

## Investigations to Improve Biodiesel Yield from High Free Fatty Acid Feedstock

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**Abstract:** High free fatty acid (FFA) feedstock present more challenges to biodiesel production requiring more careful processing. Soap formation and product losses during separation and purification can easily add to processing costs. The two-stage esterification and transesterification process used to minimize these problems is analyzed step-wisely to reduce cost and improve product yield. Ways to minimize in-situ water generation from different chemical reactions are reviewed with the objective of minimizing associated detrimental effects. A combination of two alkali catalysts (KOH and K<sub>2</sub>CO<sub>3</sub>) is investigated for the transesterification step for the first time. The objective is to maintain good catalyst activity while minimizing residual water in the reaction mixture.

**Key Words:** Biodiesel; High FFA feedstock; Cost-effective processing; esterification; transesterification

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### I. INTRODUCTION

Environmental concerns due to fossil fuels combustion have led to extensive research on renewable energy sources including geothermal, solar, wind, and biomass. Biodiesel, derived from plant oils and animal fats is an attractive alternative fuel to fossil-based diesel as it is biodegradable, non-toxic, renewable, and has a low emission profile. It consists of a mixture of mono-alkyl esters of long-chain fatty acids chemically produced by transesterification of triglycerides (TG) or esterification of free fatty acids (FFA). A catalyst is generally required to speed up the reaction and improve yield [1, 2]. Industrial production of biodiesel faces major challenges including limited supply of raw material due to the utilization of high quality refined vegetable oils and, the cost of feedstock, which accounts for 60-80% of total production cost [3]. At present, biodiesel is not economically competitive with petroleum based-fuels. In order to overcome some of these issues, use of inexpensive raw materials such as waste frying oils, non-edible oils, and animal fats have attracted attention of biodiesel producers [4, 5]. However, one main obstacle is that these low quality feedstock contain significant amounts of FFA which react with a base to produce soap and water hindering product separation during alkaline transesterification [5-7]. The problem of soap formation can be avoided by using acid-catalyzed transesterification but the slow reaction rate makes it a less attractive option [8]. A method that has received more attention due to its moderate operating conditions, higher reaction rates and relative flexibility is the two-step esterification-transesterification process [9]. In the esterification step fatty acids are converted to alkyl esters reducing FFA content to an acceptable level for the subsequent transesterification step, thus improving overall product yield. In the present study, different steps used in two-stage process are analyzed for their contributions to achieve improved conversion efficiency at lower cost. In-situ water generation from different chemical reactions is considered with the objective of minimizing its detrimental effects. For the transesterification step, a combination of potassium hydroxide and potassium carbonate is investigated with the objective to maintain good catalyst activity while avoiding detrimental effects of residual water in the reaction mixture.

### II. EXPERIMENTAL DETAILS

#### 2.1. Equipment and materials

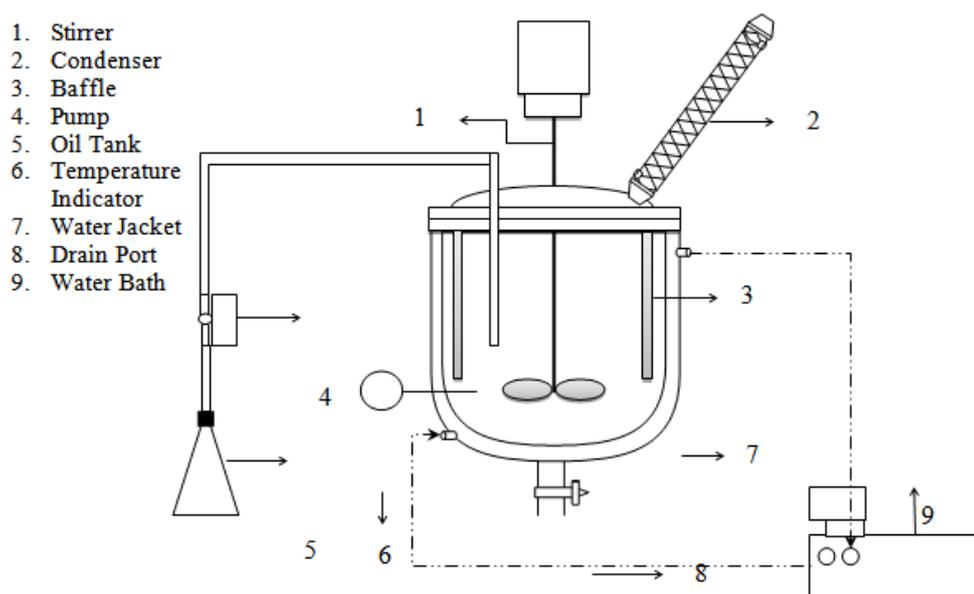
Experiments were conducted in a one liter jacketed glass reactor equipped with a reflux condenser, an impeller and four baffles evenly placed to provide a better mixing of reactants and products. A schematic set up can be seen in Figure 1. The vessel was connected to a water bath capable of maintaining a desired temperature to within  $\pm 1^\circ\text{C}$ . Three ports were accessible from the lid of the vessel, one was used to connect the condenser to the system, the other one was the inlet of the rod of the impeller, and the third was employed to feed the

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reactants into the reactor and to take intermittent samples for analysis. The impeller diameter was 63.5mm and it had three pitched blades (45°) of 5mm width, placed concentrically at 36mm from the bottom. Additionally, a drain valve was installed to empty the contents of the reactor at the end of reaction. Other equipment used during experiments included: a Brookfield viscometer, a Buchi vaporizer, a centrifuge, and separatory funnels. Anhydrous grade methanol (>99.8%), anhydrous reagent grade potassium carbonate (99%), potassium hydroxide (85%), concentrated sulphuric acid (95-98%), and anhydrous grade sodium sulfate were supplied by Caledon Laboratories Ltd. Anhydrous grade ethyl alcohol was obtained from Commercial Alcohols, oleic acid (90%) from Alfa Aesar and concentrated hydrochloric was supplied by Fisher Scientific. Canola Oil used in experiments was the Messina Brands marketed by Costco grocery stores. 1% Phenolphthalein indicator solution in 50% alcohol, and methyl orange indicator 0.1% aqueous solution were obtained from VWR (Canada). The following calibration standards and chemicals were purchased from Sigma Aldrich for GC analysis: glycerin solution, monolein solution, 1,3-diolein solution, triolein solution, tricaprin solution, reagent grade N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA), and n-Heptane (HPLC grade, >99%).



**Figure 1. Schematic of the experimental setup used**

## 2.2. Esterification reaction

For the esterification step known amounts of oleic acid were added to refined canola oil to simulate high FFA feedstock. Oleic acid was selected since it is found in abundance in several plant oils[10, 11]. Acidity was varied from 12mgKOH/g to 30mgKOH/g corresponding to 6% and 15% FFA content by weight respectively. Methanol was selected as alcohol and sulphuric acid as catalyst given their low cost and wide availability. Methanol to FFA molar ratio of 20:1 was employed for all experiments, based on previous literature studies [12]. Sulphuric acid concentration was varied from 2 to 10 wt.% of FFA in feed. The reactor was operated under batch and semi-batch mode to investigate mixing effects. For the batch mode, acidified oil was first added to the reactor and heated until the desired temperature was reached. Then, the methanol/sulphuric acid mixture was poured into the reaction system and a mixing speed of 600rpm was adjusted. The reaction was conducted for 1 hour and intermittent samples were collected for analysis.

For the semi-batch mode, methanol and sulphuric acid were initially transferred into the reactor and heated to the desired temperature at a mixing speed of 300rpm. In a separate flask, a mixture of canola oil and oleic acid was pre-heated to 60°C. A metering pump was used to add this mixture to the reactor vessel at a constant flow rate of 18 ml/min. By using this feeding rate, the reaction was allowed to proceed under a semi-batch mode in which oil was added in the first 25 minutes of esterification and then the reaction proceeded under batch mode for the remaining 35 minutes. Impeller speed was varied over the course of the reaction from 300 to 600 rpm for different runs. These variations in rpm allowed investigations of mixing intensity. During esterification, samples were withdrawn from the vessel at regular intervals to analyze progress of the reaction.

Following esterification, the contents of the reactor, for both modes, were transferred to a separatory funnel and allowed to stand overnight to ensure complete separation of the phases. The system was biphasic: a top layer was constituted by excess methanol, water and most of the catalyst and an organic bottom layer mainly

composed of methyl ester, unreacted TG and FFA. It required further purification to remove residual amounts of methanol, sulphuric acid and water.

### 2.2.1. Purification of esterified oil

The esterified oil after decantation was prepared for transesterification by evaluating different combinations of purification steps shown in Figure 2a. It contained residual amounts of methanol, sulphuric acid and water which could affect transesterification reaction. Attempts were made to determine most effective combination(s) of these steps and their operating conditions in order to achieve maximum product recovery and yield while taking into consideration processing costs. For example, methanol recovery was conducted at 60°C when it was followed by neutralization or at 100°C when both methanol and water were removed together and neutralization step was avoided.

### 2.3. Transesterification reaction

Transesterification of esterified oil was conducted in presence of alkali catalyst to convert triglyceride molecules into FAME. Two types of alkali catalysts namely potassium hydroxide and potassium carbonate, and their combination were employed. Weighed amounts of catalysts were dissolved in methanol using a molar ratio of alcohol to oil of 6:1. The selected catalyst concentrations were based on preliminary laboratory experiments. Transesterification was carried out for 1 hour at a constant temperature of 60°C followed by product separation and purification. Once the reaction was completed the mixture was allowed to stand overnight in a separatory funnel. Methanol was then removed from both phases by evaporation for later reuse. Crude methyl esters were washed once with 28vol.% (based on product) 1N HCl, to neutralize any remaining catalyst, and then with distilled water until a pH close to 7 was reached. The washed product was dried in a rotary evaporator for 20 minutes and filtered to remove any solid impurities using a micro-filter with a pore size of 45µm.

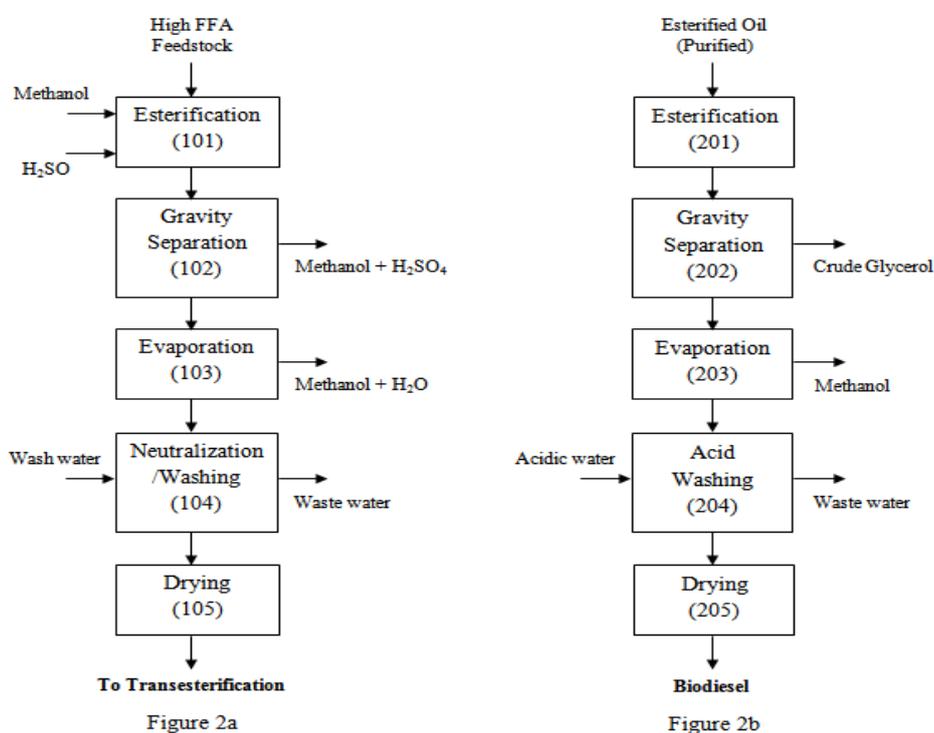


Figure 2. Block flow diagram a) esterification stage b) transesterification stage

### 2.4. Sample analysis

An acid-base titration method was used to quantify FFA content in the samples collected at specific intervals. The titration process followed in this work is a modified method of AOCS Ca 5a-40 in which smaller quantities of sample can be used as described by Rukunudin et al. [13]. In the titration analyses, ethyl alcohol was used as the solvent and phenolphthalein as indicator. The FFA content as oleic acid in the sample was calculated by the following equation.

$$\text{FFA (\%)} = \frac{\text{Volume of NaOH soln (ml)} \cdot \text{Normality of NaOH soln} \cdot 28.2}{\text{Weight of titrated sample (g)}} \quad (1)$$

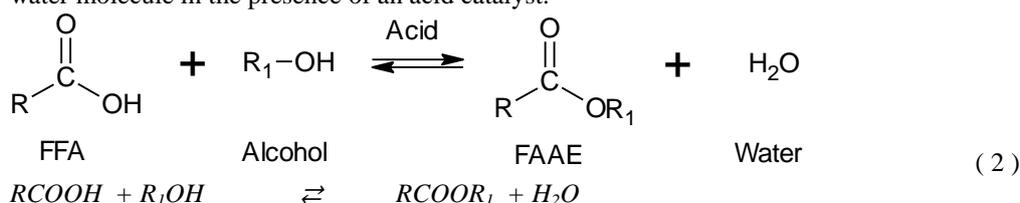
Biodiesel product was analyzed by gas chromatography (GC Shimadzu 2010) equipped with a flame ionization detector (FID) and a capillary column with dimensions of 15m in length, 0.32mm internal diameter, and 0.1µm film thickness. Sample (1µl) was injected on-column by an AOC 20s auto sampler at an oven temperature of

50°C and an injector temperature of 250°C. High purity helium was used as the carrier gas. The temperature program followed was in accordance with ASTM D6584 to determine free glycerol and total glycerol in biodiesel samples: temperature of 50°C was held for 1 min, and then it was increased at a rate of 15°C/min to 180°C; followed by a rate of 7°C/min to 230°C. Finally the temperature was increased at a rate of 30°C/min to 380°C and held for 10 min. The total operating time was 31.84 min. The FID temperature was fixed at 380°C. Glycerol, monoolein, diolein and triolein were used as standards to quantify glycerides. Calibration curves were generated from the above four standards and 1,2,3-tricaproylglycerol (tricaprin) as an internal standard. A silylating agent, N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA) was added to each GC sample to improve chromatographic properties of glycerides. Samples were prepared as per ASTM D6584 specifications.

### III. RESULTS AND DISCUSSION

#### 3.1. Esterification step

Esterification was carried out in order to reduce the FFA content in the oil feed to a level below 0.5 wt.% (<1mgKOH/g) to avoid soap formation in subsequent alkali transesterification step to produce biodiesel [14, 15]. In esterification reaction, a fatty acid molecule reacts with an alcohol molecule to produce an alkyl ester and a water molecule in the presence of an acid catalyst.



As previously mentioned, two types of mixing were studied, namely batch and semi-batch. While, batch is commonly used in industry, its mixing effects can be limited especially at the beginning of the reaction between two immiscible liquids. Mixing process can be improved and initial mass transfer limitations can be overcome by gradually feeding the oil into previously added methanol and catalyst solution in the reactor. This technique was previously proposed by Pal and Prakash [16] for methanolysis of TG to overcome mass transfer limitations commonly encountered with batch mode. As droplets of oil fall into a pool of methanol and catalyst solution, they easily get dispersed uniformly throughout the reaction system. By adding oil into the system at 18ml/min, methanol to FFA molar ratio is also enhanced specially in the early stages of the reaction with values of: 100:1 at 5min, 50:1 at 10min, 25:1 at 20min and finally a 20:1 from 25min to 60min.

The two methods were compared based on FFA conversion under different conditions. Figure 3 compares reaction progress obtained with the two methods for initial FFA of 6wt.%. It can be observed from the figure that FFA conversions obtained with the semi-batch method are higher initially, while they are nearly the same between 20 to 40 minutes interval. For higher reaction durations, conversions are higher with the batch method. It seems that any advantage of semi-batch method is lost after 30 minutes which is the end of feed flow. The reactor now operated in the batch mode for another 30 minutes and agitator mixing speed remained at 400 rpm. In case of the batch mode, however, the mixing speed of 600 rpm was kept constant from the beginning to the end. Higher conversions obtained with the batch method in the second half of reaction indicate that mixing intensity is important to facilitate the reaction.

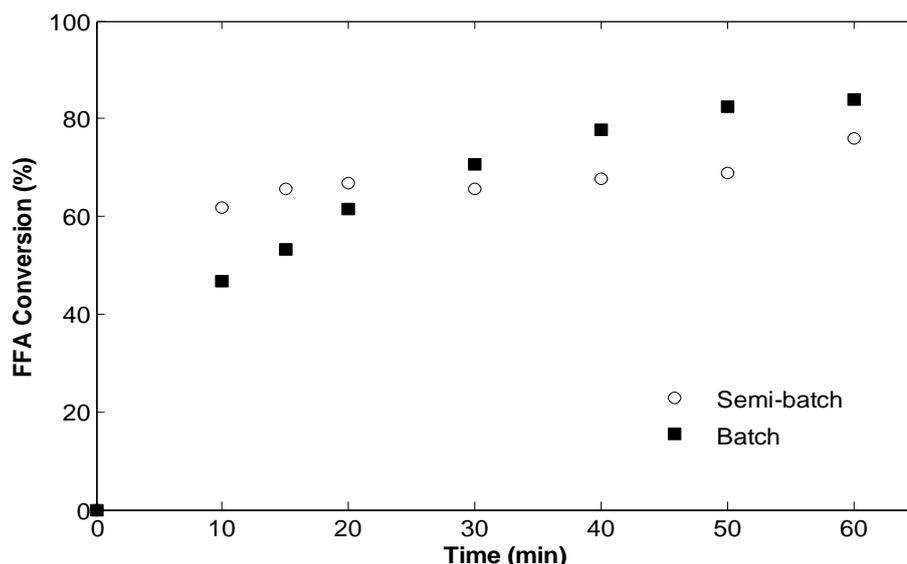


Figure 1. Comparison of batch and semi-batch method based on reaction progress (Initial FFA:6%)

The role of mixing intensity was further investigated by adjusting the rpm as follows for semi-batch mode: 300 in first 15 minutes, 400 for the next 15 minutes and 600 for the remaining 30 minutes. The FFA content in the feed was raised to 15 wt% which is more representative of the value in most nonedible oils. Moreover, higher FFA in oil feed was also expected to show clear difference between the two methods. The progress of the reaction with the above changes is shown in Figure 4 for batch and semi-batch. It can be observed that conversions obtained with the two methods are similar in the second half thus confirming the importance of agitation intensity to achieve high conversions in the reaction system.

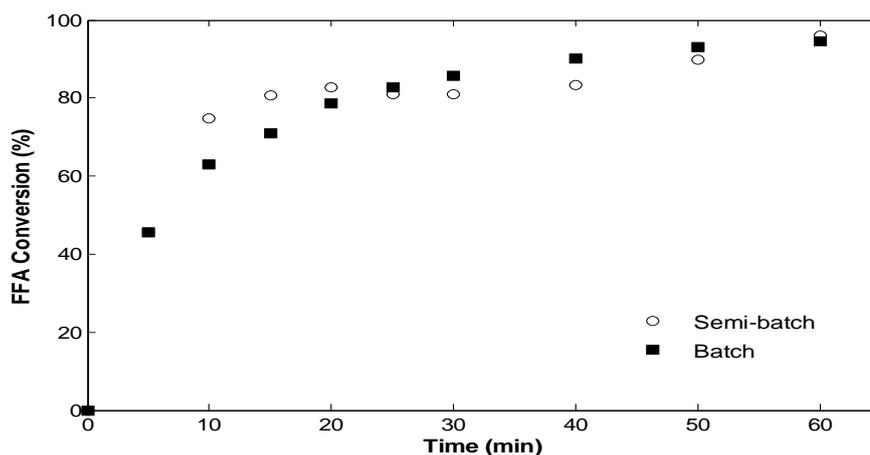


Figure 2. Comparison of esterification reaction progress obtained with the two methods for high initial FFA and increased agitation

A comparison of remaining FFA in the reaction mixture as a function of time is presented in Figure 5 for low and high initial FFA in feed. It can be seen that reduction in FFA content is rapid in the beginning but slows down significantly after about 30 minutes as the reactant concentration drops. With the progress of reaction, there is also accumulation of water produced by the esterification reaction. Since the reaction is reversible, the net reaction rate is reduced with the accumulation of product water molecules in the system. It can also be noted that the rate of decrease is faster with high initial FFA value. This can be explained by higher specific weight of catalyst and methanol for most of reaction period with high starting value of FFA in feed. It is noted from Figure 5 that final FFA content was reduced to about 0.8 wt% after one hour of reaction which was higher than targeted value of 0.5 wt% or less. The target value could be achieved by continuing the reaction for longer duration or by increasing catalyst concentration to speed up the reaction. Since, the reaction rate is

quite slow towards the end, it was decided to conduct reactions with higher catalyst concentration, while keeping the reaction time the same.

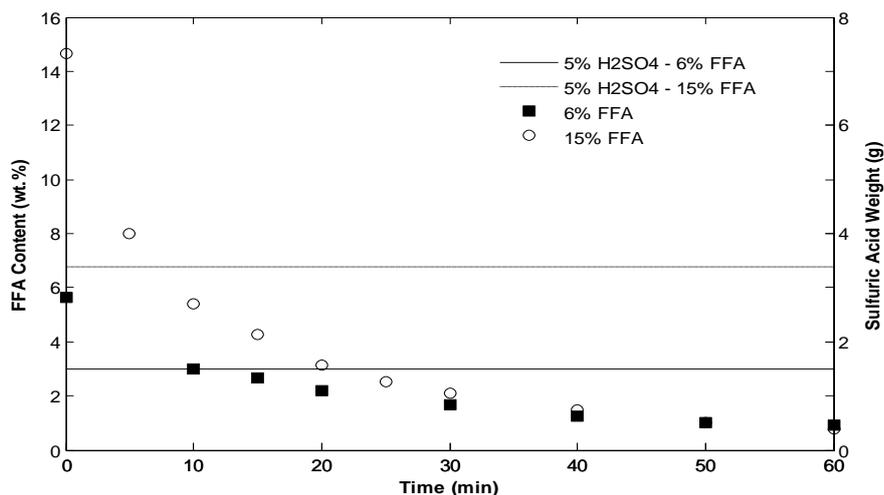


Figure 3. Change in FFA content with time for different initial FFA values

The results presented in Figure 6 show that desired final FFA content was achieved at higher catalyst concentration. These results indicate that an optimum combination of reaction time and catalyst concentration can be determined to achieve the desired FFA content.

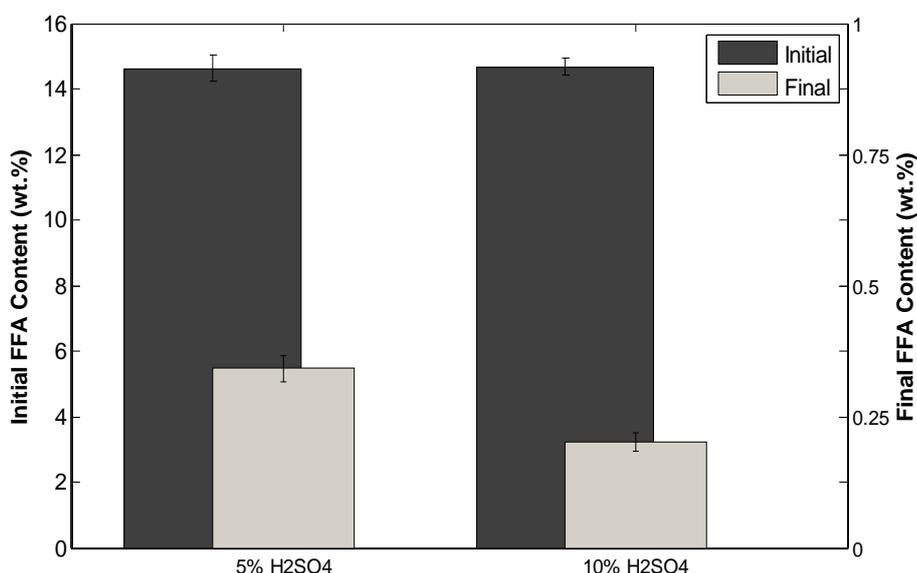


Figure 4. Comparison between 5% and 10% catalyst concentration

### 3.1.1 Purification of Esterified Oil

After the reaction the esterified reaction mixture gets separated into a methanol- rich layer and an oil-rich phase – step102 in Figure 2a. Sulphuric acid being a homogeneous catalyst is distributed between the two phases although most of it is expected to remain in methanol-rich phase due to its polar nature.

Before transesterification reaction, the oil phase was treated to remove residual amounts of methanol, sulphuric acid and water present. Three possible steps considered were methanol recovery (103), neutralization (104) and drying (105) as shown in Figure 2a. Attempts were made to determine most effective treatment scheme in order to achieve maximum product yield while minimizing processing steps. For example, methanol recovery was conducted at 60 °C when it was followed by washing or at 100°C when both methanol and water were removed together and washing step was avoided. The objective was to remove impurities which could lead to lower biodiesel product yield.

### KOH vs K<sub>2</sub>CO<sub>3</sub> for Transesterification

Experiments were conducted to determine overall effectiveness of selected alkali catalysts for the transesterification step. Figure 7 shows that compared to KOH, significantly higher concentration of K<sub>2</sub>CO<sub>3</sub> is required to obtain similar biodiesel yield. The optimum concentration is about 1 wt% with KOH and 3 wt% with K<sub>2</sub>CO<sub>3</sub>. Potassium hydroxide pellets were dissolved in alcohol phase in about five minutes while it took much longer to dissolve K<sub>2</sub>CO<sub>3</sub> due to its lower solubility.

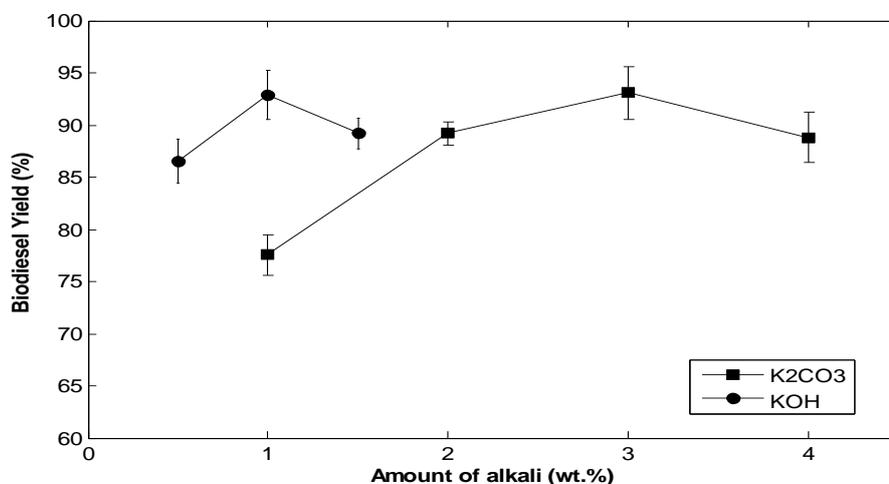
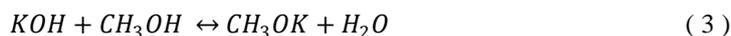


Figure 5. Biodiesel yields obtained with two alkaline catalysts

The alkali catalyst was added to methanol prior to transesterification reaction to initiate methoxide ion formation from interactions between methanol and the alkali.



Methoxide ions are responsible for initiating transesterification as they attack the carbonyl group of the tri-, di-, and monoglyceride molecules [2, 17, 18]. The amount produced is dependent on the catalyst concentration and the alkali dissociation constant. Since potassium hydroxide is a very strong base, its dissociation constant is high compared to potassium carbonate, a weaker base. Thus for a given weight of the alkali, methoxide anion produced would be higher with KOH than with K<sub>2</sub>CO<sub>3</sub>.

Although, K<sub>2</sub>CO<sub>3</sub> is a weaker catalyst for transesterification reaction, a few observations of practical significance were made with this catalyst. It was observed that after the transesterification step, glycerol phase separated out more quickly with potassium carbonate compared to potassium hydroxide. This was studied systematically and the results are presented in Figure 8 by recording glycerol phase yield as a function of time. Phase separation was achieved much faster with K<sub>2</sub>CO<sub>3</sub>. As soon as the reaction mixture was poured into a calibrated flask the denser glycerol phase settled at the bottom of the cylinder rather quickly. Around 90% of phase separation occurred within the first 8 minutes with K<sub>2</sub>CO<sub>3</sub> while it took about 15 minutes with KOH. Moreover, biodiesel phase was clear and free of cloudiness with potassium carbonate at different catalyst loadings. This quick settling of glycerol phase indicated absence of emulsion formation which usually results from soap formation with other alkali catalysts. With KOH, a layer of soap like material was observed between the biodiesel and glycerol phases in the separatory funnel at the loading of 1.5 wt% KOH. The soap formation can be attributed to following sequence of reactions with generation of water molecules.

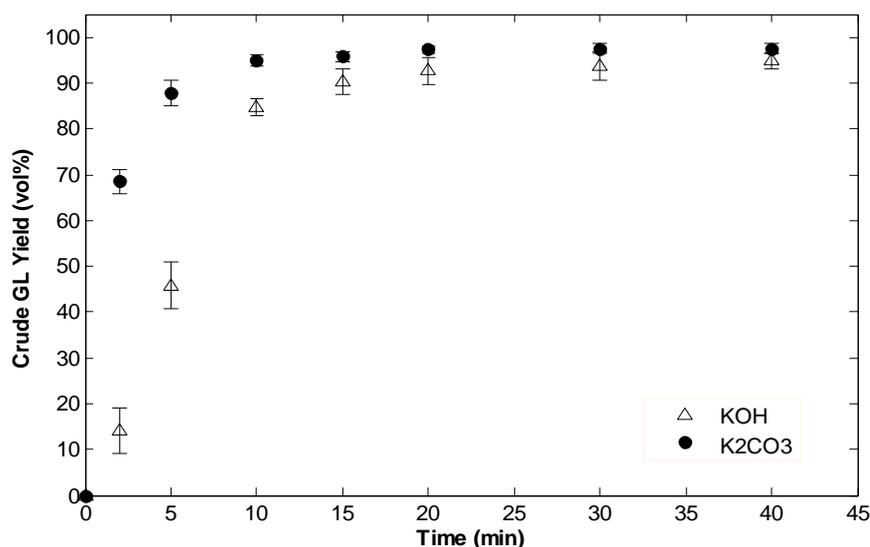
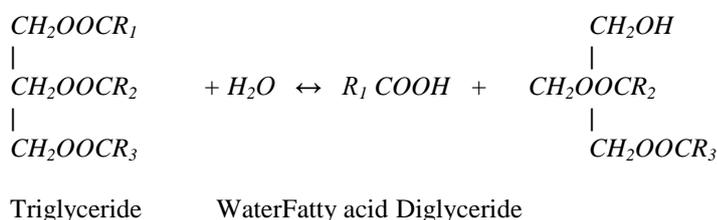


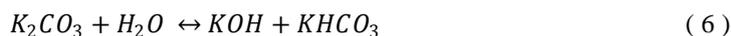
Figure 6. Crude glycerol yield at different time intervals



However, with potassium carbonate, the generation of water molecule is avoided due to the following reaction.



It was, however, noted that during the water washing step, there were more losses with K<sub>2</sub>CO<sub>3</sub> compared to KOH. It was observed that a layer of gel like material formed during the washing step between aqueous and biodiesel phase. Also compared to KOH, more washes were required in order to obtain a clear product free of cloudiness. Due to its limited solubility in methanol, all of K<sub>2</sub>CO<sub>3</sub> could not dissolve at concentrations above 2wt%. The un-dissolved amount was small at 3 wt% but increased for higher concentration which further complicated washing of final product. During washing step, potassium carbonate can react with water to produce more KOH as per following reaction.



Availability of excess KOH can aid soap formation during washing step. These observations indicated that an appropriate combination of KOH and K<sub>2</sub>CO<sub>3</sub> could provide for more effective catalysis which could be more tolerant of any residual amounts of water in the reaction mixture. As discussed below, this combination was further tested for the transesterification reaction step. Based on the above observations, a set of experiments were conducted to study effects of different processing steps (after esterification) on biodiesel yield. The results are summarized in Table 1 in an increasing order of biodiesel yield. Product yields reported in the table were calculated based on the weight of oil initially fed into the system (i.e. high acidity oil). This followed the assumption that transesterification in the first step was negligible. Although, acidic catalysts are capable of conducting both reactions, the rate of methanolysis of TG is well known to be low at temperatures below 100°C, low methanol to oil molar ratio, and short reaction times (<3hr) [19, 20].

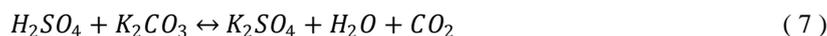
Table 1 Product analysis after transesterification conducted on esterified oils.

Run No.	Methanol Recovery	H <sub>2</sub> SO <sub>4</sub> Removal	Drying	Catalyst Type	Catalyst wt.% (wt., g)	BD Yield (%)
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1	NO	NO	NO	K <sub>2</sub> CO <sub>3</sub>	3 (15.7*)	78.7
2	YES (60°C)	NO	NO	KOH/K <sub>2</sub> CO <sub>3</sub>	0.5/1 (2.4/8.8*)	83.5
3	YES (100 °C)	NO	NO	KOH	1 (5.74*)	89.7
4	YES (100 °C)	NO	NO	K <sub>2</sub> CO <sub>3</sub>	3 (15.82*)	89.8
5	YES (100 °C)	NO	NO	KOH	1 (5.71*)	89.9
6	YES	YES	NO	KOH/K <sub>2</sub> CO <sub>3</sub>	0.5/1 (2.21/4.3)	93.6

\*Extra amount of alkali added to neutralize residual acid

It can be seen from Table 1 that lowest yields are obtained with run 1 and 2 conducted without any pre-treatment. For this run, the oil layer after phase separation from esterification was directly injected into the transesterification reactor. It can be seen that biodiesel yield is greatly affected by the impurities in the feed. It was observed that a layer of soap-like material formed after the alkaline reaction. Water generated by the neutralization reaction would have added to the residual water from esterification stage and further aided the hydrolysis of esters and glycerides and saponification of carboxylic acids (FFA).



The soap layer formation became more obvious and difficult to separate in the washing step. The product yield was greatly affected by this separation as a substantial amount of FAME was lost. For run # 2, methanol recovery step (103) was conducted at 60°C under vacuum. While most of methanol would have been removed under these conditions, some amount of associated water would also be removed. For this run, a combination of KOH and K<sub>2</sub>CO<sub>3</sub> catalysts was used to reduce total weight of alkali catalyst. Higher yield obtained with run could be attributed to use of lower catalyst and slightly lower moisture in feed to transesterification reaction. For runs 3 to 5 methanol recovery was conducted at 100°C which would have removed both methanol and associated water from esterified oil. Higher product yields obtained with these runs compared to run # 2 can be attributed to absence of water in the feed.

Although product yield increased to about 90% with runs 3 to 5, generally product yields higher than 90% are desirable for economic reasons [21]. The only impurity remaining in the feed was residual amount of sulphuric acid. For previous runs, excess alkali was used to neutralize remaining acid in feed but for run # 6, acid was removed by washing. After washing, most of the water was settled out by decantation and only trace amounts of water would enter the reacting medium in step two. In order to neutralize, the effects of any remaining water in the feed, a combination of KOH and K<sub>2</sub>CO<sub>3</sub> catalysts was used. As seen in the table, highest product yield was obtained with this run. Potassium carbonate can react with available water molecules to produce more KOH as shown by reaction 6.

As a result of this reaction, more catalytic species would be available for transesterification to occur without adding net water to the reaction mixture. Thus potassium carbonate can be used as a drying agent to remove traces amount of water while generating potassium hydroxide in situ. The quality of final product was further tested by gas chromatography to ensure ASTM standard requirements were met. Methyl ester content in the final product was > 99% and total glycerol content well below 0.2 max.

#### IV. CONCLUSIONS

Purification of esterified oil is essential to improve biodiesel yield in the two stage esterification-transesterification process. However, attempt to neutralize acid catalyst by adding excess alkali should be avoided. In-situ generation of water due to neutralization reaction adds to the problem of soap formation. Residual amount of sulphuric acid should be removed by water washing instead. A combination of KOH and K<sub>2</sub>CO<sub>3</sub> in appropriate proportions is recommended to take advantage of their respective contributions to

transesterification reaction. Drying step after water washing can be avoided by using this catalyst combination for a more cost effective operation.

### ACKNOWLEDGMENTS

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### **List of Figures:**

Figure 7. Schematic of the experimental setup used

Figure 8. Block flow diagram a) esterification stage b) transesterification stage

Figure 9. Comparison of batch and semi-batch method based on reaction progress (Initial FFA:6%)

Figure 10. Comparison of esterification reaction progress obtained with the two methods for high initial FFA and increased agitation

Figure 11. Change in FFA content with time for different initial FFA values

Figure 12. Comparison between 5% and 10% catalyst concentration

Figure 13. Biodiesel yields obtained with two alkaline catalysts

Figure 14. Crude glycerol yield at different time intervals

### **List of Tables:**

Table 1. Product analysis after transesterification conducted on esterified oils.

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