Review Article

# Catalytic Applications in Biodiesel Production: A Review

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Abstract

Biodiesel is produced from vegetable oils and animal fats by transesterification reaction in the presence of an acidic, alkaline or enzymatic catalyst. The application of biodiesel as an alternative to fossil fuels is growing; however, the optimization of reaction parameters to obtain maximum yield is still an area of research that can be further explored. The current methods of biodiesel production employ the use of acidic, basic, solid and enzymatic catalysts to obtain high yields and lower the cost of production. In this paper, various catalysts that have been explored over the past decade are reviewed to obtain an understanding of the progress made in the field of biodiesel catalysis. Areas of potential interest like the exploration of catalysts from natural sources are also explored and recommended for further studies.

Keywords: Catalysts, Transesterification, Enzymatic catalysts, Acid-Base catalysts, Biodiesel
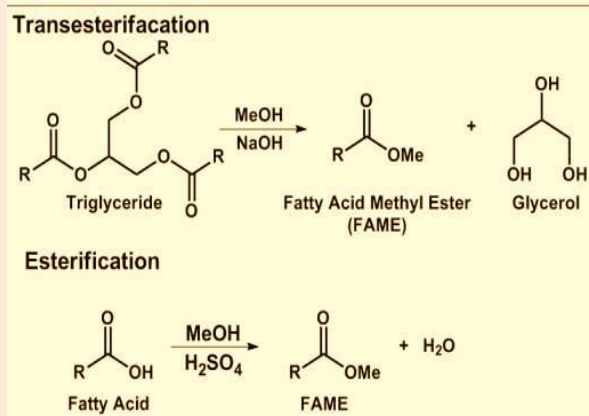
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Introduction

Biodiesel is derived from vegetable oils and animal fat. It is comprised of mono-alkyl esters of long-chained fatty acids and pure biodiesel is designated B100 [1]. This fuel is seen both as a complement as well as an alternative to fossil fuel that is currently the major source of energy. Straight vegetable oils have been directly used in diesel engines but the high viscosity of the oils causes many problems and result in poor fuel characteristics. Possible solutions to these problems are engine modifications, blending of straight oils with fossil fuels, micro-emulsification, transesterification or thermal cracking [2]. The transesterification process however, has been widely adopted because of its cost-effective technology and easy application as well as the suitable physicochemical properties of the fuel. The process occurs by reacting vegetable oil with alcohol in the presence of a catalyst. Various catalysts have been utilized with acidic and basic catalysts being the most common. However, the applications of supercritical fluids or enzymes are also being explored in order to reduce costs and increase yield. Recent studies have also reported the increased use of heterogeneous catalysts for the production of biodiesel from low-cost starting materials.

The different feedstocks for biodiesel production have a great influence on the type of catalysts used. Refined vegetable oils have been extensively used as the primary feedstocks for the transesterification process. However, waste oils from cooking oils and animal fat can also be utilized because of their availability and low cost. Other low-cost oils from non-edible plant sources are also suitable for the production of biodiesels. These methods aid in the recycling of the waste oil and the prevention of food and fuel competition for energy production. Despite their potential, the waste oils and animal fat are however seen as low-quality feedstocks compared to refined vegetable oils because of their Free Fatty acid (FFA) content. For biodiesel production to be effective for low-quality feedstocks, some form of pretreatment is required. Animal fats usually contain bone and meat particles as well as organic matter. These must be filtered using a cellulose filter and other pretreatment steps include water removal, steam distillation, and bleaching [3]. These low-quality feedstocks may be inexpensive but their high FFAs make them unsuitable for the conventional direct base catalyzed transesterification process due to soap formation. This necessitates the application of multistep acid-catalyzed pre-esterification of the FFAs before the base-catalyzed transesterification.

This method is known as the integrated process and widely applied for biodiesel production from low-cost but high FFA feedstocks [3].

Table 1 illustrates the acceptable specification limits for biodiesel. Therefore, different feedstocks and varying procedures should produce biodiesel within the acceptable limits. Catalytic applications are extensively researched to further improve yield and minimize costs of production of biodiesel both at experimental and industrial levels. Thus this review paper explores various types of catalysts used for the maximization of product yield. The study explores acidic, basic and enzymatic catalysts. It also reviews improvements in results obtained by the use of both homogeneous and heterogeneous catalysts.

Table 1 Specification for Biodiesel B100–ASTM 6751-11a

Property	ASTM Method	Limits	Unit
Kinematic Viscosity, 40°C	D445	1.9-6.0	mm^2/sec
Flash Point (Closed cup)	D93	93 minimum	°C
Calcium & Magnesium combined	EN14538	5 maximum	ppm
Alcohol control (one to be met)			
Methanol	EN14110	0.2 maximum	Mass %
Flash Point	D93	130 minimum	°C
Water and Sediment	D2709	0.05 maximum	% vol
Sulfated Ash	D874	0.02 maximum	% Mass
Sulfur			
S 15 Grade	D5453	0.0015 maximum	% Mass (ppm)
S 500 Grade	D5453	0.05 maximum	% Mass (ppm)
Copper Strip Corrosion	D130	No. 3 maximum	
Cetane	D613	47 minimum	
Cloud Point	D2500	Report	°C
Carbon Residue 100% sample	D4530	0.05 maximum	% Mass
Acid Number	D664	0.5 maximum	mg KOH/g
Free Glycerin	D6584	0.020 maximum	% Mass
Total Glycerin	D6584	0.240 maximum	% Mass
Phosphorus Content	D4951	0.001 maximum	% Mass
Distillation	D1160	360 maximum	°C
Sodium/Potassium, combined	EN14538	5 maximum	Ppm
Oxidation Stability	EN15751	3 minimum	hours
Cold Soak Filtration	D7501	360 maximum	Seconds
For use in temperatures below -12 °C	D7501	200 maximum	seconds

Literature review
Acidic catalysts

The use of acidic catalysts for the production of biodiesels has been studied extensively with reaction rates observed to be low and temperature requirements high for maximum product yields. The application of acids is seen in feedstocks with high free fatty acids with the most preferred acids being sulfuric, hydrochloric and sulfonic acids. However, acid catalyzed transesterification is not applied commercially like the base-catalyzed process due to the low yield in comparison to base catalyzed transesterification.

It is reported by Srivastava and Prasad [4] that the acid-catalyzed process is about 4000 times slower than the base-catalyzed process and this is one of the reasons for the less application of the acid-catalyzed process. However, acid-catalyzed transesterification is advantageous because the performance of the catalyst is not affected by the presence of FFAs in the feedstock and acid catalysts are known to catalyze both esterification and transesterification reactions.

In the application of sulfuric acid for transesterification, it was observed by Canakci and Gerpen [5] that a higher molar ratio is required for acid catalyzed transesterification and the efficiency is based on the molar ratio of the alcohol to oil. Acid catalyzed transesterification is also seen to be very slow with poor ester conversion at room temperature with the amount of free fatty acid having a significant effect on the reaction [5].

A study of the transesterification of soybean oil with methanol in the presence of 1 mol% H_2SO_4 by Freedman et al. [6] showed that an alcohol/oil molar ratio of 30:1 at 65°C will take 50h for the process to reach completion (>99%), while the application of ethanol (at 78°C) and butanol (at 117°C) using equal quantities of catalyst and alcohol will take 18h and 3h respectively.

In another study by Al-Widyan and Al-Shyoukh [7], palm oil was transesterified under different conditions using various concentrations of H_2SO_4, HCl and ethanol in excess. The study observed that higher catalysts concentrations (1.5-2.25M) produced biodiesel with a lower specific gravity in shorter reaction times. The effectiveness and completeness of the process were obtained by studying the variation of the specific gravity of the end product with time. The study observed that lower values of specific gravity indicate removal of heavy glycerine which means complete reaction. Comparing the two catalysts, H_2SO_4 gave better conversion levels than HCl at a catalyst concentration of 2.25M.

Heterogeneous acid catalysts have also been used in the production of biodiesel from different oil sources. A study was done by Furuta et al. using methanol and soybean oil in the presence of different solid super acids which include tungstated zirconia-alumina (WZA), sulfated zirconia alumina (SZA), and sulfated tin oxide (STO) [8]. It was observed that WZA was more effective with conversions >90% at high temperatures above 250 and over a 20 h period. Other heterogeneous catalysts which include Amberlyst-15, SZ, Nafion NR50, and WZ showed good activities at moderate temperatures, indicating that these are suitable catalysts that can overcome the disadvantage of corrosion and handling of liquid mineral acids.

Furthermore, a study by Kaita et al.[9] on the transesterification of kernel oil with methanol, synthesized aluminum phosphate catalysts with different Al/P molar ratios. The catalysts were found to be thermally stable with good reactivity and selectivity to methyl esters. The problem with the catalysts however, is the high temperature (200°C) and high methanol to oil molar ratios (60:1).

WO_3/ZrO_2, SO_4^{2-}/ZrO_2 and Amberlyst-15 heterogeneous catalysts are used with the aim of accelerating the transesterification process. Park et al. [10] tested these systems in the esterification of 4 % wt oleic acid in soybean oil. The parameters used include methanol to oil molar ratio of 9:1, 0.29 g of catalyst per mol of oil at 75 °C. A high conversion of about 93 % was obtained in all variations. The major setback however, in the application of acidic catalysts is the corrosive nature of the catalysts which is higher than that of basic catalysts.

Alkaline Catalysts

Homogeneous alkaline catalysts are currently employed in the synthesis of Biodiesel because they have faster reaction rates and several comprehensive studies have been done on alkaline-catalyzed transesterification reactions. Alkaline catalysis has been extensively used in the production of biodiesel with sodium hydroxide (NaOH), sodium methoxide ($NaOCH_3$), potassium hydroxide (KOH) and sodium ethoxide ($NaCH_2CH_3$) being the preferred alkaline catalysts for the transesterification reaction. However, alkaline catalysts have limitation for high FFA containing oils leading to soap formation and consumption of catalysts.

Heterogeneous alkaline catalysts have also been explored as viable means of optimizing the production of biodiesels with promising results because heterogeneous catalysts are reusable, non-toxic to the environment and are used in a continuous process without the need for additional purification steps. They are also potentially cheap and can be tuned to avert the effects of FFA and water during the reaction [11]. Commonly studied heterogeneous alkaline catalysts include Na_2CO_3, K_2CO_3, $CaCO_3$, CaO, MgO, BaO, and other oxides like ZnO.

Yan et al. [12] studied the transesterification of rapeseed oil catalyzed by MgO, CaO, SrO and BaO at the same parameters (64.5°C, 3.5h reaction time, 18:1 methanol/oil molar ratio and 10% catalyst dosage). The results showed methyl esters content of <5%, 58%, 60% and 86% respectively. The catalytic activities decreased in the order of BaO followed by SrO, then CaO with MgO being the least. The results indicate that the catalytic activities of alkaline earth metal oxides are associated with their alkalinity. However, the use of BaO is not practical enough since it is soluble in methanol and also forms highly toxic compounds. For SrO, the oxide has a strong tendency to react with CO_2 and water present in air to form strontium hydroxide and strontium carbonate, which will make the compound lose its catalytic ability.

In a study by Yoo et al, using CaO under supercritical state (at 200°C to 220°C, 40:1 methanol/oil molar ratio and 1.0 % wt of catalyst), the achieved conversion was near 96 %. At the same conditions, ZnO was the optimum catalyst for the transesterification of rapeseed oil with more than 96 % conversion towards biodiesel [13].

Furthermore, Verziu et al. studied the catalytic activity of nanocrystalline magnesium oxide, with three different morphologies, in the transesterification of sunflower oil. The obtained yield was 90 % at 70 °C and 4:1 methanol to oil molar ratio. However, saponification resulted in the detachment of magnesium [14].

Another study carried out by Huaping et al. [15] on the transesterification of Jatropha curcas oil with methanol catalyzed using calcium oxide as the catalyst gave a yield higher than 93% under the conditions namely the catalyst amount of 1.5 wt.%; temperature of 70 °C; molar ratio of 9:1; and reaction time of 3.5 h

Metal complexes have also been used for soybean oil methanolysis under homogeneous conditions. The complexes are in the form $M(3-hydroxy-2methyl-4-pyrone)2(H_2O_2)$ where M=Sn, Zn, Pb, and Hg. The results showed the activities of Sn and Zn complexes with yields of up to 90% and 40%, respectively, in 3 hrs, using a molar ratio of 400:100:1 (methanol:oil:catalyst) and emulsion was not formed [16].

Nonionic bases have also been explored for the transesterification of vegetable oils in homogeneous media. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) was observed to produce more than 90% of methyl esters after 1 h with only 1 mol% in the reaction mixture. The catalytic activity was also compared to conventional catalysts and the yields obtained were close to that of NaOH with no soap production which is easily formed when alkaline metal hydroxides are used. Although, TBD does not require special reaction conditions, it was observed to be less active than sodium methoxide at 0.5 mol% [17].

Liquid amine based catalysts have recently been successfully used for the transesterification of both refined and used vegetable oil [18]. Four amines (diethylamine (DEA), dimethylethanol amine (DMEA), tetramethylammonium hydroxide (TMAH) and tetramethyldiaminoethane (TEMED) (as 25% in methanol)) were compared by Cercce et al [18]. The highest conversion of 98% was achieved with TMAH as a catalyst at 65 C in 90 min. It is also observed that a large amount (13%) of liquid amine catalysts is required for the transesterification. The amine also acts as a solvent for the reactants and products, helping to shift the reaction equilibrium toward the products.

Enzymatic Catalysts

Enzymes are biological catalysts which allow many chemical reactions to occur within the homeostasis constraints of a living system. Enzymes reduce energy requirements and environmental problems in the chemicals and pharmaceutical industries. The commercial development of enzyme-catalyzed transesterification processes has not been reported. However, the application of enzymes to optimize reaction conditions in biodiesel formation has been studied over the past two decades.

Candida Antarctica lipase (Novozym 435) gave promising results in catalyzing methanolysis of triglycerides. The study by Shimada et al. [19] used Novozym 435 with methanol added stepwise to avoid the deactivation of the catalyst. It was observed that after the addition of the third methanol equivalent, methyl esters conversion was almost complete. The enzyme could be reused about 50 times without the loss of activity and the occurrence of free fatty acids did not affect the enzyme catalyst.

The optimization of alkyl ester production from grease using a phyllosilicate sol-gel immobilized lipase was studied by Hsu et al. [20]. The study concluded that the immobilized lipase was active from 40 to 70 °C and ester contents of 60-97% were highest when using a ratio of reactants of 2 mmol grease to 8 mmol alcohol with biocatalyst 10% (w/w) in the presence of a molecular sieve.

In another study by Watanabe et al. [21], the enzymatic conversion of waste edible oil to biodiesel in a fixed bed bioreactor was evaluated using a three-step and one-step methanolysis of waste oil using candida Antarctica lipase. The result showed a 90% conversion from waste oil to biodiesel in both reactions.

Furthermore, Royon et al. [22] studied the methanolysis of cotton seed oil using Novozym 435 using a batch system. The reaction rate and yield of ester was increased by adding tert-butyl alcohol to the reaction medium. A yield of 97% was observed after 24h at 50°C with reaction mixture containing 32.5% tert-butyl alcohol, 13.5% methanol, 54% oil, and 0.017g enzyme per gram of oil.

In another study, Kose et al. [23] investigated the alcoholysis of refined cotton seed oil with primary and secondary alcohols in the presence of an immobilized enzyme from Candida antarctica in a solvent-free medium and the results gave a yield of methyl ester to be 72 and 94%, respectively.

Selmi and Thomas [24] also studied the ethanolysis of sunflower oil with immobilized 1,3 specific Mucor miehei lipase in a solvent-free medium with methyl ester and reported a yield of 83%.

In general enzymatic reaction selectivity is high, and enzymes can be immobilized on support materials. However, enzymes are very expensive and exhibit unstable activities with reaction rates much lower than those possible with homogeneous base catalysts. A comparison between base catalyzed and biocatalyzed transesterification is illustrated in the table below.

Table 2 Comparison of base catalyst and biocatalyst transesterification (Shah et al. [25])

Major Factors	Base catalyst transesterification	Biocatalyst transesterification
Temperature	60-80 °C	20-60 °C
Presence of FFA's in feedstock	Soap formation	Complete conversion into methyl ester
Presence of water	More soap formation as hydrolysis of oil may take place	No effect on final product
Yield of biodiesel production	High, nearly 99%	Comparatively lower than alkali catalyst, around 90%
Downstream processing	Multi-step purification of end products	None
Biodiesel production cost	Cheap, as catalysts comparatively cost less	Really expensive as biocatalysts are expensive
Commercialization	100% commercialized	Not exactly
Waste water generation	Saline and alkaline effluents need treatment before discharge	No waste water generation

Conclusion

The advantages of biodiesel which include non-toxicity and absence of sulfur and aromatics have made the application of biodiesel to grow over the past two decades. Biodiesel also contains oxygen in its structure resulting in the production of more tolerable exhaust gas emissions. The current methods of biodiesel production involve the use of vegetable oils or animal fats with primary alcohols in the presence of acidic or alkaline catalysts. Several homogeneous acid/base, heterogeneous acid/base, enzymes and other catalysts are also being studied and applied to the synthesis of biodiesel. However, homogeneous alkaline catalyzed transesterification is the predominant method used in the commercial production of biodiesel. This is because of its short reaction time and high yield for good quality oils containing low FFAs. For poor quality raw oils containing high FFAs, the method employed involves a strong sulfuric acid catalyst esterification used as a pre-treatment step followed by a base catalyzed transesterification reaction.

Further areas of studies would involve the development of catalysts from natural sources. A recent study by Wei et al. [26] have investigated the use of waste eggshell as a low-cost solid catalyst for the transesterification of soybean oil and the results showed high activity of the catalyst. The eggshell catalyst was calcined at 1000°C and the reaction conditions were 3 wt. % catalyst, 9:1 methanol to oil molar ratio at 65°C for 3h. The yield was observed to be more than 95%. Therefore, the feasibility of using natural sources as potential catalysts can be further explored in the quest to find suitable catalysts for the production of biodiesel.

The development of efficient catalysts is important; however, the efficiency of these catalysts depend of various factors which include the type of oil, alcohol to oil molar ratio, temperature, catalyst type and even the type of reactor used. The reviewed works in this paper illustrate the advantages of acidic, alkaline and enzymatic catalysts and defined reaction parameters employed to reach optimum yields of the biodiesels. The modification of some of the parameters will encourage further and deeper research in the utilization of various catalysts for the production of biodiesel.

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