Supercritical Alcohol Technology In Biodiesel Production: A Comparative Study Between Methanol And Ethanol

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ABSTRACT

A system for non-catalytic supercritical alcohol technology was developed using a batch-type tube reactor. In the present study, methanol and ethanol were used as the source of alcohol and a comparative study on the yields of supercritical methanol and supercritical ethanol was carried out. The effects of temperature, reaction time and molar ratio of alcohol to oil on the yield of fatty acid methyl esters were investigated. The results obtained showed that supercritical methanol is superior to supercritical ethanol in terms of biodiesel yield and reaction time. Supercritical methanol reaction only required a mere 20 minutes reaction time to achieve more than 80% yield of biodiesel while supercritical ethanol only can produce 65% for a longer period of 23 minutes. Nevertheless, the study has shown that supercritical alcohol reaction have significant advantages compared to conventional catalytic methods such as lower reaction time and simpler separation and purification steps.

INTRODUCTION

Most countries in this world depend heavily on fossil fuels such as petroleum, natural gas and coal as the main source of energy. With the rapid development of some countries such as China and India, the demand of fossil fuels in the world market has been increasing substantially over the past 25 years and is projected to escalate significantly within the next two decades. On the other hand, utilization of these non-renewable energy sources has been identified as one of the main causes of environmental pollution throughout the world. Consequently, the problem has become a global issue and the quest for cleaner, affordable and renewable source of energy is inevitable.

One of the renewable energy that has been receiving a lot of attention is biodiesel due to its similarity with conventional diesel in terms of chemical structure and energy content. Biodiesel, or also known as fatty acid alkyl esters is derived from triglycerides via transesterification reaction with alcohols such as methanol and ethanol [1]. In this reversible reaction, 1 mole of triglycerides will react with 3 moles of alcohol to produce one mole of glycerol and three moles of fatty acid alkyl esters. As biodiesel is derived by utilizing inexhaustible natural resource such as biomass to produce energy in the form of liquid fuels, it does not emit excessive harmful gases or particulates to environment as in non-renewable fossil fuels. Instead, it has the potential to mitigate climate change and solve environmental pollution crisis in the world. Apart from that, biodiesel also offer a promising solution for energy security and sustainable development in the long term due to the renewable feedstock used in the production.

Currently, biodiesel is produced by using homogeneous and heterogeneous catalytic transesterification reaction. Homogeneous catalysts such as sodium hydroxide and potassium hydroxide are extensively used in commercial biodiesel plant for the past few decades. However, these catalysts are sensitive to the presence of free fatty acids in oils and subsequently cause the reaction to suffer from low yield and tedious separation and purification steps are required [2, 3]. On the other hand, there has been a growing interest in heterogeneous catalytic reaction due to its advantage in term of purification process. However, this method was found to be time consuming and susceptible to water content in vegetable oils as the efficiency of catalysts will be adversely affected [4].

Catalytic reactions have several limitations in terms of complicated purification steps and sensitivity to impurities in oils. Collectively, these weaknesses arise due to the utilization of catalysts in transesterification reaction. Hence, it is of great interest to carry out supercritical alcohol transesterification reaction which does not required the presence of any catalysts. Previously, many studies in non-catalytic supercritical methanol have been carried out to investigate the yield of biodiesel [5-7]. However, there is no attempted study to compare the effect of alcohol used, which is important as the type of alcohol influences the performance of the reaction significantly. Hence, this study aims to carry out a comprehensive comparison between methanol and ethanol in non-catalytic supercritical alcohol reaction. The parameters that were investigated include effect of temperature, reaction time and molar ratio of alcohol to oil.

MATERIALS AND METHODS

Purified palm oil was purchased from Yee Lee Edible Oils Sdn. Bhd., Malaysia. Methanol and ethanol were purchased from Merck (99%). Methyl heptadecanoate (used as internal standard) and standard references for biodiesel analysis which include alkyl myristate, alkyl palmitate, alkyl stearate, alkyl oleate and alkyl linoleate were obtained from Fluka Chemie. All those standards were used without any prior purification.

The non-catalytic supercritical alcohol transesterification reaction was carried out by using two types of alcohol which are methanol and ethanol by using a 12 ml batch-type tube reactor which can sustain high temperature and pressure needed in supercritical treatment. The material of construction for the tube reactor is Stainless Steel 316 Super Duplex® which has the strength and durability to endure the extreme conditions. The reaction temperature used in the reaction range from 270°C to 420°C with the molar ratio of alcohol to oil from 15 to 60 mol/mol. Besides, the reaction time was limited to the range of 5 to 30 minutes. Initially, alcohol and oil were charged into the tube reactor and subsequently immersed in a furnace heated at pre-determined temperature by using an automated transferring mechanism. After a fixed reaction period, the reaction tube was transferred automatically into the water bath to quench the reaction immediately. After that, the mixture of products was taken out and allowed to settle in order to separate biodiesel from glycerol. Subsequently, the biodiesel sample was collected by using micropipette and subsequently underwent a reflux process in order to remove excessive methanol. Finally, the biodiesel sample is diluted with solvent and the yield is analyzed by using gas chromatography (PerkinElmer, Clarus 500) with Nukol™ capillary column (15 m × 0.53 mm, 0.5 µm film thickness) and Flame Ionization Detector (FID) as the detector.

RESULTS AND DISCUSSION

Effect of temperature

Temperature plays a crucial role in supercritical alcohol transesterification reaction for biodiesel production. As the critical temperature of methanol and ethanol are 239°C and 243°C respectively, the reaction temperature must be higher than these critical values. Apart from that, to ensure that supercritical alcohol conditions were reached, the operating pressure must be higher than the critical pressure of methanol and ethanol which are 8.1 MPa and 6.4 MPa respectively. Figure 1 shows the effect of temperature on the yield of supercritical methanol (SCM) and supercritical ethanol (SCE) reactions which were carried out at 20 minutes reaction time and 40 molar ratio of alcohol to oil. For SCM, the yield of biodiesel increased with temperature from 270°C to 360°C with the optimum yield of 80%. Beyond the optimum temperature, the yield decreased slightly to 66%. On the other hand, similar trend is observed for SCE but the optimum temperature is relatively lower at 330°C, with optimum yield of 65% only. This observation can be best explained by the reactivity of triglycerides with alcohol, which decreases with increasing alkyl chain of alcohol [8]. This might be due to the long chain alkyl group hindering the (-OH) group in alcohol from reacting with triglycerides to form fatty acid alkyl esters. Hence, SCE reaction has lower optimum yield of biodiesel compared to SCM reaction.

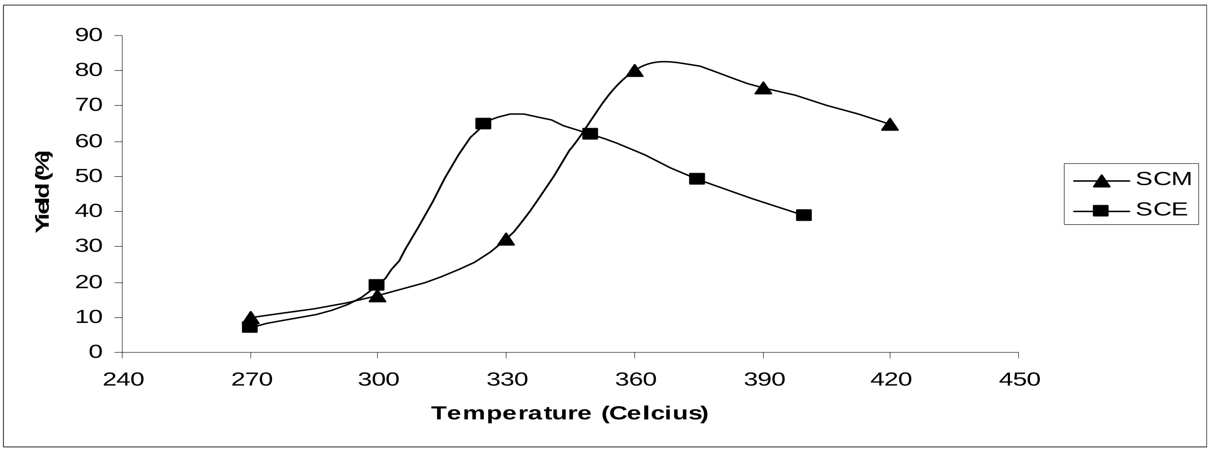

Figure 1: Effect of temperature on the yield of SCM and SCE reactions.

Effect of reaction time

Reaction time plays a crucial in biodiesel production as it can influence the productivity and economic consideration. Compared to conventional catalytic reactions which required hours of reaction time, supercritical alcohol reaction can be completed in a substantially lower duration of 20 minutes. As shown in Figure 2, the yield of biodiesel increased steadily with the increment of time for SCM and SCE reactions until the optimum conditions of 20 and 23 minutes respectively. The experiments were carried out at optimum temperature for SCM and SCE respectively as discussed previously and 40 molar ratio of alcohol to oil. At the optimum condition, the yields of biodiesel were 80% and 65% for SCM and SCE respectively. Beyond the optimum reaction time, the yield of biodiesel decreased gradually due to the instability of produced biodiesel at high temperature for a long period of time and decomposition started to take place [9]. Nevertheless, as discussed earlier, since the reactivity of methanol with triglycerides is higher than ethanol, hence SCE reaction required longer reaction time to achieve optimum yield compared to SCM reaction.

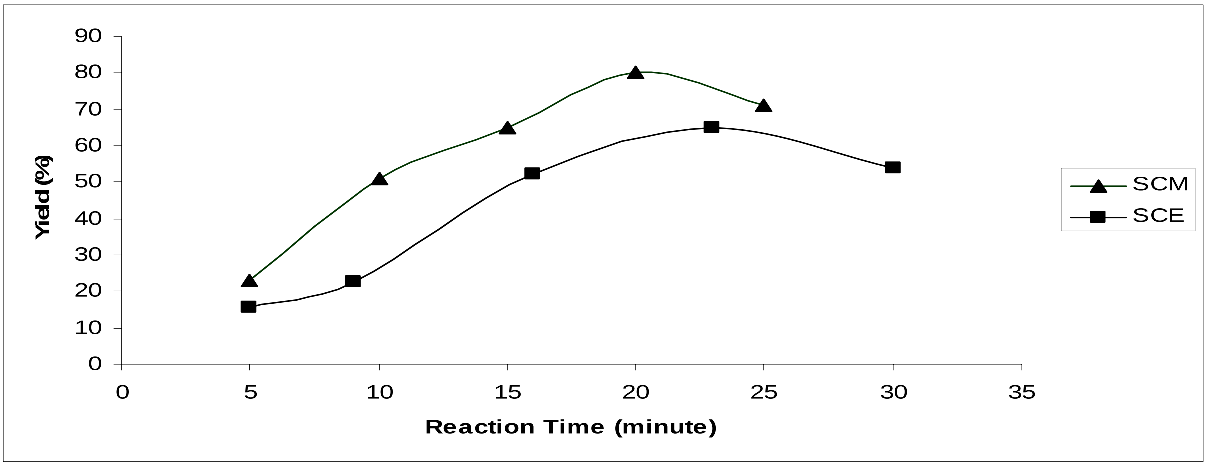

Figure 2: Comparison between SCM and SCE reactions on the influence of reaction time in biodiesel production.

Effect of alcohol to oil molar ratio

In supercritical alcohol reaction, excessive amount of methanol is employed in order to shift the equilibrium towards producing more biodiesel [10, 11]. In this study, the molar ratio of alcohol to oil was varied from 15 to 60 to investigate the effect of molar ratio on biodiesel production as shown in Figure 3. Other parameters such as temperature and reaction time were kept at optimum values as discussed earlier. From the figure, the yield increased steadily when the molar ratio increased from 15 to 40 for both SCM and SCE reactions. However, when the molar ratio exceeded the optimum value of 40, the yield of biodiesel suffers a slight drop. Although enormous amount of alcohol can enhanced the reaction rate, excessive concentration of alcohol in the reaction mixture can inhibits transesterification reaction. Moreover, purification process of biodiesel becomes energy intensive due to the extreme amount of alcohol in the product mixture. Hence, the molar ratio of alcohol to oil should be kept at 40 in supercritical alcohol transesterification reaction.

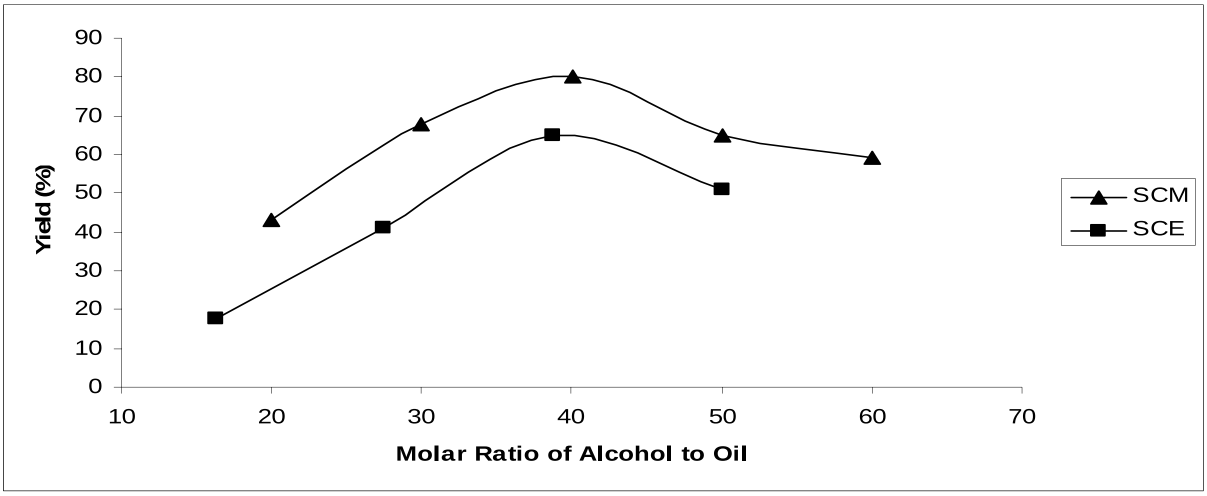

Figure 3: Effect of alcohol to oil molar ratio in SCM and SCE reactions on the yield of biodiesel.

Comparison between SCM and SCE reactions

In this study, supercritical alcohol transesterification were carried out by using two types of alcohol, which were methanol and ethanol. The effect of temperature, reaction time and molar ratio of alcohol to oil were investigated. It was found that both alcohols could be used in supercritical reaction and the yields of biodiesel were very promising. Comparatively, SCM has been shown to be more suitable to be used in biodiesel production compared to SCE. In term of optimum yield, the performance of SCM is superior to SCE with the values of 80% and 65% for the former and latter respectively. Moreover, the reaction time needed is less for SCM than SCE which were 20 and 23 minutes respectively. Although the optimum temperature for SCM is slightly higher than SCE at 360°C and 330°C respectively, the yield of SCE is significantly too low for productivity and economic consideration. As far as molar ratio of alcohol to oil is concerned, both SCM and SCE show an agreement with the optimum value of 40.

CONCLUSION

Supercritical alcohol technology has been shown to be able to produce biodiesel by using methanol and ethanol as the source of alcohol. By comparing SCM and SCE processes, it was found that SCM is significantly better than SCE in terms of reaction time and biodiesel yield. Hence, it can be concluded that methanol-based supercritical reaction is better and more suitable than SCE to be utilized in biodiesel production.

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