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Review Article

Evaluating the role of the appropriate catalysts on the efficacy of biodiesel production from waste cooking oil

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Abstract: Concerns over the rapidly depleting sources of energy have led to the need of acquiring alternative sources that are renewable and sustainable. Biodiesel has come under the spotlight as an alternative energy source that is non-toxic, can reduce the emission level of pollutants, and most importantly be produced from cheap sources. Waste cooking oil has proven to be a promising cheap and available source for biodiesel production. However, the choice of the proper catalyst for efficient production of biodiesel from cooking oil remain the key challenge. In this review, we discuss the transesterification of waste cooking oil to biodiesel using different catalysts. Mainly, focusing on homogeneous catalysts and heterogeneous catalysts for this process.
Keywords: biodiesel, cooking

INTRODUCTION

With a rapid increase in the magnitude of combustion of fossil fuel constituents, there has been an increasing concern and demand for an alternative source of energy over the last few decades. Most of the energy being used worldwide comes from fossil sources such as petroleum, coal and natural gas. However, these sources are limited, and are bound to run out eventually leading to the need to acquire fuel alternatives that are renewable and sustainable. A report available on the United States Energy Information Administration (EIA) website showed that the world total energy consumption was 406 quadrillion British thermal units (BTU) in 2000 and is expected to increase to 769.8 BTU by 2035 [1]. On the other hand, the European Commission has set the objective of 20% substitution of conventional fuels by alternative fuels in the road transport sector by the year 2020 and that energy efficiency must increase by 20% while greenhouse gases must decrease by 20% [2, 3]. Alternative and renewable fuels have the ability to solve many problems such as air pollution and global warming as well as improve environmental and sustainability issues.

Biofuels as an alternative source of energy have attracted worldwide attention due to their advantages over fossil fuels. A sustainable development of biofuel must give response to the current trilemma of energy, environment and economy. The trilemma of energy as referred to by the World Energy Council (WEC) is the triple challenge of finding solutions that simultaneously support the three aspects of energy security, energy equity and environmental sustainability [4]. From being environmentally friendly, emitting greenhouse gases in significantly lesser amounts those fossil fuels, to being renewable and increasing employment opportunities, biofuel as an alternative source of energy is sought after globally.A Global Renewable Fuel Alliance (GFRA) report on the Contribution of Biofuels to the Global Economy done with the global economic research company, Cardno Entrix, established that the global biofuels industry contributed $277.3 billion and supported nearly 1.4 million jobs in all sectors of the global economy in 2010. As the biofuels industry expands, the employment impact is projected to grow to more than 2.2 million jobs by 2020 [5]. Biofuels can be liquid, solid or gaseous hydrocarbon fuels derived from organic matter such as animal waste, wood and wood wastes, plants, fibers and many other waste materials that are available and renewable.

An example of biofuel is biodiesel. Biodiesel refers to any clean-burning alternative fuel produced from domestic, renewable resources. It is an alternative fuel defined as a mixture of monoalkyl esters of long chain fatty acids thatcan be produced from any material that contains fatty acids linked to other molecules or present as free fatty acids. Therefore, various vegetable fats and oils, animal fats, waste oils, and edible oil processing wastes can be used as feedstock for biodiesel production. As an energy source it is biodegradable, non-toxic, and as biodiesel can reduce the emission level of the pollutants. It can also be added conventional petroleum based fuels to create an efficient and safer blend.

Waste cooking is a promising source for biodiesel production. The quantity of waste cooking oil made every year by any country is immense and its disposal is a serious problem primarily in polluting the environment and water. Such negative effects of waste cooking oil can be permanently resolved by processing it into biodiesel.

Accordingly and consequently, two major problems that can be overcome by using biodiesel: waste vegetable oil disposal safely and production of environmentally friendly fuel.

Transesterification of waste cooking oil for biodiesel production

Transesterification of natural glycerides with methanol to methylesters is an important reaction that has been utilized in the soap and detergent manufacturing industry. In the production of biodiesel, a similar process is used. The transesterification process is the reaction of a triglyceride (fat/oil) with an alcohol to give esters and glycerol. A triglyceride has one glycerin molecule as its base with three long chain fatty acids attached to it. Upon reaction of the triglyceride with the alcohol in the presence of a catalyst, it results in formation of the mono-alkyl ester or biodiesel and crude glycerol.

This reaction between the fat or oil and the alcohol is a reversible reaction, so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

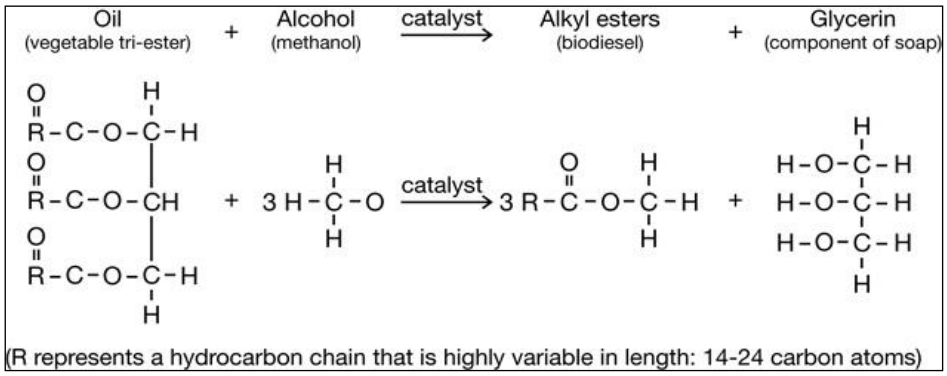

Fig 1: Chemical reaction to produce biodiesel from vegetable oil and methanol [18].

A successful transesterification reaction is signified by the separation of the methyl ester (biodiesel) and glycerol layers after the reaction time. The much heavier co-product, glycerol, settles out and can be sold as it is or purified to be used in other industries, e.g., cosmetics, detergents and pharmaceuticals.

Factors affecting the transesterification process are the concentration of catalyst, type of catalyst, temperature and the content of water. In the present review we will focus on the type of catalyst and how it affects the transesterification of waste cooking oil to produce biodiesel more efficiently.

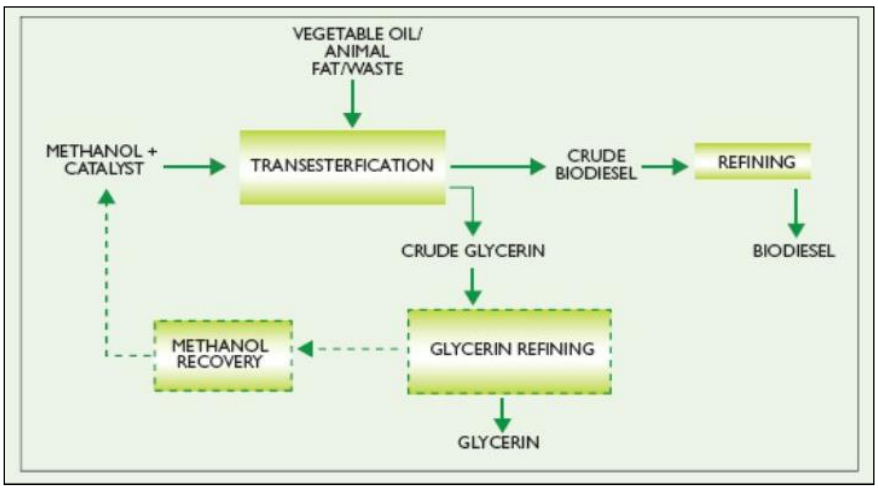

Fig 2: The basic biodiesel production process [19]

Catalysts

Two types of catalysts are generally used in the transesterification process: Homogenous catalysts and Heterogeneous catalysts. These catalysts are further divided into homogenous base and acid catalyst, and heterogeneous solid acid and solid base catalyst.

Homogeneous Base-Catalyst

Base catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) are favored over acid catalysts due to their fast reaction rate, their requirement for low reaction temperature, lower corrosive properties and higher conversion efficiency compared to acid catalysts. Even though the rate of the transesterification reaction is a thousand times faster when a base catalyst is used instead of an acid catalyst, they are not efficient when the feedstock contains water or very high acid value. The presence of water in the feedstock promotes hydrolysis of the alkyl esters to FFAs resulting in soap formation and since base catalysts are sensitive to free fatty acids content of the oil, they will react with the free fatty acids (FFA) forming unwanted soap as a by-product. The excessive amount of soap formed significantly interferes with the washing process by forming emulsions, therefore leading to substantial yield losses. Moreover, these catalysts cannot be recovered and reused.

Homogeneous Acid-Catalyst

Homogenous acid catalysts such as sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) have the advantage of being insensitive to FFA content in the oil, therefore eliminating the side reactions such as saponification. This makes them suitable for use in producing biodiesel from low-cost feedstocks that generally have high free fatty acid concentrations .Apart from this advantage, acidic catalysts can also carry out esterification and transesterification simultaneously. Esterification is the most common way to reduce the content of FFA. However these catalysts exhibit some drawbacks such as corrosion to the reactor wall, valves and pipelines due to the strong acidic properties as well as the need for high alcohol to oil molar ratio to drive the transesterification and longer reaction time.

Heterogeneous Solid Acid Catalyst

Similar to homogenous acid catalysts, heterogeneous solid acid catalysts such as Zirconium oxide (ZrO_2) and tungsten trioxide (WO_3) are insensitive to FFA content in cheap feedstocks without the need to pretreat them and have the ability to carry out esterification and transesterification simultaneously. They eliminate the washing step as well as minimize product contamination due to ease of separation from the reaction mixture. Moreover, the problems with corrosion areminimized when using these catalysts. Another advantage is that the catalysts can be regenerated and reused. However, the employment of solid acid catalysts for trans-esterification is limited due to the negative expectations on the likelihood of low reaction rates and adverse side reaction.

Heterogeneous Solid -Base catalysts

Heterogeneous base catalysts are solids with bronzed basic and lewis basic activity centers. These supply electrons (or accept protons) for (or from) reactants.Similar to their homogeneous equivalents, solid basic catalysts are more active compared to solid acid catalysts. These catalysts include alkali, alkaline oxides, large-surface-area material supported alkaline oxides, basic zeolites, hydrotalcites and organic base catalysts. Despite the promising activities that heterogeneous base catalysts have displayed, they have not substituted the homogeneous catalyst in commercial biodiesel production till now.

The Alkaline earth metal oxides are considered among the heterogeneous catalysts. The catalytic activity among alkaline earth metal oxide catalyst in transesterification is according to the following order: Barium oxide> Strontium oxide > Calcium oxide >Magnesium oxide. This order also represents the order of the number of basic sites.Even though BaO and SrO have the highest number of basic sites and catalytic activity, it was found that both BaO and SrO are soluble in methanol. Therefore they are considered to be more homogenouscatalysts insteadof heterogeneous catalysts. However, they are not utilized in homogenous system because NaOH and KOH are much inexpensive and are more effective [6]. Therefore, among the heterogeneous base catalysts, only CaO had been widely used in transesterification of various vegetable oils.

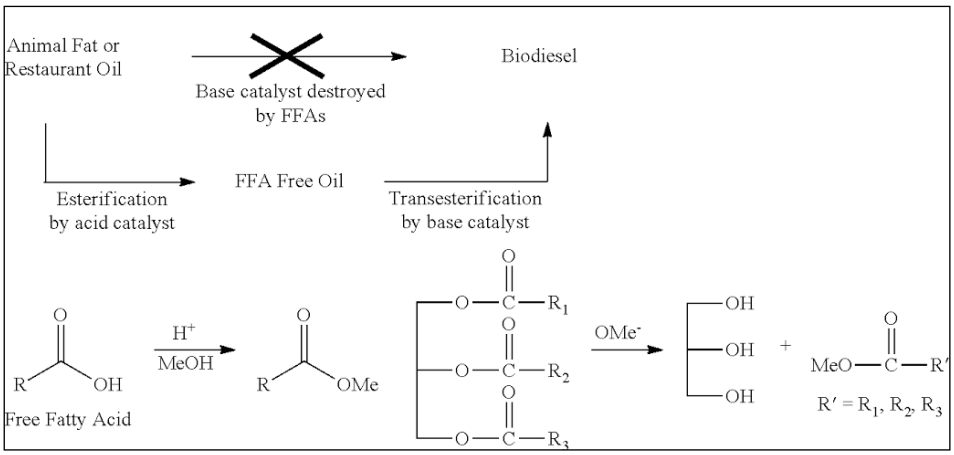

Fig 3: The schematic production of biodiesel [20].

Calcium Oxide as a promising catalyst for biodiesel production.

Calcium oxide, a heterogeneous catalyst has attracted attention as a promising catalyst for biodiesel production. It is one of the favorable catalysts because it can be prepared from cheap resources such as limestone and calcium hydroxide. It also retains qualities such as having relatively high basic sites, nontoxicity and low solubility in methanol. One remarkable feature of CaO catalyst is how the reaction system is affected by water. According to a study [7] it was reported that a small amountof water could improve the CaO catalyst activity and FAME yield. They achieved a 95% biodiesel yield by adding 2.03wt% water atoptimum condition of 8wt% catalyst amount, 12:1 molar ratio of alcoholtooil, and3hrreactiontime. More importantly, the catalyst was stable even after 20 cycles. While the presence of water in most catalyst systems has an adverse effect on the yield of FAME, CaO performance is improved in the presence of small amount of water. In the presence of a little water in methanol, it reacts to generate methoxide ion, which is highly active and is the real catalyst[8].

Another major determinant of the catalytic activity of CaO lies in its basic properties. It possesses strong basic sites due to the existence of oxygen anion generated on its surface. The function of these sites is to abstract proton from organic matter, which induces the base catalyzed reaction.

A study [9] investigated the transesterification of soybean oil and ethanol catalyzed by calcium oxides prepared from calcinations of CaO, Ca $(OH)_2$, limestone, and Ca $(OH)_2$/CaO as solid base catalysts. It was found that the catalytic activities significantly depended upon their base site strengths and their structures. The increase in CaO catalytic performance was achieved by loading Ca $(OH)_2$ on CaO.

The catalytic activity of CaO can be accelerated by an initial pretreatment with methanol at room temperature, an activation at high temperature and surface modification to the catalyst support with potassium halides in order to generate strong active basic sites.

In a study [10] aimed at studying the acceleration of the catalytic activity of CaO, an activation mechanism of pretreating CaO with methanol was proposed. Some of the CaO will convert intoCa $(OCH_3)_2$. This acts as an initiating reagent for the transesterification reaction and produces glycerin as a by-product;then, the CaO-glycerin complex, which is formed from the generated glycerin and CaO, functions as the main catalyst and accelerates the transesterification reaction.

Another method to improve the activity of CaO by modifying it with trimethylchlorosilane (TMCS) was investigated [11]. They investigated the performance of commercial CaO modified (TMCS) for transesterification of rapeseed oil and methanol to biodiesel production and concluded that the fatty acid methyl esters yield of modified CaO greatly enhanced from 85.4% to 94.6%. The reason lies in promoting the absorption of grease to CaO surface. Repeating the experiment showed that the modified catalyst had the capacity of water resistance and could be used several times without significant deactivation.

Alkaline earth metal oxides can be incorporated into metal oxides to form composite oxides [12] these are also suitable as solid base catalysts for biodiesel production. The activity of such composites is just like that of the parent alkaline earth (typically CaO). However they show greater stability and are less susceptible to dissolution, making them easier to separate from the reaction media**.**

In a study by Kawashima et al. [13] the catalytic activity of calcium based metal oxides such as $CaTiO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$ and CaO-CeO_2 in the methanolysis of rapeseed oil was looked at. As well as that, the authors also studied the change of activity on replacement of Ca with barium, magnesium, or lanthanum. The reaction was carried out in a batch reactor at 60 °C with 6:1 molar ratio of methanol to oil for 10 hours, in which the methyl esters yield reached 79-92%. It was found that $CaZrO_3$ and CaO-CeO_2 show high durability, ester yields greater than 80% and has the potential to be used in biodiesel production processes as heterogeneous base catalysts. $CaTiO_3$ had a base strength in the range of 6.8-7.2. $CaMnO_3$, $Ca_2Fe_2O_5$, $CaZrO_3$, and $CaCeO_3$ had the highest base strengths, in the range from 7.2 to 9.3. However, the Ba, Mg, and La series catalysts displayed the weakest base strengths, which were less than 6.8. These results suggest that the Ca series catalysts have high catalytic activity for the transesterification reaction, but the other catalysts have low activity.

Alkaline –earth metal alkoxides have also been found to be efficient active catalysts for the transesterification In a study conducted by Liu et al.[14],calcium methoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with methanol, the experimental results showed calcium methoxide has excellent catalytic activity and stability in the transesterification of soybean oil to biodiesel with methanol. The optimal conditions were: 1:1 volume ratio of methanol to oil, addition of 2 wt. %Ca $(OCH_3)_2$ catalysts, 65°C and about 2 hours of reaction time and yield of biodiesel obtained was 98%. The recycling experiment results showed that the catalyst had a long lifetime and could maintain activity even after being reused for 20 cycles.

The same author, in another study [15] done on calcium ethoxide as a solid base catalyst for the transesterification of soybean oil to biodiesel with

methanol and ethanol found that 95% biodiesel yield was obtained within 1.5 hours when the optimum conditions were 12:1 molar ratio of methanol to oil, addition of 3% Ca $(OCH_2CH_3)_2$ catalyst, and a 65°C reaction temperature. It also indicated that the catalytic activity of calcium ethoxide is better than that of CaO. A 91.8% biodiesel yield was obtained when it catalyzed soybean oil to biodiesel with ethanol at 75°Cin 3 hours. This catalyst has a moderate surface area, a relatively broaderparticle size distribution, and a better low solubility in methanol and ethanol.

Calcium oxide treated with ammonium carbonate solution and calcined gives super base catalyst. Some believe that treatment with ammonium carbonate results in calcium carbonate layering at the surface. CaO forms Ca $(OH)_2$ with the humidity of the air and reacts as base with ammonium salt with formation of NH_3 and $CaCO_3$. The ammonia evolution might cause the calcium carbonate layer to be porous and calcination helps the CaO in maintaining this porous structure with high surface area, high reactivity and high activity.

Huaping, et al [16] used CaO as heterogeneous catalyst for biodiesel synthesis from non-edible oil from Jatropha curcas as the feedstock. Calcium oxide was treated with ammonium carbonate solution and calcined to increase the base strength to 26.5. Calcination at 900 °C resulted in decomposition of calcium carbonate producing defects in its crystal structure. This defect favored the formation of calcium methyl oxide, which is a surface intermediate in the transesterification reaction. Under optimized conditions (70 °C temperature, 2.5 h reaction time, 1.5% catalyst amount, and 9:1 methanol to oil molar ratio) 93% conversion of jatropha oil was obtained. A study by [17] suggest that calcium oxide being treated with ammonium carbonate solution and calcinated at high temperature becomes a solid super base, which shows high catalytic activity in transesterification.

DISCUSSION & CONCLUSION

The importance of biodiesel as an alternative fuel is growing day by day. The catalysts used in the production of biodiesel are homogenous acid and base catalysts, and heterogeneous solid acid and solid base catalysts.In this review, we focused on the importance of heterogeneous solid base catalysts, mainly CaO for biodiesel production. .From the results of various experiments , it can be seen that Calcium oxide has excellent catalytic abilities as a solid base catalyst for the transesterification as well as various advantages over the other catalysts. For instance it can be prepared from cost effective resources and has relatively high basic sites that abstracts proton from organic matter and induces the base catalyzed reaction. Also, it is non toxic and has low solubility in methanol. In addition, a small amount of water can improve the CaO catalyst activity by reacting to generate methoxide ion that is highly active, that is the real catalyst.

Likewise, Ca series catalysts have signified to have a higher catalytic activity among which calcium methoxide has excellent catalytic activity that has a long lifetime that can maintain its activity even after being reused over. Another studyindicates that the catalytic activity of calcium ethoxide is better than that of CaO.

Various methods of improving this catalyst have been tried, that includes pre-treating it with methanol or modifying the surface of catalyst support with potassium halide. Furthermore, the catalyst could be modified with TMCS, making it water resistant that can be reused many times and enhances the yield of fatty acid methyl esters. Moreover, alkaline earth metals oxides can be incorporated into metal oxides to form composite oxides, making it less prone to dissolution, thus making it easier to separate from the reaction media.

The results thereby concluded that the use of CaO as a catalyst for the transesterification of waste cooking oil to biodiesel will remarkably increase its production to a significant level.

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