Production of Biodiesel from Castor Oil Using Imidazolium Based Acidic Ionic Liquid Catalyst

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Table of Contents

List of Tables

List of Figures

List of Abbreviations

FAMEs	Fatty Acid Methyl Esters
RFS	Renewable Fuel Standard
ECC	Economic Coordination Committee
OMC	Oil Marketing Companies
FFA	Free Fatty Acid
CV	Calorific Value
CN	Cetane Number
FP	Flashpoint
IV	Iodine Value
AN	Acid Number
PV	Peroxide Value
PP	Pour Point
SV	Saponification Value
STR	Stirred Tank Reactor
SDR	Spinning Disc Reactor
RTR	Rotating Tube Reactor
ACR	Annular Centrifugal Reactor
RDR	Reactive Distillation Reactor
ROI	Return on Investment
EROEI	Energy Return on Energy Investment
TGA	Thermogravimetric Analysis
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography Mass Spectroscopy

Abstract

The world's population is exponentially increasing so is the energy demand. Fossil resources are depleting at a faster pace. Not only they are not enough to meet the requirements but also they are emitting harmful emissions. Green approach is to use biodiesel which is more environmental friendly. In this study, castor biodiesel was prepared by using acidic ionic liquids i.e., 1-vinyl-3-(sulfopropyl) imidazolium hydrogen sulfate [VSIM][HSO_4] and modified 1-vinyl-3-ethylimidazolium bromide (VEtImBr) as catalysts. pH was measured to determine the acidity of catalysts. These catalysts were synthesized and used in the transesterification by using different reaction conditions (reaction time, oil methanol ratio, catalyst concentration, and temperature). Physicochemical parameters of oil and castor biodiesel were measured. TGA, FTIR, and GC-MS analysis were done. Modified VEtImBr showed a maximum biodiesel yield of 99.8%. Optimum conditions were 60 min reaction time, 6 wt% catalyst concentration, 1:06 oil methanol ratio, and 60 °C temperature. The acidity of catalysts was compatible with the inorganic acids (pH is 1.5 and 1.6 of [VSIM][HSO_4] and modified VEtImBr, respectively). All physicochemical parameters were within range except iodine value and density. TGA analysis showed that modified VEtImBr is more thermally stable (up to 270 °C) than [VSIM][HSO_4] (up to 235 °C). FTIR analysis showed characteristic peaks confirming the chemical structure. GC-MS showed that ricinoleic acid, palmitic acid, and phthalic acid are prominent in castor oil. Ricinoleic acid methyl ester, palmitic acid methyl ester, linoleic acid methyl ester and oleic acid methyl ester were the main constituents of biodiesel.

Chapter 1

Introduction

Background Information

Due to economic growth and increasing population, the energy need across the globe is increasing rapidly. Fossil fuel is insufficient to cater to this high demand. The world is now paying attention to green energy sources i.e., biofuels. Biofuel i.e., biodiesel is a source of green energy and a good replacement for fossil fuel based resources. It can minimize the use of fossil fuel diesel (Aghbashlo et al., 2016).

Biodiesel has a high cetane number, flashpoint higher than 130 °C, and low sulfur content as compared to petroleum diesel. As natural resources are depleting and energy demand is high, manufacturing and application of biodiesel as an alternative is more favored (Zulqarnain et al., 2021).

Petroleum diesel produces harmful emissions. Using biodiesel as an alternative is beneficial to the environment as it reduces the emissions of aerosol particles, carbon monoxide, nitrogen and sulfur oxides, aldehydes, and hydrocarbons. Biodiesel burning is more safe than fossil fuel burning because it does not emit carcinogenic compounds which are harmful to health. Different proportions are used to blend biodiesel with petroleum based diesel. Biodiesel have such properties which enable them to be used in an engine right away without any refinement (Zahid et al., 2020).

Biodiesel is also compatible with the internal oil and engines of the vehicle. It is beneficial as emissions are less than petroleum diesel. Emissions like organic compounds, carbon monoxide, and smoke are 20, 30, and 50% less than that of petroleum based diesel (Datta et al., 2016).

Pakistan is also facing severe energy shortages. Its dependence on fossil fuels is enormous and reliance on sustainable energy is less. The COVID-19 pandemic caused demand-side shocks and fluctuations in the economy of the country. Electricity and fuel prices in Pakistan are affected greatly by international crude oil prices. In 1986, energy consumption in Pakistan was 12 million tons of oil. It then increased to 52.17 million tons of oil in 2020. It is expected that in 2030, it will be 116 million tons of oil (Pakistan Energy Demand Forecast, 2021).

Also, fossil fuel resources are unable to cater to huge energy demand and Pakistan faces energy shortages due to it. Fossil fuel sources satisfy only 15% of energy demand (Ali et al., 2020).

In 2015, Pakistan imported 13.57 million tons of petroleum products which caused a higher fiscal deficit. The transportation sector consumes a major chunk of petroleum energy i.e., 57% (Hydrocarbon Development Institute of Pakistan, 2018). Import bills can be curtailed by the advancement of processes to improve energy efficiency and draft well-developed energy preservation policies. Due to the current situation and high energy demands, if we do not shift to other energy sources, our economy will be severely affected. Today's world cannot run without fuel and it will be a disaster when fossil resources will become so less. For our future, we need to establish an alternative system and biodiesel is the best option to cater to our needs.

1.1. Biodiesel

Biodiesel is a biofuel (derived from biomass) that is compatible with a diesel engine for efficient combustion as a substitute for petro-diesel. Rudolf Diesel, who invented the diesel engine used peanut oil to test his engine in 1900. Biodiesel is chemically different from petro-diesel as it contains oxygen in its molecular structure (Khan et al., 2022).

Biodiesel is chemically stated as fatty acid methyl esters (FAMEs). It is formed by the reaction of oil (plant or animal based) with methanol or ethanol as a solvent by using an acidic or basic catalyst (Zulqarnain et al., 2020). FAMEs composition include oleic acid, stearic acid, linoleic acid, palmitic acid, linolenic acid, arachidic acid, and palmitoleic acid. The composition of biodiesel depends on the feedstock used to synthesize it. The composition also plays a role in biodiesel characteristics i.e., oxidation stability, pour point, viscosity, density, etc. The composition of biodiesel is such that it is degradable due to which there is reduced impact on the climate systems across the globe (Zulqarnain et al., 2021).

1.2. Biodiesel Production around the Globe

Many countries have taken the impact of fossil fuels on climate change seriously. They are tending to reduce dependence on fossil fuels and are moving towards renewable resources. Vegetable oil contributes to 73% of biodiesel production globally, 31% of which is palm oil, 24% soybean oil, 21% used cooking oil, and 14% rapeseed oil. 30.7% of the total biodiesel production globally is in the European Union, and 18.4% in the United States. European Union uses palm oil, rapeseed oil, and used cooking oil for biodiesel synthesis. The United States uses soybean oil and used cooking oil for biodiesel synthesis. Indonesia, Brazil, Thailand, China and Colombia, etc. are other prime contributors producing 17.5, 13.1, 3, 2.8%, and 1.3% biodiesel globally (OECD, FAO, 2022).

It is estimated that by 2031, global biodiesel production will increase to 55 billion tons from 37 billion tons as of 2020. Renewable energy directive, RED II has set a target that 32% of transport energy will be based on renewable resources by 2030. The renewable energy share reached 22% in 2020. They aim to abolish fossil fuels and substitute it with renewable energy by year 2050 (Popp et al., 2021). In the United States, the EPA has set a post-renewable fuel standard (RFS) regime to sustain biofuel production. Its main objective is to expand biodiesel production to 3.35 billion gallons by year 2025. RFS aims to save 20% of GHG by using renewable resources relative to gasoline (Lark et al., 2022). Singapore produces biodiesel to not only reduce greenhouse gas emissions but also to export it to boost the country's economy. It is projected that in Singapore, biodiesel production from used cooking oil will increase to 1.4 billion liters. The Philippines, Malaysia, and Peru are some other countries to produce biodiesel; by 2031, production is expected to increase to 1.69 billion liters, 0.2 billion liters, and 0.3 billion liters respectively. These countries also use biodiesel blends. Malaysia uses a 10% blend, whereas 6% and 3% blend are used in Peru and the Philippines respectively. To set up blending facilities and improve infrastructure, the Malaysian government has allocated 79 million dollars for it (Mahdi et al., 2023).

1.2.1. Sustainable Development Goal to Mitigate Climate Change

Goal 7 of Sustainable Development Goals is "Affordable and Clean Energy". Prime contributor to climate change is energy. 60% of total global greenhouse gas emissions is due to energy (Hossin et al., 2023).

Apart from energy needs, biodiesel is also necessary to be opted to ameliorate climate change. In the past 10 years, 86% of carbon dioxide emissions are due to fossil fuel burning (Canadell et al., 2021). Greenhouse gases have impacted our ecosystem adversely. It has caused a rise in temperature, melting of glaciers, flooding, sea level rise, and other unusual climatic events across the globe (Sule et al., 2022). So, to address this issue we should shift from fossil fuel resources towards more green resources i.e., biodiesel.

1.3. Status of Biodiesel Production in Pakistan

To meet the energy demand, Pakistan is importing petroleum diesel immensely. In 2018, Pakistan had imported 14 million tons of petroleum diesel which was greater than previous years (Yaqoob et al., 2021). In Pakistan, policies for biodiesel implementation were given by the Alternative Energy Development Board on 14th of Feb, 2014. In a conference, the Economic Coordination Committee (ECC) of the National Cabinet gave a vision to start implementing biodiesel in Pakistan. They mentioned implementing biodiesel blends gradually in the country, to commence a scheme for the quality measures of the biodiesel blend, and provoked that oil marketing companies (OMC) must buy the biodiesel from manufacturers (Akia et al., 2014). In Pakistan, the B10 Jatropha biodiesel blend is used practically. In the future, demand will increase so that there will be a need for more Jatropha (*Jatropha curcas* L.) seeds. To meet the demands of fuel in the local transportation sector, B10 and B20 blends can be utilized. The requirement of this B10 blend in Pakistan is 0.8 million tons. Effective implementation of Jatropha biodiesel can reduce the import cost of diesel by 0.4 billion dollars. In this way, Pakistan will be able to minimize imports by using biodiesel which can positively impact economy. For this purpose, Pakistan State Oil (PSO) is working on a biodiesel blend. The government of Pakistan has set a target to use 15% blended biodiesel by 2025 (Hussain et al., 2023).

For the first trial to produce biodiesel from Jatropha seeds, 5000 trees were cultivated. A Canadian company, Kijani Energy invested 150 million dollars in 2009 to cultivate Jatropha trees on 80937 hectare area covering Khairpur, Cholistan, Umerkot, Tharparkar, and Sanghar to produce biodiesel from it. It is expected that in Pakistan 2.93 million tons of Jatropha biodiesel will be produced (Yaqoob et al., 2021)

1.4. Feedstocks for Biodiesel

Different types of feedstock are used to make biodiesel. According to the feedstock types, biodiesels are divided into four generations (Sarwer et al., 2022).

1.4.1. 1st Generation Feedstock

Currently, first-generation feedstock is mostly used (more than 95%) in biodiesel production across the globe (Zulqarnain et al., 2021). It is extracted from edible biomass or crop oil. Rapeseed, sunflower, palm, and soybean oil are some examples of first-generation feedstock. They are used extensively because of their availability. Using it extensively poses a negative impact on the price of food and leads to food insecurity. It also leads to environmental problems due to intensive plantation which includes water scarcity, food insecurity, soil degradation, biodiversity loss, and deforestation. A good yield of biodiesel is produced using this feedstock with easy conversion (Topare et al., 2023). Palm oil (*Elaeis guineensis* Jacq.) was used to synthesize biodiesel. A heterogeneous bismuth ferrite nano-catalyst was used and a 98% yield was achieved. Optimum conditions were 1:15 oil methanol ratio, 7 wt% catalyst concentration, reaction time 120 min, and 79.85 °C temperature (Razuki et al., 2023). Sunflower oil (*Helianthus annuus* L.) yielded 99.2% biodiesel by using a heterogeneous catalyst (RHA/CuO/K_2CO_3). Optimum conditions were 1:18 oil methanol ratio, 3 wt% catalyst concentration, 120 min reaction time, and reaction temperature of 65 °C (Foroutan et al., 2023). Rapeseed oil (*Brassica napus* L.) yielded 94.55% biodiesel by using dolomite as a catalyst. Optimum conditions were 1:13.71 oil butanol ratio, 5.24 wt% catalyst concentration, 480 min reaction time, and 110 °C temperature (Gaide et al., 2022).

1.4.2. 2nd Generation Feedstock

This type of feedstock is non-edible in nature and derived from different sources. Non-edible plants, waste cooking oil, animal, fat, etc. are some examples of 2nd generation feedstock. This type of feedstock does not need large land area to be cultivated and goes well with mixed crop cultivation. Some non-edible plants like *Ricinus communis* L. (Castor), *Jatropha curcas* L. (Jatropha), *Pongamia pinnata* (L.) Pierre (Karanja), *Azadirachta indica* A.Juss. (Neem), etc. are some non-edible sources of biodiesel production. They are cultivated in their natural habitat ensuring the presence of oil the whole year (Arumugam et al., 2019). Their properties are similar to 1st generation feedstock. Non-edible plants produce biodiesel which is low in aromatics and sulfur compounds. It leads to reduced toxic gas emissions to the environment when combusted. It is environmentally friendly (Mofijur et al., 2021).

Castor oil yielded 96.32% biodiesel by using $LiAlO_2$-$LiFeO_2$ catalyst. Optimum conditions were 1:15 oil methanol ratio, 5 wt% catalyst dosage, 150 min reaction time, and 65 °C temperature (Ba et al., 2022). Malabar ebony is another non-edible source and yielded 94% biodiesel by using a green CdO_2 nano-catalyst. Optimum conditions were a 1:9 oil methanol ratio, 0.5 wt% catalyst concentration, a reaction time of 180 min, and a reaction temperature of 90 °C (Arshad et al., 2023). A yield of 98.7% biodiesel was achieved by using Jatropha oil. Carbonaceous material (Sulfonic acid functional group) was used as a catalyst. Optimum conditions were 1:20 oil methanol ratio, 9 wt% catalyst concentration, reaction time of 50 min, and 120 °C temperature (Ruatpuia et al., 2023).

1.4.3. 3rd Generation Feedstock

This type of feedstock originates from algae biomass i.e., microalgae or macroalgae. They are environmentally friendly and require less area to grow. But they require sufficient sunlight, carbon dioxide, water, and nutrients to grow. They help to mitigate climate change by consuming carbon dioxide which is a greenhouse gas. It is estimated that to grow 1 kg of algal feedstock, 1.8 kg of carbon dioxide is consumed. They contain large amounts of oil in their biomass. About 70% of the dry weight of chlorella species consists of oil. About 80% of the dry weight of microalgae may consist of oil. These are huge quantities as compared to 55, and 50% of sunflower and palm plant dry weight, respectively. There are some limitations to using algal biomass to produce biodiesel. They require a large amount of water to grow. Water scarcity is also a major issue in many countries. It is expensive to produce algal biodiesel commercially due to advanced technology to scale up it (Varkkey et al., 2018).

In a study, 87.6% yield of biodiesel was produced by using microalgae. SO_4^{-2}/Fe_3O_4-Al_2O_3 nano-catalyst was used and optimum conditions were 1:9 oil methanol ratio, 8 wt% catalyst concentration, 240 min reaction time, and 120 °C temperature (Safakish et al., 2020). Dry algae yielded 87.42% biodiesel by using NaOH catalyst. Optimum conditions were 1:8 oil methanol ratio, 3.36 wt% catalyst concentration, 60 min time, and 50 °C temperature (Chamola et al., 2019). Microalgae i.e., *Spirulina* species yielded 85.28% biodiesel by using KOH as a catalyst. Optimum conditions were 1:5 oil methanol ratio, 1 wt% catalyst concentration, 120 min reaction time, and 60 °C temperature (Pradana et al., 2020).

1.4.4. 4th Generation Feedstock

Synthetic biology development has opened the gate to another type of feedstock which is fourth generation feedstock. An economical and renewable biodiesel feedstock can be generated by the incorporation of renewable energy like solar energy and purpose-designed biological systems which are modified. This type of feedstock can be formed by incorporating photovoltaics in fuel production process, through formation of cells synthetically, and by modified photosynthetic microorganisms (Singh et al., 2020). It will produce high lipid content, increased ability to absorb carbon dioxide, rapid growth rate, and high energy content. There are some limitations too. To build up such a system, capital cost is high. Research is at the infancy level so less knowledge is available (Shah et al., 2018).

1.5. Castor Oil Biodiesel

Castor oil is used in cosmetics, perfumes, lubricating oil, and plasticizers. It is not suitable for human consumption and doesn't compete with food production. Its oil contains ricinoleic acid in abundance. The castor tree is beneficial for carbon sequestration as it consumes 34.6 tons of carbon dioxide per hectare (Oprea et al., 2019). It has a good potential for carbon trading. It is cultivated in 4131 hectare area in Pakistan and 3.4 million dollar export was observed in 2021. In a study castor oil biodiesel cost was determined and found to be 0.693 US dollars per liter (Rahimi et al., 2020).

Because it is a fast-growing crop with high biomass production even in marginal soils, the castor bean plant (*Ricinus communis* L.) provides a cheap feedstock to make biodiesel. Its 40–60% seed oil content makes it a promising feedstock for producing sustainable biodiesel (Rivas et al., 2023). It is estimated that castor plants yield 481 kg/acre of oil. Oil content in castor seeds i.e., 53% is greater than that of Jatropha plant i.e., 35%. Plantation cost of castor oil is lower i.e., 77 US dollars per acre as compared to 83 US dollars per acre for Jatropha plant. Maturity time of castor plant is 4-5 months as compared to 30 months for Jatropha plant. The optimum rainfall requirement of castor plant is 600 mm as compared to 900-1200 mm for Jatropha plant. Castor plants can be cultivated on alkaline lands, marginal dry land, semiarid, and arid lands. Castor plants grow well at temperatures above 24 °C which is suitable considering Pakistan's climate (Ali et al., 2020).

In a study, 95% of castor oil biodiesel was produced by using KOH as catalysts. Optimum conditions were 1:9 oil methanol ratio, 1 wt % catalyst concentration, 30 min reaction time and 60 °C temperature (Keera et al., 2018).

By using benzilimidazolium based ionic liquid, 96% yield of castor oil biodiesel was observed. Optimum conditions were 1:12 oil methanol ratio, 5 mol% of catalyst concentration, 840 min reaction time, and 40 °C temperature (Khiratkar et al., 2018).

Alkaline ionic liquid [Bmim] OH was used and a yield of 97% castor oil biodiesel was achieved. Optimum conditions were 1:6 oil methanol ratio, 1 wt% catalyst concentration, 60 min reaction time, and 40 °C temperature (Zhang et al., 2020).

A yield of 89.82% castor oil biodiesel was achieved by using [Hmim] HSO_4 ionic liquid. Optimum conditions were 1:6 oil methanol ratio, 12% catalyst concentration, 240 min reaction time, and 77 °C temperature (Xu et al., 2015).

1.6. Catalysts for Biodiesel

A catalyst is a substance that, by enhancing surface interaction, accelerates the rate of reaction for the synthesis of biodiesel. It increases process effectiveness and consequently lowers the price of producing biodiesel (Babadi et al., 2022). They are classified into several categories which are as follows:

1.6.1. Homogeneous Catalyst

As they are affordable and effective, homogeneous catalysts like bases and acids are typically utilized in biodiesel processes. Homogenous catalysts are further categorized as homogenous acidic and homogenous basic catalysts.

1.6.1.1. Homogeneous Acid Catalyst

Typically sulfuric acid, sulfonic acid, ferrous sulfate, and hydrochloric acid are commonly used to produce biodiesel. Most preferred ones are sulfuric acid and hydrochloric acid. As oxygen and carbon atom have electronegative difference, carbonyl group enables bonding for inorganic acids. Firstly cations are formed and then alcohol behaves as a nucleophile in the carbocation. Alcohol is then separated by accepting protons. The carbon atom receives a pair of electrons from alcohol and water is removed. Oil having high free fatty acid content is efficiently transformed to biodiesel by using a homogeneous acid catalyst (Tang et al., 2020). Homogeneous acid catalyst gives higher biodiesel yield. In a study, sulfuric acid was used as a catalyst to yield 96% biodiesel from *Sterculia foetida* L. oil and waste cooking oil mixture. Optimum conditions were 1:3 oil methanol ratio, 0.6 wt% catalyst concentration, 120 min reaction time, and 60 °C temperature (Kavitha et al., 2021). In another study, sulfuric acid catalyst was used to synthesize biodiesel from waste cooking oil. A yield of 95.37 biodiesel was achieved under optimum conditions which were 1:12 oil methanol ratio, 5 wt% catalyst concentration, 180 min reaction time, and 60 °C reaction temperature (Dhawane et al., 2018).

1.6.1.2. Homogeneous Basic Catalyst

Primary homogeneous basic catalysts which are commonly used are KOH, NaOH, CH_3KO, and CH_3NaO. KOH and NaOH are mostly used as a catalyst. As sodium-based catalysts have low molecular mass and offer a good separation phase; they are preferred over potassium-based catalysts. The mechanism include formation of radical compound by interaction of catalyst and alcohol as base catalyst accepts hydrogen. This radical compound then reacts with carbonyl group. After bond breakage ester is produced along with radical carbon chain compound. Radical compound then accepts hydrogen from base catalyst and base catalyst remains intact at the end of process. Oils that contain free fatty acid concentration less than 0.5% are efficiently catalyzed by the homogeneous basic catalyst. They show good efficiency for transesterification reactions (Mohadesi et al., 2019). NaOH catalyst produced 97% biodiesel from sunflower oil. Optimum conditions were 1:6 oil methanol ratio, 1.5 wt% catalyst concentration, 60 min reaction time, and 60 °C temperature (Maheshwari et al., 2022). KOH catalyst was used to produce biodiesel from soybean oil and yielded 95% biodiesel. Optimum conditions were 1:12 oil methanol ratio, 1.5 wt% catalyst concentration, 60 min reaction time, and 60 °C temperature (Brito et al., 2020).

1.6.2. Heterogeneous Catalyst

A catalyst that has a distinct reactant or product phase is said to be a heterogeneous catalyst. Heterogeneous catalysts can greatly save costs and make it simple to recover biodiesel (Bashir et al., 2022).

1.6.2.1. Heterogeneous Acid Catalyst

Despite their lower catalytic activity, heterogeneous catalysts are favoured over homogeneous acid catalysts. Acidic strength is less in heterogeneous catalysts but they are preferred due to efficient recovery. Heterogeneous acid catalysts examples are sulfonated solids, cation exchange resins, heteropoly acids, and different metal oxides, etc. They resist moisture and carry transesterification reactions effectively with a feedstock having low free fatty acid content (Bashir et al., 2022).

Nano-sulfated zirconia as a catalyst yielded 97% biodiesel by using waste sheep fat. Optimum conditions were 1:15 oil methanol ratio, 8 wt% catalyst concentration, 300 min reaction time, and 65 °C temperature (Booramurthy et al., 2020). ZrO_2-TiO_2-SO_3H yielded 98.6% biodiesel from palmitic acid as feedstock. Optimum conditions were 1:20 oil methanol ratio, 5 wt% catalyst concentration, 300 min reaction time, and 100 °C temperature (Fan et al., 2019).

1.6.2.2. Heterogeneous Basic Catalyst

It is better than homogeneous base catalysts as it leads to lower saponification which enables a better detachment of glycerol from the alkyl ester layer. One limitation of using heterogeneous basic catalyst is their tendency to absorb moisture when they are kept for a large period of time. When it is used with a feedstock having high free fatty acid content, soap formation occurs. Yield of biodiesel fuel is affected by it (Jain, 2019).

CaO was used with soybean oil to yield 97.61% biodiesel. Optimum conditions were 1:11 oil methanol ratio, 3.68 wt% catalyst concentration, 120 min reaction time and 60 °C temperature (Bharti et al., 2019). Cobalt doped ZnO was used with *Mesua ferrea* L. oil to yield 98.03% biodiesel. Optimum conditions were 1:9 oil methanol ratio, 2.5 wt% catalyst concentration, 180 min reaction time, and 60 °C temperature (Borah et al., 2019).

1.6.3. Enzyme Catalyst

The most familiar enzyme used in the transesterification process is lipases. Lipases are hydrolases that's why triglycerides are hydrolyzed to be converted into fatty acids and glycerol (Su et al., 2019). They are environmental friendly and can even carry out transesterification of high free fatty acid feedstock and presence of water. It can react effectively at low temperature and mild conditions of reaction. The limitation of enzyme catalysts is the high cost associated with its practical application. Some enzymes take a long time to produce biodiesel (Wang et al., 2020)

Lipase enzyme yielded 88% biodiesel from waste cooking oil feedstock. Optimum conditions were 1:3 oil methanol ratio, 1.5 wt% catalyst concentration, 240 min reaction time, and 60 °C temperature (Jayaraman et al., 2020). A yield of 92% was observed when

Lipase-PDA-TiO_2 was used as a catalyst. Jatropha oil was used as a feedstock. Optimum conditions were 1:6 oil methanol ratio, 10 wt% catalyst concentration, 1800 min reaction time, and 37 °C temperature (Zulfiqar et al., 2021).

1.6.4. Nano-catalyst

Nanotechnology is used to form nano-catalysts to use in a transesterification reaction. They have cross section of less than 100 nm and are of different shapes and morphologies. Their properties lie between homogenous and heterogeneous catalysts. They show high activity and are very stable. They can function in even mild reaction conditions and produce biodiesel with the higher yield. They can also be reused again to produce biodiesel. The limitation of using nano-catalyst is high cost during its synthesis (Hosseini et al., 2022).

$NaAlO_2$-Al_2O_3 nano-catalyst was used to produce biodiesel from palm oil. A yield of 97.65% biodiesel was achieved under optimum conditions. Optimum conditions were 1:20.79 oil methanol ratio, 10.89 wt% catalyst concentration, 60 min reaction time, and 65 °C temperature (Zhang et al., 2020). $CaO/CuFe_2O_4$ nano-catalyst was used to produce biodiesel from chicken oil. A yield of 94.52% was obtained by using 1:15 oil methanol ratio, 3 wt% catalyst concentration, 240 min reaction time, and 70 °C temperature (Seffati et al., 2019).

1.6.5. Ionic Liquid Catalyst

Ionic liquids (ILs) are organic salts that are in liquid state at room temperature due to a melting point below 100 °C. It is made of anions and cations and is used as solvents and catalysts for different reactions. Due to their properties and applications, they have gained interest in the past 10-20 years (Ullah et al., 2018).

Ionic liquids are unique and do not follow like dissolve like rule as they can dissolve both polar and non-polar compounds. As they consist of anions and cations, they individually affect the ionic liquid physicochemical properties. These properties include melting point, viscosity, conductivity, density, etc. They can also introduce some features in their application like adding functional groups for catalysis purposes, chirality, controlling the solubility of solute, and influencing hydrophobicity or hydrophilicity in reaction medium (Ong et al., 2021).

Some common organic cations of ionic liquid are imidazolium, quaternary ammonium, phosphonium, and pyridinium. Common anions include halides (bromides, chloride, etc.), hexafluorophosphate, tetrafluoroborate, etc. (Cheng et al., 2022).

1.7. Properties of Ionic Liquid

They are categorized as green solvents because of their excellent properties. These properties include less sensitivity to heat, high catalytic activity, easy recyclability, low flammability, flexible design ability, high aqueous solubility, low volatility, superior conductivity, and low melting point. So, they are a good alternative to other organic solvents which are harmful and volatile (McNeice et al., 2020).

Ionic liquids are also called designer compounds because their chemical and physical properties can be easily tunable. We can select and modify anions and cations for desired characteristics and requirements for different usage (Szepinski et al., 2020).

Applications of ionic liquid include catalysis, biomass conversion, electrochemistry, pharmaceutical engineering, fuel production, biotransformation, and nanotechnology (Sehrawat et al., 2020).

1.8. Applications of Ionic Liquid as Catalyst

Ionic liquids, most commonly acid ionic liquids are commonly used in the transesterification reaction to produce biodiesel. Currently, to manufacture biodiesel from different feedstock, Bronsted and lewis acidic ionic liquids are being extensively used. These feedstocks include castor oil, soybean oil, and even oils with high free fatty acid values (Brzeszek-Szafran et al., 2021).

Some new acidic ionic liquids were used to produce biodiesel from oleic acid in the presence of methanol. It was observed that catalytic activity was higher even in the presence of mild reaction conditions. The temperature range for such reactions was 25-60 °C (Zhang et al., 2023).

A yield of 97.58% biodiesel was achieved by using [EDA-PS] [P-TSA] ionic liquid with oleic acid. Optimum conditions were 1:13 oil methanol ratio, 3 wt% catalyst concentration, 108 min reaction time, and 70 °C reaction temperature (Li et al., 2021).

92.38% biodiesel was produced from the *Thlaspi arvense* L. seed oil by using graphene oxide supported ionic liquid catalyst. Optimum conditions were 1:10 oil methanol ratio, 25 wt% catalyst concentration, 240 min reaction time, and 60 °C temperature (Zhao et al., 2021).

[$NiFe_2O_4$@BMSI]Br ionic liquid was used with palm oil to produce 74.6% biodiesel. Optimum conditions were 1:12 oil methanol ratio, 5 wt% catalyst concentration, 480 min reaction time, and 80 °C temperature (Naushad et al., 2021).

1.9. Applications of 1-Vinyl-3-(Sulfopropyl) Imidazolium Hydrogen Sulfate

1-vinyl-3-(sulfopropyl) imidazolium hydrogen sulfate [VSIM][HSO_4] ionic liquid was made magnetic after copolymerization. It was observed that along with magnetic nanoparticles, catalytic efficiency was enhanced. 93.3% biodiesel was achieved by the transesterification of soybean oil. Optimum conditions were 1:35 oil methanol ratio, 9 wt% catalyst concentration, 360 min reaction time, and 120 °C temperature (Xie et al., 2020).

In a study, poly ionic liquid based on [VSIM][HSO_4] and sodium p-styrene sulfonate was synthesized. Enrichment and swelling properties in solvents were observed. Due to hydrogen bonding interactions, enrichment and swelling properties were greater. It was also used as a catalyst for alkyne hydration. Catalytic activity was greater than other catalysts which are homogeneous or heterogeneous in nature (Chen et al., 2021).

A yield of 92.6% biodiesel was achieved when poly(ionic liquid) based on [VSIM][HSO_4] was used in the transesterification of oleic acid. Optimum conditions were 1:12 oil methanol ratio, 8.5 wt% catalyst concentration, 270 min reaction time, and 80 °C temperature (Wu et al., 2016).

[VSIM][HSO_4] monomer was used to make acidic magnetic polymer catalyst. This acidic catalyst was used to synthesize 1, 1-diacetyl from aldehydes. It gave good yield in mild conditions. Even at room temperature and solvent free conditions, yield was high i.e. 94% (Pourjavadi et al., 2012).

[VSIM][HSO_4] was used as a catalyst for the acetylation of cellulose. Good catalytic activity was observed. 88.8% yield of cellulose acetate was achieved by using only 9 mol% of ionic liquid (Tian et al., 2014).

A polymer of [VSIM][HSO_4] was synthesized. It was then used as an organocatalyst to synthesize dihydropyrimidines under mild conditions by using Biginelli synthetic route. A yield of 90% was observed which was higher than that of H_2SO_4 (88%) (Pourjavadi et al., 2012).

1.10. Applications of 1-Vinyl-3-Ethylimidazolium Bromide

1-vinyl-3- ethylimidazolium bromide (VEtImBr) polymer was obtained and used as a catalyst to synthesize diethyl carbonate from propylene oxide. Propylene glycol was also produced as a byproduct. A yield of 54.4% diethyl carbonate and 59.8% of propylene glycol was achieved (Wang et al., 2017).

In a study poly ionic liquid nanoparticles were created by using 1-vinyl-3-ethyl imidazolium. Magnetic nanoparticles were also used in this synthesis of polymer which was formed by distillation precipitation polymerization process. The resultant catalyst was utilized to produce 4H-benzo[b]pyrans in water using a magnetic heterogeneous base (Pourjavadi et al., 2013).

In a study, VEtImBr was grafted on a heterogeneous catalyst. It was then used in the cycloaddition reaction of epichlorohydrin with CO_2. Conversion rate of 98.5% was observed to obtain cyclic carbonates (Wang et al., 2021).

A polymer of 1-vinyl-3- ethylimidazolium bromide was supported on reduced graphene oxide along with AuPt@Pt nanocrystals. Electrocatalytic performance was observed in the ethylene glycol oxidation reaction. It was observed that catalytic efficiency was higher than commercially used Pt/C (20 wt%) catalyst (Shao et al., 2016).

1-vinyl-3- ethylimidazolium bromide was used to make a polymer that acted as a sacrifice agent to make carbon nanotube catalyst. It was then used as a cathode catalyst for Li-O_2 batteries. Comparing the catalyst's activity to samples without polymer ionic liquid, it exhibited increased activity (Ni et al., 2017).

1-vinyl-3-ethyl-imidazolium bromide was polymerized to create micro particles that contained tyrosinase. Tyrosinase was successfully used to create a catechol amperometric biosensor. The biosensor was used to find phenol chemicals in samples of wastewater. Recoveries of 91-96% were observed (Lopez et al., 2018).

1.11. Processes of Biodiesel Production

There are four main processes for biodiesel production which are as follows:

1.11.1. Direct Blending and Dilution

It involves blending and mixing of animal or vegetable oil with petroleum biodiesel to be used as a fuel in diesel engine. To reduce the high viscosities of crude oils, vegetable blend is often used to dilute the diesel fuel. However it causes issues like gum formation because polymerization and oxidation occur during its storage. Carbon deposition, agglomeration, and solidification of lubricating oil, and acid generation are some other issues associated with it (Singh et al., 2020).

1.11.2. Micro Emulsification

It is a technique to decrease the high viscosity problems of vegetable oils through the formation of micro-emulsions with various solvents. It is a thermally stable, clear mixture of surfactant, oil, and water which is isotropic in nature (same properties in different directions). These surfactants (nbutanol, methanol, hexanol, etc.) act as an emulsifying agent and disperse oil into small droplets. Limitation includes carbon accumulation in diesel engines and insufficient combustion (Zulqarnain et al., 2021).

1.11.3. Pyrolysis

In this conversion, the reaction is carried out in high heat and anaerobic conditions. It is also known as thermal cracking. When the catalyst is used it is called catalytic cracking. This process is quite similar to the one in which petroleum biodiesel is synthesized. It produces less waste and negligible pollution. They are classified into three types on the basis of operational temperature. Conventional pyrolysis (275-625 °C), fast pyrolysis (575-975 °C), and flash pyrolysis (775-1025 °C) are different types. Some byproducts formed in this process are not desirable (Karmakar & Halder, 2019).

1.11.4. Transesterification

This process is most frequent and commercially used in the production of biodiesel. In this process feedstock oil is reacted with alcohol and fatty acid alkyl ester (biodiesel) is produced along with a byproduct i.e., glycerol. Catalysts are also used in this reaction to increase the reaction rate. Stoichiometric calculations suggest using 1 mol of triacylglycerol (animal or plant oil) and 3 mol of methanol or ethanol. It is a reversible reaction so a higher concentration of methanol favors more product yield by shifting the reaction equilibrium forward (Mishra & Goswami, 2018). Initially, one methanol molecule is used to convert triglyceride to diglyceride, fatty acids are released which then react with methanol and one molecule of fatty acid methyl ester is formed. Then, another methanol molecule reacts with diglyceride to form monoglyceride along with another molecule of fatty acid methyl ester. In the last step, monoglyceride reacts with the third molecule of methanol to generate the last molecule of fatty acid methyl ester and glycerol is produced (Chozhavendhan et al., 2020). Layers are being formed after some time with biodiesel at the upper and glycerol at the bottom layer. Important parameters for the optimization are the nature of alcohol and molar ratio with oil, catalyst nature and dosage, time and temperature of reaction, free fatty acid content, etc. (Mathew et al., 2021).

1.12. Effects of Transesterification Parameters on Biodiesel Yield

1.12.1. Catalyst Concentration

It is an important parameter for the transesterification reaction. Feedstock with low free fatty acid (FFA) concentration gives better yield with base catalyst whereas feedstock with high FFA concentration gives better yield with acid catalyst (Mansir et al., 2018).

When less concentrations of catalysts are used, it gives a lower yield of biodiesel. This is due to less catalytic surface given by lesser quantity of catalyst. Less concentration results in a surplus amount of methanol which is left unreacted. It then dissolves in glycerol and biodiesel production process is hindered. After an optimum concentration when we increase dosage, yield may decrease. It is due to increased viscosity, slurry formation, and soap formation (Korkut et al., 2018).

1.12.2. Oil to Alcohol Ratio

Among methanol, ethanol, butanol, propanol, etc. methanol is preferred for commercial applications as it is cheaper (Rehan et al., 2018). Methanol can be recycled for biodiesel production as it does not form azeotrope (mixture with constant boiling point) with water. Acid catalysts require a high oil to methanol ratio as compared to base catalysts.

Less and excessive methanol concentration results in a lower yield of biodiesel. When less methanol is used, a reverse reaction occurs as equilibrium is not shifted towards the formation of products. Excess feedstock is left unreacted as methanol is not available for the reaction (Rad et al., 2018). When excessive amount of methanol is applied in a reaction, yield is reduced as active sites of the catalyst are occupied with it and are not available for the oil. A high concentration of methanol also causes difficulty in separation of glycerol (Sharma et al., 2018).

1.12.3. Reaction Temperature

Reaction temperature is an important factor as transesterification is an endothermic reaction. A certain temperature is required by feedstock to overcome the barrier of activation energy (Hanif et al., 2018). Biodiesel yield generally increases by increasing temperature as it lowers the viscosity of oil.

When the temperature is low, the viscosity of oil is low resulting in poor mixing. When the temperature is increased above the optimum point, biodiesel yield is decreased. It is because at high temperature boiling of alcohol occurs resulting in reduced availability. As less alcohol has remained, alcohol oil contact time is reduced (Baskar et al., 2018).

1.12.4. Reaction Period

Generally, yield of biodiesel increases with increased reaction duration. The optimum time depends on the nature and concentration of the catalyst, and type of feedstock. Base catalysts require less time as compared to acid catalysts. Enzyme catalysts require a longer reaction time to give a high biodiesel yield (Dhwane et al., 2018). The optimum reaction period is time within 120 min for acid and base catalysts. Enzyme catalysts generally require more than 24 h to give a high yield of biodiesel. As transesterification is a reversible reaction, a longer time results in hydrolysis of ester and saponification. As a result, biodiesel yield is reduced (Mohiddin et al., 2021).

1.13. Uses of Glycerol

Our main target is biodiesel in the transesterification process. Glycerol is a byproduct that is an organic solvent and non-toxic having high boiling point (290 °C) (Babadi et al., 2022). This byproduct can be used in different applications to make this overall process cost effective.

In food industry it is used as a solvent, sweetener and humidifier. In the pharmaceutical and personal care industries, it finds use in cough syrups, mouthwashes, and allergen immunotherapies. Additionally, it is used in botanical extracts as a preserving agent (Jancikova et al., 2020), and an alcohol free alternative. In the automotive industry, it serves as an antifreeze, and it acts as a chemical intermediate in soap formation, nitroglycerin synthesis, and sublingual tablets.

Leaf Resources is a leading company that uses the glycerol produced from biodiesel production. It is used in the biomass conversion technology. In this process, plant biomass is deconstructed and a high yield of cellulose and hemicellulose sugars are formed (Egas et al., 2021).

1.14. Biodiesel Fuel Properties

1.14.1. Calorific Value

Calorific value (CV) gives estimation of energy content stored in a fuel. During the combustion of fuel a certain amount of heat is released. This amount of heat when unit quantity of fuel undergo combustion is calorific value. Fuel with impurities have low calorific value as compared to the one with less or no impurities. When water is present in the fuel, calorific value is lower. The methyl ester components of biodiesel determine its calorific value (Wahyudi et al., 2019).

1.14.2. Cetane Number

The ignition quality of fuel is determined by the cetane number (CN). This property is crucial for effective utilization in diesel engine. It quantifies the capacity of fuel for ignition when heated. Lower cetane fuels have a longer delay period means that it will not ignite immediately when heated. It causes injected fuel to build up. This would result in faster pressure increase rates, which would weaken the engine's structure and impair its thermal efficiency. Additionally, cetane number has a considerable impact on NO_x emissions. It is desirable to burn fuel with a higher cetane number when using standard diesel (Marri et al., 2021).

1.14.3. Density

Fuel is measured by volume in vehicle fuel injection systems. Fuel density have an impact that how much fuel will be injected in the engine. The fuel-to-air ratio distribution inside the diesel engine is also influenced by the density of the fuel. Diesel density is typically lower than that of biodiesel. Depending on its content and purity, biodiesel has a density that ranges from 0.85 to 0.89 g cm^{-3}. Fuel with more unsaturated methyl esters are denser as compared to the one with saturated methyl esters. Biodiesel with low density shows good atomization when injected to the diesel engine for the combustion (Gulum & Bilgin, 2021).

1.14.4. Flashpoint Temperature

The lowest temperature at which heated gasoline produces a brief flash when interacted with the ignition source is the flashpoint (FP) temperature. It is a proximate indicator of fuel volatility. It is the important parameter that denote the safety of the fuel when handled and stored in accordance with approved fire codes. Biodiesel has a higher flashpoint temperature than diesel fuel, which is in the range of 100-190 °C. In terms of mobility and storage, biodiesel is therefore safer than diesel. Biodiesels with different fatty acid methyl ester show different flashpoint temperature (Alviso et al., 2020).

1.14.5. Iodine Value

The amount of iodine which is absorbed in biodiesel sample (100 g) at the recommended conditions is the iodine value. It stands for the unsaturated methyl ester components of biodiesel, which have an impact on oxidative stability. During storage and handling, the biodiesel's unsaturated methyl esters are prone to oxidation. Peroxides and hydroperoxide, which are regarded as primary oxidation products, are produced when they interact with ambient oxygen. A number of secondary oxidation products are created when peroxides and hydroperoxide react. Additionally, the level of biodiesel unsaturation and iodine value both affect NO_x emissions. It is also related to other fuel properties like viscosity, cetane number, and pour point temperature (Huang et al., 2022).

1.14.6. Acid Number

Acid number (AN) is determined by the amount of free fatty acids contained in the biodiesel sample. Its unit is mg KOH g^{-1}. High free fatty acid content causes a high acid value that causes corrosion of the engine. The level of lubrication in the fuel channel can also be indicated using the acid number value. The acid number for biodiesel fuel is empirically calculated in accordance with ASTM D664, and EN 14,104. The highest permissible value of acid number is 0.5 mg KOH g^{-1} according to these criteria (Sakthivel et al., 2018).

1.14.7. Peroxide Value

Peroxide value (PV) is used to determine whether there are any oxidative moieties in the fuel (biodiesel). Fuel contains oxidative molecules in the form of hydroperoxides. Hydroperoxide is produced as a result of the methyl ester's interaction with oxygen (in the air). The production of hydroperoxides is the first stage in the oxidative breakdown of methyl ester (Singh et al., 2019).

1.14.8. Pour Point

The lowest temperature at which a fuel stops to flow is the pour point (PP) temperature of the fuel. A crucial component of the cold flow process is the pour point. Just above the pour point value, fuel is appropriate for the process. Compared to biodiesel fuels, diesel fuel often has a lower pour point. Castor oil has the lowest pour point value for raw oil while mahua oil has the greatest pour point value. Using biodiesel with high pour point at low temperatures causes an increase in carbon monoxide and hydrocarbon emissions at high speed (Sun et al., 2022).

1.14.9. Saponification Value

The total number of units of oil that can be saponified per unit weight of oil is known as the saponification value (SV). Low molecular weight fatty acid chains are present in significant amounts, as indicated by a comparably increased saponification value. The average molecular weight is directly measured by the saponification value of biodiesel fuel. It is the amount of KOH needed to saponify 1 g of fat in milligrams. The presence of a high fatty acid proportion in raw oil is indicated by a greater saponification value, which may aid in the synthesis of soap bubbles during the biodiesel production process (Tamilselvan et al., 2020).

1.15. Biodiesel Reactor

For practical application, biodiesel is synthesized in reactors. There are different types of reactors which are as follows:

1.15.1. Rotating Reactor

It has rotating elements such as discs, impellers, or tubes. The rotational parameters such as speed and power, are important for rational reactors. Mass and heat transfer conditions are provided by rotational agitators. Stirred tank reactor (STR), spinning disc reactor (SDR), and rotating tube reactor (RTR) are different types of rotational reactors (Tabatabaei et al., 2019).

STR consists of heating and cooling elements, vessels, and stirrers which are connected to the axial shaft. In SDR, reactants mixture is added through the center portion and then mixed through rotation of the disc. Velocity can be increased for efficient mixing. For the scale up of SDR, disc size is not increased instead disc numbers are increased. In RTR, the reactants mixture is pumped into the rotating tube. Through rotation, thin liquid film of reactants is formed. RTR has a simpler design and a more compact structure. RTR produces cost-effective biodiesel (Chanthon et al., 2021).

1.15.2. Plug Flow Reactor

It is the simplest form of a chemical reactor in which mixing occurs as the reactants mixture is added. At a specific flow rate and residence time, reactants are streamed through pipes. Through high turbulent flow, reactants are mixed effectively. Considering the fluid inside the pipes, the size of the reactors is also adjusted.

This reactor is more economical and involves efficient mixing. It requires less maintenance. Initial capital cost is also lower and it requires less space. Limitation includes variation in pressure and temperature in its long pipes. It is not suitable for a slow reaction process. Temperature is difficult to be controlled (Gupta et al., 2020).

1.15.3. Cavitation Reactor

In this reactor, shock waves, micro turbulent eddies, and acoustic streaming are used for the effective mixing and transport of reactants (Okolie et al., 2022). Free radicals are produced which enhance the chemical reactivity. There are two main types of cavitation reactors, ultrasonic and hydrodynamic reactors.

In ultrasonic reactor, sound waves are used to boost up chemical reactions, which are produced from acoustic cavitation. Its performance is good for transesterification reaction. It requires less catalyst loading, alcohol molar ratio, reaction time and temperature. Power consumption is half as compared to other conventional methods (Nasim et al., 2023). A hydrodynamic reactor consists of a pump and a channel near the pump discharge. Cavitation is due to pressure differentiation through the flow of fluid and the structure of the system. Its design is simple and feasible to operate as it requires less maintenance and is easy to scale up. It consumes 10 times less energy as compared to an ultrasonic reactor. Through unsuitable pressure differentiation, the reaction rate may be decreased. It prevents agglomeration of the catalyst (Sun et al., 2023)

1.15.4. Microwave Reactor

This type of reactor includes microwaves in the range of 0.01 to 1m wavelength. Inside the metallic chamber, the source of the microwave reactor is enclosed. On an industrial scale, mechanical stirrers are incorporated in this reactor so that a uniform electric field is formed. Microwave irradiation activates ions and polar molecules (Hsiao et al., 2021). This type of reactor takes some minutes to a few hours for a complete biodiesel reaction. Among other alcohols, methanol is best suited for this reactor. Heat transfer is more efficient in the case of microwave reactor (Khan et al., 2021).

It is favored due to good time and energy efficiency. Limitation includes less controllability of power and temperature in the system. Scale up is difficult for this reactor and can only be used for small scale production (Leonelli et al., 2015).

1.15.5. Simultaneous Reaction Separation Reactor

In this type of reactor, after a chemical reaction, products are separated from unreacted reactants. Through separation, the process is intensified resulting in equilibrium towards the right direction. Membrane reactor, annular centrifugal reactor (ACR), and reactive distillation reactor (RDR) are two types of this reactor (Mohiddin et al., 2021).

A membrane reactor separates the fluids through different mass transfer rates. The yield and quality of biodiesel are reported to be good by using this reactor. It consumes less energy and occupies less space (Hafeez et al., 2020). Limitation includes a high capital cost. ACR involves centrifugal separation to separate the liquid. This reactor has low solvent requirements and enhances the contact area of fluid. It has a low residence period which results in incomplete transesterification (Polyakova et al., 2020). RDR separates the liquid through distillation after a chemical process. As fluids have different vapor pressure and boiling point, they are separated through distillation. It consumes less energy and can be operated for a long time. Cost can be much higher as extra equipment is often used in this reactor (Rocha-Meneses et al., 2023).

1.16. Economic Analysis of Biodiesels

The type of feedstock used for the biodiesel process determines the overall cost of the process. Using inexpensive feedstock can reduce the cost of the production process (Gebremariam & Marchetti, 2018).

Economic analysis of biodiesel produced from *Azadirachta indica* A.Juss. oil using a heterogeneous biocatalyst was determined. To perform the economic analysis ASPEN Batch Process Developer V10 was used. It was calculated that the unit cost of biodiesel is 1.06 US dollars. An annual production capacity of 3300 tons per year and annual production cost of 3,537,105 US dollars was determined. The internal rate of returns was 43% and payback time was determined to be 2.67 years. It was predicted that this process was economically feasible (Oke et al., 2021).

In another study, an economic analysis of biodiesel produced from Nile tilapia viscera oil was determined. An alkaline catalyst was used. It was calculated that payback time will be 1.9 years and the return on investment (ROI) will be 26%. A production cost of 0.22 US dollars was determined. It proved to be economically viable also implying a positive impact on the environment (Mota et al., 2019).

Biodiesel was produced from microalgal oil (*Scenedesmus* species) in an open pond. Algae-derived catalyst was used for transesterification. Economic analysis was determined and unit production cost was found to be 1.70-1.75 US dollars per kg. It was lower as compared to 2.03 US dollars per kg cost from the process in which a homogeneous acid catalyst was used. It was estimated that the payback period will be 1.32-5.57 years. This process was economically feasible (Mustapha et al., 2022).

Economic analysis of castor oil by using heterogeneous CaO nano-catalyst was determined. The Super Pro model was used in this study. 12000kg of castor oil was added in a continuous stirred tank reactor in a single batch. 4561.63 kg methanol and 356.7 kg of catalyst were added. Reaction conditions were 70 min reaction time, and 57 °C temperature. In the end, 10135.68 kg of biodiesel was produced. It was estimated that 23.7 million kg of castor oil to be used annually to produce 20.3 million glycerol. Initial investment of the plant was 2,148,000 US dollars and revenue generated was 14,048,000 US dollars per year. The payback period was calculated to be 2.88 years (Naveenkumar & Baskar, 2021).

1.17. Life Cycle Assessment of Biodiesel Production

Life cycle assessment (LCA) is crucial to assess the environmental impact of biodiesel production. The process begins with extracting resources and ends with the synthesis of the final product and waste disposal. Life cycle assessment includes analyses and quantification of energy input and output of products considering environmental concerns. It includes four stages; scope and goal analysis in the first stage, inventory analysis in the second stage, impact analysis in the third stage, and the fourth stage includes interpretation of results (Hosseinzadeh-Bandbafha et al., 2021). The LCA of biodiesel formed by soybean oil was determined. As compared to conventional processes, carbon dioxide emissions were less than 174 times in this process (Sieira et al., 2015). For the life cycle assessment of microalgae, all steps from cultivation to transesterification were analyzed. It was concluded that carbon dioxide emissions were reduced by 25% (Campbell et al., 2011). Biodiesel production from rapeseed reduced carbon dioxide emissions by 24% and about 75-79% was reduced by biodiesel production from vegetable oil (Al-Mawali et al., 2021). The life cycle assessment of castor oil biodiesel was determined. A positive carbon balance was observed with the energy return on energy investment (EROEI) of 2.60 contributing to the reduction in climate change. It was found that castor oil biodiesel production will save greenhouse gas emissions by 68.8% as compared to diesel produced by fossil fuels (Amouri et al., 2017).

1.18. Objective of the Study

- To investigate the effect of two different acidic imidazolium based catalysts on the yield and quality of castor biodiesel.

Chapter 2

Materials and Methods

2.1. Sample Collection

Castor oil was purchased from Hermain Chemicals (33°36′58″ N, 73°03′02″ E), Raja Bazar Rawalpindi on 31st October 2022. It was purchased at the rate of 710 Rupees kg^{-1}.

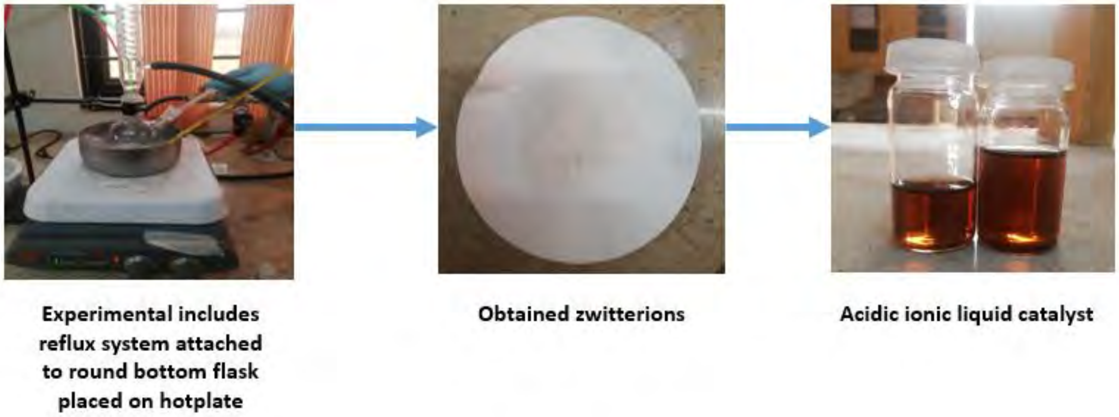
Figure 1. Map showing sample collection location.

2.2. Synthesis of Ionic Liquid Catalysts

Two ionic liquid catalysts were prepared to be used in the transesterification reaction. 1-vinyl-3-(sulfopropyl) imidazolium hydrogen sulfate was prepared and denoted as IL_1. The second catalyst, 1-vinyl-3-ethylimidazolium bromide was prepared and then it was modified to make it acidic. It was denoted as IL_2.

2.2.1. Synthesis of 1-Vinyl-3-(Sulfopropyl) Imidazolium Hydrogen Sulfate

A simple two-step reaction was used to make 1-vinyl-3-(sulfopropyl) imidazolium hydrogen sulfate (Xie et al., 2021). 4.7 g 1-vinylimidazole was mixed with 60 ml ethyl acetate. In this solution, 6.1 g 1, 3-propanesultone was added slowly in an ice bath and stirred vigorously. After this, temperature was increased to 25 °C and mixture was stirred for next 24 h. White precipitates were formed which were washed with ethyl acetate after separation through filtration. In the next step, these zwitterion ionic liquid salts were mixed with 5 ml of distilled water until dissolved. In the ice bath, an equimolar ratio of H_2SO_4 was added dropwise under constant stirring. Temperature was increased to 60 °C again stirred for 12 h. The obtained solution is the dual acidic ionic liquid catalyst.



Experimental includes reflux system attached to round bottom flask placed on hotplate

Obtained zwitterions

Acidic ionic liquid catalyst

Figure 2. Synthesis of 1-vinyl-3-(sulfopropyl) imidazolium hydrogen sulfate.

2.2.2. Synthesis of Modified 1-Vinyl-3-Ethylimidazolium Bromide

In an ice bath, 22 g 2-bromoethane was slowly added to 10 g 1-vinyl imidazole under vigorous stirring on a reflux system. After that, the temperature was increased to 80 °C and the mixture was stirred at this temperature for 20 h. Zwitterions were formed after that which were separated through filtration. It was thoroughly washed with ethyl acetate (Detrembleur et al., 2011).

For modification, this ionic liquid was made acidic which was basic in nature. Zwitterions were dissolved in 5 ml water and an equimolar of H_2SO_4 was added dropwise in an ice bath. It was stirred for 12 h at 60 °C temperature. The obtained solution is a modified acidic ionic liquid.

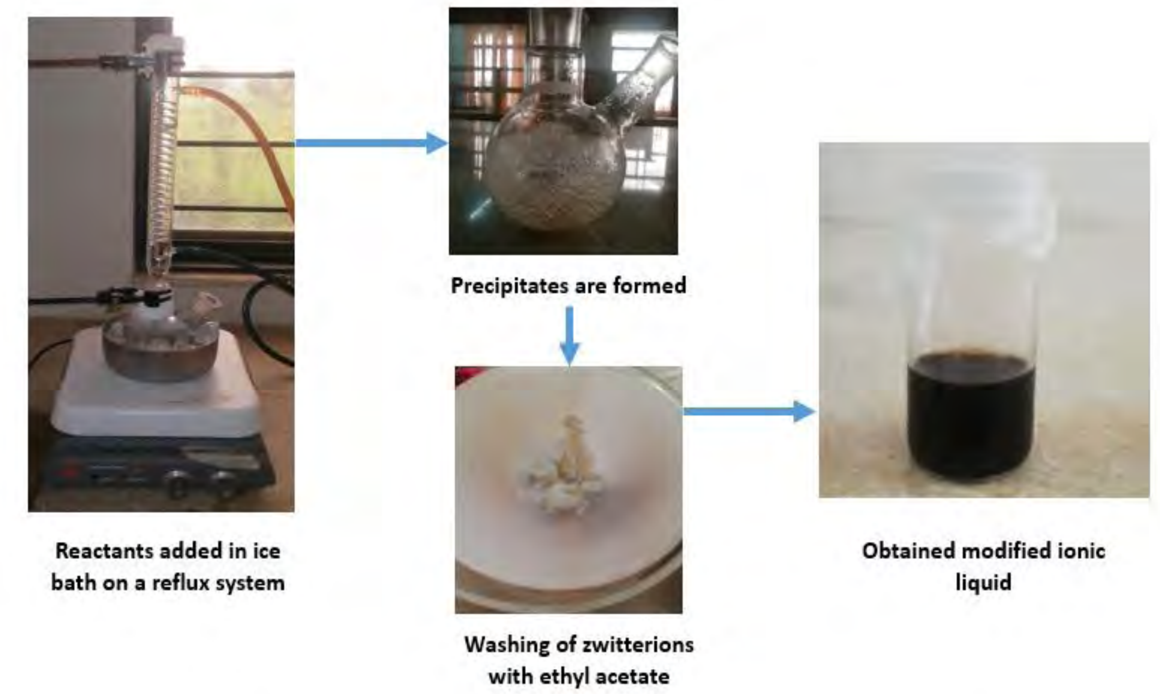


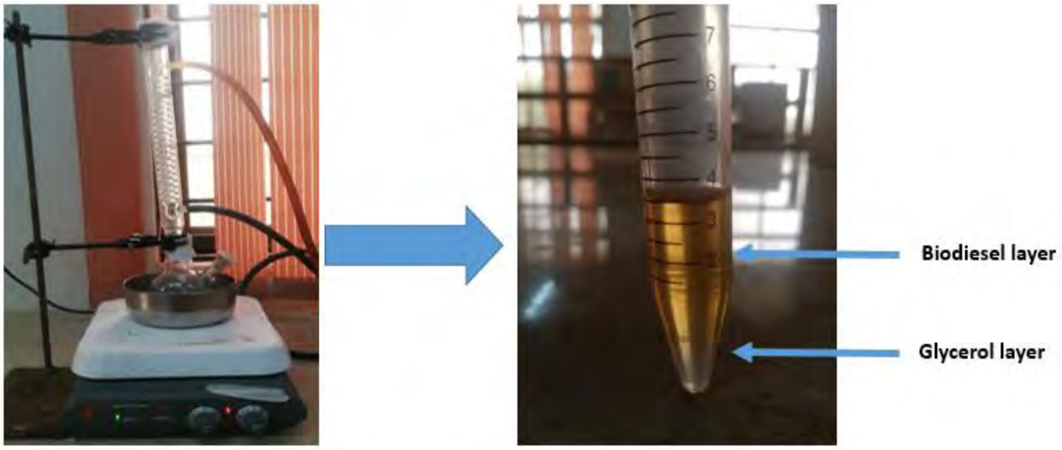
Figure 3. Synthesis of modified 1-vinyl-3-ethylimidazolium bromide.

2.3. Transesterification Process

Transesterification of castor oil was done in a round bottom flask on a hotplate in a reflux system. The reflux condenser was connected to the water circulating system (Dawood et al., 2022). The oil was preheated and when the desired temperature was maintained, catalyst and methanol were added and stirred. Under continuous stirring after maintaining the desired temperature, different concentration of methanol and catalyst was added to castor oil. After a certain time, the reaction was stopped. The obtained mixture was centrifuged at 2000 rpm for half an hour. Different layers were formed where the lower layer includes glycerol, upper layer biodiesel, and top layer catalyst. Biodiesel was separated and weighed to calculate yield. Yield was calculated by the formula:

$$Biodiesel\,Yield\,(\%) = \frac{Weight\ of\ biodiesel\ produced\ (g)}{Weight\ of\ oil\ used\ (g)} \times 100$$

Optimization experiments were done by using different reaction conditions. Reaction time (30, 60, 120, 180 min), catalyst concentration (3, 6, 9, 12 wt%), oil methanol ratio (1:03, 1:06, 1:09, 1:12), and temperature (45, 60, 75, 90 ℃) was used.



Transesterification reaction conducted on reflux system

Obtained biodiesel

Figure 4. Production of biodiesel through transesterification reaction.

2.4. Acidity Analysis of Ionic Liquids

The acidity of ionic liquids was determined by preparing 0.02 ml L^{-1} solution of H_2SO_4, HCl, IL_1, and IL_2. pH of the solutions was determined by a pH probe. The acidity of ionic liquids was then compared with H_2SO_4 and HCl (Fan et al., 2017).

2.5. Testing of Oil and Biodiesel

2.5.1. Acid Value Determination

5 g of sample was added to 25 ml of absolute ethanol and mixed. Phenolphthalein indicator was then added (3 drops). It was heated for 5 min and then titrated against 0.1 N KOH. When a pink color appeared, titration was stopped. A consumed volume of 0.1 N KOH was recorded (Kyari et al., 2008). The acid value was then calculated by the formula:

$$Acid\ Value\ (AV) = \frac{56.1 \times V \times N}{m}$$

Where 56.1 is the molecular weight of KOH, V= volume of KOH used, N= normality, and m= mass of sample.

2.5.2. Saponification Value Determination

A 2.5 ml sample was mixed with 25 ml ethanolic solution. It was then heated for 30 min at 70 °C temperature. Phenolphthalein indicator (3 drops) was added and 0.5 mol HCl was used for titration. Blank was also prepared in which water was used instead of the ethanolic solution. Titration was stopped when a pink color appeared (Nora et al., 2018). The saponification value was calculated by the formula:

$$Saponification\ Value\ (SV) = \frac{56.1 \times N \times (V_b - V_s)}{m}$$

Where 56.1 is the molecular weight of KOH (ethanolic solution), N = normality, V_b = volume of HCl used in the blank, V_s = volume of HCl used in the sample, m = mass of sample.

2.5.3. Free Fatty Acid Determination

Free fatty acid (FFA) value is based on acid value (Kyari et al., 2008). It was determined by the following formula:

$$\%FFA = \frac{AV}{2}$$

2.5.4. Iodine Value Determination

0.25 g of sample was added to a 250 ml conical flask and mixed with 10 ml chloroform. After that 30 ml of Hanus solution was added and mixed. It was stored in the dark for 30 min. Next 10 ml of 15% potassium iodide solution was added (a yellow color appeared) and under continuous stirring, 100 ml deionized water was added. 2-3 drops of starch solution was added. Sodium thiosulfate solution was used for titration until the color disappeared. Blank was also prepared and the same process was repeated for it (Omari et al., 2015). The iodine value was calculated by following the formula:

$$Iodine\ Value\ (IV) = \frac{126.9 \times N \times (V_b - V_s)}{m}$$

Where 126.9 is the molecular weight of iodine, N = normality, V_b = volume of sodium thiosulfate solution used for blank, V_s = volume of sodium thiosulfate solution used for sample, m = mass of sample.

2.5.5. Peroxide Value Determination

1 g of sample was added to a 250 ml Erlenmeyer flask. 20 ml of solvent mixture (chloroform/glacial acetic acid, 2/3 by volume) and 1 g of potassium iodide were added and mixed. The mixture was then heated and then added to an Erlenmeyer flask containing 20 ml of 5% potassium iodide solution. After adding starch solution (3 drops), it was titrated with 0.025 N sodium thiosulfate solution until the color disappeared. Blank was

also prepared and the same process was repeated for it (Kyari et al., 2008). Peroxide value was calculated by the following formula:

$$Peroxide\ Value\ (PV) = \frac{V \times N \times 1000}{m}$$

Where, V = volume of sodium thiosulfate used, N = normality, m = mass of sample.

2.5.6. High Heat Value Determination

High heat value is determined by using the saponification value, iodine value and mass of the sample (Dagne et al., 2019). It is calculated by the following formula:

$$High\ Heat\ Value = \frac{49.43 - (0.041 \times SV) + 0.015 \times IV}{m}$$

Where, SV = saponification value, IV = iodine value, and m = mass of sample.

2.5.7. Cetane Number Determination

The cetane number is also determined by using saponification value and iodine value (Dagne et al., 2019). It is calculated by the following formula:

$$Cetane\ Number = 46.3 + \frac{5458}{SV} - (0.225 \times IV)$$

Where, SV = saponification value, IV = iodine value.

2.5.8. Density Determination

The density of sample was determined by measuring the mass to volume ratio of the samples at 40°C (Ismail et al., 2015). It is calculated by the following formula:

$$Density = \frac{m_2 - m_0}{m_1 - m_0}$$

Where, m_0 = weight of empty container, m_1 = weight of biodiesel in the container, and m_2 = mass of container with water.

2.5.9. Flash Point Determination

It was determined by using the open cup method (Viraj et al., 2022). The container was in contact with outside air and a biodiesel sample was added to it. It was placed on a hotplate to increase the temperature. With the gradual increase in temperature, an ignition source was passed over it. When flash was observed and biodiesel caught fire, that temperature was noted down.

2.5.10. Pour Value Determination

For pour value determination, the sample was placed using a container and after heating allowed to cool. After it reached the predicted pour point temperature of 9 °C, it was then examined at consecutive intervals of 3 °C temperature. The sample container was tilted to observe biodiesel surface movement. The temperature at which it stopped flowing was noted down. It is the final flowable point (Bhale et al., 2009).

2.6. Characterization Techniques

Thermogravimetric analysis (TGA) was done to access the thermal properties of IL_1 and $1L_2$ catalysts by using a thermogravimetric analyzer (NETZSCH TG 209F3). Temperature range was set to 30-800 °C. Fourier transform infrared spectroscopy (FTIR) of catalysts, castor oil and biodiesel samples was analyzed by FTIR spectrometer (Agilent Technology). The range was set to 650-4000 cm^{-1}. Background scans were fixed to 8. Gas chromatography mass spectrometry of castor oil and biodiesel samples was analyzed by GC-MS spectrophotometer (Agilent Technology 5977B). The main components of castor oil and biodiesel were identified by it.

Chapter 3

Results

3.1. Effect of Reaction Parameters on Biodiesel Yield

Different yields were obtained on varying the reaction variables. In a reaction, all variables were kept constant except one to check its effect on biodiesel yield.

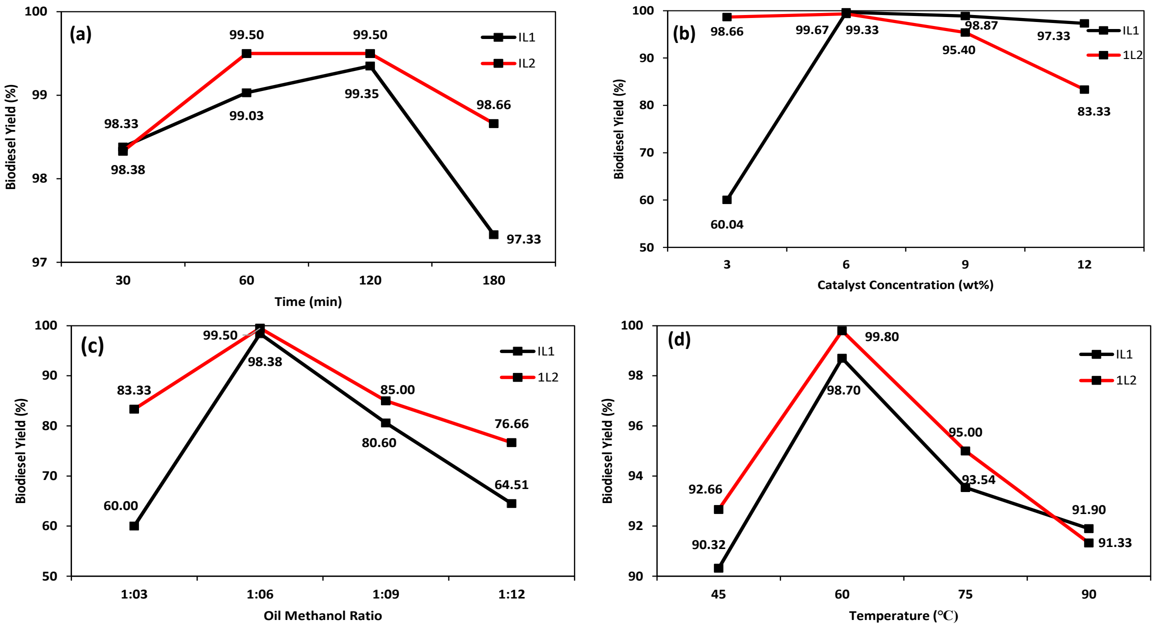


Figure 5. Effect of different parameters (a) time, (b) catalyst concentration, (c) Oil methanol ratio, and (d) temperature on biodiesel yield by using IL_1 and IL_2 catalyst.

3.1.1. Effect of Reaction Time

Figure 5 (a) shows the effect of reaction time on biodiesel yield. To check the effect of reaction time on biodiesel yield, all variables i.e., catalyst concentration, oil methanol ratio, and temperature were kept constant. Reactions proceeded at different reaction times i.e., 30, 60, 120, and 180 min. It is observed that while using IL_1 as a catalyst, biodiesel yield obtained at 30 min is 98.38%. It increased to 99.03% at 60 min and further increased to 99.35% at 120 min. At a reaction time of 180 min, the yield decreased to 97.33%. While using IL_2 as a catalyst, the yield obtained was 98.33% at 30 min, it increased to 99.50% at 60 min, and then the yield remained constant i.e., 99.50% at 120 min. At 180 min reaction time, yield then decreased to 98.66%.

3.1.2. Effect of Catalyst Concentration

Figure 5 (b) shows the effect of catalyst concentration on biodiesel yield. To check the effect of catalyst concentration on biodiesel yield, all other variables were kept constant. Different catalyst concentrations were used i.e., 3, 6, 9, and 12 wt%. It is observed that by using IL_1 as a catalyst, a yield of 60.04% biodiesel yield was observed at 3 wt% catalyst concentration. It increased to 99.67% at a catalyst concentration of 6 wt%. At 9 wt% it decreased to 98.87% and further decreased to 97.33% at 12 wt% catalyst concentration. While using IL_2 as a catalyst, a 98.66% yield was observed at 3 wt% catalyst concentration. It increased to 99.33% at 6 wt% catalyst concentration and then decreased to 95.40 and 83.33% at 9 and 12 wt%, respectively.

3.1.3. Effect of Oil Methanol Ratio

Figure 5 (c) shows the effect of oil methanol ratio on biodiesel yield. To check the effect of oil methanol ratio on biodiesel yield, all other variables were kept constant. The oil methanol ratios used in these experiments were 1:03, 1:06, 1:09, and 1:12. It is observed that by using IL_1 catalyst, at 1:03 oil methanol ratio, 60% biodiesel yield was produced. It increased to 98.38% at the 1:06 oil methanol ratio and decreased to 80.60 and 64.51% at the 1:09 and 1:12 oil methanol ratio, respectively. While using IL_2 a yield of 83.33% was observed at 1:03 oil methanol ratio. It increased to 99.50 at 1:06 oil methanol ratio and then decreased to 85.00 and 76.66% at 1:09 and 1:12 oil methanol ratio respectively.

3.1.4. Effect of Temperature

Figure 5 (d) shows the effect of temperature on biodiesel yield. To check the effect of temperature on biodiesel yield, all other variables were kept constant. Different temperatures used in these experiments were 45, 60, 75, and 90 °C. It is observed that while using the IL_1 catalyst, at 45 °C, biodiesel yield was 90.32%. At a temperature of 60 °C, the yield obtained was 98.70%. It then decreased to 93.54 and 91.90% at a temperature of 75 and 90 °C, respectively.

While using IL_2, a yield of 92.66% was observed at 45 °C. It increased to 99.80% at 60 °C. It then decreased to 95.00 and 91.33% respectively.

3.2. Maximum Yield Obtained of Biodiesel

In Fig 6, maximum yields of IL_1 and IL_2 are shown. The maximum biodiesel yield obtained is 99.80% by using an IL_2 catalyst. Optimum reaction conditions were 60 min reaction time, 6 wt% catalyst concentration, 1:06 oil methanol ratio, and 60 °C temperature. When using IL_1, the maximum yield obtained was 99.67%. It is slightly lower than that of the one obtained with the IL_2 catalyst. Optimum conditions were 120 min reaction time, 6 wt% catalyst concentration, 1:06 oil methanol ratio, and 60 °C temperature.

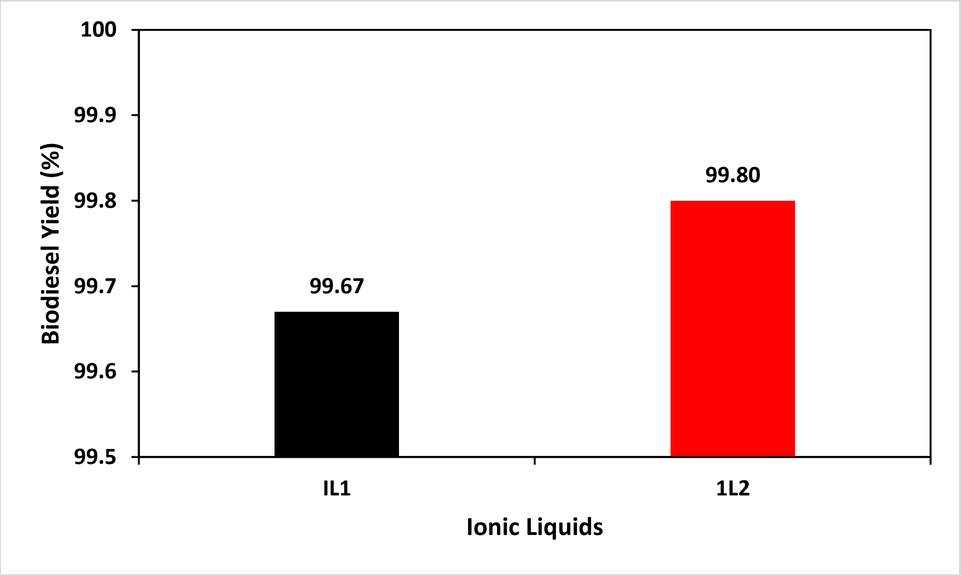


Figure 6. Maximum yield obtained by using IL_1 and IL_2 catalyst.

3.3. Acidity of Ionic Liquids

In Table 1, the acidity of ionic liquids and acids is shown. It is observed that the pH of IL_1 is 1.5. It is more acidic than that of HCl (pH=1.8), and its acidity is closer to that of H_2SO_4 (pH=1.4). The acidity of IL_2 is less than that of IL_1 but it is more acidic than HCl.

Table 1. pH of ionic liquids along with inorganic acids.

	H_2SO_4	HCl	IL_1	IL_2
pH	1.4	1.8	1.5	1.6

3.4. Physicochemical Properties of Oil and Biodiesel

Table 2 shows the physicochemical properties of oil and biodiesel. The acid value of castor oil was found to be 0.25 mg KOH g^{-1}. In IL_1 biodiesel it was 0.36 mg KOH g^{-1} and slightly higher in IL$_2$ biodiesel i.e., 0.41 mg KOH g^{-1}. These values are within limits of ASTM D6751 standard i.e., <0.5 mg KOH g^{-1}. Saponification value of castor oil was found to be 198.62 mg KOH g^{-1}. It was lower in biodiesel i.e., 104.58 and 108.64 mg KOH g^{-1} in IL$_1$ and IL$_2$ biodiesel respectively. Biodiesel values were within AOCS Cd 3-25 limit i.e., 175-187 mg KOH g^{-1}. The free fatty acid value of castor oil was found to be 0.13%. 1L$_1$ and IL$_2$ biodiesel showed free fatty acid values of 0.18 and 0.20%, respectively. The iodine value of castor oil was found to be 83.50 gI$_2$/100g. IL$_1$ and IL$_2$ biodiesel showed iodine values of 83.46 and 82.51 gI$_2$/100g, respectively. It was slightly lower than the AOCS Cd 1-25 limit i.e., 84-112 gI$_2$/100g. The peroxide value of castor oil was found to be 15.22 meq kg^{-1}. IL$_1$ and IL$_2$ biodiesel showed peroxide values of 16.27 and 15.94 meq kg^{-1}, respectively. The high heat value of castor oil was found to be 42.53. IL$_1$ and IL$_2$ biodiesel showed high heat values of 46.93 and 46.21, respectively. The cetane number of castor oil was found to be 54.99. It was higher in biodiesel i.e., 79.71 and 77.97 in IL$_1$ and IL$_2$ biodiesel, respectively. It was within limits as values should be greater than 47 according to ASTM D6751. The density of castor oil was found to be slightly higher than biodiesel i.e., 0.97 g ml^{-1}. In IL$_1$ and IL$_2$ biodiesel, density was found to be 0.93 and 0.92 g ml^{-1}, respectively. It was higher than the ASTM D1298 limit which is 0.83-0.89 g ml^{-1}, respectively. The flash point of IL$_1$ and IL$_2$ biodiesel was 196 and 198 °C, respectively. ASTM-D97 limit is 130-170 °C. The pour point of IL$_1$ and IL$_2$ biodiesel was found to be -10 and -12 °C, respectively. ASTM D97 limit is -17 °C.

Table 2. Physicochemical properties of castor oil, IL$_1$ biodiesel, and IL$_2$ biodiesel.

Properties	Castor oil	IL$_1$ Biodiesel	IL$_2$ Biodiesel	Standard limits
Acid Value (mg KOH g^{-1})	0.25	0.36	0.41	<0.5 (ASTM D6751)
Saponification value (mg KOH g^{-1})	198.62	104.58	108.64	175-187 mg KOH g^{-1} (AOCS Cd 3-25)
Free fatty acids (%)	0.13	0.18	0.20	-

Iodine value (gI_2/100g)	83.50	83.46	82.51	84-112 gI_2/100g (AOCS Cd 1-25)
Peroxide value (meq kg^{-1})	15.22	16.27	15.94	-
High heat value	42.53	46.39	46.21	-
Cetane number	54.99	79.71	77.97	>47 (ASTM D6751)
Density (g ml^{-1})	0.97	0.93	0.92	0.83-0.89 g ml^{-1} (ASTM D1298)
Flash point (℃)	-	196	198	130-170 ℃ (ASTM-D97)
Pour point (℃)	-	-10	-12	-17 ℃ (ASTM D97)

3.5. Characterization of Catalyst

3.5.1. TGA Analysis of Ionic Liquids

Fig 7 shows the Thermogravimetric analysis (TGA) curve of the IL_1 and IL_2 catalysts. In this analysis, sample's weight and rate of weight loss as a function of the increased temperature are measured under controlled atmosphere.

Significant mass loss of IL_1 started from 235℃. A peak is formed at 235 ℃. From 235-360 ℃, mass loss was 81.46%. It was 18% of its mass at 0-235 ℃. Another peak starts at 360 ℃. From 360-558 ℃ almost all of the mass was lost at 558 ℃.

In IL_2, 10.02% mass was reduced from 100-270 ℃. Major mass loss was observed afterward. It was seen that from 270-378 ℃, 77.22% of further mass loss has occurred. From 378-573 ℃, further mass loss occurred and almost all mass was lost at 578 ℃.

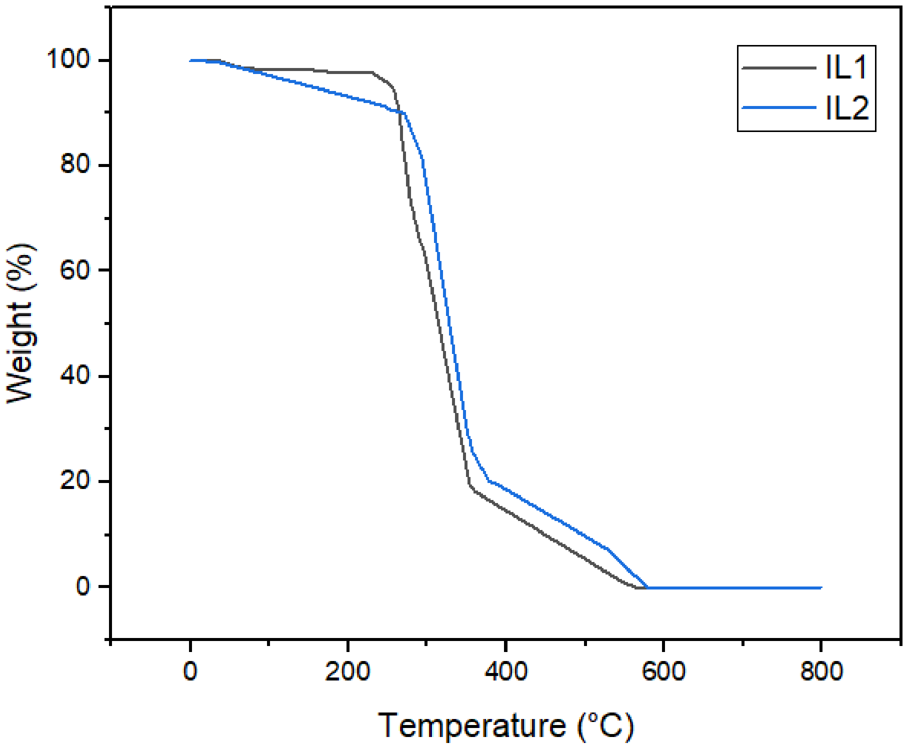


Figure 7. TGA curve of IL_1 and IL_2 catalyst.

3.5.2. FTIR Analysis of Ionic Liquids

Figure 8 shows the Fourier transform infrared spectroscopy (FTIR) spectrum of ionic liquids. In Fig (a) FTIR spectrum of IL_1 is shown with characteristic peaks. The peak at 2145 cm^{-1} shows stretching vibrations of N=C=N, and at 1644 cm^{-1} there was stretching vibrations of C=C and C=N. Peaks at 1134 and 1029 cm^{-1} show symmetric and asymmetric S=O stretching vibrations of the HSO_3 group. The peak at 858 cm^{-1} is showing $[HSO_4]^-$ anion vibrations.

Fig 8 (b) shows FTIR spectrum of IL_2 with characteristic peaks. A peak at 3421 cm^{-1} is indicative of OH^- vibrations. The peak at 3112 cm^{-1} is showing =C-H stretching vibrations. At 2962 cm^{-1}, the peak is showing CH_3 stretching vibrations. The peak at 1575 cm^{-1} shows stretching vibrations of C=C. At 1454 cm^{-1}, the peak is showing stretching vibrations of C=N. Peak at 1151 cm^{-1} shows C-C-N stretching vibration. The peak at 1052 cm^{-1} is indicative of symmetric and asymmetric S=O stretching vibrations of the HSO_3 group.

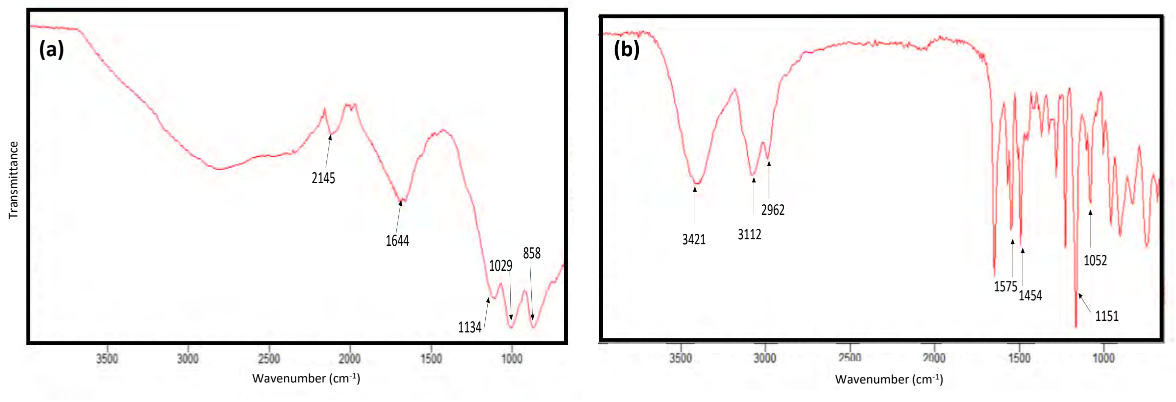


Figure 8. FTIR analysis of (a) IL_1, and (b) IL_2.

3.6. Characterization of Oil and Biodiesel

3.6.1. FTIR Analysis of Oil and Biodiesel

Fig 9 shows the FTIR spectrum of castor oil and biodiesels. In Fig 9 (a) FTIR spectrum with characteristic peaks of castor oil is shown. A peak at 3380 cm^{-1} is indicative of OH^- stretching vibrations. At 3005 cm^{-1}, the peak is showing stretching vibrations of C-H in a double bond of unsaturation. Peaks at 2924 and 2856 cm^{-1} show aliphatic $–CH_2$ fatty acid hydrocarbon symmetric and asymmetric vibrations. The peak at 1738 cm^{-1} is indicative of a stretching band of C=O in triglyceride. The peak at 1450 cm^{-1} is showing $–CH_2$ aliphatic group bending vibrations. Peaks at 1167 and 1042 cm^{-1} are showing carbonyl group C=O bending vibrations. Peak at 975 cm^{-1} shows HC=CH (Trans) bending out of the plane. The peak at 857 cm^{-1} indicates wagging vibrations of $=CH_2$. At 719 cm^{-1}, the peak shows overlapping out-of-plane vibrations of $-CH_2$ of cis di-substituted olefins.

In Fig 9 (b), and (c) FTIR spectrum with characteristics peaks of biodiesel formed by IL_1 and IL_2 is shown, respectively. Peak 3380 cm^{-1} of IL_1 biodiesel and 3380 cm^{-1} of IL_2 biodiesel is showing OH^- stretching vibrations. Peak 2920 and 2851 cm^{-1} of IL_1 biodiesel and 2924 and 2853 cm^{-1} of IL_2 biodiesel show stretching vibrations of methyl, methylene, and methane group. Peak 1741 cm^{-1} of IL_1 biodiesel and 1742 cm^{-1} of IL_2 biodiesel indicates a stretch of the carbonyl group (C=O) which is located at carboxylic ester. Peaks 1455 and 1452 cm^{-1} of IL_1 biodiesel and 1452 and 1421 cm^{-1} of IL_2 biodiesel show the bending of a methyl group ($-CH_3$). Peak 1210 cm^{-1} of IL_1 biodiesel and 1213 cm^{-1} of IL_2 biodiesel shows C-N stretching. Peaks 1149 and 1011 cm^{-1} of IL_1 biodiesel and 1148 and

1008 cm^{-1} of IL_2 biodiesel is showing C-O stretching. Peak 852 and 714 cm^{-1} of IL_1 biodiesel and 854 and 716 cm^{-1} of IL_2 biodiesel show the bending of =C-H.

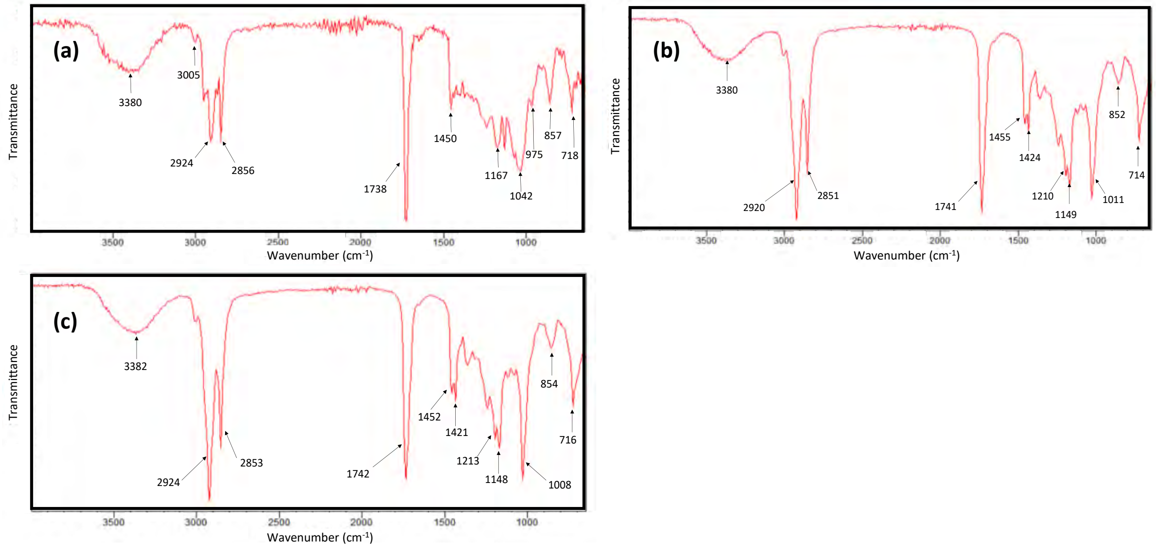


Figure 9. FTIR analysis of (a) castor oil, (b) IL_1 biodiesel, (c) IL_2 biodiesel.

3.6.2. GC-MS Analysis of Oil and Biodiesel

In Fig 10. Gas chromatography mass spectrometry (GC-MS) chromatogram of castor oil is shown. It is evident that methyl ricinoleic acid ($C_{18}H_{34}O_3$) is the dominant fatty acid i.e., 47.353%. It is an unsaturated fatty acid. Other prominent fatty acids are 6.41% palmitic acid ($C_{16}H_{32}O_2$) which is a saturated fatty acid and 17.25% phthalic acid ($C_8H_6O_4$) which is also saturated in nature. Arachidic acid ($C_{20}H_{40}O_2$), oleic acid ($C_{18}H_{34}O_2$), and stearic acid ($C_{18}H_{36}O_2$) are also present in this castor oil.

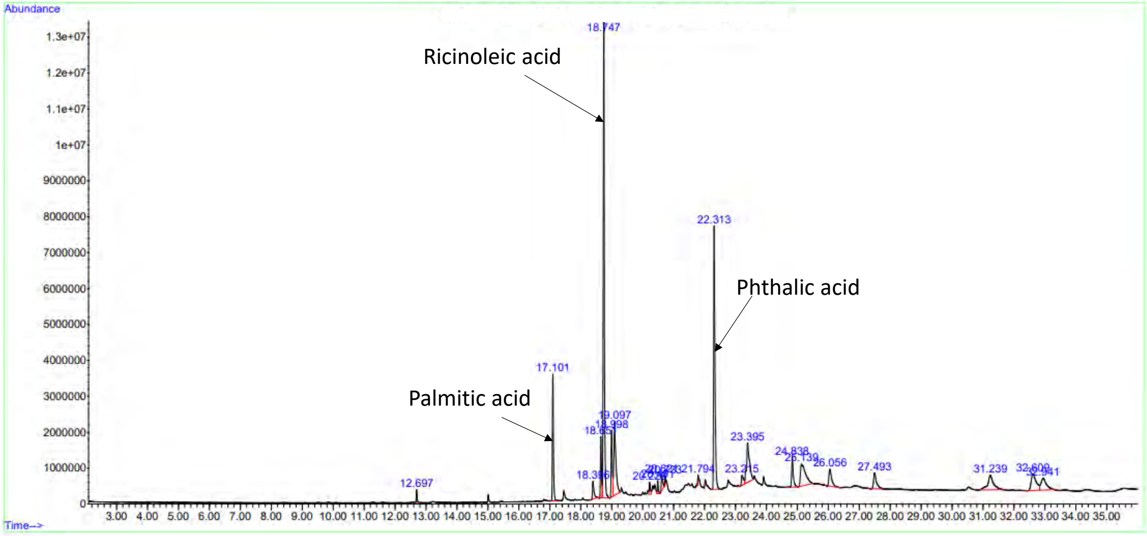


Figure 10. GC-MS analysis of castor oil.

Figures 11 and 12 show GC-MS chromatogram of IL_1 biodiesel and IL_2 biodiesel, respectively. The dominant fatty acid methyl ester is ricinoleic acid methyl ester ($C_{19}H_{36}O_3$) which is 62.79% in IL_1 biodiesel and 60.54% in IL_2 biodiesel. Palmitic acid methyl ester ($C_{17}H_{34}O_2$) is 3.19% in IL_1 biodiesel and 3.13% in IL_2 biodiesel. Oleic acid methyl ester ($C_{19}H_{38}O_2$) is 7.52% in IL_1 biodiesel and 7.60% in IL_2 biodiesel. Linoleic acid methyl ester ($C_{19}H_{34}O_2$) is 9.81% in IL_1 biodiesel and 9.76% in IL_2 biodiesel. Stearic acid methyl ester ($C_{19}H_{38}O_2$) is 3.04% in IL1 biodiesel and 3.01% in IL_2 biodiesel. Phthalic acid methyl ester ($C_{10}H_{10}O_4$) is 0.58% in IL_1 biodiesel and 1.02% in IL_2 biodiesel.

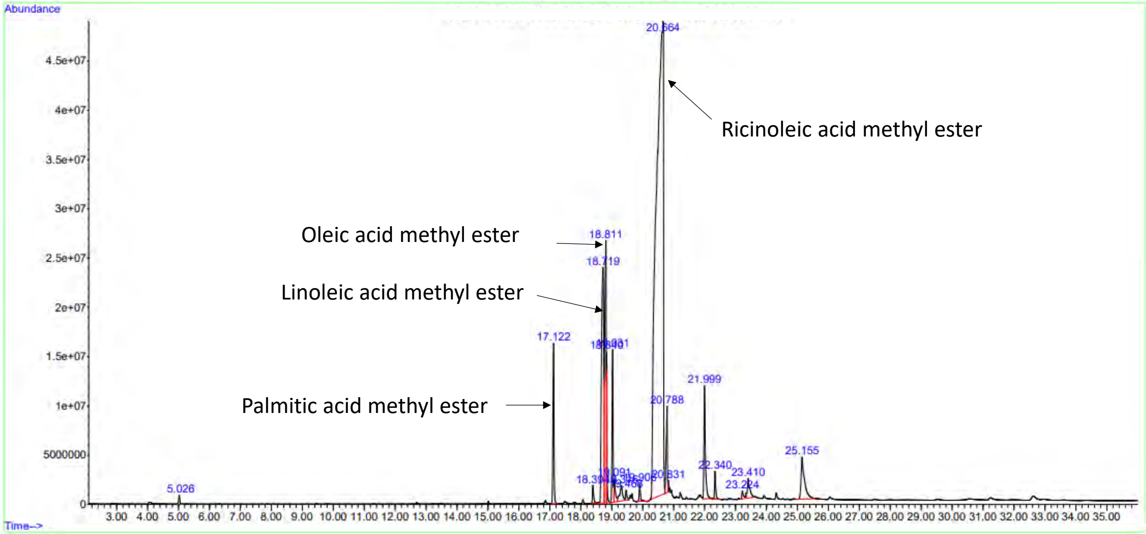


Figure 11. GC-MS analysis of IL_1 biodiesel.

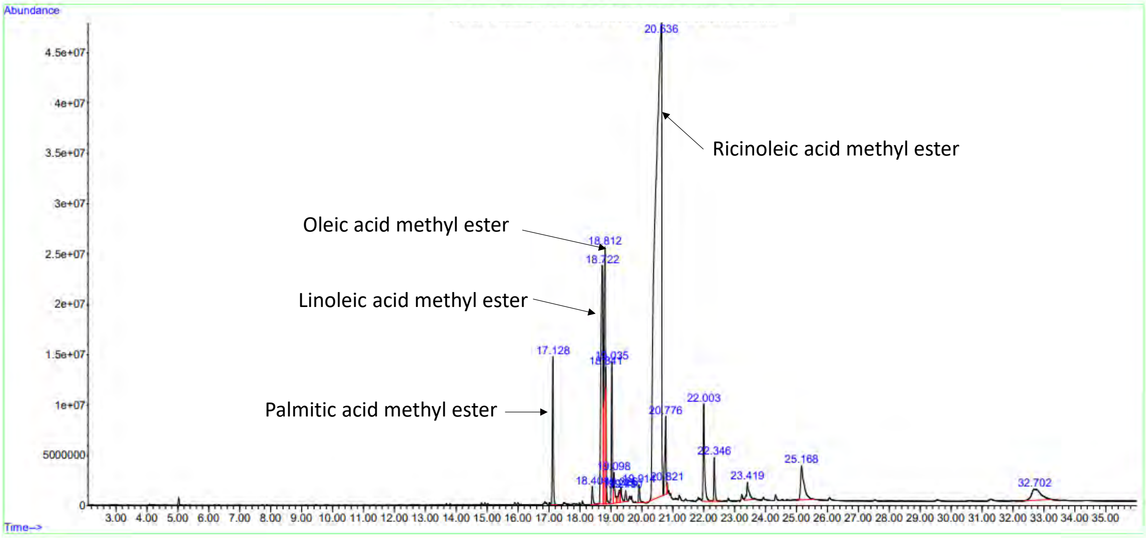


Figure 12. GC-MS analysis of IL_2 biodiesel.

Chapter 4

Discussion

Yield of biodiesel is influenced by the four variables i.e., reaction time, catalyst concentration, oil methanol ratio, and temperature. Reaction time is crucial to investigate the biodiesel production cost. It is observed that reaction reached steady state within 30 min reaction time. It is due to high polarity of methanol and ricinoleic acid which is dominantly present in castor oil (Keera et al., 2018). Using IL_1 as a catalyst, more time i.e., 120 min were required to reach maximum efficiency as compared to IL_2 which required only 60 min. At 180 min reaction time, yield decreased in both cases. It is due to the fact that reversible reaction occurs and products are converted into reactants (Dawood et al., 2022).

To produce a good quality biodiesel with a high yield, role of catalyst is very important. By using different catalyst concentrations it was found that 6 wt% is optimum catalyst concentration in case of both IL_1 and IL_2 catalysts. By using 3 wt%, yield was very low by using IL_1 catalyst as compared to that of IL_2 catalyst. It may be due to presence of less catalytic sites which are insufficient for the reaction to reach equilibrium state (García-Moreno et al., 2014). At high concentration i.e., 9 and 12 wt%, biodiesel yield was reduced. It may be due to disturbed reaction equilibrium due to reduced mass transfer between catalyst and reactant. High catalyst concentration also leads to soap formation which prevents separation of biodiesel from glycerol (Munir et al., 2021).

Effect of different oil to methanol ratio was also observed. Optimum oil methanol ratio was 1:06. This methanol concentration was suitable to shift the equilibrium towards forward direction leading towards more product formation. At this ratio there was more collision between reactant molecules and as a result biodiesel with higher yield was produced. At 1:03 oil methanol ratio, low yield of biodiesel was observed. This is due to the fact that transesterification is a reversible reaction and low methanol concentration resulted in shift in equilibrium towards backward direction and obtained bioiesel and glycerol reacted to form oil and methanol (Ba et al., 2022). Using oil methanol ratio i.e., 1:09 and 1:12 lead to decrease in biodiesel yield. Lowest yield was observed by using 1:12 oil methanol ratio. It is due to dilution effect, reducing the concentration of catalyst and reactants. Also by using high methanol concentration, glycerol starts dissolving in it and difficult to be separated (Nisar et al., 2017).

Reaction temperature is an important factor to enhance the yield of biodiesel production. At 30 °C relatively low biodiesel yield was observed in case of both catalysts. This indicate that this temperature is not sufficient to overcome the activation energy. By increasing the temperature, biodiesel yield increases. At 60 °C maximum yield was observed. At this temperature interaction between reactants was enhanced due to sufficient kinetic energy. Castor oil has high viscosity and increasing the temperature reduce viscosity which results in more mass transfer between reactant phases (Foroutan et al., 2021). Biodiesel yield was decreased at 75 °C and further decreased at 90 °C. This may be due to evaporation of methanol. As a result less methanol is remained so reaction equilibrium was shifted towards left i.e., obtained biodiesel was converted into oil and methanol. At high temperature >65 °C, triglycerides undergo saponification reaction with a faster pace than transesterification reaction (Matawea et al., 2018).

Maximum biodiesel yield in this study is 99.67 and 99.80% by using IL_1 and IL_2 catalyst, respectively. This is greater than other acidic ionic liquid which were used in the transesterification reaction of castor oil. Khiratkar et al. (2018) used benimidazolium based acidic ionic liquid catalyst for transesterification of castor oil. Maximum yield was 96% and reaction time was also high i.e., 840 min. Wei et al. (2015) used 1-methyl imidazole hydrogen sulfate ionic liquid catalyst for transesterification of castor oil. Maximum yield was 89.82% with a reaction time of 240 min.

In this study acidic ionic liquids were successfully prepared. It is the first time that 1-vinyl-3- ethyl imidazolium bromide (VEtImBr) was modified and used as a catalyst for biodiesel production. It was basic in nature and was modified by adding acidic functional groups. Acidity of 1-vinyl-3-(3-sulfopropyl) imidazolium hydrogen sulfate was close to that of sulfuric acid. Acidity of VEtImBr was more than HCl. It means it was stronger acidic catalyst than HCl. Instead of these inorganic acids we can use these acidic ionic liquids. It will also lead to avoid disadvantages associated with these inorganic acids. These disadvantages include high corrosion leading towards reactor deterioration (Maleki et al., 2022). Inorganic acid i.e., H_2SO_4 also liberates harmful gases. Ionic liquids as green catalysts having similar acidic strength can overcome these issues. Acidity in ionic liquids is due to sulfonic acid (-SO_3H) covalently bonded to it. Another source is hydrogen sulfate (HSO_4^-) as acidic counter anion in it (Vafaeezadeh et al., 2016).

Physicochemical properties of castor oil and formed biodiesels were measured to check whether they comply with international standards or not. It helps to better understand whether fuel can be used as diesel substitute or not. Acid value of castor oil and biodiesels were found to be within range of ASTM D6751 standard. Value obtained was low and it is suitable for biodiesel production (Hussain et al., 2022). Acid value of IL_1 and IL_2 biodiesel corresponds with the study by Attia et al. (2018), in which obtained acid value of biodiesel (0.3 mg KOH g^{-1}) was also within limits. Saponification of castor oil exceeded the limit but obtained biodiesels were within limit range. As acidic catalysts were used, saponification value decreased after transesterification. These values corresponds with the reported saponification value by Encinar et al. (2010) which was also within standards limit. High value of free fatty acids hinders the transesterification reaction and reduces the biodiesel yield. Free fatty acids (FFA) of biodiesels was low. Minimum FFA value of biodiesels enables it to be used as a substitute of diesel (Hussain et al., 2022). Iodine value of castor oil and biodiesel was slightly lower than standard limits. If iodine value is high it means that it can cause polymerization and forms deposits on piston rings and nozzles. Iodine value of some other biodiesels were high as compared to castor biodiesel. It was lower than soybean, rapeseed, and sunflower oil biodiesel. It means that castor biodiesel is more stable and can be used as diesel substitute (Negm et al., 2016). Peroxide value give us estimation of oxidative rancidity. Its value was low in castor oil and biodiesel. This may be due to double bond on ricinoleic acid (carbon no 9) protected from oxidation (hydroperoxide formation) by hydroxyl group on carbon no 12. 38 meq kg^{-1} peroxide value of castor oil was measured by Yusuf et al. (2015) which was even higher than peroxide value in this study. High heat value is an important parameter to understand the fuel consumption. Fuel consumption is lower when there is high heating value. High heating value of castor biodiesel in this study was greater than reported by Attia et al. (2020). Cetane number is an important parameter to access the ignition quality of fuel. Higher the cetane number, higher will be the ability to fuel to ignite quickly after injection. Cetane number was found to be within standard limits. It was higher than the cetane number of castor biodiesel reported by Negm et al. (2016). Density of the castor biodiesel has exceeded the international limits. Reason for high density is the presence of OH^- group in ricinoleic methyl ester which was dominant in castor biodiesel. This problem can be overcome by using biodiesel blends which are also recommended by policies in different countries (Keera et al., 2018). Flash point gives us estimate that at what temperature fuel can ignite when exposed to heating source. Flash point of biodiesel was found to be higher. It means that it is safe to handle, store and transport to other places. There is less risk of explosion when exposed to heating source. Observed value also corresponds with reported flash point value by Osorio-González et al. (2020). Pour point is that temperature at which fuel cannot flow. Pour point of castor biodiesel was low and within international standards limit. Low value shows that it is suitable to be used in cold places and in winter season. This is the characteristic of castor biodiesel that it works efficiently even if surrounding temperature is very low. Castor biodiesel pour point value corresponds with the value observed in a study by Desari et al. (2016).

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability of obtained ionic liquid catalysts. In case of IL_2 mass loss was observed from 100 to 270 °C. It is due to evaporation of water molecules which are adsorbed to it, as 100 °C is the boiling point of water. It corresponds to the study by Li et al. (2020). Onset temperature for significant mass loss was 235 °C in IL_1 and 270 °C in IL_2. It means that IL_2 backbone shows more resistant to temperature than IL_1. It is evident from literature that mass loss in these temperature ranges are attributed to structure loss of ionic liquid. From 200-280 °C, mass loss is due to combustion of SO_3H group and from 280-400 °C is due to decomposition of alkyl long chain as suggested by Li et al. (2020). Ionic liquid decomposes significantly from 316-373 °C as suggested by Ding et al. (2018). Pourjavadi et al. (2012) correlated mass loss from 300-450 °C with imidazolium groups $(CH_2)_3SO_3H$ and temperature from 450 °C onwards with complete decomposition of alkyne chain. Chen et al. (2021) correlated mass loss from 300-600 °C with decomposition of imidazolium rings and sulfonic groups. It is also due to disruptions of polymer networks.

Fourier transform infrared spectroscopy (FTIR) was analyzed to confirm the chemical structures of the sample. FTIR analysis of IL_1 shows N=C=N stretching indicating that it is vinyl ionic liquid as mentioned in the study by Kim et al. (2014). Peaks at 1134 and 1029 cm^{-1} shows that in this ionic liquid sulfonic acid groups were successfully synthesized. At

858 cm^{-1} HSO_4^- vibration is due to stable structure after treatment with acid (Yassin et al., 2015). Peak 1644 cm^{-1} showed vibrations of C=C, C=N which are constituents of imidazole ring as suggested by Ding et al. (2018).

FTIR of IL_2 showed stretching vibrations of C=C, C=N, and =C-H which are present in imidazolium ring. =C-H stretching vibrations is due to hydrogen bond interaction in imidazolium ring. It means that imidazolium ring was intact in this ionic liquid. Asymmetric stretching vibrations of HSO_3^- and S=O symmetric vibrations indicate that acidic functional groups were successfully introduced as a modification. This also corresponds to the study by Ding et al. (2018).

FTIR of castor oil was analyzed to identify characteristics functional groups. Peak at 1738 cm^{-1} shows presence of ester carbonyl group in triglycerides which is a structural constituent of castor oil. Peak 3380 cm^{-1} indicates that hydroxylated ricinoleic acid which is a dominant constituent of castor oil. C-H and $–CH_2$ vibrations indicate unsaturation and presence of fatty acid chains in castor oil. All observed peaks corresponds well with the study of Panhwar et al. (2019).

FTIR of synthesized biodiesel by using both catalysts doesn’t show any major difference. Both contains same functional groups with slight difference in wavenumbers. It was found that =C-H was the most abundant group. Unsaturated functional groups are indicated at peaks 852 and 714 cm^{-1} of IL_1 biodiesel and 854 and 716 cm^{-1} of IL_2 biodiesel. Peak at 3380 and 3382 cm^{-1} of IL_1 and IL_2 biodiesel, respectively shows overtone of ester group. Presence of ester groups indicates successful synthesis of castor biodiesel. All the peaks of both biodiesel corresponds well with the literature (Ndana et al., 2013; Utami et al., 2022).

Gas chromatography mass spectrometry (GC-MS) analysis showed that in castor oil major constituents were ricinoleic acid, palmitic acid and phthalic acid. Omari et al. (2015) also showed that ricinoleic acid is the major constituent of castor oil. They also showed that palmitic acid is second main constituent of castor oil. Presence of ricinoleic acid in high concentration was also confirmed by Naveenkumar et al. (2022). Presence of phthalic acid in castor oil indicates that it was added during manufacturing process. For many industrial uses it is added to enhance the properties to be used as plasticizer as mentioned by Mehta et al. (2014).

Gas chromatography mass spectrometry (GC-MS) of both biodiesel showed that ricinoleic acid methyl ester is the main constituent followed by oleic acid methyl ester, linoleic acid methyl ester, and palmitic acid methyl ester. Abundance of ricinoleic acid methyl ester was showed by Fitranda et al. (2020). Presence of oleic acid methyl ester, linoleic methyl ester, and palmitic acid methyl ester in castor biodiesel corresponds with the study of Elango et al. (2019).

Chapter 5

Conclusions

Using imidazolium based acidic ionic liquids gave promising results to be used in biodiesel production. Maximum yield of castor biodiesel produced by using 1-vinyl-3-(sulfopropyl) imidazolium hydrogen sulfate [VSIM][HSO_4] catalyst was 99.67%. Optimum conditions were 120 min reaction time, 6 wt% catalyst concentration, 1:06 oil methanol ratio, and 60 °C temperature. Modified 1-vinyl-3-ethylimidazolium bromide (VEtImBr) catalyst gave a maximum yield of 99.80%. Optimum conditions were 60 min reaction time, 6 wt% catalyst concentration, 1:06 oil methanol ratio, and 60 °C temperature. The acidity of [VSIM][HSO_4] catalyst (pH=1.5) was close to that of H_2SO_4 (pH=1.4). Acidic functional groups were successfully incorporated in VEtImBr catalyst as the pH measured was low i.e., 1.6. The physicochemical properties of castor oil and biodiesel complied with international standards except iodine value and density. The iodine value was slightly lower than the recommended limit. The density of biodiesel was high i.e., 0.93 and 0.92 g ml^{-1} (ASTM D1298 limit 0.83-0.89 g ml^{-1}). This problem can be solved by using biodiesel blends as recommended by policies in different countries. Thermogravimetric analysis (TGA) showed high thermal stability. [VSIM][HSO_4] catalyst was found to be stable up to 235 °C. The thermal stability of modified VEtImBr was higher i.e., 270 °C. FTIR analysis of catalysts, castor oil, and biodiesel showed characteristics peaks showing catalysts and biodiesel were successfully prepared. GC-MS showed that the main constituent of castor oil is ricinoleic acid, palmitic acid, and phthalic acid. GC-MS of both biodiesel samples showed that ricinoleic methyl ester, palmitic acid methyl ester, oleic acid methyl ester, and linoleic methyl ester were dominant constituents. Thus, modified 1-vinyl-3-ethylimidazolium bromide showed valuable potential to be used as a catalyst for the production of biodiesel from castor oil.

Chapter 6

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