Methods of stopping kinetic transesterification reactions

Abstract

The realisation that fossil fuel resources are limited, together with the need to reduce greenhouse gas emissions, contributed to the development of alternative fuels. Among the alternatives that have captured the world's attention are biofuels and of particular importance is biodiesel. Transesterification reaction, the most preferred method of biodiesel production, is a reversible reaction driven by excess alcohol and in the presence of a catalyst. One of the critical aspects in the kinetics of transesterification is the stopping of the reaction or quenching the reaction. Quenching is done upon the completion of the reaction in a batch reaction and this is deemed crucial because of the reversibility of the reaction and the need to prevent the degradation of the extent of reaction by the reverse reaction. Three views are held concerning quenching of the reaction: removal of the reaction residual-alcohol; removal of the catalyst and separation of the reaction products. However each option has an interactive impact on the others and consequentially on the degree of progress of the reaction. This paper analysed how to effectively stop the transesterification reaction using two of the three methods described above. Transesterification reaction was carried out and the methods of stopping the reaction were applied to determine their effects on the extent of the reaction. Results obtained showed that removal of the catalyst alone is not effective in stopping the reaction. Dilution with a solvent proved to be the most effective method of stopping transesterification reaction.

1. Introduction

Biodiesel is defined as the monoalkyl esters of vegetable oils or animal fats. The most commonly used method of production of biodiesel is transesterification which is a reaction between a lipid and an alcohol in the presence of a catalyst to form esters and glycerol. The catalyst can be basic or acidic depending on the amount of free fatty acids (FFA) in the feedstock. For free fatty acid values equal to or greater than 2mg KOH/g, a two stage process is recommended (Wenzel et al. 2006). The first step is the acid catalysed esterification where FFA is converted to esters, then followed by base catalysed transesterification. The basic catalyst normally used is sodium hydroxide because it is cheaper and safer to handle than potassium hydroxide and the alcohol preferred is methanol which is also cheaper than the other alcohols and it gives short chain fuels with desirable properties. Transesterification reaction is a step-wise and reversible reaction. It can be driven to the right by either removal of one of the products or supply of excess alcohol. Because the products need to settle before separation, the latter approach is mostly used. The reactions can be represented as follow:
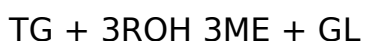
Step-wise reactions:

(1)

TG + ROH DG + RCO2R1

(2)

DG + ROH MG + RCO2R2

(3)

MG + ROH GL + RCO2R3

(4)

The overall reaction is:

TG + 3ROH 3ME + GL

One of the critical aspects of kinetic study that has not been much attended to is how to stop transesterification reaction. Stopping the reaction in a batch reaction is done after the completion of the reaction. This is crucial due to the reversibility of the reaction and the need to prevent the degradation of the desired extent of the reaction by the reversed process. In the kinetic study, samples are drawn at specific time intervals and the reaction needs to be stopped in order to determine the rate of change of the reactant to product at that particular time.

Three approaches have been suggested on how to effectively stop the reaction:

(i) removal of the reaction residual-alcohol; (ii) removal of the catalyst and (iii) separation of the reaction products

(http://www. gbanalysts. com/Reading%20Room/Situation%20Analysis/BiodieselTechs/quenchbdreactions. html).

However each of these options has its interactive impact on the others and consequentially on the degree of progression of the reaction. Because of the reversibility of the reaction, the removal of the excess alcohol alone would result in the reverse reaction to create new equilibrium and therefore degrade the preferred extent of reaction. Removing the catalysts which preferentially drives the reaction forward while the alcohol still remains in the reaction mixture, also establishes a different equilibrium condition with reverse reaction. This task alone therefore is also likely to degrade the extent of reaction realized by the catalysis. Through forcing a final disruption of the reaction state by separating the reaction products while the catalysts and the residual alcohol are still present would also lead to the occurrence of the reverse reaction towards establishing a new equilibrium, and again degrade the extent of reaction.

The authors of the article sited argue that the reversible reaction state is not so critical because it takes place in an heterogeneous state and it depends on the total interfacial surface available unlike the forward reaction which is homogeneous. For that matter, the quenching procedure could begin with the removal of alcohol, followed by the removal of catalyst and finally separation of the reaction products. However, the physico-chemical properties of the reaction mixture could influence their behaviours such that this step may be reversed. For example, alcohol is more volatile than hydroxide (catalyst) so the catalyst should be removed first.

Several researchers did studies on the kinetics of transesterification but very few have studied the methods of stopping the reaction. Maria Jesus et al., (2009), Kusdiana and Saka (2003) and Ma and Hanna (1998) all used acetic

acid for stopping the reaction while Gemma et al., (2005) used hydrochloric acid in water, Darnoko and Cherryan (2000) used a solvent; tetrahydrofuran and hydrocloric acid and Noureddini and Zhu (1998) used ice water. Kimmel (2004) investigated base-catalysed glycerolysis of fatty acid methyl esters. He optimized a procedure for stopping the reaction and reported that the reaction still proceeded in most of the cases even if a means of stopping it was applied on the sample. The degradation of the product of reaction could be minimized through effective equipment design using correct rate constants obtained from real parameter determinations. In this work, alkali catalyzed transesterification of jatropha and castor oils were carried out under constant conditions of temperature, agitation speed, alcohol to oil molar ratio and catalyst concentration while different methods of stopping the reaction were used. Kinematic viscosity of the resultant fatty acid methyl ester was analyzed as a means of assessing the results of the treatments.

2. Materials and Methods

Jatropha seeds were obtained from Arusha region, while castor seeds were obtained from Dodoma, both in Tanzania. The oil was extracted using a mechanical press machine. Crude oils so obtained were degummed using water at 70oC – 80oC for 30 minutes. The degummed oils were neutralized to reduce the FFA as follow:

Free fatty acids of the degummed oils were determined using ASTM D664 and on the basis of these values, calculated strength of sodium hydroxide solutions were prepared and used to treat the oils. The alkali solution was added to jatropha oil at about 70 oC while stirring and the reaction was allowed to continue for 30 minutes after which the soap formed was

separated by centrifuging at 4500 rpm for 20 minutes. The oil was washed thrice with warm water (50oC) and dried at 105 oC on a hot plate for 15 minutes and it was ready for use. Neutralization of castor oil followed a similar process but it needed a further step of salting out the soap formed with a 10% solution of sodium chloride.

Experimental Procedure

Transesterification reaction was carried out in a 2-litre round bottomed flask as a reactor. The reactor was fitted with a reflux condenser (to minimize alcohol loss), a mechanical stirrer, a thermometer and a sampling port. One litre of oil was pre-heated at 110 oC for 30 minutes to drive off water that might have been present in it before being charged into the reactor. Calculated amount of methanol and sodium hydroxide were dissolved separately while the oil was drying. The methanol-sodium hydroxide mix was then transferred into the reactor while stirring started immediately. The reaction was timed for 2 hours.

A sample of 150 mL was drawn after 30 minutes interval and the mixture put in separate flasks as follow: Three flasks contained 5mL of different concentrations of sulphuric acid of 0. 1M, 2. 5M and 5. 0M; one flask contained 5mL tetrahydrofuran and one flask was empty (control). The drawn sample was rapidly distributed into these flasks and shaken to mix the contents before analysis. Analysis of viscosity was performed after various storage times as shown in the results.

3. Results and Discussions.

As seen from Fig. 1, tetrahydrofuran shows good signs of stopped reaction. Tetrahydrofuran forms a homogeneous mixture with the methyl ester formed and hence lower viscosity. Whereas 0. 1M, 2. 5M, and 5M become stable after 8 hours and control shows almost similar trend but it smoothens out indicating that the reaction might have come to a natural end due to exhaustion of the reactants. The trends of 0. 1M, 2. 5M and 5M indicate respective dilutions. This may mean that since the catalyst has been removed by the concentrated acids, excess acids remaining catalyse the esterification of the remaining fatty acids in the mixture forming more esters.

In Figure 2, the dilution trend is completely reversed for 5M, 2. 5M and 0. 1M respectively. This could mean that after 1 hour of reaction time (60 minutes), the reaction may have reached equilibrium end. No more acid catalysing the reaction and therefore the viscosity is just that of the mixture. Tetrahydrofuran and control both remain consistent meaning natural end of the reaction and homogeneous mixture as before. Figures 3 and 4 show similar trends, although with lower viscosities presumably due to longer reaction times when the reactants have been exhausted.

Taking into account the following physico-chemical properties of the mixture:

- The viscosity of biodiesel is much lower than that of glycerol;
- Biodiesel has much lower specific gravity (0. 88) than glycerol (1. 261);
- Solubility of water is higher in glycerol (miscible) than in biodiesel (immiscible) and

- Solubility of hydroxide is higher in biodiesel than in glycerol.

It can be recognized that the viscosity changes that have taken place in this study may not reflect the reality of the mixture. The reaction product should have been separated first and the biodiesel purified before viscosity analysis in order to give a real reflection of what is taking place in the reaction mixture.

Figure 5 shows viscosity against storage time for THF stopped reaction for all the reaction times of 30 minutes through 120 minutes. The difference in time 0 reflect the residence time difference when reactions were beginning (30 and 60 minutes) and viscosity value of 7. 0 mm2/s and when they were ending (90 and 120 minutes), viscosity value of 4. 5 mm2/s respectively.

As an additional measure, we also wanted to check whether storage time, residence time and concentrations have any effects on the viscosity and hence on quenching procedures. A further analysis was done on the data using ANOVA to find out these effects. Results are given in Tables 1 and 2.

From Table 1, reaction time (Sample) has very high significant effect (p= 0. 000029) on viscosity whereas storage time (Columns) has no significant effect (p= 0. 1202564) on the viscosity. On the other hand, Table 2 reveals that reaction time (Sample), concentration of quenching reagent (Column) and interaction among them have very high significant effects on viscosity. There is a possibility that excess sulphuric acid catalyses the esterification reaction with the free fatty acids and glycerols to produce more ester.

4. Conclusion

The study of methods of intermittent stopping of transesterification reaction showed that different concentrations of sulphuric acid alone are not able to effectively stop the reaction until after 8 hours. The reactions still proceeded even after applying the different concentrations of sulphuric acid up to the time they stabilize (8 hours). Tetrahydrofuran was able to stop the transesterification reaction only after 4 hours. Different concentrations of sulphuric acid and their interactions with reaction time have very high significant effects on viscosity.

5. Recommendation

As stated earlier, the interferences by the physico-chemical properties of the reaction mixture may not have given a true picture of the study. It is recommended that a separate study be carried out, but the reaction mixture be separated and purified and the viscosity of pure methyl ester measured to ensure a true reflection of the above presuppositions.