

International Journal of Chemical and Biochemical Sciences (ISSN 2226-9614)

Journal Home page:www.iscientific.org/Journal.html



© International Scientific Organization

Advancements in Transesterification of Triglycerides for Sustainable Biodiesel Production

Subodh Srivastava¹, Souvik Sur², Beemkumar N³

¹Department of Physics, Vivekananda Global University, Jaipur, India,²Department Of Chemistry, Teerthanker Mahaveer University, Moradabad, Uttar Pradesh, India, ³Department of Mechanical Engineering, Faculty of Engineering and Technology, JAIN (Deemed-to-be University), Bangalore, India.

Abstract

Lipids, which are fatty acids derived from glycerol, mostly consist of triglycerides. The most alluring diesel renewable energy is biodiesel (mono alkyl esters), which has many more ecological advantages than made from petroleum fuel. Transesterification is the most practical technology for producing biodiesel with concentrations similar to diesel fuel from lipids. Previous studies have shown that compression ignition engines can run on biodiesel-diesel mixtures without any adjustments. The high manufacturing costs for biodiesel, however, continue to restrict its adoption. In this regard, the transesterification process plays a key role in deciding how much biodiesel will ultimately cost to produce. In the industrial setting, homogenous base-catalyzed transesterification is the typical process for making biodiesel. However, this approach has both economic and ecological drawbacks. There are studies on transesterification, however they often concentrate on a single kind of transesterification procedure and cannot offer an exhaustive summary. This research summarizes the most recent findings from studies reported in papers published by reputable scientific publications in the last two decades on all aspects of transesterification technology. The most innovative technology and proposed changes to the standard approach are the main topics of the evaluation. Investigations are also conducted on the possibility of producing biodiesel from subpar feedstock using each process.

Keywords: starch esterification, biodiesel, biodiesel feedstock, triglycerides, transesterification

Full length article *Corresponding Author, e-mail: <u>srivastava.subodh@vqu.ac.in</u>

1. Introduction

A crucial step in the creation of biodiesel, a renewable and sustainable substitute for diesel derived from fossil fuels, is the transesterification of triglycerides. The transesterification procedure has undergone a number of improvements throughout time to increase its effectiveness and sustainability [1]. Heterogeneous catalysts including sodium hydroxide (NaOH) or potassium hydroxide (KOH) have historically been used to accelerate transesterification processes. Hydroxide catalysts can have certain drawbacks, however, such as the necessity for high reaction temperatures, prolonged reaction durations, and soap production as a byproduct. Acid catalysts, enzyme catalysts, and heterogeneous catalysts have all been researched as solutions to these problems [2]. The process of transesterification has been improved through the use of microwave irradiation. Microwave-helped transesterification offers quicker response rates, decreased response times, and better control of response conditions. Using microwaves can possibly help both the warming of the response combination Srivastava et al., 2023

and the association between the reactants and impetus, bringing about expanded efficiency [3]. As alternatives to homogeneous catalysts, solid acid or base catalysts like zeolites and metal oxides have gained attention. Because these catalysts can be easily separated from the reaction mixture, they can be used again and the purification process is made easier [4]. Transesterification under supercritical conditions, in which the reaction medium is above its critical temperature and pressure, is called supercritical transesterification. The transesterification process is enhanced by the unique properties of supercritical fluids, such as supercritical methanol or ethanol, which improves mass transfer and shortens reaction times. The method has demonstrated the potential to produce biodiesel with greater efficiency [5]. Transesterification can be carried out directly on the feedstock, such as microalgae, without the need for separate triglyceride extraction in situ transesterification. The process of making biodiesel is made easier thanks to this method, which eliminates the need for lipid extraction. In the context of producing integrated and sustainable

biodiesel from microalgae, it has gained attention [6]. Transesterification of triglycerides has improved efficiency, sustainability, and economic viability of biodiesel production as a result of these advancements. Biodiesel is expected to become an even more appealing alternative to conventional diesel fuel as a result of ongoing research and development in this field [7]. Fatty substances, which are the primary parts of vegetable oils and creature fats, act as a significant feedstock for reasonable biodiesel creation. When compared to conventional diesel fuel, biodiesel derived from triglycerides has a number of advantages for the environment and the economy [8]. When compared to diesel derived from fossil fuels, biodiesel derived from triglycerides emits significantly fewer greenhouse gases. Biodiesel emits carbon dioxide $(^{CO}_2)$ when burned, but the carbon dioxide absorbed by plants during growth offsets the CO₂ released during combustion. As a result, the net carbon footprint is significantly reduced, which aids in climate change mitigation [9]. Triglyceride-based biodiesel can be seamlessly integrated into diesel infrastructure and engines. It can be combined with petroleum diesel in various ratios, such as B20 (20% biodiesel, 80% diesel), or used as a direct A smooth transition to replacement. sustainable transportation fuels is possible without requiring significant modifications due to biodiesel's compatibility with existing engines and fueling infrastructure [10]. Biodiesel based on triglycerides is easily biodegradable, so it can be broken down by the environment's natural processes. In case of spills or unplanned deliveries, biodiesel represents a lower chance to biological systems contrasted with petrol based diesel. It has lower levels of toxicity and persists in water and soil, lowering its potential impact on the environment [11].

The study important factors that affect how well heterogeneous catalysts work, talked about the reaction parameters that affect how much biofuel can be made from different vegetable oil feedstock's, talked about how heterogeneous catalysts work to make biodiesel, and talked about process opportunities and challenges that could lead to more research [12]. Either traditional chemical catalysts (Acid or Alkali Transesterification) or enzyme-mediated transesterification are used to produce biodiesel. However, since enzymes are natural catalysts that operate in environmentally friendly conditions, the enzyme-mediated transesterification process is proposed to overcome the disadvantages of chemical synthesis [13]. Transesterification is examined in relation to a variety of nanocatalyst types and manufacturing procedures in this review. It examines the significance of nanocatalysts in boosting biodiesel production, identifies potential obstacles, and offers suggestions [14]. Nanocatalysts are unique due to their selective reactivity, high activation energy, and controlled reaction rate, ease of recovery, recycling potential and other characteristics. In this paper, they examine the various feedstocks used to make biodiesel and their properties and composition. The fundamental target of the study is to assess the portrayal of nanocatalysts, their effect on the development of biodiesel, and biodiesel creation methods [16].

2. Integrated Catalysis

2.1. Base-catalyzed integrated transesterification

Base catalysts for virgin vegetable oil often work well with oils that have more free fatty acids than are needed to make soap. These free fatty acids prevent glycerol from being made and fatty acids from being divided into biodiesel and glycerin are limited. Financially speaking, hydroxides are cheap, and they are also easy to handle while being stored. It is advised to use methoxides in alcohol to maintain biodiesel generation. The species that is active in both situations is the methoxide as ion created by the interaction among hydroxides alkaline metals and alcohol in formula (1) the methoxide is salt in formula (2).

$$CH_3ON_a \to CH_3O^- + Na^+ \tag{1}$$

$$N_a OH + CH_3 OH \leftrightarrow CH_3 O^- + H_2 O + Na^+$$
(2)

Using a variety of basic catalysts, including sodium methoxide, potassium methoxide, sodium hydroxide, and potassium hydroxide, sunflower oil was metabolized. The findings revealed that all catalysts had a biodiesel purity of one hundred percent by weight. However, the biodiesel yields could only be achieved in full by using methoxide catalysts. A number of homogeneous caustic catalysts have been used for study to create biodiesel from canola oil that and it has been shown that methane catalysts produce more than caustic catalysts and those potassium-based catalysts perform higher. Because they are less corrosive, create biodiesel with a higher simplicity, and generate it more rapidly than acid catalysts, approximately base catalysts are chosen for the manufacture of biodiesel in industrial operations. Homogeneous base catalysts, on the other hand, cannot tolerate the substantial amounts of free fatty acids (FFAs) present in the feedstock. Particularly, the overall (FFAs) oil content cannot exceed 0.5 weight percent. In any case, as shown by (Condition (3)), the impetus is spent on the grounds that cleansers create. The base methodology isn't fitting for feedstocks with high FFA focuses, for example, certain non-eatable vegetable oils, disposed of cooking oil, or creature fats. The hydrolysis of alkyl esters into FFAs Equation (4) is made easier by the water in the feedstocks, which results in the formation of soap. Alcohol and the catalyst must therefore be nearly waterless. The production of soap makes it more difficult to separate glycerol from an alkyl ester. Alkali-hydroxide homogenous catalysis generates a lot of wastewater that is released into the environment to remove the dissolved catalyst from the produced biodiesel.

$RCOOH + NaOH \text{ or } (CH_3ONa) \rightarrow RCOONa +$	
$H_2O \text{ or } (CH_3OH)$	(3)

$$RCOOH_3 + H_2O \leftrightarrow RCOOH + CH_3OH \tag{4}$$

The ethanol to oil molar ratio was 4.25:1, and the reaction temperature was 55 °C. A sum of 1.06 g of sodium methoxide impetus was added to 100 g of oil all through each phase of the interaction. This two-stage salt catalyzed transesterification merits modern thought since it could create biodiesel with the required standard all out glycerin content, with less liquor and impetus utilization, and with a

more noteworthy biodiesel yield than one-stage transesterification. Vegetable oils that have been transesterified are often referred to as "biodiesel". As compared to diesel, Figure 1 displays the differences in regularity among oils and transesterified oils.

2.2. Acid-Catalyzed Homogeneous Transesterification

The second most popular way to make biodiesel is using this industrial process. The two most often utilized acids are hydrochloric. Alkyl esters give exceptionally significant returns while utilizing this sort of impetus. While FFAs in the feedstock have no effect on it, it cannot be employed in production because to its slow reaction time and high alcohol requirements. Under acid catalysis, the transesterification of used frying oil was the subject of The alcohol's effects were examined by investigation. researchers: oil molar extents in soybean oil during the corrosive catalyzed transesterification process by utilizing an exceptionally thought sulfur acidic (1 wt %) depending on the weight of the oil at a temperature close to what causes methanol to bubble up. At 3 and 18 hours, they had conducted pilot studies with molar ratios of 6:1 and 20:1. Esters could not be changed in a way that was acceptable. After nine hours at 95 °C, 99.7 wt% of biodiesel was produced; after 24 hours at 80 °C, the yield was comparable. In point of fact, even 24 hours later, methylation at 75 °C was sluggish and insufficient. At the point when temperature is considered, corrosive catalyzed transesterification requires a great deal of energy. Acids have the potential to catalyze both transesterification and etherification processes by prorogating the fatty acids and triglycerides. Consequently, the corrosive catalyzed approach is fitting for assembling biodiesel from modest feedstock with high FFA fixation since acids may both etherification simultaneously catalyze and transesterification processes. The production of biodiesel through the base-catalyzed method and the acid-catalyzed method are now economically comparable. An alkalicatalyzed procedure employing waste cooking oil was determined to be less practicable, more costly, and more challenging to execute by a techno-economical study.

2.3. Two-Step Acid-Base Catalyzed Process

When making biodiesel from feedstock's with a lot of FFAs, this method works well. To begin, an acid-catalyzed pretreatment is carried out in order to esterifies FFAs and reduce their concentration to less than 1% by weight. In step two, an alkaline catalyst is used to transesterify the triglycerides to complete the process. Charoenchaitrakool and Thienmethangkoon produced biodiesel by utilizing the two-step catalytic pretreatment method. Methyl ester accounts for 28% of the product at 90.56 percent. Before being subjected to alkaline-catalyzed transesterification, Mahua oil underwent a two-step pretreatment process, reducing the concentration of FFAs from 19 percent to less than 1 percent. They discovered that the amount of FFAs present is influenced by both reaction time and methanol concentration. Obviously a huge amount of methanol was spent all through the two pretreatment techniques. In order for this method to be useful in a commercial setting, it is necessary to recover some of the methanol that is removed Srivastava et al., 2023

from the water mixture at the top following each stage. Acidic ionic liquids (ILs) are used in a unique heterogeneous catalytic technique that converts feedstock with high FFA levels into biodiesel. Despite being more expensive than common catalysts like NaOH, KOH, and H2SO4, ionic liquids have the advantages of being biodegradable and reusable.

2.4. Transesterification double step process (TDSP)

The biodiesel/glycerin phase may be effectively separated using this technique. Basic accelerated transesterification is the initial step, which is carried out by the development of an acidic impulse. Acid is added to the second stage to speed up and disintegrate the lather. Because of the high conversion rate, the whole process is rapid and yields goods that are very pure. According to 1 H-NMR, it was possible to produce biodiesel of high quality and purity from linseed and sunflower oils using the TDSP. Over 97% of the oil was converted into fatty acid methyl ester, according to the 1 H-NMR analysis. Castor oil and other hydroxyl vegetable oils are exceptionally solvent in ethanol and glycerin. Consequently, using a basic catalyst to ethanolyze such vegetable oils is impractical. It has been shown that the TDSP must be used in order to improve the separating glycerin from the fatty acid methyl ester that is produced during castor oil transesterification. In addition to producing sufficient ethyl esters and 95.76 % pure glycerin, they also produced less free and bound glycerol than was needed. A few vegetable oils and waste vegetable oils were ethanolyze utilizing a changed TDSP. Comparing recoveries from a single basic catalysis to the triglyceride conversion to biodiesel, all of the oils examined achieved values more than 97%. With a faster conversion rate than the traditional process and a shorter running period than acid catalysis, TDSP is being evaluated as a revolutionary biodiesel manufacturing technology.

3. Heterogeneous Catalysis

All problems associated with homogeneous catalysts seem to be solved by the heterogeneous catalytic system. Currently, heterogeneous catalysts are preferred due to the following significant advantages: 1) the rapid separation and purification of finished goods; 2) the capacity to be recycled and rebuilt; furthermore (3) capacity to be utilized in persistent cycles without requiring corrosive or water treatment during the partition step, making them harmless to the ecosystem. Heterogeneous catalysis has gotten the interest of scholastics a great deal due to this multitude of advantages. Strong bases or strong acids might be heterogeneous impetuses. In environments that are either acidic or basic, the fundamental mechanism of heterogeneous catalysis is comparable to that of homogeneous catalysis. By coating porous materials with active compounds, solid catalysts are routinely created. This approach reduces the quantity of catalyst needed to complete the transesterification process while increasing catalytic activity.

3.1. Process with a heterogeneous base catalyst

The rate at which various vegetable oils are converted into biodiesel and the ideal conditions for using a solid base catalyst are shown in Table 1. A CaO/mesoporous silica catalyst was used to transesterify soybean oil. To achieve the highest yield (95.2%), the mesoporous silica catalyst was loaded with 15 wt percent Ca, the reaction temperature was set at 60 degrees Celsius for eight hours, and the catalyst to oil ratio was found to be 5% (w/w). Even though, this aid has a mild corrosiveness because of the concentrated non-polar silanol bunches on the pore walls. A loading weight of 5% applied to the metal. When Zr atoms were added to the SBA-15 framework, Bronsted acid sites were easier to generate and the size of the Na species' particles was reduced. Increasing the Zr content of the catalysts increased the yield of the fatty acid methyl ester (FAME). Oils having an acid value higher than two are where esterification first started. The findings demonstrated that CaSn(OH)6 performed differently for the various tested oils, producing more than 90% biodiesel with catalysts weighing 3 weight percent.

3.2. Heterogeneous Corrosive Catalyzed Interaction

Contrasted with homogeneous corrosive impetuses, heterogeneous corrosive impetuses are less toxic and destructive and cause less ecological issues. In place of the troublesome homogeneous two-step method, a new method has been devised that utilizes powerful caustic catalysts to etherify and transesterify oils that aren't fit for human consumption all at once. Utilizing a meso-primary impetus changed by euphonic corrosive, vegetable oils that were refined and those that were not were transesterified. Even though there were free fatty acids present, this catalyst shown exceptional activity for both the simultaneous etherification and transesterification of molecules. Utilized a 4-sulfophenyl enacted carbon-based strong corrosive impetus (ACPhSO3H) and Amberlyst-15, a modern grade strong corrosive impetus, to inspect the etherification responses of rapeseed oil unsaturated fats and rapeseed oil (RO) blend. At 65 °C and a molar ratio of 1/20 RFA to methanol, the etherification reaction took 0-7 hours. After seven hours of reaction, the RFA/RO mixture reached 95% and 92%, respectively. With a drink: The catalyst (pyrolyzed cork at 600 °C) was able to convert fatty acids methyl esters (FAMEs) at a maximum rate of 98% at a ratio of 25:1, a catalyst loading of 1.5% w/v, and 65 °C. Table 2 introduces new heterogeneous strong corrosive impetuses for the age of biodiesel from subpar feedstock.

In one step, fly ash with a high concentration of SO3 (27 wt %) and CaO (47 wt %) produced biodiesel from discarded frying oil. An oil-to-methanol ratio of 6:1 and a process temperature of 45 °C after 9 hours generated biodiesel with an oil content of 81.96 %. The SO3H group esterifies FFAs and the CaO transistors raw material triglycerides simultaneously.

3.2.1. Co-Solvent's Function in Heterogeneous Catalyst

Meso-structural catalysts that had been euphonic acid-modified were used to transesterify both refined and unrefined vegetable oils. This impetus has solid etherification and transesterification action paying little heed to free unsaturated fat. 5:1 oil's transesterification of soybean oil: It was shown that biodiesel may be a helpful co-dissolvable to accelerate the transesterification cycle lighted by a strong corrosive impetus by involving n-hexane as a co-dissolvable in a n-hexane molar proportion heterogeneous impetus. The yield of unsaturated fat methyl ester was 30% higher than it would have been without a codissolvable. In a study, heterogeneous catalysis was used to transesterify rapeseed oil using methanol and butanol.

3.2.2. Nano-Heterogeneous Catalysis

Nanotechnology may be used by researchers to create creative materials with certain physical and chemical properties. Therefore, nanotechnology is essential for a fresh, potential approach to solving the mass interchange problem. Nonmaterials' vast surface area considerably increases the reaction area and active center, producing in catalytic reactions that are very energy- and time-efficient. Because KCaF3 has greater Lewis F and Lewis Ca2+ than CaO, it may release the active anion CH3O more readily in the response medium. These two molecules cooperate to deprotonate CH3OH and draw the liberated CH3O concurrently. At 338 Kelvin and a molar ratio of 9:1 methanol to oil, the biodiesel yield after 8 hours in a liquid batch reactor was 96.67% 1.7. The catalyst's 3 wt% addition to canola oil effectively increased the process of the glycerol in canola oil. The new technique of electromagnetic incineration was used to create an iron aluminum oxide nano-catalyst. Under these conditions (65 degrees Celsius, 3.5 weight percent catalyst, 12 miles of methanol to one mole of oil, and four hours of reaction time), the highest biodiesel production (96.70 percent) was obtained. At least three transesterification processes could be catalyzed successfully using the KOH/calcium aluminum oxide nanocatalyst. Chinese tallow oil was transesterified into biodiesel at a rate of over 95%. The magnetic field separation enabled the catalyst to be recycled up to 14 times without significantly affecting its activity, resulting in catalyst recovery of over 90%. Some promising new nanoheterogeneous-based catalysts for biodiesel synthesis are included in Table 3.

3.3. Heterogeneous Catalysis Based on Natural/Waste

Numerous heterogeneous catalysts for biodiesel generation have been documented in the study; however they are either prohibitively costly or very labor intensive to produce. This limits their industrial application. Cheap solid base catalysts that can support environmentally acceptable biodiesel production may be made from waste materials from enterprises and the outside world.

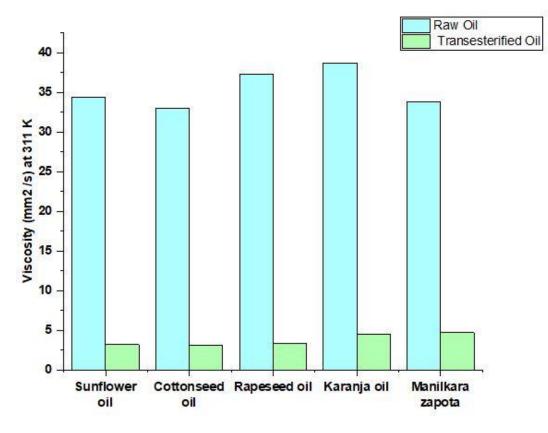


Figure 1: Transesterification's impact on the viscosities of vegetable oils

			Reaction Parameters			
Catalyst	Catalyst to oil %(w/w)	Feedstock	Conversion %	Methanol to oil molar ratio	Reaction time h	Temperatu re ∘C
BaAl ₂ O ₄	12	Used cooking	93.27	22:4	2.4	64
f-MgO	NA	Canola oil	93.2	17:1	2.3	180
Na/Al-SBA-15	3	Canola oil	96	75:5	4	64
Na/Zr-SBA-15	NA	Canola oil	97	53:3	5	73
CaO/Mesoporous	5	Soybean oil	95.4	14:1	7	65
CaSn(OH) ₆	3	Oils with high free fatty acids	93–95	12:1	5–12	64

 Table 1: Strong fundamental catalysts for the production of biodiesel

IJCBS, 23(2) (2023): 355-365

	Acid Value (mgKOH/g)			
Catalyst	Initial Value	Final Value	Reaction Time	Biodiesel yield wt%
Graphene Oxide-(5 wt%) Alumina	NA	NA	20	98
Fly ash	6.75	NA	8	82.94
Fe ₂ O ₃ /KOH oil	75.93	-	-	97.24
Fe2O ₃ /CaO	41.04	5	4.46	95
Ca-B	9.4	0.4	3	93
Ca-La	16.3–22.86	0.9	4	96.75

Table 2: Producing biofuel from inferior feedstocks using new homogeneous solid acid catalysts

Table 3: Several brand-new catalysts based on nanoheterogeneity for the production of biodiesel

		Reaction I	Parameters				
Method of Preparation	Feedstock (oil)	Catalyst Reusabili ty Loading wt%	Methanol to Oil Molar Ratio	Temper ature ∘C	Time h	Conversi on or Yield wt%	Reusability
Step-wise co- precipitation	Crude Jatropha oil	7	9:1	80	3.5	97%	9
Solvothermal method	Oleic acid	8.9	6:9	120	4	95.8%	7
Impregnation	tallow seed oil	3	14:1	65	2.5	96.7%	14
Impregnation	canola oil	2	8:4	125	8	97.67%	4
Acile chemical co- precipitation	Soybean with high FFAs	7	33:2	140	8	95.3%	3
Microwave combustion/impregnati on	96.7%	3.4	14:1	64	4	96.9%	2
CaO@yFe2O3/encaps ulation	Soybean oil	3	14:8	70	3	96.7%	5
facile impregnation m	Stillingia oil	5	13:5	75	3	35%	13

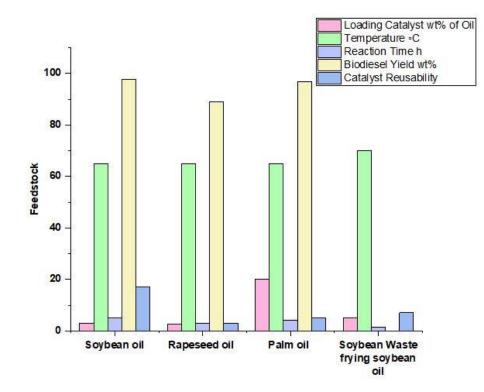


Figure 2: Solid base catalysts made from waste from industry are used in the generation of biodiesel

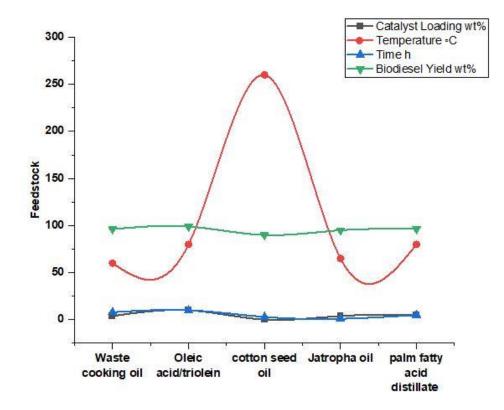


Figure 3: Solid acid catalysts based on carbon for the manufacture of biodiesel

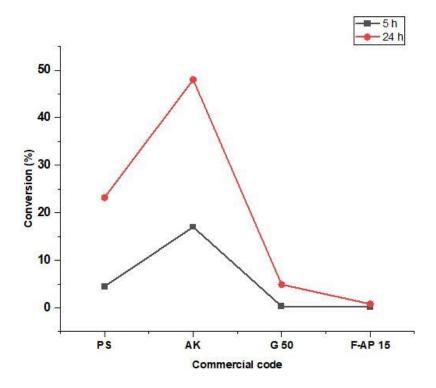


Figure 4: Commercial crude lipases are tested for their ability to alcoholism pure triolein with methanol in n-hexane

Alcohol/Solvent	Critical Temperature (°C)	Critical Pressure (MPa)
Methanol	238	8.07
Ethanol	245	6.37
Water	373.94	22.13
Acetic acid	316	5.70
1-propanol	265	5.05
1-butanol	289	4.8
1-octanol	384	2.85
Methyl acetate	236	4.67
Dimethyl carbonate	285	4.64

Table 4: Important characteristics of several alcohols and other solvents

Many scientists working in this area are attempting to create heterogeneous catalysts that are less expensive and more natural. Industrial debris may be properly disposed of by being used in the manufacturing of catalysts, which also lowers the cost of making catalysts. Catalyst preparation may be done using waste that is abundant, inexpensive, biodegradable, and ecologically benign.

3.3.1. Solid Basic Catalysis

It has been demonstrated that industrial waste shells can be utilized as an inexpensive natural source of CaO that can be utilized as a solid base catalyst with excellent efficacy rather than spending money on expensive compounds used as analytical reagents. The ideal conditions for producing biodiesel from high-base impetuses using modern waste shells are shown in Figure 2. After being calcined at 700 to 1000 C for 2 to 4 hours, the resultant catalysts were used in various reactions. It is believed that mixing used seashells with fly ash would produce inexpensive supported-base catalysts with better catalytic capacity. By placing waste shells on an active basis, they might have their CaO activity level raised. The shrimp shells that contained KI were partially carbonized, leading to the creation of the following locations of activity on the outside of the resulting catalyst.

3.3.2. Solid acidic catalysis

These problems include a lack of acid sites, micro porosity and hydrophilicity on the catalyst substrates, leaching, and expensive prices. These materials undergo incomplete carbonization, which results in amorphous aromatic carbon structures with wide holes that suffocate to trap the acidic groups (-SO3H). Because the aromatic groups' influence on electron drawing makes the resulting solid acid catalyst so stable. Additionally, this derived catalyst's hydrophobic properties allow it to tolerate the presence of water in the feedstock. They created a carbonbased catalyst using the shell of a palm kernel. Chlorosulfonic acid (ClSO3H) was applied to the carbonaceous catalyst's surface for four hours at 70 degrees to trap the active SO3H sites. The synthesized catalyst continued to function catalytically for up to four cycles in a row. To make it easier to separate the reaction medium from the PKS (PKS-SO3H) catalyst. Employed a mixture of biochar made from PKS and ferrite Fe3O4 to suffocate a magnetized form of PKS-SO3H. The first four cycles showed adequate catalyst performance. To lessen the leaching of Fe, the scientists suggested covering the catalyst with an additional layer. Figure 3 provides an overview of the investigations done on carbon solid acid catalysts for biodiesel synthesis.

4. Enzymatic Catalysis

Enzyme-based catalysis may be used to get rid of soaps and polymeric pigments unwanted byproducts that make it hard to separate glycerol, di, and monoacylglycerols from the biodiesel produced by chemical catalysis. The most promising new technique is the synthesis of biodiesel by enzymatic catalysis. Numerous articles published during the last two decades on the topic of enzymatic transesterification of lipids provide evidence of this. Enzymes known as lipases hydrolyze a broad range of esters by breaking them down into glycerol and water. They catalyze the reversible etherification and transesterification processes, which allow their synthetic activity to be increased even under low water circumstances. Many different kinds of microbes create lipases in nature. Low-quality FFAs and fatty substances may be etherified and transesterified concurrently by lipases under mild reaction circumstances, resulting in little to no downstream activity, fewer cycles, a reduced liquorto-oil ratio, and simple product division. By modifying proteins, lipase's performance as a biocatalyst may be enhanced. Since lipases are involved in the storage of carbon in soil or other organic matter, they are seen from an environmental perspective as being of prime significance in natural ecosystems. So, compared to enzymatic transesterification traditional procedures, provides a more appealing environmental alternative. Therefore, to facilitate the manufacture of biodiesel on a wide scale, the influence of water must be maintain Srivastava et al., 2023

experimentally. The presence of phospholipids in the feedstock also reduces lipase activity. Because of this, lipase-catalyzed transesterification is very sensitive to the types of contaminants present in the feedstock.

4.1. Screening of lipases

Extracellular lipases and intercellular lipases the two main classifications of lipases. The both containing the liveproducing microorganisms are used to extract and purify extracellular lipases. Either within the cell or in the wall that produces new cells, intercellular lipase stays. Because pure lipase has a limited catalytic activity, it immobilizes both external and intracellular lipases. To examine their susceptibility to the alcoholysis reaction, free lipases are utilized. Six separate crude microbial lipases were investigated as part of a study the impact of various parameters on the catalytic alcoholysis produced by sunflower oil (Figure 4). As an organic solvent, they metabolized triolein in n-hexane. Only three enzymes demonstrated significant catalytic activity from the starting rate of the alcoholysis process with the degree of deactivation. Since the short alcohol present in the triglycerides and the alcohol droplet clinging to the immobilized enzyme are incompatible, the enzyme is inactivated. After being thoroughly rinsed tert-butanol, the totally trapped, disabled recovered 56% and 75% of its initial activity. In contrast, submerged preparation with these alcohols might boost the enzyme's activity tenfold compared to an enzyme that has not been pretreated. These alcohols have the capacity to disperse the methanol molecules that have been deposited around the digestive enzyme. The conventional approach of gradually adding methanol, which calls for high accuracy to keep the methanol content low and the reaction rate low, was deemed impractical in favor of this alternative.

4.2. Methods of Lipase Deactivation Treatment

Added methanol in three 1/3 molar equivalent increments to counteract its toxicity. In a 48-hour reaction, 98.4 percent of the oil was transformed into methyl esters. Even after 50 cycles (100 days), the catalyst was still effective in converting ester at a rate of above 95%. In light of this, adding methanol gradually might lower the price, particularly if done in permanent solid base reactors. They showed that linear alcohols, which are less soluble in the triglyceride, blocked the enzymatic activity more effectively than branched alcohols. Additionally, the linear alcohol's carbon chain length had an inverse relationship

4.3. Immobilization of Lipases

The greatest barrier to the practical generation of biodiesel using enzymatic glycerol alcoholysis is the expense of the lipase enzyme. Immobilized lipases' economic viability is influenced by the encapsulation techniques and support materials used. Support materials for enzymatic reactions should be inexpensive, have a sufficient amount of surface area, and have the least amount of diffusion restriction. Several methods exist for immobilizing lipase, including encapsulation, covalent attachment to a solid support, physical trapping using a polymer matrix support, and cross linking. Using a natural biopolymer as a matrix for immobilizing lipase may make biodiesel production more economically and ecologically feasible. In a 24 hour process, the highest biodiesel yield of 93% was attained at 25 °C under ideal circumstances. Throughout ten successive batch processes, the immobilized lipase maintained its activity. Immobilized microbial entire cells containing internal lipases on biomass support particles (BSPs) are more cost-effective than a free and immobilized enzyme.

5. Ultrasonic and microwave irradiation for transesterification

5.1. Using microwave radiation to aid in catalysis

Alcohols and other weakly polar compounds may have their magnetic fields altered by microwave radiation. Heat is produced as a consequence of the molecules' rotating movement being accelerated. Microwave radiation speeds up chemical processes by transferring heat more efficiently than traditional heating methods. Electromagnetic heating's shallow penetration depth is its main flaw or restriction. Since a microwave's range is just a few millimeters, its power would quickly fade in the event of a response. The effects of microwave heating that are not thermal are another point of contention. Due to the fact that they might cause harm through sparks from metal, microwave sensitivity, or even high temperatures at welded or sharp edges. Catalyst quantity, temperature, and reaction time were three parametric conditions that were changed. With conventional heating, equivalent results were reached in 30 minutes less time.

6. Production for Non-Catalytic Biodiesel

Without the aid of anv catalysts. the transesterification of supercritical alcohol and triglycerides takes place. Alcohol molecules begin to function as an acid catalyst when their hydrogen bonding substantially reduces once they reach the supercritical zone. Methanol is a compressible fluid with a density that falls between that of a liquid and a gas because of its low surface tension and viscosity, giving it good mass transfer capabilities. It acts like a supercritical fluid when heated to 240 °C and compressed to 78.60 bars. Due to its lack of a catalyst, supercritical alcohol technology may overcome the limitations of both homogeneous and heterogeneous traditional catalytic processes. When alcohol is heated to its supercritical temperature, it takes on qualities normally associated with a gas, such as high density and high kinetic energy. The dielectric constant of supercritical alcohol is also lower than that of alcohol liquid. As a consequence, the deleterious effects of alcohol polarity on the reactions with non-polar triglycerides are lessened. Triglycerides and alcohol form a completely miscible 1phase system after being converted to fatty acids alkyl ester without the need of a catalyst. Heating alcohol until its critical pressure and temperature are attained is the procedure. Table 4 shows the critical pressure and temperature for a few solvents and alcohols.

7. Intracellular transesterification

Prior to esterification or transesterification, oils from materials containing triglycerides must be extracted and purified in order to produce conventional biodiesel. Because biodiesel requires many processing steps, refined feedstock accounts for 70% of the entire cost of production. A method of producing biodiesel called in situ transesterification was created to lower the cost of producing the fuel. Alcohol serves as both an extraction solvent and a transesterification reagent during one phase of in situ transesterification, which comprises direct extraction and transesterification. Reactive extraction, also known as in situ transesterification, has the benefit of requiring less solvent and processing time. Additionally, it is ecologically friendly since it may avoid using dangerous air pollutants like hexane. Improvements in cottonseeds oil extraction and conversion were seen with increased catalyst amount, greater methanol's, extended reactions time, and decreased percentage of moisture and seed particle size. Biodiesel production is not much affected by temperature changes. The ideal circumstance led to 99% and 98% recovery and conversion costs of oil from cottonseeds, as follows: Cottonseed flour with a moisture content of less than 2%, a particle size of 0.3-0.335 mm, metabolic sodium hydroxide solutions. Moreover, by combining 0.2 ratios of new and recycled methanol, the removal and transformation of the oil from cottonseeds maintained consistent.

8. Conclusion

FAME, often known as biodiesel, is a fuel made from plant oils that may be used in conventional compression ignition vehicles. Interest in and progresses toward biofuels have skyrocketed in recent years in response to the need of producing ecologically friendly energy sources and combating climate change. The sustainability of the biodiesel sector in terms of both business and the environment is still up for dispute. Research to make the production of biodiesel more economical and ecologically friendly is advancing quickly. A special focus has to be placed on creating novel transesterification pathways that make it possible to produce biodiesel from low-quality feedstock with fewer downstream procedures. For the transesterification of lipids necessary to produce biodiesel, several non-edible plant oils are employed. Since they have a direct impact on the process' overall cost, stable catalysts that are long-lasting, recyclable, and affordable are crucial. In spite of their more slow response rate and side responses, strong corrosive impetuses may change over oils wealthy in FFA into biodiesel in a solitary step. The efficiency and response time of nano-catalyzed transesterification are improved by the high active surface area and superior selectivity of nano-heterogeneous catalysts.

Reference

 S. Wu, C. Gao, H. Pan, K. Wei, D. Li, K. Cai, H. Zhang, (2022). Advancements in tobacco (Nicotiana tabacum L.) seed oils for biodiesel production. *Frontiers in Chemistry*, 9, 834936.

- M. A. Bashir, S. Wu, J. Zhu, A. Krosuri, M. U. Khan, R. J. N. Aka, (2022). Recent development of advanced processing technologies for biodiesel production: A critical review. *Fuel Processing Technology*, 227, 107120.
- B. H. H. Goh, C. T. Chong, Y. Ge, H. C. Ong, J. H. Ng, B. Tian, V. Józsa, (2020). Progress in utilisation of waste cooking oil for sustainable biodiesel and biojet fuel production. *Energy Conversion and Management*, 223, 113296.
- B. Panchal, Z. Zhu, S. Qin, T. Chang, Q. Zhao, Y. Sun, S. Rankhamb, (2022). The current state applications of ethyl carbonate with ionic liquid in sustainable biodiesel production: A review. *Renewable Energy*, 181, 341-354.
- B. Maleki, S. A. Talesh, M. Mansouri, (2022). Comparison of catalysts types performance in the generation of sustainable biodiesel via transesterification of various oil sources: A review study. *Materials Today Sustainability*, 18, 100157.
- A. A. Babadi, S. Rahmati, R. Fakhlaei, B. Barati, S. Wang, W. Doherty, K. K. Ostrikov, (2022). Emerging technologies for biodiesel production: processes, challenges, and opportunities. *Biomass and Bioenergy*, 163, 106521.
- M. Ahmed, K. A. Ahmad, D. V. N. Vo, M. Yusuf, A. Haq, A. Abdullah, M. Athar, (2023). Recent trends in sustainable biodiesel production using heterogeneous nanocatalysts: Function of supports, promoters, synthesis techniques, reaction mechanism, and kinetics and thermodynamic studies. *Energy Conversion and Management*, 280, 116821.
- M. Salaheldeen, A. A. Mariod, M. K. Aroua, S. A. Rahman, M. E. M. Soudagar, I. R. Fattah, (2021). Current state and perspectives on transesterification of triglycerides for biodiesel production. *Catalysts*, 11(9), 1121.
- 9. G. Dwivedi, S. Jain, A. K. Shukla, P. Verma, T. N. Verma, G. Saini, (2022). Impact analysis of biodiesel production parameters for different catalyst. *Environment, Development and Sustainability*, 1-21.

- J. Gardy, E. Nourafkan, A. Osatiashtiani, A. F. Lee, K. Wilson, A. Hassanpour, X. Lai, (2019). A core-shell SO4/Mg-Al-Fe3O4 catalyst for biodiesel production. *Applied Catalysis B: Environmental*, 259, 118093.
- A. N. Gutiérrez-López, V. Y. Mena-Cervantes, S. M. García-Solares, J. Vazquez-Arenas, R. Hernández-Altamirano, (2021). NaFeTiO4/Fe2O3–FeTiO3 as heterogeneous catalyst towards a cleaner and sustainable biodiesel production from Jatropha curcas L. oil. *Journal of Cleaner Production*, 304, 127106.
- E. A. Mohamed, M. A. Betiha, N. A. Negm, (2023). Insight into the Recent Advances in Sustainable Biodiesel Production by Catalytic Conversion of Vegetable Oils: Current Trends, Challenges, and Prospects. *Energy & Fuels*, 37(4), 2631-2647.
- 13. G. M. Mathew, D. Raina, V. Narisetty, V. Kumar, S. Saran, A. Pugazhendi, P. Binod, (2021). Recent advances in biodiesel production: Challenges and solutions. *Science of the Total Environment*, 794, 148751.
- G. Yang, J. Yu, (2023). Advancements in Basic Zeolites for Biodiesel Production via Transesterification. *Chemistry*, 5(1), 438-451.
- S. Z. Hossain, S. A. Razzak, A. F. Al-Shater, M. Moniruzzaman, M. M. Hossain, (2020). Recent advances in enzymatic conversion of microalgal lipids into biodiesel. *Energy & Fuels*, 34(6), 6735-6750.
- 16. A. P. Ingle, A. K. Chandel, R. Philippini, S. E. Martiniano, S. S. da Silva, (2020). Advances in nanocatalysts mediated biodiesel production: a critical appraisal. *Symmetry*, *12*(2), 256.