utilising a polar solvent. The type and quality of feedstock used, microwaves intensity, the volume and properties of the solvent used, and the temperature are the primary factors of MAE extraction efficiency. (Krishnan et al., 2020).

MAE usage was reported by Hu *et al*. (2021) in which they followed certain steps in the extraction process: the seed kernel powders (20 g) and 200 ml of solvent, were added to a two-neck round bottom flask. A reflux condenser and a temperature sensor were individually linked to the flask's left and right neck sections. Then, in accordance with the needs of the experiment, microwave extraction was carried out at 300 W of powers with boiling temperature of n-hexane and 40 mins time. Following MAE, filter paper was used to filter the suspension, and a rotating vacuum evaporator recycled the solvent at a temperature of 55 °C. The 25% oil yield was determined.

1.3.4. Ultrasound-Assisted Extraction (UAE)

The search for sustainable and eco-friendly extraction methods has led to the development of innovative techniques such as ultrasound-assisted extraction (UAE) and aqueous enzymatic extraction (AEE) of biomass oil. UAE uses ultrasound to induce high- and low-pressure cycles, creating intense liquid jets during cavitation that physically damage the cell makeup of the material, promoting mass transfer and making oil extraction easier (Tiwari *et al*., 2015). AEE, on the other hand, offers numerous benefits, including minimal energy utilization, product safety, gentle process conditions, and simultaneous segregation of protein and oil (Gao *et al*., 2021).

1.3.5. Aqueous Enzymatic Extraction (AEE)

Enzymes are used in this approach such as cellulase, hemicellulase, phospholipase, pectinase, and protease to break down the cell walls of organic materials and encourage the extraction of oils, with some studies suggesting that enzyme combinations are more effective than single enzymes (Zhang *et al.*, 2007). Additionally, commercially available enzymes can degrade cellulose, hemicellulose, and pectin, further boosting oil recovery (Mwaurah *et al.*, 2020). Table 1.2 provides an overview of the advantages and disadvantages of this method.

Table 1.2.
Benefits and drawbacks of oil extraction methods

Extraction Techniques	Benefits	Drawbacks	Reference
Mechanical extraction	• Less time consumption. • Cost effective. • Environment loving technology. • No use of harmful chemicals.	• Oil contains unwanted impurities like phosphatide. • Less amount of oil extracted. • By product still contain large amount of oil. • Oil press type determined the yield.	• (Jahirul *et al.*, 2013) • (Mohiddin *et al.*, 2021)
Solvent extraction	• High quality product. • High yield of extracted oil. • Cost effective because solvent can be recovered.	• Not so environmentally friendly. • Need for special instruments. • Use of volatile solvents like n-hexane.	• (Sakurag *et al.*, 2019) • (Mubarak *et al.*, 2015)
Enzymatic extraction	• Environment safe method. • Use plant-based material for extraction. • Oil content contain less FFA content.	• AEE has extra step of demulsification. • Cost of enzyme is high. • Time taking process.	• (Mohiddin *et al.*, 2021) • (Pikula *et al.*, 2020)

1.4. Biodiesel Production Methods

There are several methods that may be used to produce biodiesel, including direct usage, or mixing, Cracking by heat (pyrolysis), micro emulsion, and transesterification, which is the most common. since this process is simple, can be used under typical circumstances, and provides the greatest conversion and fuel efficiency.

- Direct usage of oils has typically been regarded as undesirable and unfeasible. There are several evident issues with this product, such as its high viscosities, acid component, free fatty acid concentration owing to degradation, polymerization during preservation and thickening of the crude oils. Whereas oils lose the density and viscosity as a response of dilution or blending. adding 4% ethanol to petroleum diesel improves performance. (Gebremariam *et al*., 2017).
- By using micro emulsion method, the high viscosity problem can be solved by using solvents like ethanol. This method utilizes relatively less energy as well as it is simple and easy technique with no need of purification step (Zare e*t al.,* 2020).
- Pyrolysis or thermal cracking method involves the heating of a substance at a high temperature varying from 300 – 1300 °C without evolvement of air or oxygen as a result breakdown the chemical bond and convert the substance into smaller molecules (Karmakar *et al*., 2019).
- Transesterification is the process is which alcohol (methanol) and oil molecules react in a specific molar ratio like 3:1 stoichiometrically (although excess amount of alcohol is favorable) with the help of catalyst and as a product 3 molecules of FAME and 1 molecule of glycerol as a byproduct is formed (Hajjari *et al.,* 2017). The easiest chemical equation of transesterification is shown in Figure 1.5.

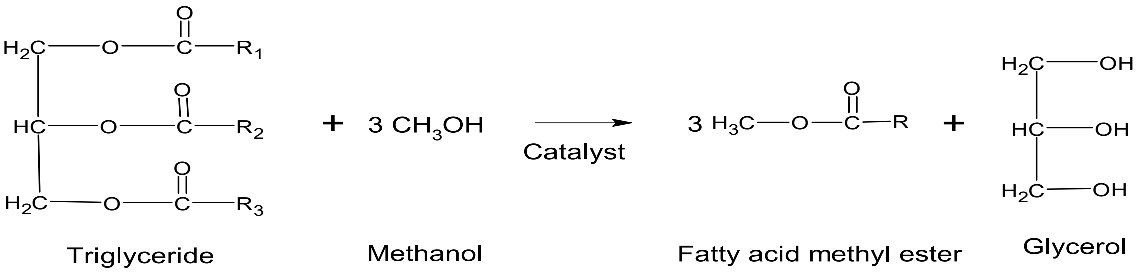


Figure 1.5. Transesterification process for biodiesel production (adopted from Wang *et al*., 2021).

It is well known that the catalytic transesterification process can make oil virtually as viscous as diesel, making it suitable for use in engines without any additional modifications. The effectiveness of transesterification is necessary to produce more biodiesel and basic catalyst performs better than weak acidic catalyst in the process.

Hence this review focuses on only catalytic transesterification of non-edible oil mentioned in Table 1.3. Transesterification could be utilized to make biodiesel in a variety of methods. Figure 1.6 depicts the basic schematics diagram for various potential methods.

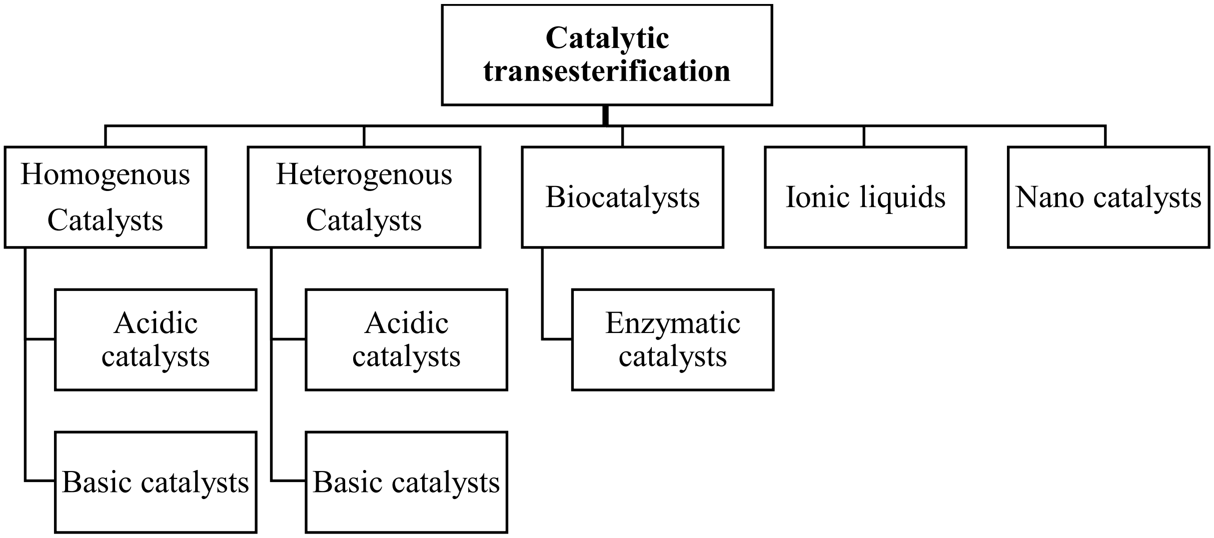


Figure 1.6. Classification of catalytic transesterification (Mohiddin *et al.*, 2021).

1.4.1. Homogenous Catalytic Transesterification

Biodiesel production using homogenous base catalysts is the most widely used technique in the industry. In this reaction triglycerides or oils are reacted with methanol in the presence of basic catalysts such as hydroxides, carbonates, or methoxide to create biodiesel and glycerol. However, the existence of moisture and free fatty acids (FFA) within the vegetable oil can cause soap synthesis, making separating glycerol from biodiesel difficult and reducing fuel quality. Acidic catalysts such as HCl, H_2SO_4, and H_2PO_4 are preferred when the FFA value of the oil is greater than 1% as they result in less soap production and easier glycerol removal, although they require a longer retention time than base catalysts. However, the use of acid catalysts is hazardous to machinery and storage, making it less commonly used in the industry (Williams *et al.*, 2015;

Pairiawi *et al.*, 2010; Lam *et al.*, 2010). Figure 1.7 shows the soap formation during the transesterification process (Akçay *et al.*, 2010).

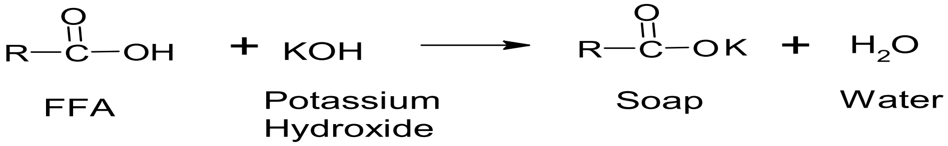


Figure 1.7. Soap formation during transesterification process (Akçay *et al.*, 2010)

1.4.2. Heterogeneous Catalytic Transesterification

Scholars have been enthralled by heterogeneous catalyst due to its capability to reduce chemical and time wastage. As a result of catalyst's excellent selectivity, separation of the catalyst from the product is simple (Al-Jammal *et al.*, 2016). Additionally, it is non-corrosive and reusable. Compared to homogeneous catalyst, it is less sensitive to both water and FFA (Uprety *et al.*, 2016). The three main categories of heterogeneous solid catalysts are acid solids that can catalyze the esterification of FFA, base solids that can catalyze the transesterification of oil, and dual-functional solids (acid-base personality) that can catalyze the transesterification of reactions all at once. (Borges *et al.,* 2012). Examples of acidic heterogeneous catalysts are ZnO/I_2, ZrO_2/ SO_4^{2-}, niobic acid, and sulfated zirconia. On the other hand, examples of basic catalysts are CaO, $CaZrO_3$, CaO-CeO_2, $Ca_2Fe_2O_5$, KOH/Al_2O_3 and alumina/silica supported K_2CO_3 (Mohiddin *et al.,* 2021).

1.4.3. Enzymatic Catalytic Transesterification

The process for producing biodiesel is typically catalyzed by basic or acidic catalysts, which have their own limitations in terms of soap formation, glycerol separation, and toxicity. To overcome these limitations, an alternative catalyst called an enzyme catalyst or biocatalyst has been developed (Semwal *et al.*, 2011). Lipases, a type of enzyme, have shown promising results in catalyzing the transesterification reaction on various oils with attractive properties such as low processing speed, reuse of enzyme, and resistance to heat and alcohol (Bajaj *et al.*, 2010). Recent studies have explored the use of lipases coupled with magnetic nanoparticles and genetically engineered free liquid lipases, resulting in high biodiesel yields from low-quality biomass and spent cooking oil, respectively (Sharma *et al.*, 2019; Chang *et al.*, 2020). Table 1.3 provides additional examples of reported works in this area.

1.4.4. Ionic Liquid Catalytic Transesterification

Ionic liquids, commonly known as salts, are made up of anions and cations with melting temperatures lower than 100 °C. (Fang *et al.*, 2014). The chemical characteristics of IL are primarily due to anions, while physical properties are due to cations. They are eco-friendly and easily recyclable, and their solubility in organic and inorganic solvents makes them ideal for various applications (Muhammad *et al.*, 2015). One of the key features of ILs is their adjustable structure, which can be modified by changing either the cation or anion. ILs have served the purpose of catalysts for transesterification and co-solvents in biodiesel synthesis (Gamba *et al.*, 2008). The resulting biphasic system in biodiesel synthesis allows separation of the synthesis biodiesel and glycerol from the insoluble IL layer. However, ILs are not without their limitations, including high cost and viscosity in liquid form (Gholami *et al.*, 2020).

Figure 1.8 shows the cations and anions of an ionic liquid (Ramadhan *et al.,* 2015), and Table 1.3 lists some reported works on the use of ILs in transesterification.

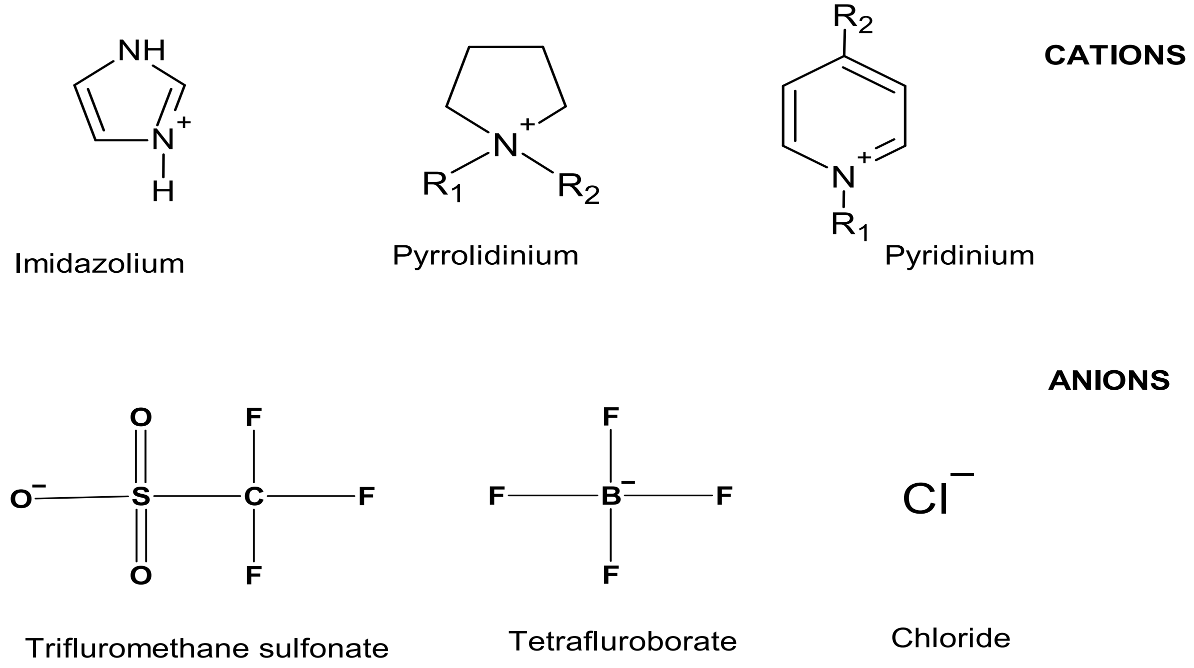


Figure 1.8. Cations and anions of ionic liquid (Ramadhan *et al.*, 2015).

1.4.5. Nano Catalytic Transesterification

Because of their great catalytic performance, nano-catalysts have gained special attention in the generation of biodiesel (Ambat *et al.,* 2018). The large surface area and surface charge of nano catalysts results in strong enzymatic performance. nano catalysts increase reaction sensitivity by letting reactions to take place at reduced temperatures, limiting the incidence of side reactions, increasing recyclability, and recovering energy costs (Sharma *et al.,* 2015). Nano-catalysts may be synthesis through Vacuum deposition and evaporation, gas condensation, precipitation, impregnation, sol-gel processing, and electrochemical deposition which are the most often employed processes (Rajput, 2015). Gupta *et al.* (2016) studied the nano particles fabrication and characterization of CaO to produce FAME from soybean oil. According to their findings, the Nano catalyst made from shell snail has excellent catalytic performance.

Table 1.3.
Types of catalyst used for biodiesel production.

Catalyst		**Feedstock**	**CD % *(w/w)***	**M:O**	**T (°C)**	**Rp**	**Yield (%)**	**Reference**
Homogenous acidic	H_2SO_4	Dry algae	3.361	8:1	50	60.4	89.58	(Chamola *et al*., 2019)
	H_2SO_4	*Sterculia foetida* oil and waste cooking oil	0.6	3:1	60	120	95	(Kavitha *et al.,* 2019)
	H_2SO_4	Waste cooking oil	5	12:1	60	180	95.37	(Dhawane *et al*., 2018)
Homogenous basic	NaOH	Sunflower oil	1.5	6:1	60	60	97	(Brito *et al*., 2020)
	KOH	Soyabean oil	1.5	12:1	60	60	95	(Brito *et al*., 2020)
	KOH	Waste cooking oil	1.16	9.4:1	62.4	60	98.26	(Mohadesi *et al*., 2019)
Heterogenous acidic	Nano-sulfated zirconia	Waste sheep fat	8	15:1	65	300	97	(Booramurthy *et al*., 2020)
	ZrO_2-TiO_2-SO_3H	Palmitic acid	5	20:1	100	300	98.6	(Fan *et al*., 2019)
	SO_4/Mg-Al-Fe_3O_4	Waste cooking oil	3	10:1	90	50	98.50	(Gardy *et al*., 2019)
Heterogenous basic	CaO	Soybean oil	3.68	11:1	60	120	97.61	(Bharti *et al*., 2019)
	Li/ZnO-Fe_3O_4	Rapeseed oil	0.8	12:1	35	58	99.8	(Kelarijani *et al*., 2020)
	Cobalt doped ZnO	*Mesua ferrea* oil	2.5	9:1	60	180	98.03	(Borah *et al*., 2018)
Enzymatic	Lipase enzyme	Waste cooking oil	1.5	3:1	60	240	88	(Jayaraman *et al*., 2019)
	Lipase-PDA-TiO_2	*Jatropha curcas* L. oil	10	6:1	37	1800	92	(Zulfiqar *et al*., 2021)
	Lipases from Candida rugosa and *Rhizomucor miehei*	Waste cooking oil	1	6:1	45	1440	96.5	(Binhayeeding *et al*., 2020)
Ionic liquid	[EDA-PS] [P-TSA]	Oleic acid	3	13:1	70	108	97.58	(Li *et al*., 2020)
	Fe_3O_4/graphene oxide-phenylalanine bisulfate ionic liquid	*Thlaspi arvense* L. Seed oil	25	10:1	60	240	92.38	(Zhao *et al*., 2021)
	$NiFe_2O_4$[BMSI] Br	Palm oil	5	12:1	80	480	74.6	(Naushad *et al*., 2021)
Nano catalyst	$NaAlO_2$-Al_2O_3	Palm oil	10.89	20.79:1	64.72	60	97.65	(Zhang *et al*., 2020)
	$Ni_{0.5}Zn_{0.5}Fe_2O_4$	Soybean oil	2	12:1	180	60	99.38	(Dantas *et al*., 2018)
	CaO/$CuFe_2O_4$	Chicken oil	3	15:1	70	240	94.52	(Seffati *et al*., 2019)

CD = Catalyst dosage, M:O = Methanol ratio oil, T = Temperature, Rp = Reaction period.

1.5. Effects of Transesterification Parameters on Biodiesel

1.5.1. Catalyst Types and Concentrations

The nature and quantity of the catalyst play a critical role in the transesterification process. The selection of basic or acidic catalysts depends on the FFA level of the feedstocks used. The quantity of catalyst also used effect yield of the biodiesel, with a higher concentration leading to an increase in yield due to the availability of more binding sites. However, using excessive catalyst can result in soap formation, slurry development, and higher viscosity, leading to uneconomical and ineffective production. On the other hand, using a lower amount of catalyst decreases biodiesel production, as fewer active sites are available for methanol binding. Therefore, finding the optimal amount of catalyst is crucial for transesterification, which depends on the methanol and oil ratio (Mansir *et al.*, 2017; Tan *et al.*, 2015; Korkut *et al.*, 2018).

1.5.2. Methanol and Oil Ratio

The molar ratio of methanol and oil is a significant factor that affects the transesterification process. Methanol is preferred over other alcohols due to its low cost and chemical properties. In the process, 1 mole of oil is transformed into 3 moles of FAME using 3 moles of methanol according to stoichiometric ratio. Excessive use of alcohol can increase biodiesel production by reacting with additional FFA present in the oil, but using an excessively high oil to methanol ratio can decrease biodiesel production by drowning the catalyst's active sites. Therefore, a balanced oil to methanol molar ratio is necessary for optimal biodiesel production. (Rehan *et al.*, 2018; Maneerung *et al.*, 2016; Gebremariam *et al.*, 2018; Lokman *et al.*, 2014).

1.5.3. Temperature

The temperature is a significant parameter in transesterification, affecting both the speed of reaction and the amount of yield o biodiesel produced. Reaction is a slow process, and is usually endothermic, requiring an optimum temperature for maximum efficiency. As the temperature increases, the viscosity of the oil decreases, leading to higher biodiesel yield (Encinar *et al.*, 2010). However, a lack of reaction temperature leads to poor reactant mixing due to high viscosity, resulting in low yield (Takase *et al.*, 2014). High reaction temperatures can also lead to reduced polarity of methanol, limiting the amount of alcohol available, and ultimately decreasing the yield of biodiesel (Baskar *et al.*, 2018).

1.5.4. Reaction Time

In overall, response time improves biodiesel output. However, the kind of biomass, catalyst utilized, and its dosage all affect the optimal transesterification reaction time. When compared to acidic catalyst, basic catalyst often synthesis the biodiesel at a average rate of 4000 times faster. In contrast, enzyme as a catalyst requires a longer time for reaction (Dhawane *et al.,* 2018). Additionally, longer reaction times can also result in less biodiesel since transesterification is a reversible process that causes esters to be lost and soap to develop.

1.6. Qualities of Biodiesel Generated from Inedible Sources

Biodiesel is a renewable and sustainable fuel that has become an attractive alternative to conventional diesel in recent years due to its environmental benefits. However, it is crucial to ensure that biodiesel produced from non-edible sources is efficient enough to be used in CI and compatible with traditional diesel and blend diesel. Moreover, biodiesel must comply with the worldwide biodiesel standards, including the (EN 14214) for Biodiesel or American Standard for Testing Materials (ASTM 6751-3), to ensure its effectiveness and other characteristics. The treatment and purification of biodiesel have a significant impact on its quality and should be optimized throughout the manufacturing process according to these guidelines (Table 1.4).

Iodine value measures the degree of unsaturation of the (FAMEs) in biodiesel, and a lower iodine value indicates higher oxidative stability. Viscosity is the resistance to flow, and low viscosity is preferred over high viscosity for efficient flow and injection processes. Cetane number (CN) measure the ignition standard, and higher value CN biodiesel result in a smoother and more efficient combustion. Flash point is the temperature which is the lowest in scale at which fuel ignites and should be higher in biodiesel than conventional diesel, according to ASTM D93 standards, which requires a minimum flash point of 130 °C. FFA content and cloud point are also essential parameters to consider while testing biodiesel for quality assurance.

Table 1.4. ASTM D6751 and EN 14214 specifications of biodiesel fuels.

Properties specification	**ASTM 6751 limit**	**EN 14214 limit**
Acid value (mg KOH g^{-1})	Max. 0.50	Max 0.50
Iodine value (g I_2 $100g^{-1}$)	-	Max. 120
Density at 15 °C (kg m^{-3})	880	860-900
Viscosity at 40 °C (mm^2 s^{-1})	1.9-6.0	3.5-5.0
Cloud point (°C)	-3 to -12	-
Flash point (°C)	Min. 130	Min. 101
Cetane number	Min. 47	Min. 51
Pour point (°C)	-15 to -16	-

1.7. Economic Aspect

The primary barrier to commercialization of biodiesel is their higher production costs, which may be reduced by modifying different process parameters that are required for biodiesel production shown in figure 1.9. The expense of biomass, the sale price of the biodiesel that is generated, as well as the cost of its byproducts (glycerol), all have a significant effect on whether biodiesel manufacturing is economically viable (Rezania *et al.*, 2019).

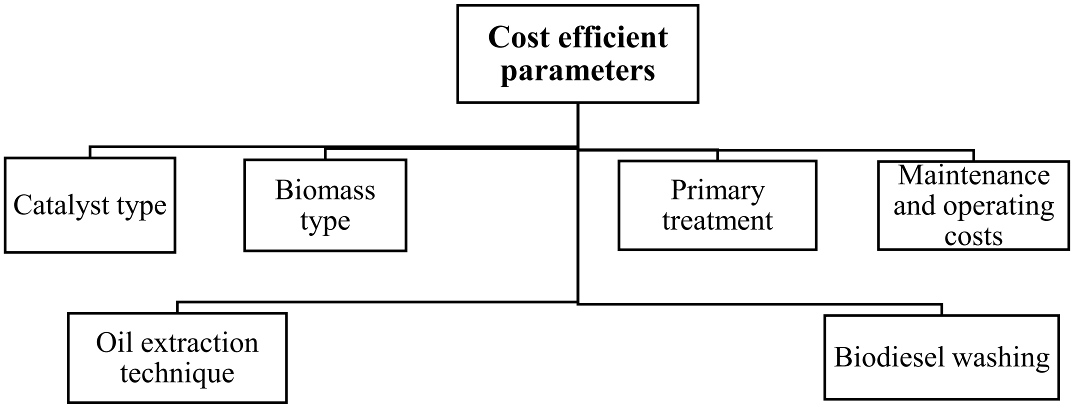


Figure 1.9. Cost efficient parameters for biodiesel synthesis (Rezania *et al.*, 2019).

1.8. Production and Consumption

Large portions of the world's total biodiesel are not accounted for by more advanced methods based on cellulosic feedstock (such as agricultural wastes, crops grown specifically for energy, or wood). Government initiatives with the following three main objectives: farmer support, decreased GHG emissions, and greater energy independence, have a significant impact on the worldwide biodiesel industries.

The International Energy Agency (IEA) reports that palm oil-based biodiesel makes up a significant portion of EU environmental concerns related to palm oil production. On the other hand, output of biodiesel from other vegetable oils is predicted to fall as well, while projected to increase from spent cooking oils. The EU is anticipated to continue to be the global top producer of biodiesel in 2030 based on demand predictions for the industry, even if worldwide manufacturing rates are anticipated to drop from 32% to 28%. Feedstock used and the production of biodiesel from different states were mentioned in table 1.5.

In China, expense of producing biodiesel from oil extracted from algae was expected to be 2.29 USD kg^{-1} from 2019 to 2022, which is much more expensive than conventional diesel (1.08 USD kg^{-1}). This contrast supports the absence of future prosperity (Sun *et al.,* 2019). Comparison of overall biodiesel and diesel prices mentioned in table 1.6. It should be highlighted that using wet consolidated algal biomass for oil extraction which eliminates additional drying can lower the cost of producing biodiesel from algae (Ghasemi *et al.,* 2016).

Table 1.5. Feedstock used and the production of biodiesel from different states.

Countries	Production of biodiesel (Based period)	Feedstock used for biodiesel
United States	2 (18.1%)	Used cooking oil, soybean oil
European union	1 (32.3%	Used cooking oil, rapeseed oil, palm oil.
Brazil	4 (12.2%)	soybean oil
China	9 (2.3%)	Used cooking oil
India	15 (0.5%)	Used cooking oil
Canada	13 (0.7%)	Used cooking oil, canola oil, soybean.
Indonesia	3 (15%)	Palm oil
Argentina	5 (5%)	Soybean oil
Thailand	7(3.8%)	Palm oil
Colombia	11 (1.3%)	Palm oil
Paraguay	19 (0.03%)	Jatropha

Numbers represent a country's position in the global production rankings; % represents a state's production share during the base period.
(Source: “OECD-FAO Agricultural Outlook”, OECD Agriculture statistics (database) 2021).

Table 1.6. Comparison of Biodiesel and diesel prices, April 2022

States	Biodiesel	Diesel
US	2.0 USD per liter	1.1 USD per liter
Europe	1.7 USD per liter	1 USD per liter
Asia	0.6 USD per liter	-

(Source: IEA, Biodiesel, and diesel prices, 2019 to April 2022, IEA, Paris)

1.9. Cost and Benefit Analysis

Cost efficiency of biodiesel depends upon its life cycle which involves the input and output of production shown in figure 10. (Deng *et al*., 2012) determined the cost and benefit of cultivating *Jatropha* plant in China for the sole purpose of producing biodiesel by using non agriculture land to avoid land competition with the food source land. *Jatropha* seed oil had shown high oil content, but it took 3 years to reach its matured age to be used. The total input cost investigated for afforestation of *Jatropha* was about 1430 USD ha^{-1} including 35 USD ha^{-1} land cost which is far less than the cost used for agricultural. The major contributor of input cost in *Jatropha* cultivation was labor (60%) along with fertilizers, however the output was less than the fossil fuel and the profit were sensitive to seed price still the positive net benefit was achieved that is up to 3978 USD ha $^{-1}$. Mohammad Shirazi *et al.*, 2014 investigated the economic feasibility of using used cooking oil to produce biodiesel based on energy use for input and output. The total energy input consumption was about 30 MJ L^{-1} with major consumer being waste cooking oil (70%) and chemical (19.4%) whereas the total output energy efficiency obtained was 40.9 MJ L^{-1} with the input output energy ratio of about 1,49 MJ L^{-1} which describe that 1.49 MJ L^{-1} energy was produced when each MJ of energy consumed to obtained biodiesel. Because the energy cost is beneficial, it is determined that energy is conserved during biodiesel manufacturing. It is also suggested for manufacturing owing to its positive energy output.

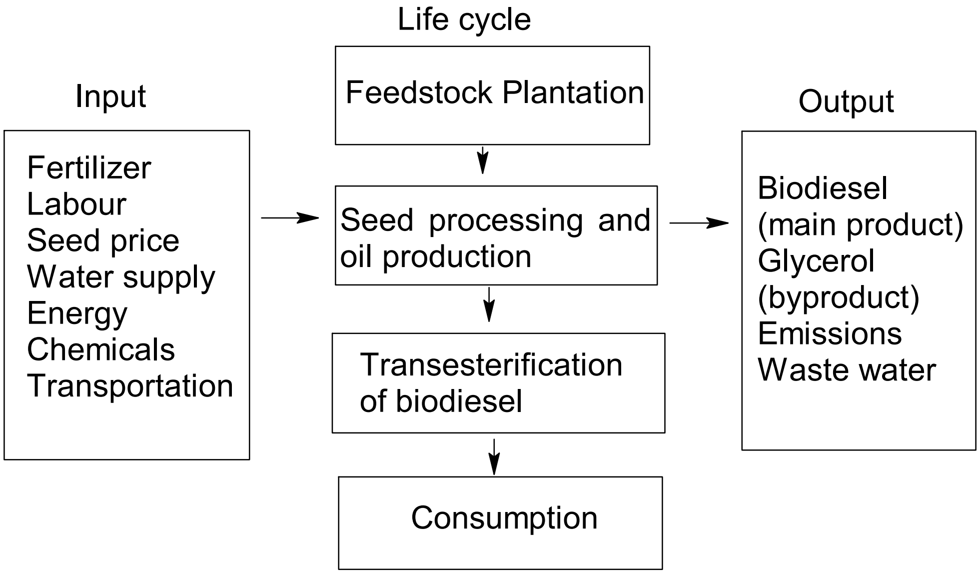


Figure 1.10. The life cycle of biodiesel production system (Shirazi *et al.*, 2014)

1.10. Problem statement

Despite the increasing global demand for biodiesel as a substitute source, the biodiesel produced from non-edible feedstocks faces challenges in terms of cost-effectiveness, feedstock availability, and compliance with international quality standards. In addition, concerns have been raised regarding the environmental impact of using certain feedstocks such as palm oil and the carbon footprint of the process of biodiesel synthesis. Therefore, there is a need for research that addresses these challenges and explores innovative solutions for improving the sustainability and competitiveness of biodiesel production from non-edible feedstocks.

1.11. Objectives

1. To analyze the feasibility of oil extracted from *Melia azedarach* L. seeds through Soxhlet apparatus and producing biodiesel from it as a sustainable alternative to traditional feedstocks.

2. To produce an acidic IL and evaluate its capacity to catalyze transesterification process.

3. To examine the influence of different reaction parameters (catalyst quantity, time, oil and methanol ratio, and temperature) on the production and quality of biodiesel generated from non-edible sources (Melia azedarach L. seeds).

4. To evaluate the biodiesel's physicochemical qualities to worldwide biodiesel standards (ASTM 6751).

1.12. Current Study

The current study aims to investigate the feasibility of using *Melia azedarach* L. seeds as a biomass for oil extraction and synthesizing biodiesel through transesterification process. The study also focuses on synthesizing Bronsted acidic ionic liquids and comparing their catalytic activity with KOH-based catalysts in the transesterification of Extracted oil (EO).

The Soxhlet apparatus and solvent extraction technology were utilized for the oil extraction procedure. The oil was then subjected to transesterification using the synthesized Bronsted acidic ionic liquid namely 1-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulphate, and KOH-based catalysts. The effect of varying reaction conditions such as catalyst quantity, time, and temperature on biodiesel output and quality were also evaluated. The physicochemical properties of the biodiesel produced from *Melia azedarach* L. seeds were analyzed and compared with international biodiesel standards (ASTM 6751).

CHAPTER 2

MATERIALS AND METHODS

2.1. Selection and Drying of Biomass

Melia azedarach L. seeds were collected from various locations of the Quaid-i-Azam University campus during different seasons. The seeds collected during the winter season appeared yellow, while those collected during the summer season appeared green. The seeds were rinsed with distilled water after being collected to eliminate any dirt or debris. The kernels were extracted from the seeds, which were then sun-dried to remove any excess moisture. The seeds were crushed using a high-power electric grinder, and the resulting powder was sieved to obtain a fine powder.

2.2. Oil Extraction

The oil was extracted from *Melia azedarach* L. seeds, 30 g of the seeds were placed in a cellulose thimble within a separatory tube of Soxhlet apparatus capped with a condenser. As an organic solvent, 200 ml of n-hexane was introduced to a round bottom flask in the apparatus. For 8 hours, the extraction was being carried out at an unchanged temperature of 60 °C. The extraction was completed after 5 to 6 cycles of extraction. The solvent was also removed from the extracted oil using Soxhlet, and the extracted product was oven-dried for 1 hr. at 60 °C to eliminate any leftover solvent and water. After drying, the resultant oil sample was measured and kept in a tight container. (Hamesh *et al.*, 2018).

The yield of oil obtained was calculated by using the equation (1) (Dagne *et al.*, 2018).

$$\text{Oil yield (\%)} = \frac{\text{Oil extracted (g)}}{\text{dry sammple used(g)}} \times 100 \qquad \text{eq. (1)}$$

2.3. Synthesis of Bronsted Acidic Ionic Liquid by Two Step Method

To create 1-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulphate [SO_3H-$(CH_2)_3$-IM-vinyl] [HSO_4] (referred to as IL), a simple two-step process was used. In Step 1, 4.7 g of 1-vinylimidazole was dissolved in 60 ml of ethyl acetate as the solvent, and 6.1 g of 1,3-propanesulfonate was progressively added in an ice bath while aggressively stirring. The resulting mixture stirred in room temperature; it was allowed to react for 24 hr. The white precipitates (zwitterion) that were formed were then filtered and cleaned with ethyl acetate to make your all impurities was washed out. For the second step, the resultant zwitterion IL salts were mixed in 5 ml of water that had been deionized. An equimolar of H_2SO_4 was introduced in solution slowly while stirring in a cold bath. The solution was further agitated for 12 hr. at 60 °C to synthesize IL. After completing the steps, a brown viscous liquid was produced, which was stored in a tightly packed glass bottle. The acidic value of the synthesized IL was checked and compared with that of H_2SO_4 acidic (Figure.2.1) (Xie *et al*., 2021).

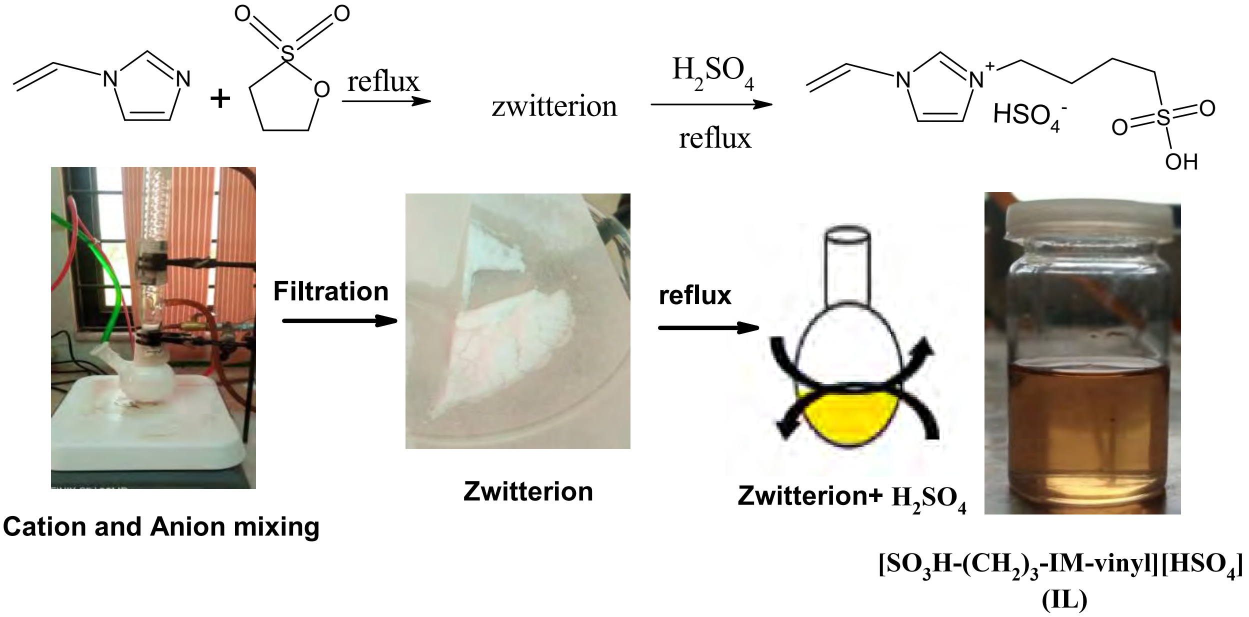


Figure 2.1. Pathway for the preparation of IL

2.4. Acidity of IL

In this study, the acidity of IL was predicted and justified by electron induction theory and by pH. Induction effects are the shifting of electrons from less electronegative atom toward more electronegative atom in a covalent bond (Fan *et al*., 2017).

2.5. Transesterification Process

The transesterification process was performed using two types of catalysts IL as acidic and KOH as basic catalyst. To obtain the highest biodiesel yields, different parameter conditions were investigated in the transesterification process for both catalysts. The reaction was taken place in a reflux system with varying ratios of methanol and oil (1:3, 1:6, and 1:9), and the oil was put to a two-necked round-bottom flask with a thermometer embedded in it and heated to the desired temperature (60, 80, and 100 °C). Methanol was then added, along with the calculated dose of catalysts (1, 2, and 3% *w/w*), and the solution was stirred at 500 rpm. The reaction was stopped at a specific time (60, 90, and 120 min), and the solution was put into a falcon tube and centrifuged for 10 mins at 3000 rpm to obtain the required layers. The mixture was separated into separate layers, with the layer at bottom comprising glycerol, the top layer comprising biodiesel. The biodiesel was left to dry in an oven for 40 min to make sure that all the solvent and water evaporated and stored in a closed container (Wang *et al*., 2020).

2.5.1. Mechanism of Transesterification through IL

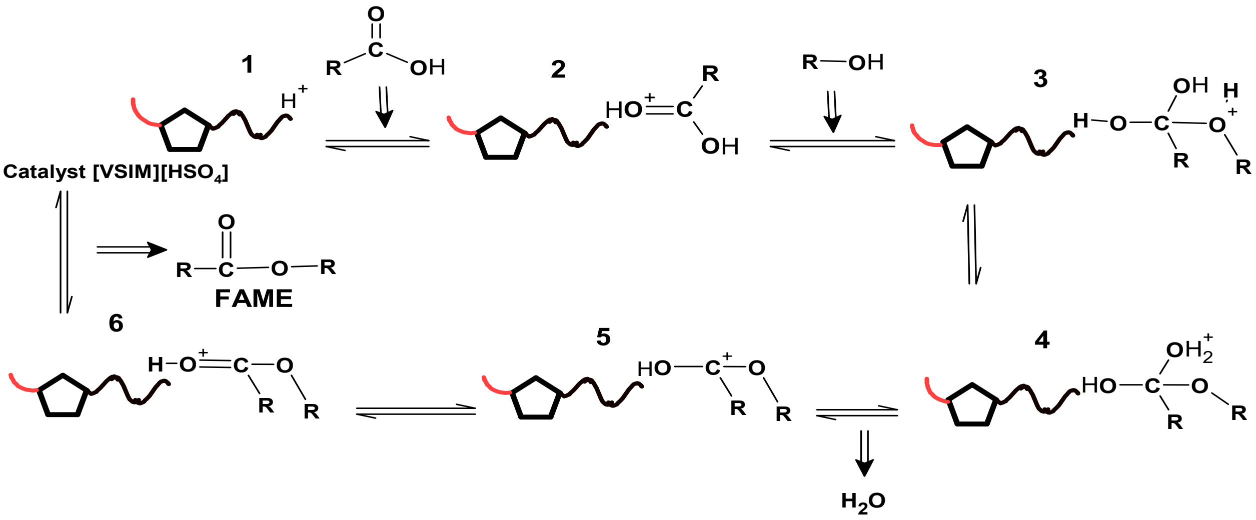


Figure 2.2. Mechanism of IL catalyzed transesterification (adopted and modified from Xie *et al*., 2021).

To understand the process of the transesterification mechanism catalyzed by IL (Figure 2.2). Throughout the biodiesel synthesis process, FA protonation and nucleophilic assault occur. Critical processes were thought to be the protonation of the acid by the alcohol. The H^+ proton was provided by repeating active units of $-HSO_3$ and $-HSO_4$, and fatty acid was protonated, yielding carbocation. The alcohol molecule then carries nucleophilic attack towards the produced carbocation. Biodiesel was created when the hydrogen-oxygen connection in product 5 was disrupted and the catalyst IL formed a cloudy layer between glycerol and biodiesel from which all three layers get separated, however KOH catalyzed biodiesel only produced two layers (Figure 2.3) (Xie *et al.*, 2021).

Biodiesel yield can be calculated through the following equation (2).

$$\text{Biodiesel yield } (\%) = \frac{\text{obtained yield (g)}}{\text{oil used (g)}} \times 100 \qquad \text{eq. (2)}$$

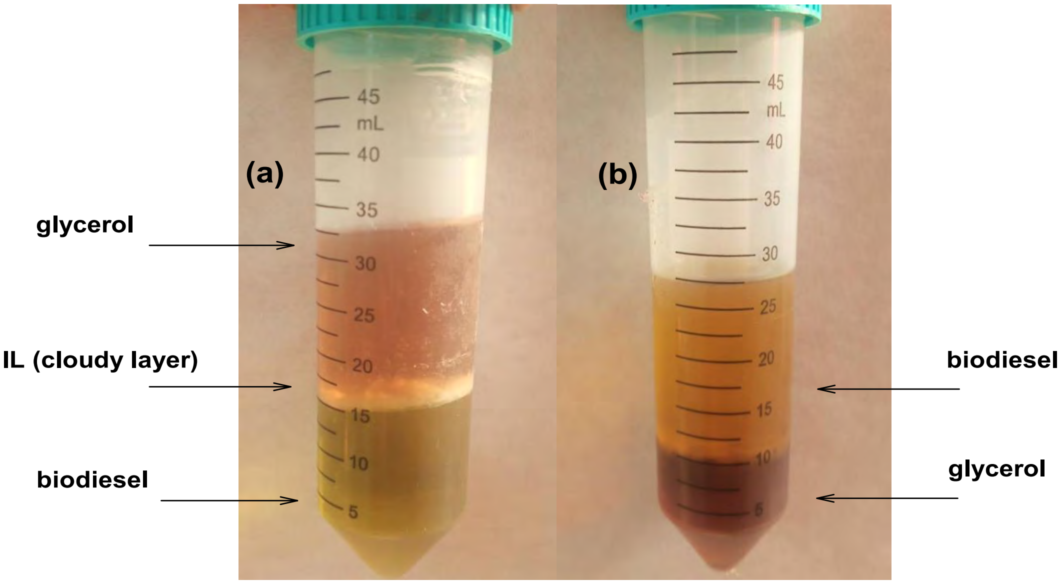


Figure 2.3. Layers distribution after transesterification, **(a)** IL catalyzed biodiesel, **(b)** KOH catalyzed biodiesel.

2.6. Parameters Analysis for Biodiesel

2.6.1. Acid Value test (AV):

The acid content of the sample was calculated using the method outlined by Feleke *et al.* (2019), which entails using KOH to neutralize the amount of free fatty acids found in 1 g of the substance or sample.

Material and Procedure:

In a 250 ml flask, 2 g of the oil sample was combined with 40 ml of neutralized ethanol-ether solution and heated at 60 °C until the oil dissolved. A couple of drops of phenolphthalein as an indicator were added, and the solution was titrated with 0.1 N KOH until a pink color developed and lasted for more than 10 seconds (AOAC 940.28).

The acid value was calculated using equation (3):

$$\mathrm{AV} = \frac{\mathrm{M} \times \mathrm{N} \times \mathrm{V}}{\mathrm{W}} \qquad eq.(3)$$

where M is the molecular weight of KOH, N denotes the normalcy of KOH, V denotes the volume of titrate, and W denotes the weight of oil.

2.6.2. Saponification Value (SV):

The saponification value (SV) test involved treating oil samples with KOH, which degraded the lipids into glycerol and fatty acids.

Material and Procedure:

2 g of oil sample was heated for 30 minutes at 70 °C in a reflex system with 25 ml of 0.5 N ethanoic solution. After cooling, few drops of phenolphthalein as indicator were incorporated, and the resulting mixture was diluted with 0.5 mol of a solution of HCl until the sample became pink. A blank sample (AOAC 920.160) was also used in the titration. The saponification value was calculated using equation (4):

$$\mathrm{SV} = \frac{\mathrm{M} \times \mathrm{N} \times (\mathrm{Vb} - \mathrm{Vs})}{\mathrm{W}} \qquad eq.(4)$$

Where Vb indicates the sum of the volumes of HCl used in the blank, Vs represents the volume of HCl in the sample being tested with oil, and W is the weight of the oil used. SV stands for the saponification value. M is the molecular mass of KOH.

2.6.3. Iodine Value (IV):

The quantity of double bonds in a sample of oil was determined using the iodine value test (Getahun *et al*., 2013).

Material and Procedure:

2 g of oil were dissolved in 10 ml of chloroform in an Erlenmeyer flask to create a solution. After that, 25 ml of the Hanus solution (a combination of 6 ml of bromine liquid, 400 ml of glacial acetic acid, and 13 g of iodine) was added. The mixture was then left in the dark for 30 minutes. A few drops of starch indicator were added after adding 10 ml of 15% KI solution until a yellow color was seen. With 0.1 N sodium thiosulfate solution, the solution was titrated until the color vanished, at which point the final reading was taken. The blank sample underwent the exact same procedure.

The following equation was used to calculate the iodine value:

$$\mathrm{IV} = \frac{\mathrm{MI} \times (\mathrm{Vb} - \mathrm{V\,t}) \times \mathrm{N}}{\mathrm{Ma}} \qquad eq\,.(5)$$

In this equation, IV stands for iodine value, MI for iodine molecular weight, Vt for the total volume for oil sample, Vb for total volume for blank, N for sodium thiosulfate normality, and Ma for mass of measured oil.

2.6.4. Peroxide Value (PV):

The PV of a fat or oil sample was measured by determining the amount of iodine produced by the interaction of peroxides formed in the sample with the iodide ion. The base generated in the process absorbs the excess acetic acid present in the sample (Getahun *et al*., 2013).

Material and Procedure:

30 ml of a 3:1 acetic acid-chloroform solution was combined with 2 g of oil, and the mixture was agitated to create a homogenous mixture. After that, 30 ml of distilled water and 1 ml of saturated KI solution were added and well mixed for 1 minute. 0.5 ml of starch indicator was added to the solution as it was being titrated with 0.01 N sodium thiosulfate solution. The reading from the burette was recorded after the titration was completed and the color had vanished. The blank solution underwent the same procedure.

The peroxide value test can be calculated using the following equation:

$$\mathrm{PV} = \frac{\mathrm{V} \times \mathrm{N} \times 1000}{\mathrm{Ws}} \qquad eq.(6)$$

Where Ws is the weight of the measured oil, N is the sodium thiosulfate normalcy, PV is the peroxide value, V is the volume of titrate in the sample, and N represents the peroxide value.

2.6.5. High Heat Value (HHV):

According to Dagne *et al*. (2019), the high heat value (HHV) is "the amount of heat created when fuel was burned, and the temperature that was brought back to its pre-combusted temperature has been referred to as the latent heat of vaporization that occurs in combustion and stated as high heat value of biodiesel". The HHV was calculated using equation (7):

$$\mathrm{HHV} = \frac{49.43 - (0.041 \times \mathrm{SV}) + 0.015 \times \mathrm{IV}}{\mathrm{Ma}} \qquad eq.(7)$$

2.6.6. Cetane Number (CN) Value:

The Cetane Number (CN) is an estimation of the fuel's consumption speed, and it is calculated using the equation (8) published and suggested by Dagne *et al*., (2019):

$$\mathrm{CN} = 46.3 + \frac{5458}{\mathrm{SV}} - (0.225 \times \mathrm{IV}) \qquad eq.(8)$$

2.6.7. Biodiesel Density:

The density of biodiesel samples was estimated by measuring the mass over volume of the samples at 40 °C, as described by Ismail *et al*., (2015). The formula used for calculating density is as follows:

$$\mathrm{Density} = \frac{\mathrm{m}_2 - \mathrm{m}_0}{\mathrm{m}_1 - \mathrm{m}_0} \qquad \text{eq. (9)}$$

where m_0 represents the weight of an empty bottle, m_1 is the weight of biodiesel in the bottle, and m_2 is the mass of the bottle with water.

2.6.8. Flash Point of Biodiesel:

The flash point of biodiesel was determined using the open cup method, as described by Nolan *et al.* (2014). The biodiesel sample was placed in a container, which was exposed to the outside air and placed on a hotplate. The temperature increased slowly, and an ignition source passed over it after every 2 °C increased in temperature. The temperature was noted down when the biodiesel caught fire or started to flash.

2.6.9. Pour Point:

The pour point is an important indicator of fuel quality that measures how likely a fuel becomes viscous and less capable of flowing in cold temperatures. The pour point was determined following the procedure described by ASTM D97. The oil sample was placed in a vessel, preheated, and then cooled in a refrigerator until it reached the predicted pour point temperature of 9 °C. The sample was then examined at consecutive intervals of 3 °C. The examination involved taking the vessel out of the cooling system and tilting it to check for any biodiesel surface movement. The pour point of the biodiesel was determined by adding 3 °C to the temperature at which it stopped flowing (because this is the final flowable point) (ASTM D97).

2.7. Methods for Characterization of Samples

2.7.1. Fourier Transform Infrared Spectroscopy (FTIR)

The functional group for the IL, oil, and biodiesel samples was identified using Fourier transform infrared spectroscopy (SHIMADZU, FTIR-8400). With a spatial resolution of 4 cm-1, the observed spectrum range for FTIR was 4000 cm-1 to 400 cm-1. FTIR analysis was performed on the materials using sodium cells.

2.7.2. Thermogravimetric Analysis (TGA) of IL

To prepare a sample for thermogravimetric analysis of the synthesized IL (Ionic Liquid), a mixture of IL and a 10% CA (cellulose acetate) solution was created. The mixture was then used to cast uniform membranes, with a diameter of 0.5 mm and labeled as IL. To acquire thermal degradation curves, a thermogravimetric analyzer (NETZSCH TG 209F3) was used. The samples were heated in an aluminum oxide (Al_2O_3) crucible under a nitrogen stream. The heating process involved gradually increasing the temperature at a rate of 20 °C every 10 minutes until reaching a terminal temperature of 800 °C (Sofia *et al*., 2022).

2.7.3. GC-MS for Biodiesel and Extracted Oil

The biodiesel samples were analyzed using a Shimadzu QP2010S Gas Chromatography Mass Spectrometer to assess the FAME content. A HP 88 cylinder with a length of 60 m, an inner diameter of 0.25 mm, and a film with a thickness of 0.20 m was used. During the analysis, a scanning mode was used. The gas used as the carrier was helium, with an ongoing velocity of 2.0 mL/min. A 2.0 L methylene chloride-dissolved sample was administered using the split mode at a split ratio of 1:50. The injection heat was set at 250 °C.

The GC oven conditions were originally kept at 175 °C for 10 minutes during the procedure. The temperature was then scaled up at a speed of 3 °C/min until it achieved 220 °C. The end point temperature was kept constant for 5 min. The temperature of the GC-MS interface was kept at 250 °C, whereas the temperature of the MS electron source was kept at 230 °C. The NIST05 mass spectral library (NIST, 2012) was utilized as a reference for comparing spectral data acquired after analysis (Sang *et al*., 2019).

CHAPTER 3

RESULTS

3.1. Extracted Oil Yield

The seeds of *Melia azedarach* L. obtained in winter were yellow in color, whereas those obtained in summer were green, and this was also observed in the extracted oil color. Furthermore, the summer seeds had a higher yield of 35%, compared to the winter seeds which had a yield of 23%, as indicated in Figure 3.1. Therefore, we selected the seeds harvested in summer for further testing.

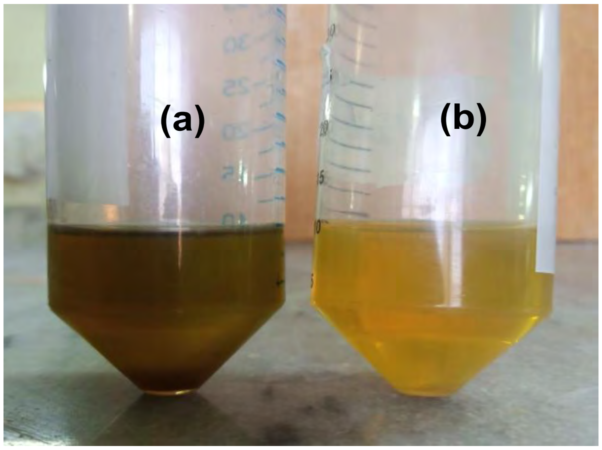


Figure 3.1. Oil extracted from seeds of *Melia azedarach* L., **(a)** winter season, **(b)** summer season.

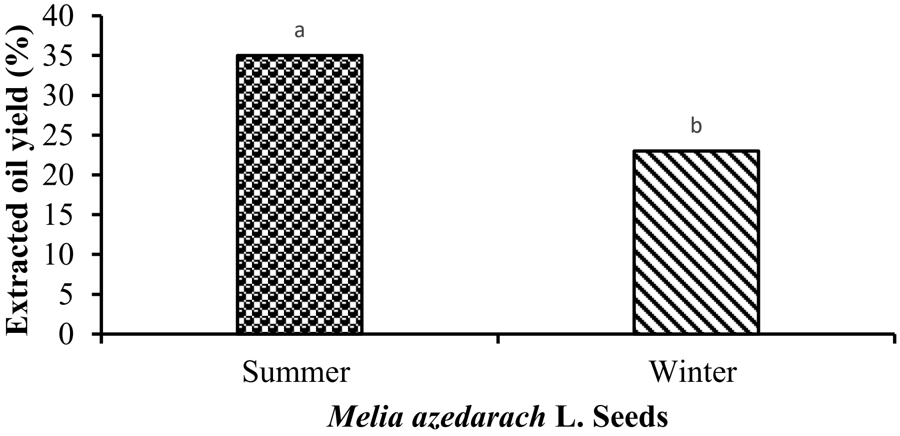


Figure 3.2. The yield of oil extracted from *Melia azedarach* L. Seed.

3.2. Catalytic Activity of IL and KOH for Transesterification Reaction

Four parameters were tested to check the optimum concentrations for producing high yield and best quality biodiesel.

3.2.1. Catalysts Dosage

The biodiesel yield showed a decrease pattern as the catalyst dosage increased during the transesterification process. Specifically, when using 1, 2, and 3% (*w/w*) of KOH as basic catalysts (CB), the corresponding biodiesel yields were 73, 70, and 40%, respectively. Similarly, when using 1, 2, and 3% (*w/w*) of IL as catalysts (CIL), the corresponding yields were 83, 77, and 63%, respectively. Figure 3.3 shows that the optimal catalyst dosage for both CB and CIL were 1% (*w/w*), which resulted in the highest biodiesel yield.

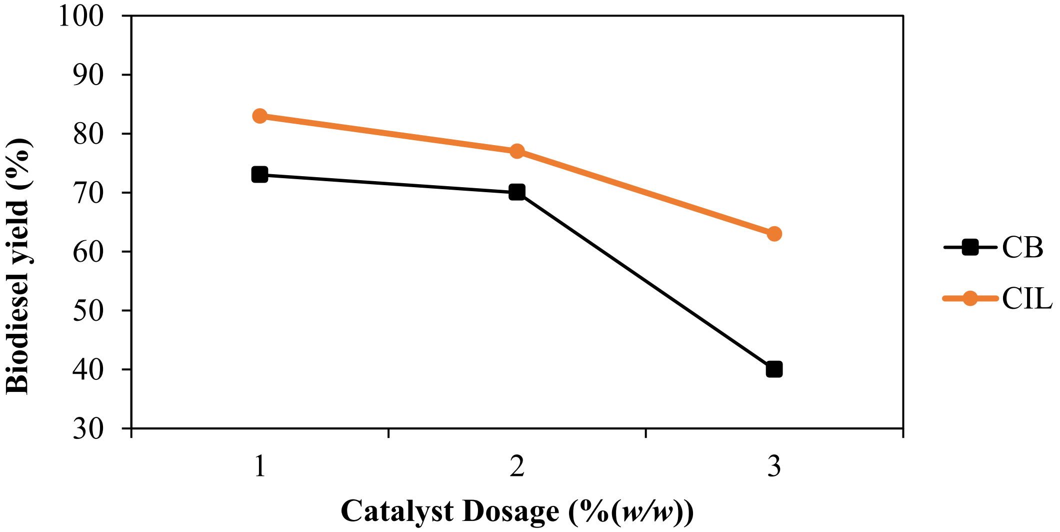


Figure 3.3. Catalysts dosage influence on KOH and IL catalyzed biodiesel.

3.2.2. Oil to Methanol Molar Ratio

When different molar ratios of oil to methanol (1:3, 1:6, and 1:9) were used, the CB-catalyzed transesterification process resulted in biodiesel yields of 73, 86, and 60%, respectively. Meanwhile, the CIL-catalyzed process produced biodiesel yields of 83, 84, and 90%, respectively. The highest yield for CB was obtained at a 1:6 molar ratio, whereas for CIL, the highest yield was obtained at a 1:9 ratio. As shown in Figure 3.4, the biodiesel yield decreased as the molar ratio increased from 1:6 to 1:9 in the CB-catalyzed process.

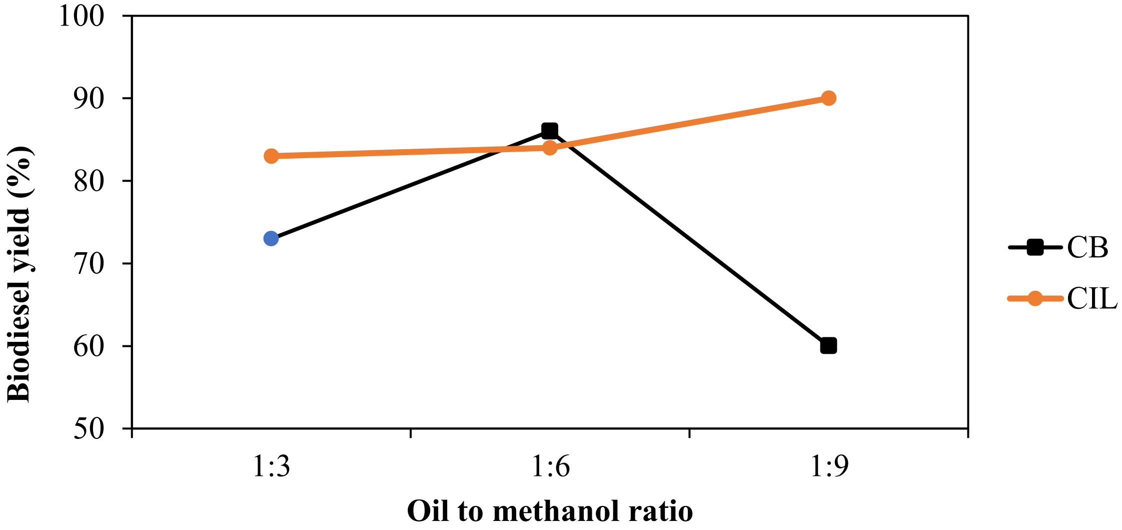


Figure 3.4. Oil to methanol ratio influence on KOH and IL catalyzed biodiesel.

3.2.3. Reaction Temperature

For both catalysts, the reaction was carried out at three distinct temperatures (60, 80, and 100 °C). The CB catalysts yielded biodiesel in amounts of 86, 87, and 97% at these temperatures, respectively. Meanwhile, the CIL catalysts produced biodiesel in amounts of 90, 98, and 93% at the same temperatures, respectively. Although the CIL catalyst had the highest conversion rate at 80 °C, the CB catalyst produced the highest output at 100 °C (Figure 3.5).

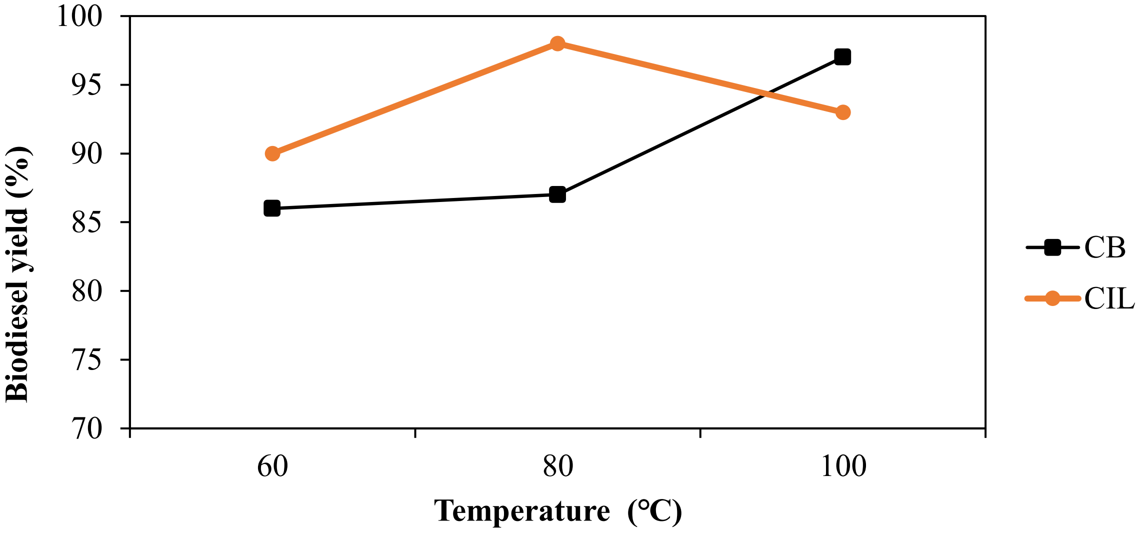


Figure 3.5. Temperature influence on KOH and IL catalyzed biodiesel.

3.2.4. Reaction Time

When using both CB and CIL catalysts, three different reaction times (60, 90, and 120 min) were tested, and the resulting biodiesel yields were as follows: 93, 97, and 81% for CB, and 92, 98, and 100% for CIL, respectively. The CB catalyst produced the maximum yield at 90 min, which decreased as the reaction time increased to 120 min. In contrast, the CIL catalyst produced the highest yield at 120 min, (Figure 3.6).

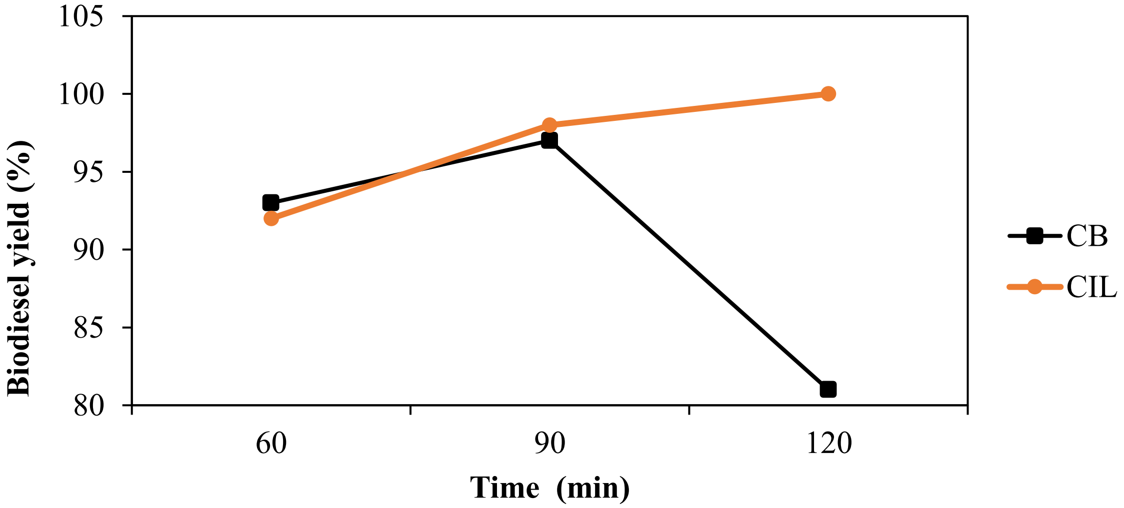


Figure 3.6. Time influence on KOH and IL catalyzed biodiesel.

3.2.5. Optimum Reaction Conditions

The best parameters for generating the maximum yield of CB-catalyzed biodiesel were determined to be 1% (w/w) catalyst dose, a molar ratio of oil to methanol of 1:6, a temperature of 100 °C, and a reaction duration of 90 minutes, yielding 97%. The best parameters for CIL-catalyzed biodiesel were 1% (w/w) catalyst dose, a 1:9 oil to methanol molar ratio, an 80 °C reaction temperature, and a 120-min reaction period, resulting in a 100% yield (Figure 3.7).

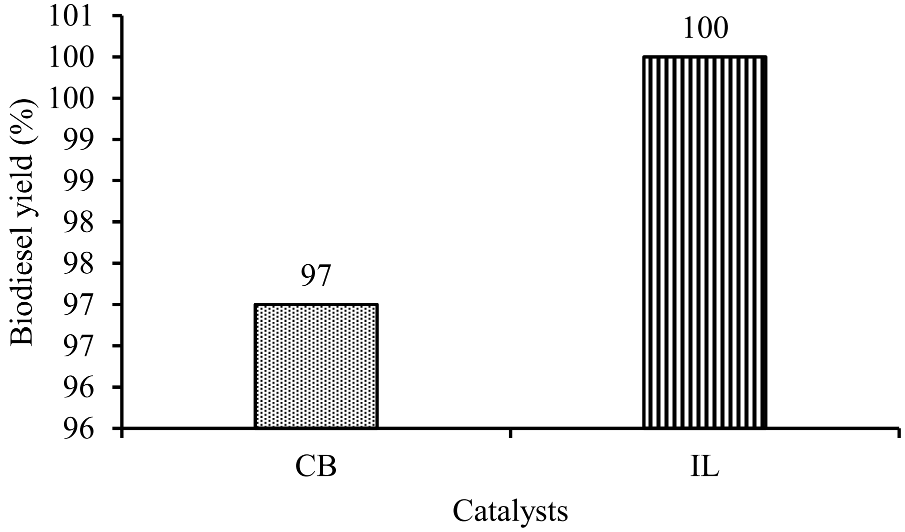


Figure 3.7. Biodiesel yield from using KOH (CB) catalysts and IL catalysts at optimum reaction conditions.

3.3. Acidity of synthesis IL

The acidity of [VISM][HSO_4] or IL predicted was very high because the presence of sulfonate-bearing alkyl chains in the IL which introduces a dominant spatial effect. As the carbon chain length increases, the Coulomb force between the cation and the anion weakens due to the larger volume of the cation. Consequently, the -SO_3H component in the IL finds it easier to lose H^+ ions. The prediction was confirmed with the pH of IL obtained which was rather higher than the HCL (Table 3.1).

Table 3.1. Comparison of acidity of IL with strong acids

	HCL	H_2SO_4	IL
pH	1.8	1.4	1.5

3.4. Physical and Chemical Properties of Extracted Oil and Biodiesel

Table 3.2. The physical-chemical properties of oil and biodiesel produced from the *Melia azedarach* L. seed by using KOH as base catalysts (CB) and IL.

Parameter	**Extracted Oil**	**KOH Catalyzed Biodiesel**	**IL Catalyzed Biodiesel**	**ASTM Standard**
Acid value (mg KOH g^{-1})	3.6	0.5	0.8	max.0.8
Saponification value (mg KOH g^{-1})	259	169	154	NA
Peroxide value (m Eq kg^{-1})	51	4.5	3.2	NA
Iodine value (g I_2 $100g^{-1}$)	73	68.39	68.77	max 120
HHV (MJ kg^{-1})	NA	22.07	21.76	max 43
Cetane value	NA	63	66	min 47
Density (g ml^{-1})	0.9	0.76	0.8	0.86-0.90
Flash point (^{o} C)	NA	140	135	min 130
Pour point (^{o} C)	NA	-6	-8	max -15

3.4.1. Acid Value Test

The acid value (AV) of the oil was 3.6 mg KOH g^{-1}, which decreased after it was converted to biodiesel. The AV of KOH and IL-catalyzed biodiesel was 0.5 and 0.8 mg KOH g^{-1}, respectively, which was within the maximum limit of 0.8 mg KOH g^{-1} set by the American Society for Testing and Materials (ASTM) (Table 3.1). CB had a lower AV than IL-catalyzed biodiesel.

3.4.2. Saponification Value Test

The saponification value of the extracted oil was 259 mg KOH g^{-1}, which decreased after it was transformed into biodiesel. IL-catalyzed biodiesel had a lower saponification value of 154 mg

KOH g^{-1} compared to KOH-catalyzed biodiesel (169 mg KOH g^{-1}), and there was no set limit provided by ASTM (Table 3.1).

3.4.3. Peroxide Value Test

The peroxide value (PV) of the extracted oil was 51 m Eq kg^{-1}, which decreased after trans-esterification into biodiesel. The PV of KOH-catalyzed biodiesel (4.5 m Eq kg^{-1}) was higher than that of IL-catalyzed biodiesel (3.2 m Eq kg^{-1}), and there was no stated limit for PV by ASTM (Table 3.1).

3.4.4. Iodine Value Test

The iodine value (IV) of the extracted oil was 73 g I_2 $100g^{-1}$, which decreased after conversion into biodiesel. Both KOH-catalyzed and IL-catalyzed biodiesel had IV values of 68.39 and 68.77 g I_2 $100g^{-1}$, respectively, which were within the ASTM standards (Table 3.1). There was no significant difference between the IV values of the two biodiesels.

3.4.5. High Heat Value and Cetane Number Test

The high heat value (HHV) of KOH-catalyzed and IL-catalyzed biodiesel was 22.07 MJ kg^{-1} and 21.76 MJ kg^{-1}, respectively, and the cetane number (CN) values were 63 and 68, respectively. All the values were within the ASTM standards (Table 3.1). However, IL-catalyzed biodiesel had better results in both HHV and CN values than KOH-catalyzed biodiesel.

3.4.6. Flash point and Pourpoint

The flash point values of KOH-catalyzed and IL-catalyzed biodiesel were 140 °C and 135 °C, respectively, and the pour point values were -6°C and -8°C, respectively. All the obtained values were within the ASTM limits (Table 3.1). However, IL-catalyzed biodiesel had a lower flash point and higher pour point than KOH-catalyzed biodiesel.

3.4.7. Density

The density of the extracted oil was 0.9 g ml^{-1}, which decreased after conversion into biodiesel by both KOH and IL catalysts. The density values obtained were 0.7 and 0.8 g ml^{-1}, respectively, which were within the ASTM limits (Table 3.1). However, KOH-catalyzed biodiesel had a lower density compared to IL-catalyzed biodiesel.

3.5. Characterization of Ionic Liquid, Extracted Oil and Biodiesels

3.5.1. FTIR of [VSIM][HSO4] (IL)

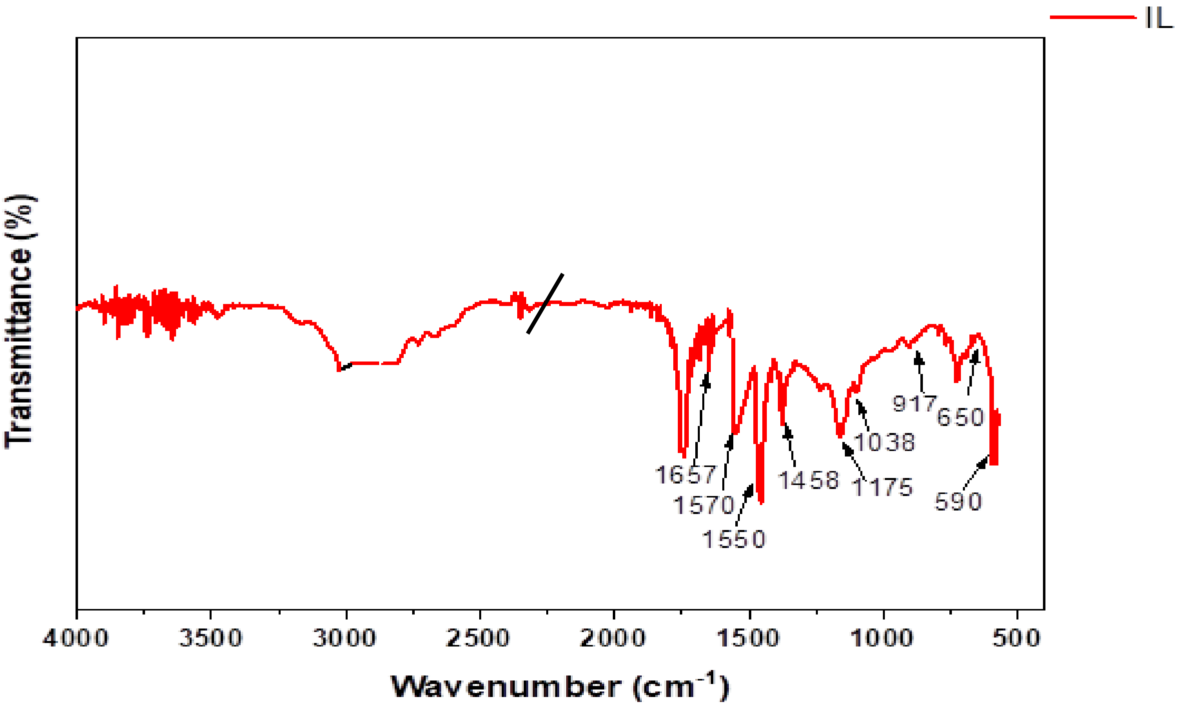


Figure 3.8. FTIR spectrum of [VSIM][HSO4] or Bronsted Acidic Ionic Liquid.

The existence of S=O asymmetrical and symmetrical vibrations that stretch at 1175 and 1038 cm^{-1} was seen in the [VSIM][HSO4] spectra shown in Figure 3.8. At 1550 and 1570 cm^{-1}, the C=N and C=C double-bonded stretching vibrations found in the imidazole rings were discovered. At 1458 cm^{-1}, the =CH asymmetrical bending vibration was measured. The existence of the sulfonic -HSO_4 group was shown by the spectrum of bands around 650 and 1120 cm^{-1}. The C=C vibration of stretching was measured at roughly 1657 cm^{-1}, while the vinyl group's =CH out-of-plane bending was recorded at 917 cm^{-1}.

3.5.2. FTIR Overlay for Extracted Oil and Biodiesels

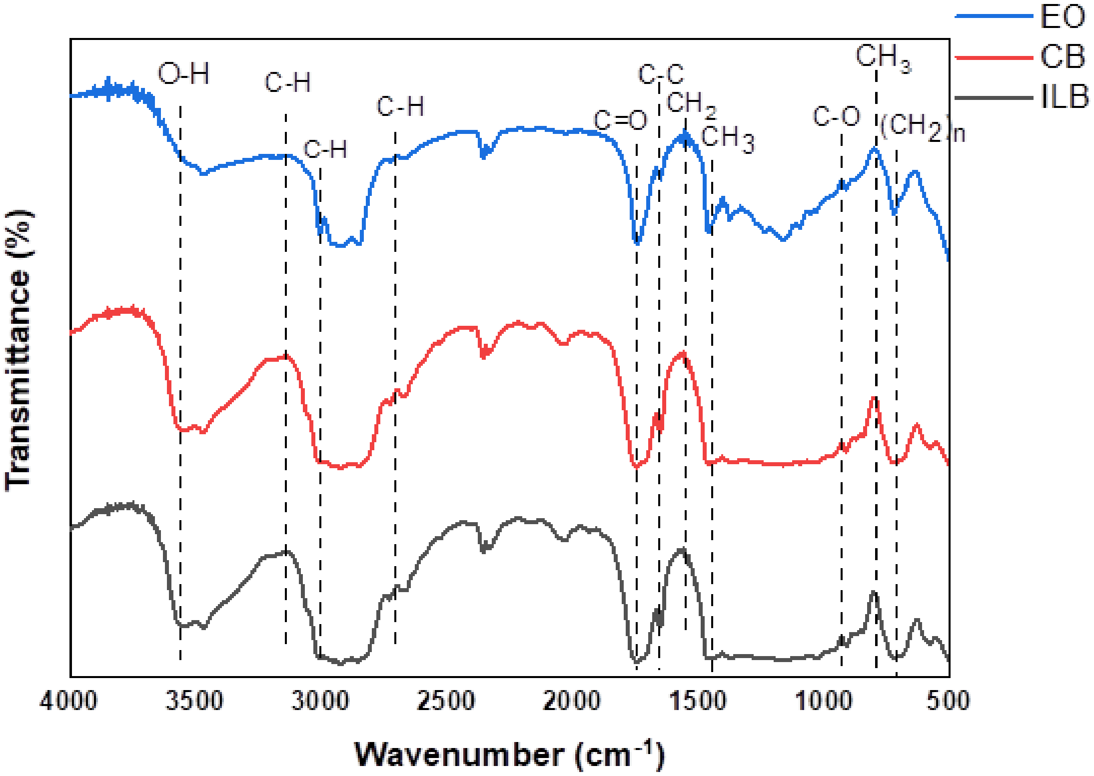


Figure 3.9. The FTIR spectrum of extracted oil (EO), KOH catalyzed biodiesel (CB), and ionic liquid catalyzed biodiesel (ILB).

Figures 3.9 displayed an overlay of the FTIR spectra for extracted oil (EO), KOH catalyzed biodiesel (CB), and IL catalyzed biodiesel (ILB). Several correlations were found among the peak areas. Firstly, a peak in the range of 1094 and 1155cm^{-1} was related to the stretched production of a C-O, which can be carboxylic acid, esters, or phenolic groups. The detected peak at 1454 cm^{-1} correlated to a C-H (methyl) group with bending vibration, while the peak at 1651 cm^{-1} showed a C=C group with bend bond type, and the strong elongating peak at 1742 cm^{-1} showed carboxylic acid or ester properties. The establishment of peaks in the range 2851 - 2915 cm^{-1} was due to the C-H group with stretching that are both asymmetric and symmetric, while the peak appeared in the range 3005 cm^{-1} related to the C-H group primarily aromatic substance with stretching vibrations. The last pattern was detected in the 3416 cm^{-1} area corresponds to the stretched bond kind of O-H group and H- bonded, which were mostly alcoholic or phenolic groups. The peaks from 3005 and 3416 cm^{-1} were only detected in the biodiesel FTIR and not in the oil (EO).

Additionally, the existence of a functional group C-H with a rock bond implied a long chain vibration, and the peak at 1454 cm^{-1} correlated to a C-H (methyl) group with bending vibration.

3.5.3. Thermal Gravimetric Analysis (TGA) of IL

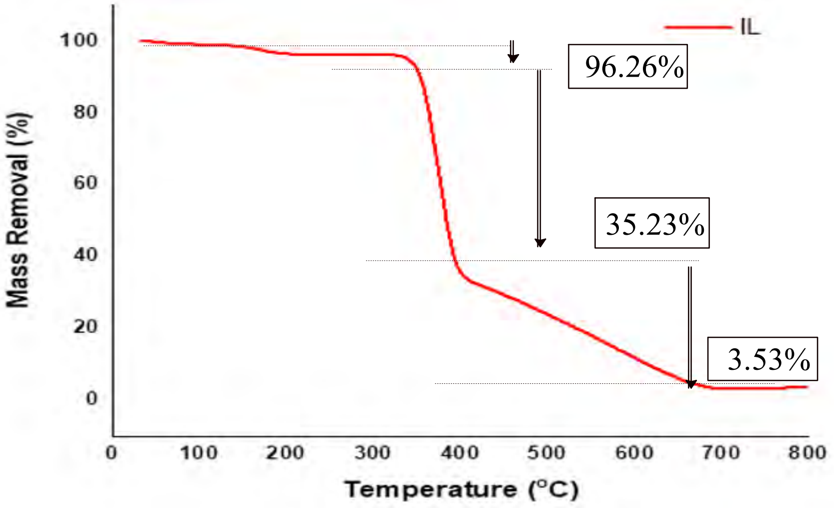


Figure 3.10. TGA curve of synthesis IL

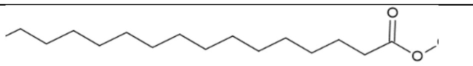
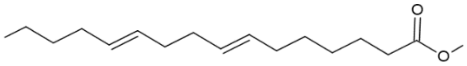
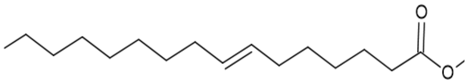
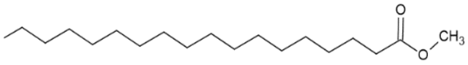
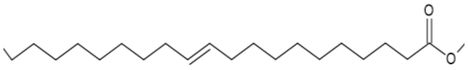
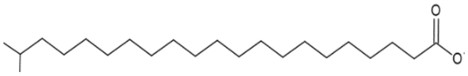
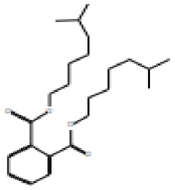
The recorded thermograms illustrate the expected mass loss in relation to temperature. The thermal patterns, as shown in Figure 13, indicate that the synthesized samples underwent complete combustion in the nitrogen atmosphere prior to reaching 800 °C. This resulted in minimal residue, indicating a high level of purity.

The thermogram exhibits three clear peaks, each corresponding to a distinct mass loss event. Initially, the sample experienced degradation at 294 °C, leading to a weight loss of 3.74%, while 96.26% of the sample remained. Subsequently, at 400 °C, further degradation occurred, resulting in a total weight loss of 64.77%, leaving behind 35.23% of the sample. The final weight loss event took place at 700 °C, during which almost all the sample was degraded, leaving a biomass residue of 3.53%.

3.5.4. GC-MS Analysis for Fatty Acid Composition of Extracted Oil

The GC-MS analysis (Table 3.3) yielded the FA makeup of the extracted oil. The extracted oil contains the following percentages of fatty acids: 1.41% Palmitic acid (C16:0), 75.96% Linoleic acid (C18:2), 17.23% Oleic acid (C18:1), 4.56% Stearic acid (C18:0), 0.25% Gondoic acid (C21:2), 0.12% Nonadecanoic acid (C21:2), and 0.36% Benzoic acid (C24:4). Linoleic acid is the most abundant fatty acid, followed by Oleic acid and Steric acid in Melia azedarach L. extracted oil, which contains more unsaturated fatty acid than saturated fatty acid.

Table 3.3. Fatty Acids composition of extracted oil from *Melia azedarach* L. seeds.

Peaks	Fatty Acids	Number of carbons	Retention Time	FFA%	Name of compound	Chemical structure	Molecular weight
1	Palmitic acid	C16:0	25.788	1.41	Hexadecenoic acid, methyl ester		270
2	Linoleic acid	C18:2	27.988	75.96	9,12-Octadecadienoic acid (Z, Z)		294
3	Oleic acid	C18:1	28.041	17.23	9-Octadecenoic acid (Z)-, methyl ester		296
4	Stearic acid	C18:0	28.326	4.56	Methyl stearate		298
5	Gondoic acid	C 21:0	30.381	0.25	cis-Methyl 11-eicosenoate l		324
6	Nonadecanoic acid	C 21:2	30.659	0.12	Methyl 18-methylnonadecanoate		326
7	Benzoic acid	C 24:4	32.877	0.36	Di-n-octyl phthalate		390

3.5.5. GC-MS Analysis for FAME composition of IL catalyzed biodiesel

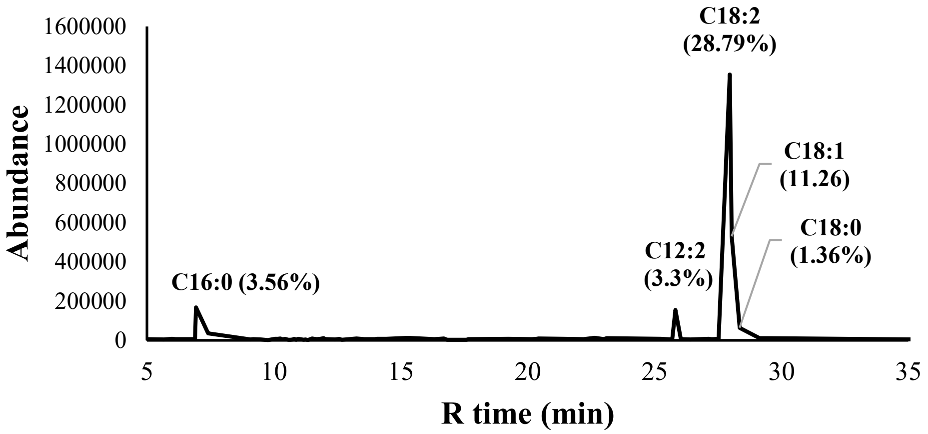


Figure 3.12. FAME composition of IL catalyzed biodiesel

Through GC-MS analysis (Figure 3.12), the FAME composition of the IL-catalyzed biodiesel was determined. The biodiesel consists of the following percentages of fatty acid methyl esters: 3.56% Hexadecenoic acid, methyl ester (C16:0), 3.3% Pentadecanoic acid, 14-methyl (C12:2), 28.79% 9,12-Octadecadienoic acid, (Z-Z) methyl (C18:2), 11.26% 9-Octadecenoic acid (Z) methyl (C18:1), and 1.36% Methyl stearate (C18:0). Notably, 9,12-Octadecadienoic acid, methyl ester (C18:2), was found in abundance compared to the other fatty acids.

3.5.6. GC-MS Analysis for FAME composition of KOH catalyzed biodiesel

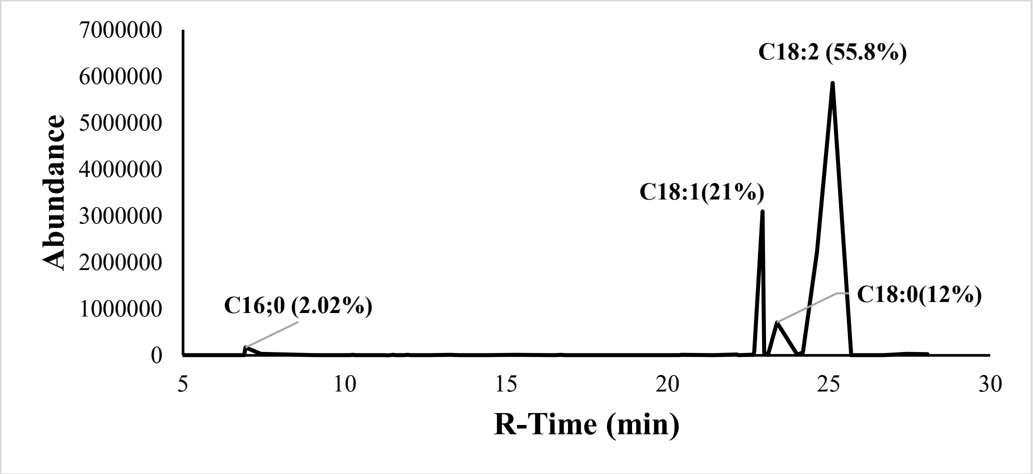


Figure 3.13. FAME composition of KOH catalyzed biodiesel.

The FAME composition of the IL-catalyzed biodiesel was determined through GC-MS analysis (Figure 3.13). It consists of the following percentages: 2.02% Hexadecenoic acid, methyl ester (C16:0), 21% 9-Octadecenoic acid (Z) methyl (C18:1), and 12% Methyl stearate (C18:0). The most abundant fatty acid methyl ester present in the biodiesel is 9,12-Octadecadienoic acid, (Z, Z) methyl ester (C18:2), accounting for 55.8% of the composition, surpassing the other acids in quantity.

CHAPTER 4

DISCUSSION

4.1. Characteristics of Extracted Oil

The differences in oil pigmentation and quality observed in the seeds are attributed to the varying levels of chlorophyll and carotenoids present in them. Chlorophyll, which is responsible for the green coloration of plant tissues, has a pro-oxidative effect that can cause degradation of the oil quality and produce strong odors. On the other hand, carotenoids, which are pigments responsible for the yellow to red hues in plant tissues, have antioxidant properties that can protect the lipids from oxidation and improve the nutritional quality of the oil.

The harvesting time of the seeds also plays a significant role in the oil quality. The summer seeds, which were harvested before maturity, had higher levels of chlorophyll, and produced oils with dark colors and strong odors. In contrast, the winter seeds were harvested when they were fully matured, resulting in low chlorophyll content and high levels of carotenoids that produced oils with lighter colors and less oily odors (Wang *et al.*, 2016).

4.2. Parameters of Transesterification

The current study's findings show that transesterification parameters are critical for estimating optimum biodiesel output. The concentration of the catalyst is an important parameter that affects the yield of biodiesel. A low concentration of catalyst results in high yield because of the availability of more active sites for binding with methanol. On the other hand, an increased concentration of catalyst leads to soap formation, slurry formation, and increased viscosity, which reduces the availability of active sites for attachment with methanol, resulting in lower biodiesel conversion (Tan *et al.*, 2015).

The oil to methanol ratio is another important parameter that affects the yield of biodiesel. The use of excessive methanol is desirable because it reacts with the additional FFA present in the oil, thereby increasing the production of biodiesel. However, excessive use of methanol can lead to drowning of the catalyst's active sites, reducing the probability of the catalyst-oil contact, and decreasing biodiesel production (Lokman *et al*., 2014).

Temperature is also an important parameter that affects biodiesel yield. Transesterification is an endothermic reaction, and an increase in reaction temperature decreases the viscosity of the oil, leading to increased biodiesel yield. However, an excessively high reaction temperature can reduce methanol polarity and evaporate methanol, limiting the amount of alcohol available for the reaction, which ultimately diminishes the total yield of biodiesel (Baskar *et al*., 2018; Dhawane *et al*., 2017).

Reaction time is also an important parameter affecting the yield of biodiesel. Longer reaction times can result in less biodiesel production as transesterification is a reversible process that causes esters to be lost and soap to develop. However, the optimal transesterification reaction time depends on the biomass, catalyst utilized, and its dosage (Dhawane *et al*., 2018).

4.3. Physical and Chemical Properties of Extracted Oil and Biodiesel

Acid value of oil was 3.6 mg KOH g^{-1} which is higher because in oil there is always free fatty acid was presents which can affect the biodiesel production, but the biodiesel results of this study indicated that the both the catalysts gave good result in reducing the acid value up to the suggested ASTM standard i.e., 0.8 mg KOH g^{-1}.

The existence of oxidative components (i.e., the part of a molecule with distinctive oxidative characteristics) in a sample is determined using the PV test. Hydroperoxides were created when oxygen from the air combines with alkyl esters commonly present in biodiesel. This is often the initial step in biodiesel's oxidative breakdown cycle. According to Dunn, (2005) increased in PV of biodiesel raises the cetane number, shortening the ignition time.

The peroxide value of biodiesels produced by using CB and IL catalysts obtained were 4.5 m Eq kg^{-1} and 3.2 m Eq kg^{-1}. These data suggested that biodiesels made from EO treated with CB and IL catalysts are less susceptible to oxidative rancidity. Oxidation produces hydroperoxide molecules, which react with metals and synthetic rubbers, by generating acids. Another negative effect of oxidation is that it initiates polymerization processes, which result in the development of gum and silt that clog filters and injectors of engine (Galão *et al.,* 2013).

The saponification value of biodiesel produced was lower than the EO but still its values were high. A higher SV implies that the oil has a larger percentage of low molecular weight fatty acids (Diwakar *et al*., 2009). The IL catalyzed biodiesel showed lower SV than CB catalyzed biodiesel because it is acid in nature and acid catalysts take longer time in reaction by giving more time to reactant to react together, hence produce less soap (Lam *et al*., 2010).

The IV is a valuable measure for determining the oxidative degradation and chemical stability of various oil and biodiesel products. A larger concentration of double bonds in the sample has a higher polymerization potential and hence poor stability. The EO obtained is considered nondrying because its IV was less than 110 g I_2 $100g^{-1}$. Oils with an IV greater than 125 g I_2 $100g^{-1}$ are categorized as drying oils, whereas those with an IV between 110 and 140 g I_2 $100g^{-1}$ are classified as semidrying oils. Oils with IV less than 110 are classified as nondrying. Whereas the IV of biodiesel produced from this oil using CB and IL catalysts was 68.39 g I_2 $100g^{-1}$ and 68.77 g I_2 $100g^{-1}$, respectively. The smaller the IV, the greater the fuel as a biodiesel will be (Ismail & Ali, 2015). IV may also be used to determine the total level of saturation of the oil, which is significant for estimating viscosity and cloud points. Higher IV may reduce engine performance but provide better viscosity properties in colder circumstances (Caye *et al.,* 2008).

The CN and HHV were determined using an equation in this study, and their values were dependent on the IV and SV. The lower the IV value, the greater the cetane number, hence the biodiesel generated in this research from both CB and IL catalysts had a low IV and thus a high CN output. According to (Lawan, 2018), *Calophyllum apetallum* wild has IV 97.6 g I_2 $100g^{-1}$ and CN value 51.57 min, whereas *Moringa concanensis* has IV 76.0 g I_2 $100g^{-1}$ and CN value 56.32 min both the data support the result this of study.

Cold weather creates another problem for biodiesel fuels, known as the cold flow or low-temperature flow issue (Islam *et al*., 2016). In general, biodiesel fuels have such challenges throughout the winter season and in colder places. The two key qualities for fuel that affect cold flow specification are cloud point (CP) and pour point (PP) (Boros *et al*., 2009). The biodiesel produced from using CB and IL catalysts had PP -6 and -8 ° C, respectively which indicated they were best qualitatively when compared to ASTM limit categorized for biodiesel.

4.4. TGA of IL

In the IL sample, the first and second weight losses were observed at lower temperatures (100-400 °C), which can be attributed to the removal of moisture, water, hydroxyl groups, organic matter, and alkyl groups. Specifically, the second weight loss suggests a significant decomposition process, resulting in a substantial reduction in the IL's weight (Behnezhad *et al*., 2020).

The third weight loss, occurring at 700 °C, indicates the complete degradation of the sample. This high-temperature degradation suggests that a significant amount of external heat is required to overcome the carbon structure, demonstrating the thermal stability of the sample.

The functionalized and stable IL requires more heat energy due to the presence of strong Van der Waals forces within its structure. These forces contribute to the increased resistance to thermal decomposition, thus necessitating higher temperatures for the degradation process to occur (Alonso *et al*., 2010).

CONCLUSION

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This study confirms the feasibility of producing biodiesel from non-edible oil crops, specifically *Melia azedarach* L., utilizing base (KOH) or Bronsted acidic ionic liquid [VISM][HSO_4] catalysts. When employing the organic solvent n-hexane, a 35% oil yield was attained from summer seed oil extraction. The prominent fatty acid within the oil was identified as linoleic acid. Notably, the IL catalyst exhibited stability up to 400 °C prior to decomposition. The optimization of transesterification conditions for both catalysts disclosed that IL-catalyzed transesterification outperformed KOH-catalyzed, yielding 100% and 97% biodiesel, respectively, under optimized parameters. The optimal conditions for IL-catalyzed transesterification encompassed a 1:9 oil methanol molar ratio, 1% (*w/w*) catalyst dose, 80 °C reaction temperature, and a 120-minute reaction duration. The resulting biodiesel adhered to the international ASTM standard. FTIR and GC-MS analyses further endorsed the potential of *Melia azedarach* L. as a biodiesel feedstock, attesting to the successful synthesis of both IL and biodiesel products.

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