Review

Catalysis in Biodiesel Production by Transesterification Processes-An Insight

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Abstract: Biodiesel is the mono-alkyl esters of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils and animal fats, for use in compression ignition (diesel) engines. The conversion of component triglycerides in oils to simple alkyl esters with short chain alcohols like methanol and ethanol amongst others is achieved mainly by transesterification. The transesterification reaction, a reversible process proceeds appreciably by the addition of catalysts, which can be acidic, basic or organic in nature, usually in molar excess of alcohol. The economy of the process depends on the type and quantity of catalyst used among other factors. The catalyst can be homogeneous or heterogeneous depending on whether it is in the same or different phase with the reactants; oils and alcohols. This paper attempts to give an insight into some of the various types of catalysts that have been used to effect the transesterification of vegetable, waste and animal oils in biodiesel production.

Keywords: Biodiesel, Transesterification, Free fatty acids, Lipase, Guanidines.

Introduction

Chemical transesterification or alcoholysis of triglycerides or the esterification of free fatty acids using short-chain alcohols in the production of alkyl esters or biodiesel was first reported¹ on August 31st 1937 in a Belgian Patent by Chavanne of the University of Brussels². In the early 1940s researches that did not actually anticipate the production of alkyl esters as fuel were patented³⁻⁸. The original objective of the work was to develop a simplified method for extracting glycerol during soap production⁹. The glycerol was needed

for wartime explosives production. The glycerol could be separated since it is insoluble in the esters and has a much higher density that makes settling or centrifugation a choice process in its removal.

Transesterification reaction of vegetable oils can be represented as in Scheme 1. The reaction does not proceed to any appreciable extent in the absence of catalysts or supercritical condition. Various homogeneous and heterogeneous catalysts, ranging from base, acid to enzyme^{10,11} as well as carbon catalysts produced from sugar starch and cellulose have been developed for use in biodiesel production.

Scheme 1. A typical transesterification reaction.

Different catalyst systems used in biodiesel production

Base-catalyzed processes

Several conventional and non-conventional base-catalyzed transesterification processes have been reported in a review by Knothe *et al*¹². Boiler ashes, potassium hydroxide (KOH) amongst other catalysts were successfully used in the ethanolysis and methanolysis of palm and coconut oils with yields as high as 90%¹³⁻¹⁷. It has also been reported that methyl and ethyl esters with 90% yield can be obtained from palm and coconut oil from the press cake and oil mill and refinery waste with the ashes of the wastes (fibers, shell, and husks) of these two oil seeds, and with lime, clay, zeolites, *etc*¹⁸⁻²¹. Methanolysis has been reported to yield 96-98% esters when palm oil is refluxed 2 h. Using coconut-shell ash and other ashes from the combustion of plant wastes such as fibers of palm tree that contain potassium and sodium carbonate²². Calcium oxide on magnesium oxide has been shown, at 60-63 °C, to be the best catalyst system amongst potassium carbonate, sodium carbonate, iron(III) oxide, sodium methoxide, sodium aluminate, zinc, copper, tin, lead and zinc oxide in the methanol transesterification of low-erucic rapeseed oil²³.

Generally, the mechanism of the base-catalysed transesterification of vegetable oils involves four steps. The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The second step is the nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generating a tetrahedral intermediate²⁴⁻²⁶. The third step involves the formation of the alkyl ester and the corresponding anion of diglyceride. The final step involves deprotonating the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. The above steps are summarized in Scheme 2.

The base-catalyzed transesterification of vegetable oils are reported to proceed faster than the acid-catalyzed reactions²⁷. Because of this and the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favour base catalysts, such as alkaline metal alkoxides²⁸ and hydroxides²⁹⁻³¹ as well as sodium or potassium

carbonates^{22,32}. Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts. They give yields greater 98% in a relatively short reaction time of 30 min. even at low molar concentrations of about 0.5 mol%, but their requirement of the absence of water makes them inappropriate for typical industrial processes in which water cannot be avoided completely³³.

R^1 = Carbon chain of fatty acid, R = Alkyl group of alcohol

Scheme 2. Mechanism for base catalysed transesterification process.

Alkaline metal hydroxides (*e.g.* KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide and the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester (Scheme 3), with consequent soap formation³³. In 2003, metal complexes of the type $\text{M}(3\text{-hydroxy-2-methyl-4-pyrone})_2(\text{H}_2\text{O}_2)$, where M = Tin(Sn), Zinc (Zn), Lead (Pb) and Mercury (Hg) were used for soybean oil methanolysis under homogeneous conditions³⁴. The Sn complex at a molar ratio of 400:100:1 methanol:oil:catalyst gave 90% conversion in 3 h. while the Zn complex gave only 40% conversion under the same conditions. This undesirable saponification reaction reduces the ester yields and considerably makes difficult the recovery of the glycerol due to the formation of emulsions, increase in viscosity and greatly increased product separation cost.

Scheme 3. Hydrolysis of esters and formation of soap by the presence of water.

Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation³⁵. This can be explained by the formation of bicarbonate instead of water (Scheme 4), which does not hydrolyze the esters. There are other heterogeneous base catalysts which have been tested with promising results^{36,37}. Also, solid bimetallic Sn-Ni³⁸, exchange resins and zeolites^{39,40}, organometallic compounds⁴¹ and mixed oxides⁴²⁻⁴⁴ have been developed and used in transesterification reactions. In addition, P(RNCH₂CH₂)₃N⁴⁵, multifunctionalized⁴⁶ as well as organosulphonic acid functionalized mesoporous silicas⁴⁷, all of which for industrial applications require high temperature and pressure are available.

Scheme 4. Equation of reaction for bicarbonate formation.

The base-catalyzed reaction is most often used because:

- ❖ It uses low temperature (60 °C) and pressure (20Psi) processing.
- ❖ It achieves high conversion (98%) with minimal side reactions and low reaction time.
- ❖ Conversion to methyl ester is direct with no intermediate steps.

Shortcomings of homogeneous alkali catalyzed processes

Reports already reviewed showed that base-catalyzed transesterification of vegetable oils results in good yields of the esters. Nevertheless, there are obvious problems encountered by their use. Some of these problems have been identified to include:

- High energy demand
- Post-reaction treatment to remove the catalyst from the product-biodiesel
- Interferences occasioned by the presence of free fatty acid and water during the reaction
- Difficulty in the recovery of glycerol after the reaction and
- Post-reaction treatment of the alkaline waste-water to obviate the environmental effects of its disposal

The development of acid and heterogeneous catalyst systems, some of which run in continuous reactors, have addressed many of these problems which ordinarily meant higher production costs and less economic viability relative to petroleum-based diesel.

Acid-catalyzed processes

The mechanism of the acid-catalyzed transesterification of vegetable oils is as shown in Scheme 5 for a monoglyceride. The protonation of the carbonyl group of the ester leads to the carbocation which after a nucleophilic attack of the alcohol produces the tetrahedral intermediate. This in turn eliminates glycerol to form the new ester, and to regenerate the catalyst. The mechanism can be extended to *di*- and triglycerides⁴⁸. Carboxylic acids can be formed by reaction of the carbocation with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids, which reduce the yield of alkyl esters.

R' = carbon chain of fatty acid, R = alkyl group of the alcohol

Scheme 5. A typical mechanism of acid catalyzed transesterification of vegetable oils.

The transesterification process in biodiesel production is catalyzed by Bronsted acids like HCl, BF₃, H₃PO₄, H₂SO₄ and sulphonic acids^{49,50}. Preferably, sulphonic and sulphuric acids are mostly used. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring typically, temperatures above 100 °C and from 3–48 h to reach complete conversion^{51–56}. Freedman et al showed that the methanolysis of soybean oil, in the presence of 1 mol% of H₂SO₄, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50h to reach complete conversion of the vegetable oil (>99%), while the butanolysis (at 117° C) and ethanolysis (at 78 °C) using the same quantities of catalyst and alcohol take 3 h and 18 h, respectively²⁷.

Peter *et al.*⁵⁷ studied the methanolysis of palm oil in a 6:1 molar ratio of methanol to oil using the following metal salts of amino acids; cadmium, cobalt, copper, iron, lanthanum, nickel and zinc. Arginate of zinc was shown to result in the highest yield and the reasonable rate of reaction estimated to be obtained at temperatures higher than 130 °C. Report also indicated that soybean oil can be transesterified in methanol using sulphated zirconia-alumina and tin oxide as well as tungstated zirconia-alumina acid catalysts, though the latter was adjudged most effective as it gave 90% conversion in 20 h at 250 °C⁵⁸. Other sulphated compounds of zirconium have also been studied with varying results^{59–60}. New solid acid/base catalysts as well as metal oxides have also been used in the transesterification process^{61–64}.

Reaction rates in acid-catalyzed processes may be increased by the use of larger amounts of catalyst. Typically, catalyst concentrations in the reaction mixture have ranged between 1 and 5 wt % in most academic studies using sulphuric acid²⁷. Canakci and Van Gerpen⁶⁵ used different amounts of sulphuric acid (1, 3 and 5 wt %) in the transesterification of grease with methanol. In these studies, a rate enhancement was observed with the increased amounts of catalyst and ester yield went from 72.7 to 95.0% as the catalyst concentration was increased from 1 to 5 wt%. The dependence of reaction rate on catalyst concentration has been further verified by the same authors and other groups^{66–67}. A further complication of working with high acid catalyst concentration becomes apparent during the catalyst neutralization process, which precedes product separation. Since CaO addition during neutralization is proportional to the concentration of acid needed in the reactor, high acid concentration leads to increased CaO cost, greater waste formation, and higher production cost.

The liquid acid-catalyzed transesterification process does not enjoy the same popularity in commercial applications as its counterpart, the base-catalyzed process. The fact that the homogeneous acid-catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction has been one of the main reasons⁶⁸. However, acid-catalyzed transesterification holds an important advantage with respect to base-catalyzed ones;

the performance of the acid catalyst is not strongly affected by the presence of free fatty acids in the feedstock. Thus, a great advantage with acid catalysts is that they can directly produce biodiesel from low-cost feedstocks, generally associated with high free fatty acid concentrations. A two step esterification process in which the free fatty acid is converted to fatty acid methyl esters in an acid-catalyzed treatment followed by base-catalyzed process has been proposed⁶⁶.

In the transesterification of triglyceride feedstock using acid catalysts, Mittelbach *et al.*⁶⁹ compared the activities of a series of layered aluminosilicates with sulphuric acid for the transesterification of rapeseed oil. These researchers used an initial molar ratio of 30:1 alcohol-to-oil and 5wt% catalysts. Among the catalysts tested, sulphuric acid showed the highest activity. The solid catalysts showed varied activities depending on reaction conditions. The most active catalysts were activated by sulphuric acid impregnation. For instance, activated montmorillonite KSF showed a 100% conversion after 4 h of reaction at 220 °C and 52 bar. However, leaching of sulphate species compromised the re-usability of this clay. Thus, to maintain clay activity at constant values, sulphuric acid re-impregnation had to be carried out after each run. It is also likely that some degree of homogeneous catalysis was taking place due to sulphuric acid leaching, they concluded.

Kaita *et al.* designed aluminum phosphate catalysts with various metal-to-phosphoric acid molar ratios and used these materials for the transesterification of kernel oil with methanol⁷⁰. According to the authors, durable and thermostable catalysts were obtained with good reactivity and selectivity to methyl esters. However, the use of these materials still needed high temperatures (200 °C) and high methanol to-oil molar ratios (60:1) in order to be effective.

In a related study, Waghoo *et al.*⁷¹ reported on the transesterification of ethyl acetate with several alcohols over hydrous tin oxide to obtain larger esters. Linear and aromatic alcohols were tested in a temperature range of 170-210 °C. All reactions were completely reflective for transesterification. In particular, this catalyst presented an appreciable activity for reactions involving *n*-butyl alcohol, *n*-octyl alcohol and benzyl alcohol.

Amberlyst-15 has also been studied for transesterification reactions. However, mild reaction conditions are necessary to avoid degradation of the catalyst. At a relatively low temperature (60 °C), the conversion of sunflower oil was reported to be only 0.7% when carrying out the reaction at atmospheric pressure and a 6:1 methanol-to-oil molar ratio⁷². Also, hydrochloric, organic, sulfonic, formic, acetic and nitric acids have been investigated by other authors^{33,73-75}.

Variables affecting the acid-catalyzed processes

The acid-catalyzed process is thought to be more suitable for the production of biodiesel from low feedstocks (used frying oil, waste animal fat), mainly because of the fact that these feedstocks contain greater amounts of free fatty acids (FFAs)⁷⁶. The base- and acid-catalyzed transesterification processes were compared with respect to the FFAs content of the feedstock. The greater tolerance of an acid catalyst to the FFA content compared to an alkaline catalyst was confirmed in a report by Canakci and Van Gerpen⁶⁵. They also showed that acid catalyzed reactions are more susceptible to water content of the feedstock than the base-catalyzed process and that the presence of more than 0.5% water in the oil will decrease the ester conversion to below 90%^{66,77-78}. The fact that the water content is more crucial in acid catalysis than in alkaline catalysis is mainly caused, according to Siakpas *et al.*⁷⁶, by the greater affinity of water by sulphuric acid, which will lead to the acid catalyst preferentially interacting with water rather than alcohol with the consequent deactivation of the catalyst. Also, there is evidence that large quantities of acid catalyst in biodiesel production may lead to ether formation by alcohol dehydration⁷⁹ and the consequent high

use of calcium oxide in the acid neutralization after production with its attendant high production cost and waste generation. It has been suggested that acid-catalyzed transesterification achieves greater and faster conversions at high alcohol concentrations⁷⁴.

Non-ionic base-catalyzed processes

Schuchardt *et al.*⁸⁰ in a comprehensive review had reported that in order to obtain milder reaction conditions and to simplify manipulations, a great number of organic bases have been developed and used as catalyst or reactant for organic synthesis. Among these bases, amines such as triethylamine; piperidines like 1,2,2,6,6,-pentamethyl piperidine; pyridines like 2,6-ditert-butylpyridine^{81,82} and 4-dimethyl-amino pyridine (DMAP)⁸³; amidines such as 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU) and 1,5diazabicyclo(4,3,0)non-5-ene (DBN)⁸¹; guanidines such as 1,5,7-triazabicyclo (4,4,0)dec-5-ene (TBD)⁸⁴, 1,1,3,3-tetramethylguanidine (TMG)⁸⁵, 1,1,2,3,3-pentabutylguanidine⁸⁶ (PBG), 1,3-diphenylguanidine⁸⁷, 1,2,3-triphenylguanidine⁸⁸ and amino- and nitroguanidines⁸⁹; triamino(imino)phosphoranes such as tert-butyl imino-2,2-diethylamino-1,3-dimethyl-perhydro-1,3,2-triazaphosphorane (BEMP)⁹⁰ and tris(dimethylamino) methyliminophosphorane (Me₇P), shown in Scheme 6 are frequently used in organic synthesis⁸⁰. The activity and efficiency of such non-ionic bases as catalysts for the transesterification of vegetable oils were studied. In a first series of studies, according to Schuchardt *et al.*⁸⁰, the catalytic activity of some guanidines was compared to that observed using other bases such as the amidines, DBU and DBN, and the triamino (imino) phosphoranes, BEMP and Me₇P. It was observed that TBD, even if applied at only 1 mol% produces more than 90% of methyl ester after 1 h. Using the other bases, under the same experimental conditions, the yields were not higher than 66%. The order of the catalytic activity is not directly related to the relative basicity of these compounds, since BEMP and Me₇P should be the more efficient catalysts, followed by TBD. However, the guanidines are more active catalysts and the activity follows their relative basicity.

Schuchardt⁸⁰ inferred that according to the observed results and to the mechanism of the base-catalyzed transesterification, it seemed that the good performance of TBD, when compared to BEMP and Me₇P, is related to its kinetic activity. The catalytic site (unshared electron pair of the SP² N) of TBD is practically unhindered allowing an easy access of the methanol for proton transfer, while the steric hindrance shown by the triamino (imino) phosphoranes is so significant that they are practically inert to alkylating agents, such as isopropyl bromide, as well as extremely resistant to react with thionyl chloride and thiophosgene⁹¹.

Scheme 6. Structures of some non-ionic bases⁸⁰.

In a second series of studies⁸⁰, the catalytic activity of TBD was compared to that observed for typical industrial catalysts (*e.g.* NaOH and K₂CO₃). The reaction yields obtained with TBD were close to those observed with NaOH and no undesirable by-products such as soaps (easily formed when alkaline metal hydroxides are used) were observed. When compared to potassium carbonate, TBD was always more active, even at low molar concentrations. Although TBD is less active than sodium methoxide (at only 0.5%, CH₃ONa produces more than 98% of methyl esters after 30 min), its use does not require any special condition. Due to the excellent performance of TBD in the transesterification of vegetable oils, the catalytic activity of other alkylguanidines was also investigated, in order to establish and understand all factors that may affect their catalytic properties.

In a third series of studies, the catalytic activity of several alkylguanidines was compared⁹². According to the authors, TBD was always the most active, however, 1, 3-dicyclohexyl -2- octylguanidine (DCOG); 1, 1, 1, 2, 3, 3- pentamethylguanidine; 7- methyl-1, 5, 7-triazabicyclo (4, 4, 0) dec-5-ene (MTBD) and 1, 2, 3- tricyclohexyl guanidine (TCG), also showed a good catalytic performance. The activity order of the catalysts TBD > TCG > DCOG > MTBD > PMG corresponds to their relative base strength, which is increased by structural factors such as number and type of subsistent (cyclic or acyclic chain). The excellent performance of DCOG and TCG is also assigned to the high symmetry of their guanidine cations, as observed earlier for the symmetric 1, 2, 3- trimethylguanidine⁹³.

Results obtained in the transesterification of soybean oil with methanol show that 1, 2, 3, 4, 5- pentacyclohexyl biguanidine (PCBG) is even more active than TCG, as an 82% yield of methyl esters is obtained with PCBG after 1 h, compared to 69% with TCG under the same conditions⁹⁴.

Lipase- catalyzed processes

Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvent⁷⁶. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools⁹⁵. Immobilized *Candida Antarctica* lipase has been used for ethyl esterification of docosahexanoic acid⁹⁵ and latter used to effect over 98.5% fatty acid methyl ester conversion^{96,97}.

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patents⁹⁸. A solution to the inhibition of enzyme activity by high concentration of methanol as well as water generated during the reaction have been proffered by many authors^{96, 99-101} to include carrying out the reaction with immobilized enzymes and the use of multiple stages. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, *etc.*) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base- catalyzed reaction systems, though Shimada and co-workers reported that the stepwise addition of methanol gave 98% conversion of oil to methyl ester with an amazing re-use of the immobilized enzyme for 50 times⁹⁸. Several reports exist on lipase catalyzed transesterification process with extracellular and intracellular lipases as catalyst in either aqueous or non-aqueous systems⁹⁹⁻¹⁰⁴. The incubation of *Candida antarctica* lipase consecutively in methyl ester (oleate) for 30 min and in soybean oil for 12 h has been reported to lead to a dramatic increase in the efficiency of the enzyme, giving almost 100% conversion¹⁰⁹. While Du *et al*¹⁰ reported lipase-catalyzed transformation of soybean oil for biodiesel

production with different acyl acceptors, others¹¹¹⁻¹¹³, reported the use of other enzymes like *Chlorella vulgaris* and *Candida cylindracea* in the conversion of other oils to biodiesel.

The variables affecting the use of enzymes like temperature, solvent, water content, immobilization or free enzyme use as well as pH and time of reaction have been studied with a view to obtaining optimum conditions for improved conversions¹¹⁴⁻¹¹⁶.

Use of organic catalyst from carbonized sugar

Japanese researchers have devised a low-cost, ecologically friendly solid catalyst for the production of biodiesel: a carbon catalyst produced from sugar, starch or cellulose¹¹⁷. The separation of the liquid catalyst from the reaction mixture is costly and wasteful. Other catalysts such as nafion or sulphonated naphthalene are either expensive or offer less or rapidly diminishing catalytic activity.

The researchers avoided all those issues by devising a mechanism to incompletely sulphonate (treat with sulphuric acid) carbonized natural organic material such as sugar, starch or cellulose to prepare a more robust solid catalyst. Incomplete carbonization of these natural products results in a rigid carbon material. The team found that sulphonation of this material generates a stable solid with a high density of active sites, enabling the inexpensive preparation of a high performance catalyst. The team found that the activity of the solid sulphonated carbon catalyst is more than half that of a liquid sulphuric catalyst¹¹⁷.

Conclusion

The industrial homogeneous catalysts will have to be substituted in the near future by heterogeneous catalysts due to environmental reasons. Good strong-base heterogeneous catalysts are still in development. One possibility would be the use of zeolites with strong basic sites. Enzymes, especially lipases, are also becoming catalysts of choice in transesterification reactions in biodiesel production despite their cost. This is because they offer some advantages as far as pretreatment of process streams are concerned. Efforts are being made by scientists to develop novel catalysts that will offer best environmental practices as well as relatively good cost.

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