



Comparison of Performance of Various Homogeneous Alkali Catalysts in Transesterification of Waste Cooking Oil

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Biodiesel is an excellent substitute for fossil diesel, which received a significant attention in recent decades. Catalyst methods are frequently used to produce biodiesel at low temperatures and pressures. The present work investigates the methanolysis of waste cooking oil with the acid value of 1.86 mg KOH/g employing a variety of homogeneous base catalysts, including KOH, NaOH, CH₃OK and CH₃ONa. Among the studied catalysts, CH₃OK produced the highest biodiesel yield at 99.0%, followed by CH₃ONa, KOH and NaOH under the identical reaction conditions. The reaction was carried out for 30 min at 600 °C and a speed of 600 rpm with a molar ratio of 6:1 for methanol-to-waste cooking oil (WCO) and a 1 wt.% catalyst. However, the viscosity, flash point, density and acid value of the biodiesel all met ASTM criteria, indicating that biodiesel made from KOH, NaOH, CH₃OK and CH₃ONa is of high quality.

Keywords: Biodiesel, Catalyst, Homogenous catalyst, Transesterification, Waste cooking oil.

INTRODUCTION

Fossil fuels are the world's principal source of energy. Thus, worldwide demand for fossil fuels increases daily as the world's population grows. Fossil fuel demand for 2030 is estimated to be 116 million barrels per day [1]. As a result, the search for alternative renewable energy sources has become critical in the sphere of energy production. Additionally, pursuing ecologically friendly and renewable energy sources is one strategy for mitigating and reversing the effects of global warming and climate change [2]. Thus, in light of the numerous hurdles associated with renewable energy sources, biodiesel is one of the most viable substitutes for petroleum based diesel fuel [3].

Biodiesel is a non-hazardous alternative fuel that has a high flashpoint, a high cetane number, a high lubricity, low volatility or flammability, superior transport and storage qualities and produces less carbon monoxide [4]. Transesterification is the primary chemical reaction that occurs between triglycerides and alcohol in the presence of a catalyst to produce monoesters in the standard method of biodiesel manufacturing. The triglyceride molecules are converted to monoesters and glycerol during this reaction. As a result, the transesterification reaction

is composed of three reversible reactions. Thus, transesterification changes triglycerides to diglycerides, diglycerides to monoglycerides and glycerides to glycerol, each stage yielding a single ester molecule [5]. Transesterification is a chemical reaction (Fig. 1), also known as alcoholics, transforming feedstock into fatty acid alkyl esters (FAAE). Additionally, when methanol is utilized in the transesterification procedure, the resulting fatty acid methyl esters (FAME) are produced [6].

Transesterification of a triglyceride with primary alcohol in the presence of a catalyst can be used to obtain biodiesel. However, transesterification reactions can be catalytic or non-catalytic. The non-catalytic transesterification reaction occurs at supercritical temperatures. High temperatures and pressures are required for the supercritical approach, which increases the parasitic energy required for the operation. As a result, catalyst methods are the most frequently utilized for low temperature and low-pressure biodiesel production [7]. The catalyst increases the solubility of the reactant and accelerates the reaction [8,9].

The type of catalyst used in the transesterification reaction is mainly determined by the amount of free fatty acid (FFA) and raw materials used in the feedstock. When oils include a significant proportion of free fatty acids and water, the acid

required to promote good conversion (6:1 is frequently cited as the optimal methanol-to-oil molar ratio); and mixing rate should be as high as possible to promote reactant mixing, which is especially critical given the system's two-phase behaviour (oil and alcohol with dissolved catalyst); the most frequently used catalysts are KOH, NaOH, CH₃ONa and CH₃OK (metal alkoxides generally perform better than hydroxides); (the amount of catalyst used varies between 0.2 and 2 wt.%, with a typical value of 1 wt.% [20]. From an economic stand-point, alkaline metals are less expensive than alkaline metal alkoxides, which is a benefit. However, their activity is greater than that of KOH and NaOH, since the former produces a higher yield in a shorter reaction time than the latter [11].

According to literature [21-24], the cost of producing biodiesel is mainly determined by raw material prices other than the catalyst, remarkably the price of the oil source. The cost of raw materials can be decreased by producing biodiesel from waste cooking oil (WCO), as WCO has little commercial value and inappropriate disposal results in a multitude of problems, including water and soil pollution, human health concerns and disruptions to the aquatic ecology. Producing biodiesel from waste vegetable oils reduces the cost of the product and assures a steady supply of raw materials [22]. Therefore, WCO may be used in place of virgin vegetable oil as a raw material for biodiesel synthesis. The WCO's biodiesel production aids the environment by reusing while delivering affordable, clean and renewable energy.

Therefore, the yield of biodiesel produced with various homogeneous catalysts must be distinguished as a result. Therefore, the transesterification of WCO is investigated in this work using a range of homogeneous base catalysts, including KOH, NaOH, CH₃OK and CH₃ONa.

EXPERIMENTAL

Pre-treatment: A sample of waste cooking oil (WCO) was collected from a local market in Colombo, Sri Lanka. Filtration and preheating at 110 °C were employed to remove suspended matter and moisture content from WCO.

Determination of acid value: According to ASTM D664-0, the acid value of pretreated WCO was determined. Pretreated WCO (1 g) was added to a titration flask containing 125 mL isopropyl alcohol and 5-6 drops of phenolphthalein as an indicator. Titration with 0.1 M KOH was performed and the volume required for a colourless solution to turn pale pink was determined. A similar procedure was used for the blank sample devoid of oil and then the KOH consumption was recorded. The entire procedure was repeated three times for each sample. The acid value and FFA content of each corresponding sample were then determined using the eqns. 1 and 2:

$$\text{Acid value} = \frac{56.1 \times 0.1 \times (V_1 - V_2)}{W} \quad (1)$$

$$\text{FFA (\%)} = \frac{\text{Acid value}}{2} \quad (2)$$

where V_1 is the 0.1 M KOH volume required for the sample, V_2 is the 0.1 M KOH volume required for the blank sample, W is the weight of WCO.

Transesterification: Transesterification was carried out in the manner as described by Miyuranga *et al.* [25]. The transesterification was performed in a closed container, since the acid value was less than 2 mg KOH/g. Methanol (6:1 molar ratio by molar of oil) was mixed with a catalyst such as KOH, NaOH, CH₃OK and CH₃ONa (1 wt.% by oil weight). The transesterification reaction was initiated when the methanol-catalyst solution was added to WCO. The reaction was carried out at a speed of 600 rpm for 30 min at 60 °C. After 30 min, the solution was transferred and allowed to cool to ambient temperature for 4 h to separate the glycerin and biodiesel layers using a separatory funnel. The top layer, biodiesel, was removed and washed with hot water to eliminate any leftover catalyst. Any leftover water and alcohol were eliminated by heating it at 110 °C for 20 min. The biodiesel was washed and dried until the pH reached around 7. The proportion of biodiesel produced was determined using eqn. 3:

$$\text{Biodiesel yield (\%)} = \frac{\text{Biodiesel dry weight}}{\text{WCO dry weight}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

The acid value of pretreated WCO and FFA concentration was 1.86 mg KOH/g and 0.93%, respectively. As a result, direct transesterification was employed because the acid value was less than 2 mg KOH/g. It is widely believed that the mechanism of biodiesel production comprises of an initial mass transfer-controlled region followed by a kinetically controlled region [26]. However, by encouraging mixing, the mass transfer regulated phase can be bypassed. However, kinetically regulated steps should require less activation energy to overcome. As a result, catalysts are crucial in the transesterification. This phenomenon is explained by the fact that without a catalyst, biodiesel cannot be produced. As a result, this study investigated the effect of various homogeneous base catalysts on transesterification. As shown in Fig. 3, the yields of biodiesel produced with various homogeneous base catalysts were measured. Compared to alkaline metal hydroxide, alkaline metal alkoxide produced much larger biodiesel yields. This could be explained by the fact that CH₃OK and CH₃ONa contain only a trace of hydroxide group required for saponification, resulting in high biodiesel yields (99 wt.% and 96.65 wt.%, respectively). Because of the use of KOH and NaOH as catalysts, biodiesel yields decreased to 94.01 wt.% and 76.65 wt.%, respectively. This is because the hydroxide group is present, responsible for the formation of soaps *via* triglyceride saponification. Since their polarity made them dissolvable, the soaps dispersed into the glycerol phase during the separation stage of the procedure. Additionally, the solubility of the methyl ester in glycerol was increased due to the dissolved soaps, which was a source of yield loss when the methyl ester was dissolved into the glycerol phase during the subsequent separation stage following the reaction. Additionally, dissolved soaps increased the solubility of methyl ester in glycerol, which resulted in a reduction in the yield of the reaction. Thus, the yield of biodiesel produced by each alkaline homogeneous catalyst can be arranged in the following manner:

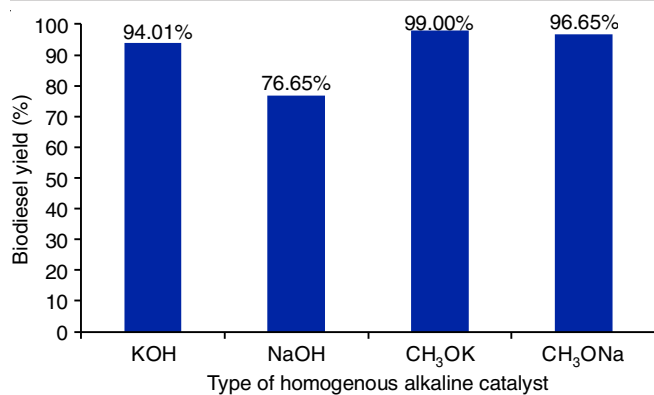


Fig. 3. Effect of type of homogenous base catalyst on biodiesel yield (reaction condition: catalyst amount 1 wt.%; alcohol-to-oil molar ratio of 6:1; reaction temperature 60 °C reaction time 30 min, reaction stirring speed 600 rpm)



The separation of glycerol is complicated by the soap, which has increased viscosity, resulting in the formation of gels that reduce ester yield and complicate the separation process [27-29]. This was also discovered to be true in the course of this investigation. When compared to NaOH-added reaction system to KOH-added reaction system, a significant amount of soap was produced. In order to make phase separation more complicated, the manufacture of soap was induced in the experiment.

The efficient species of catalysis in transesterification is methoxide ions (CH_3O^-). A catalyst's activity is proportional to the amount of methoxide ions available for the reaction [30]. Since chemical molecular weight range, the quantity of methoxide accessible for each mole of triglyceride will vary, even while the weight concentration remains constant. Therefore, the reliable comparisons of catalyst efficacy should be made using the catalyst composition's molar concentration rather than the catalyst composition's weight concentration. Table-1 summarizes the molecular weights of the catalyst compositions and their corresponding molecular weights.

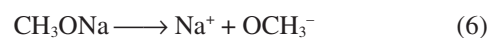
Type of homogenous base catalyst	Molecular weight (g/mol)
KOH	56.1
NaOH	40.0
CH ₃ OK	70.1
CH ₃ ONa	54.0

Transesterification is a three-step reversible reaction. Each of these stages begins with the methoxide ion attacking the triglyceride, diglyceride or monoglyceride molecule's carbonyl carbon atom. In case of KOH and NaOH, the methoxide ion (CH_3O^-) is formed *in situ* through a reaction between the hydroxide and methanol (eqn. 4):



Consequently, the amount of methoxide anion generated is proportional to the amount of hydroxide ion formed and the alkali dissociation constant used in the reaction. The dissociation

constants of KOH and NaOH are exceptionally high due to the fact that they are strong bases. In this regard, the amount of methoxide ion produced is solely determined by the concentration of catalyst. Additionally, as demonstrated in reaction (eqn. 3), this process results in the formation of water, which remains in the reaction media. Hydrolysis of triglycerides and alkyl esters may occur in the presence of water, resulting in the generation of FFA and consequently, results in the formation of unwanted soap. It is also possible for saponification to occur in the presence of a strong base [31]. Despite the high concentration of methoxide ions generated by NaOH, biodiesel yield was lowered due to the reaction medium's high-water content. This is because the increased moles of hydroxide ion (OH^-) in the reaction medium promote the creation of water molecules. However, the hydroxide ion is an impurity in the basic methoxides. They do not create soap by triglyceride saponification in this way. Therefore, in case of CH_3OK and CH_3ONa , their dissociation in methanol results in the formation of methoxide anion required to initiate the reaction and no water was produced as shows in eqns. 5 and 6:



Sodium catalysts had more considerable activation energy than potassium catalysts [14], since $\text{CH}_3\text{O}^- \text{Na}^+$ ion pair is more stable than $\text{CH}_3\text{O}^- \text{K}^+$ ion pair, making potassium catalysts more effective. As a result, alkaline metal alkoxide exhibited the highest yield. Interestingly, the results of this experiment corroborated those of Singh *et al.* [32], who found that potassium-based catalysts outperformed sodium-based catalysts and that methoxide catalyst outperformed comparable hydroxide catalysts as follows:



Since, the transesterification reaction mechanism consists of a mass transfer-controlled initial step followed by kinetically regulated final phase [26]. The order of efficiency for each catalyst in dispersion and methanolysis can be as shown below, which was further clarified the yield variance observed in this study.



Mandari & Devarai [14] concluded that in the dispersion step, K-containing catalysts outperformed their Na analogs, while methoxides outperformed comparable hydroxides.

The physical and chemical properties of WCO-derived biodiesel were examined from each homogenous base catalyst. Table-2 summarizes the findings of comparing the measured properties to ASTM requirements. The density, kinematic, acid value, viscosity and flash point of biodiesel derived from various homogenous base catalysts (KOH, NaOH, CH_3OK and CH_3ONa) were determined and found to be within the ASTM standard.

Conclusion

A range of homogeneous base catalysts (KOH, NaOH, CH_3OK and CH_3ONa), were used in the current study to explore the methanolysis of waste cooking oil (WCO). Following CH_3ONa (96.65%), KOH (94.01%) and NaOH (76.65%)

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF BIODIESEL DERIVED FROM DIFFERENT HOMOGENOUS BASE CATALYSTS

Physico-chemical property	Test method	ASTM D6751 standard values	WCO biodiesel with KOH	WCO biodiesel with NaOH	WCO biodiesel with CH ₃ OK	WCO biodiesel with CH ₃ ONa
Density at 15 °C (g/cm ³)	ASTM D4052	0.860-0.900	0.882	0.898	0.894	0.891
Kinematic viscosity at 40 °C (cSt)	ASTM D445-19a	1.9-6.0	4.2	4.4	5.8	5.8
Acid value (mg KOH/g)	ASTM D664	< 0.5	0.35	0.45	0.25	0.25
Flash point (°C)	ASTM D93-20	> 130	138	142	135	138

produced the maximum amount of biodiesel under the identical reaction conditions, followed by CH₃OK (99.0%). A molar ratio of 6:1 for methanol-to-WCO, as well as a 1 wt.% catalyst, were maintained throughout the reaction, which was carried out for 30 min at 60 °C and a speed of 600 rpm. The saponification reaction, which increased soap production and made phase separation more difficult, resulted in the substantial reduction in biodiesel yield for NaOH. However, the biodiesel's viscosity, flash point, density and acid value all met ASTM standards, showing that biodiesel derived from KOH, NaOH, CH₃OK and CH₃ONa is of good quality, as demonstrated by the results of the study. Thus, from an economic point of view, KOH is a suitable catalyst since, it is less expensive than alkaline metal alkoxides and produces more yield than NaOH with satisfactory physico-chemical characteristics.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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