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SOLID HETEROGENEOUS CATALYSTS FOR PRODUCTION OF BIODIESEL FROM TRANS-ESTERIFICATION OF TRIGLYCERIDES WITH METHANOL : A REVIEW

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ABSTRACT

Biodiesel is the main alternative to fossil diesel and it may be produced from different feed stocks such as semi refined vegetable oils, waste frying oils or animal fats. The new process technologies developed during the last years made it possible to produce biodiesel from recycled frying oils comparable in quality to that of virgin vegetable oil biodiesel with an added attractive advantage of being lower in price. Increasing number of researches focusing on the use of solid heterogeneous catalysts for the production of biodiesel provides evidence that these catalysts continue to evolve as viable alternatives. While liquid alkaline metal alkoxides remain to be appealing in the industries, it is expected that solid base catalyst will soon become more attractive due to the economics and environmental concern. Limited researches have shown that the conversion by solid base catalysts was comparable to that of the existing alkoxide system. In this review article various types of heterogeneous solid acids and bases in the production of biodiesel from trans-esterification of triglycerides and their yields and conversion from various catalytic systems are compared.

Key words: Heterogeneous catalyst, Biodiesel, Trans-esterification, Triglycerides, Methanol.

INTRODUCTION

Biodiesel is a liquid fuel similar to petroleum diesel in combustion properties, but essentially free of sulphur, making it a cleaner burning fuel than petroleum diesel. Biodiesel is derived from renewable energy sources, such as vegetable oils and animal fats. It has similar physical and chemical properties with petro-diesel fuel. However, biodiesel properties can sometimes be superior than that of petro-diesel fuel because the former has higher flash point, ultra-low sulphur concentration, better lubricating efficiency, and better cetane number[1]. The standards for biodiesel and petroleum based diesel are provided in Table 1 for the comparison.

Biodiesel is commonly produced by the trans-esterification of the vegetable oil or animal fat feedstock. There are several methods for carrying out this trans-esterification reaction including the common batch process, supercritical processes, ultrasonic methods, and even microwave methods. Chemically, trans-esterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. The most common form uses methanol (converted to sodium methoxide) to produce methyl esters (commonly referred to as Fatty Acid Methyl Ester-FAME) as it is the cheapest alcohol available, though ethanol can be used to produce an

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ethyl ester (commonly referred to as Fatty Acid Ethyl Ester-FAEE) biodiesel and higher alcohols such as isopropanol and butanol. Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester at the cost of a less efficient trans-esterification reaction. A lipid trans-esterification production process is used to convert the base oil to the desired esters. Any free fatty acids (FFAs) in the base oil are either converted to soap and removed from the process, or they are esterified (yielding more biodiesel) using an acidic catalyst. After this processing, unlike straight vegetable oil, biodiesel has combustion properties very similar to those of petroleum diesel and can replace it in most current uses[1,2].

Table 1: Comparison of the standards for Diesel and Biodiesel based on American Society for Testing and Materials (ASTM)

Property	Diesel	Biodiesel
Standard number	ASTM D975	ASTM D6751
Composition	Hydrocarbon (C_{10}–C_{21})	Fatty acid methyl ester (C_{12}-C_{22})
Specific gravity (g/mL)	0.85	0.88
Flash point (K)	333–353	373–443
Cloud point (K)	258–278	270–285
Pour point (K)	243–258	258–289
Carbon (wt. %)	87	77
Water (Vol. %)	0.05	0.05
Cetane number	40–55	48–60
Sulphur (wt. %)	0.05	0.05
Hydrogen (wt. %)	13	12
Oxygen (wt. %)	0	11

Trans-esterification reaction

Nowadays, there are four known methods to reduce the high viscosity of vegetable oils to enable their use in conventional compression ignitions engines: blending with diesel, pyrolysis, emulsification and trans-esterification. The pyrolysis and the emulsification, however, produce heavy carbon deposits, incomplete combustion, an increase of lubricating oil viscosity and undesirable side products such as alkanes, alkenes, alkadienes, aromatic compounds and carboxylic acids[1]. Regarding the direct use of vegetables oils as fuel for combustion engines, this requires the engines to be modified. Also, the direct use of vegetables oils is not feasible due to their high viscosity and low volatility which affect the atomization and spray pattern of fuel, leading to incomplete combustion, severe carbon deposits, injector choking and piston ring sticking. Thus, the most common way to produce biodiesel is by trans-esterification of triglycerides of refined/edible types of oils using alcohol, in presence of an acid or a basic catalyst. The alcohol used for trans-esterification is usually methanol. Producing biodiesel is a bulk process; the general scheme of the trans-esterification reaction is presented in Fig. 1, where R is a mixture of various fatty acid chains[3].

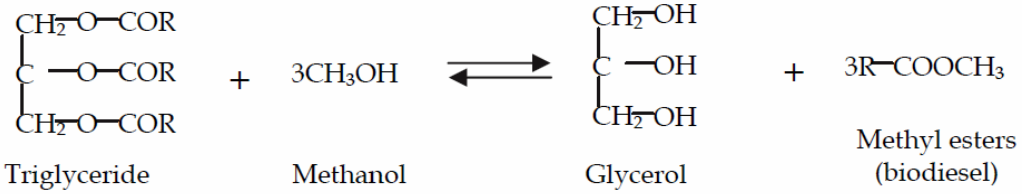

Fig. 1: Reaction for oil trans-esterification

Biodiesel production from vegetable oils

Biodiesel in another definition is a non-petroleum based fuel consisting of alkyl esters derived from trans-esterification of triglycerides (TG) or by the esterification of free fatty acids (FFA) with low molecular weight alcohols. The fuel properties of the esters produced from the trans-esterification can vary depending on the types of vegetable oils used. Table 2 enlists fuel properties of methyl esters derived from different vegetable oils[4].

Table 2: Fuel properties of methyl esters of different vegetable oils

Methyl ester of vegetables oil	Cloud point (^{o}C)	Pour point (^{o}C)	Flash point (^{o}C)	Density (kg/L)	Iodine value	Cetane number
Cotton seed	-	-4	110	-	-	51
Soybean	1	-7	178	0.885	117-143	45
Ground nut	5	-	176	0.883	80-106	54
Palm	13	-	164	0.880	35-61	62
Sunflower	1	-	183	0.860	110-145	49
Diesel	-	-16	76	0.885	-	50

Biodiesel production has become an area in which many researchers have increasing interest. This is due to its potential as an alternative fuel that offers a complementary strategy for sustainability. The most common approach of biodiesel production is by trans-esterification of vegetable oils and animal fats. This is a well established process introduced since 1853. Varieties of vegetable oils have been exploited in the past and present for biodiesel production with varying but promising results. The oils used include cotton seed, soybean, waste cooking, rapeseed, sunflower seed, winter rape, and frying, jojoba and jatropha curcas. The choices of alcohols used are mainly methanol, ethanol and butanol. The catalysts used in the trans-esterification include sodium hydroxide, potassium hydroxide, sulphuric acid supercritical fluids or enzymes such as lipases[1,3,4].

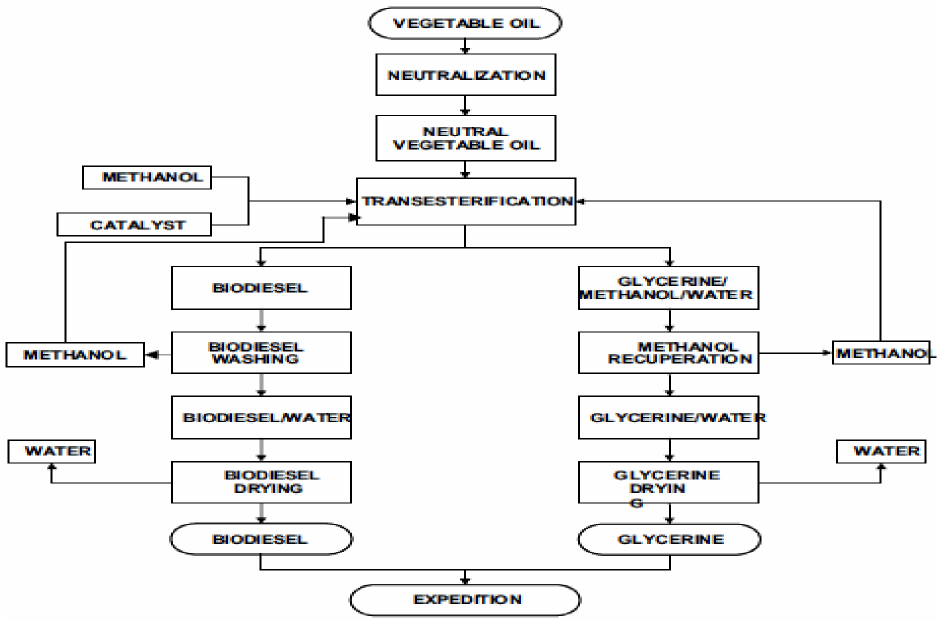

Fig. 2: Block diagram of Biodiesel production process

Heterogeneous catalysts

It is appropriate to begin the discussion on heterogeneously catalyzed trans-esterification with a comparison of factors in relation to the corresponding homogeneously catalyzed reaction[1]. Such a comparison is summarized in Table 3. In heterogeneous catalysis, a number of operating parameters such as temperature, extent of catalyst loading, mode of mixing, alcohol/oil molar ratio, presence/absence of impurities in the feed stock and the time of reaction are important. In a similar manner, trans-esterification reaction can also be carried out under supercritical conditions and this method may also evolve as a viable alternative to catalytic routes[5].

Table 3: Comparison of homogeneous and heterogeneously catalyzed trans-esterification

Sr. No.	Factors	Heterogeneously catalysis	Homogeneously catalysis
1.	Reaction rate	Moderate conversion	Fast and high conversion
2.	Processing methodology	Continuous fix bed operation possible	Limited used of continuous methodology
3.	Presence of water/ free fatty acids	Sensitive	Not sensitive
4.	Catalyst reuse	Possible	Not possible
5.	Cost	Potentially cheaper	Comparatively costly

Solid acid catalysts

Solid acid catalysts have the potential to replace strong liquid acids to eliminate the corrosion problems and consequent environmental hazards posed by the liquid acids. However, the efforts at exploiting solid acid catalysts for trans-esterification are limited due to the pessimistic expectations on the possibility of low reaction rates and adverse side reaction. As a result, the factors governing the reactivity of solid catalysts have not been fully understood. For example, simple correlations between acid strength and activity of the catalyst have not been clearly formulated. Second, due to diffusion restrictions the catalyst must have a porous system with interconnecting pores, so that the entire surface of the solid is available for promoting the trans-esterification reaction. Even though, it is possible to generate these features in the solids, it is not yet routinely possible to obtain uniform pore architecture with absolute control over the size or radius or geometry of the pores as well as the stability of the solid in the system. Zeolites, due to their uniform pore structure, appear to have definite advantages for this application. In order to be favorable, the surface should be made hydrophobic in order to promote preferential adsorption of oily hydrophobic species on the catalyst surface and to avoid deactivation of catalytic sites by strong adsorption of polar by products like glycerol or water. It is essential that a reliable quantitative measure of the hydrophobicity of solids is evolved so that one can appropriately correlate this function with the observed activity[1,5,6].

Zeolites

Zeolites can be synthesized with extensive variation of acidic and textural properties. They can be synthesized to overcome the diffusional limitations so that optimum biodiesel production can be achieved[1]. Zeolites can also be modulated to exhibit hydrophobic characteristic without compromising its functionalized acidic sites. This can be done by incorporating certain organic species like heteropoly acids into their pore structures. In spite of this, the predictive capability for the zeolites and the necessary functionalization to alter their hydrophobicity is still in the stage of trial and error. Once an estimated hydrophobicity scale is established, it is possible that some predictive capacity of heteropoly acids for the adsorption of benzene/water will emerge[2].

Other solid acid catalysts

The other types of solid acid catalysts that were exploited for use in esterification and trans-esterification reaction studies in the past include tungsten oxides, sulphonated zirconia (SZ), sulphonated saccharides, Nafion1 resins, and organosulphonic functionalized mesoporous silicas. Even though solid acid catalysts have been applied effectively in the esterification of carboxylic acids, the use of these catalysts to obtain high conversion of triglycerides to biodiesel necessitates much higher reaction temperatures than base catalysts because of their lower activity for transesterification. Some resins, may be considered an exception as these catalysts catalyze appreciably both esterification and trans-esterification reactions under mild reaction conditions due to their high concentrations of acid sites. However, thermal stability becomes an issue when resin-type catalysts are used at higher temperatures in order to achieve higher reaction rates in an application such as reactive distillation. The other issue is associated with catalyst regeneration[1,2,7].

Solid base catalysts

Basic zeolites

The base strength of the alkali ion exchanged zeolite increases with increasing electropositive nature of the exchanged cation. The occlusion of alkali metal oxide clusters in zeolite cages through the decomposition of impregnated alkali metal salts results in an increase in the basicity of these materials. These exchanges can affect the water tolerant behavior of the basic zeolite system[2]. A micro-porous inorganic lithium containing zeolite has been shown to be a new generation solid base catalyst for trans-esterification. Most of these catalysts contain the basic sites (cation) generated by thermal decomposition of the supported salt. It has been shown that the conversion to methyl ester over NaX faujasite zeolite that was ion exchanged with more electropositive cations was higher than that of the parent zeolite[5]. Fig. 3 illustrates the point where the intermediate electro negativity of the solid is correlated with the yield of the methyl ester. This type of correlation has become one of the preferred methods for catalyst selection. Although some guidelines on these aspects are available, a general concept has yet to be developed to facilitate the catalyst selection for trans-esterification[7].

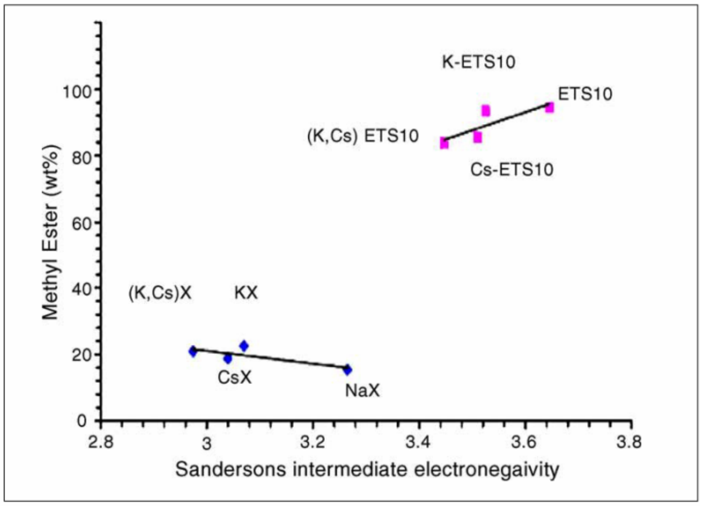

Fig. 3: Methyl ester (wt %) at 393 K as a function of intermediate electro-negativity calculated from Sanderson intermediate rule

Alkaline metal salt on porous support

Table 4 summarizes different types of heterogeneous catalysts supported on porous substrates and their conversion rate at different operating parameters reported previously. The non-loaded alumina support did not yield methyl oleate or glycerol within 1 h, and yielded only 7% methyl oleate over 12 h at 423 K. Alumina loaded with K_2CO_3, KF, $LiNO_3$ and NaOH, on the other hand, produced glycerol and higher yield of methyl oleate over 1 h at 333K. This provides evidence that porous supports can be functionalized effectively by loading alkaline metal salts, with the exception of KOH/Al_2O_3 that reportedly exhibited low catalytic activity[8].

Table 4: Different heterogeneous catalysts used for transesterification of vegetable oils[1,4]

Vegetable oil	Catalysts	Ratio MeOH/Oil	Reaction time (h)	Temperature (^oC)	Conversion, (%)
Blended vegetable oil	Mesoporous silica loaded with MgO	8	5	220	96
Palm oil	$Mg–Al–CO_3$ (Hydrotalcite)	30	6	100	86.6
Soybean oil	La/Zeolite beta	14.4	4	160	48.9
Sunflower oil	CaO/SBA-14	12	5	160	95
Jatropha curcas oil	CaO	9	2.5	70	93
Cotton seed oil	$Mg–Al–CO_3$ HT	6	12	190	87

CONCLUSION

The development of efficient heterogeneous catalysts is important since it opens up the possibility of another pathway for biodiesel production. The efficiency of the heterogeneous process depends, however, on several variables such as type of oil, molar ratio alcohol to oil, temperature and catalyst type. This review suggests that the interest in heterogeneous catalysis for biodiesel production has been growing. From the commercial point of view, solid base catalysts are seen more effective than acid catalysts and enzymes. However, more researches on solid base catalysis are needed to substantiate this because the favorable results from previously reported works were at the expense of high temperatures and high pressures.

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