Effects Of Free Fatty Acids, Water Content And Co-Solvent On Biodiesel Production By Supercritical Methanol Reaction

Kok Tat Tan*, Keat Teong Lee, Abdul Rahman Mohamed

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia.
* E-mail address: koktat@hotmail.com Fax: +604-5941013.

ABSTRACT

In the present study, non-catalytic supercritical methanol (SCM) reaction was utilized to produce biodiesel from palm oil. The effects of free fatty acids and water content on the yield of biodiesel were investigated and subsequently compared with conventional catalytic reaction. In addition, the feasibility of utilizing co-solvents to reduce the operating conditions needed in SCM was carried out as well. Results show that catalytic reaction suffers from low yield with the presence of high water content in oil. However, it was found that the yield of SCM did not drop but instead increased with the increment of water content. Hence, SCM has been shown to have a high tolerance for water content in oil, which is important in order to utilize other sources of triglycerides such as waste cooking oil. On the other hand, non-polar solvents such as heptane were found to have potential to decrease the temperature required in the reaction.

INTRODUCTION

Generally, alcohol and vegetable oil are not miscible to form a single phase of solution which leads to the introduction of catalysts to improve the reaction rate. However, the presence of catalysts, either homogeneous or heterogeneous causes some other problems to arise in the process. For instance, application of homogeneous catalyst such as sodium hydroxide in high free fatty acids (FFA) content of oil causes the catalyst to react with FFA to produce saponified product [1]. Consequently, complex purification and separation steps are needed to obtain pure biodiesel in the downstream process. Hence, it is well known that FFA content in oil should be minimized when homogeneous catalyst is applied. On the other hand, the presence of water in vegetable oils/fats should be minimal as well since water can consume catalyst and reduce efficiency.

Recently, we have developed a non-catalytic SCM process to produce biodiesel from triglycerides/fats. The optimum condition of the SCM method is at 360°C, 22 MPa and reaction time of 20 minute with a molar ratio of alcohol to oil of 40. As there is no catalyst involved, SCM method was found to have high tolerance of FFA and water content. Previously, there has been a reported study on the effect of FFA and water content in homogeneous catalysts [2]. However, with the growing interest in heterogeneous catalyst in biodiesel production, this study aims to investigate these effects on solid catalysts and subsequently compared with SCM treatment.

As supercritical conditions require high temperature and pressure, applicability of co-solvent to reduce the operating conditions was conducted as well. In this study, heptane was utilized as a non-polar co-solvent which helps to dissolve triglycerides and subsequently increases the mutual solubility between oil and alcohol. Although numerous studies have been carried out regarding co-solvents, to be best of our knowledge this is the first study which apply heptane as potential co-solvent in supercritical treatment [3, 4].

MATERIALS AND METHODS

Materials

Purified palm oil was purchased from Yee Lee Edible Oils Sdn. Bhd., Malaysia. Methanol, heptane and pure palmitic acid were purchased from Merck (99%). Methyl heptadecanoate (used as internal standard), solid catalyst Montmorillonite KSF and standard references for methyl esters analysis which include methyl myristate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate were obtained from Fluka Chemie. All those standards were used without any prior purification.

SCM process

The non-catalytic SCM transesterification reaction was carried out 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. Experiments were conducted at optimum conditions of 360°C, 22 MPa and reaction time of 20 minute with a molar ratio of alcohol to oil of 40. To investigate the effect of FFA on biodiesel yield, initially a pre-determined amount of palmitic acid was measured and added into the reaction mixture. Similar procedure was applied to study the effect of water except water was purposely added, instead of palmitic acid.

Catalytic process

Heterogeneous catalytic reaction was carried out by using Montmorillonite KSF as catalyst in order to investigate the effect of free fatty acids and water content in oil. The catalytic reaction was carried out by using an electrothermal mantle with temperature controller, two-neck round bottom flask with a reflux system and a magnetic stirrer. A pre-determined amount of palmitic acid or water was measured and added to reactant mixtures of oil, methanol and catalyst. The reaction conditions for heterogeneous treatment was set at 190 oC, reaction time of 3 hours, molar ratio of oil/methanol at 1:8 and amount of solid catalyst of 4 wt%. These optimum conditions were chosen based on the optimization studies carried out by Kansedo and co-workers [5].

Co-solvent application

Heptane was utilized as co-solvent in SCM process as discussed earlier. The experiments were conducted at a temperature range of 240-320°C and heptane to methanol molar ratio of 0.05 to 0.20. Other parameters such as reaction time and alcohol to oil molar ratio were kept at optimum conditions.

RESULTS AND DISCUSSION

Effect of water

Water content in oil is a major concern which could adversely affect the yield of biodiesel. Hence, in this experiment water is purposely added to reaction mixtures with varied amount from 4 to 20% for SCM method and 5% to 15% for KSF reaction, respectively. As shown in Figure 1, the yield of biodiesel in SCM treatment is not affected by the presence of water in oil. Instead, the yield increased steadily with increasing amount of water content. On the other hand, the yield of KSF reaction suffers a significant drop from 80% to 13% when the water content increased from 0% to 15%. This might be due to the inhibition of acidic KSF catalyst by water since it has a strong affinity for acidic compounds. Hence, the efficiency of catalyst to catalyze transesterification reaction will be severely affected and low yield was observed. Hence, SCM treatment is superior to catalytic reaction in term of water tolerance which is important to utilize wide range of edible and non-edible triglycerides/fats as feedstock which usually contain high portion of water.

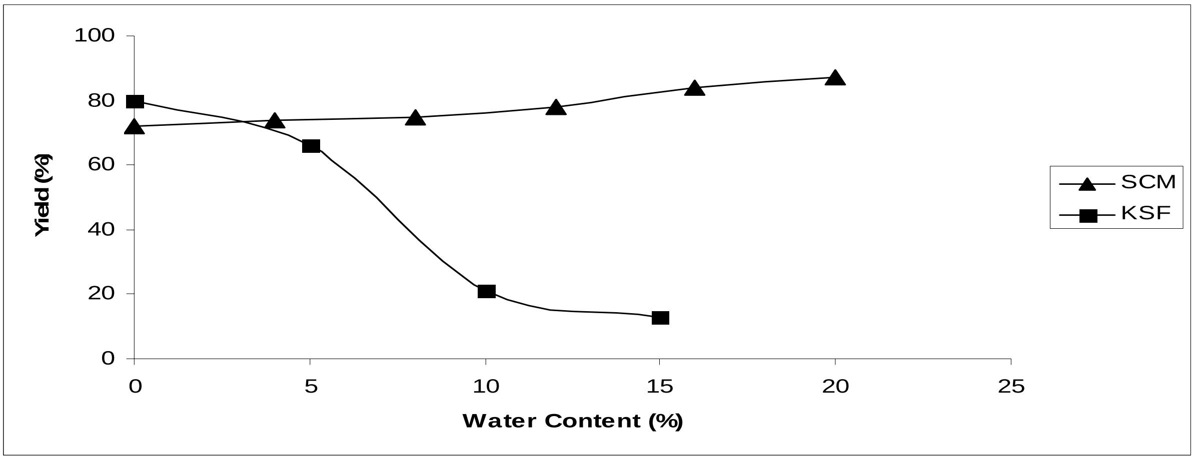

Figure 1: Effect of water content on the yield of biodiesel for SCM and KSF reaction.

Effect of Free Fatty Acid (FFA)

Apart from water, FFA content in triglycerides sources is also one of the major nuisances in biodiesel production. However, as shown in Figure 2, FFA contained in oil does not affect negatively the yield of biodiesel. Heterogeneous catalyst such as KSF is capable to esterify the FFA since the catalyst is in different phase and no side reaction occurs. On the other hand, for SCM treatment, the yield is not sensitive to the presence of FFA as well since the FFA can be simultaneously esterified with methanol to produce methyl esters. Compared to homogeneous reaction involving established catalysts such as sodium hydroxide, the reported yield of biodiesel is very low due to the side formation of soap from FFA and sodium. Hence, the biodiesel yield of SCM in high-FFA oils is comparable with conventional heterogeneous catalysts such as Montmorillonite KSF.

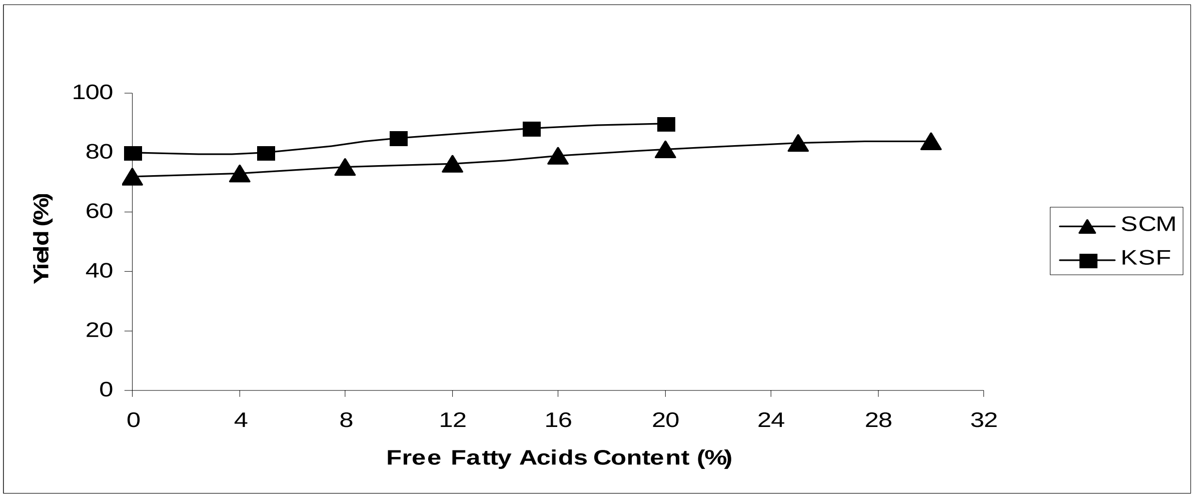

Figure 2: Effect of FFA content on the yield of biodiesel for SCM and KSF reaction.

Application of co-solvent

Utilization of co-solvent in SCM method is an important aspect of research that need to be carried out to improve the process. The introduction of heptane inside the reaction mixture will reduce the critical point of the mixture and subsequently lower the operating conditions as well. As shown in Figure 3, considerable high yield of biodiesel can be achieved at lower temperature with the addition of heptane compared with those without co-solvent. Without co-solvent, the optimum conditions were found to be at 360°C and 22 MPa with the yield of 80%. However, when a small amount of 0.2 molar ratio of heptane to methanol was added, a substantial amount of 66% could be achieved at relatively lower temperature and pressure of 280°C and 15 MPa respectively. On the other hand, the relationship between molar ratio of heptane to methanol and optimum temperature is shown in Figure 4. It can be observed that the optimum operating condition of SCM decrease significantly with the increment of heptane to methanol molar ratio until it reaches the constant temperature of 280°C. Hence, it can be concluded that heptane has a high potential to be utilized as co-solvent in supercritical alcohol technology.

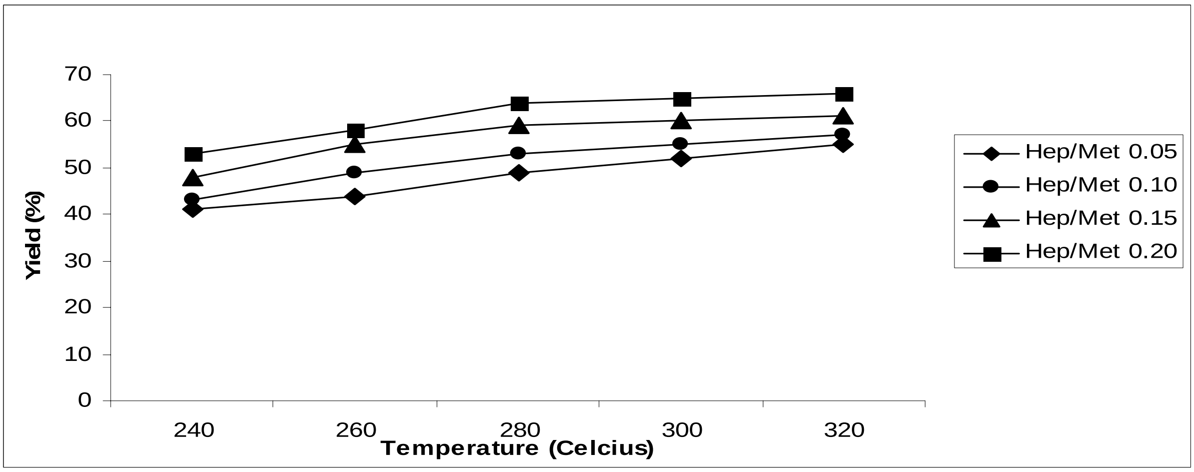

Figure 3: Effect of heptane as co-solvent in SCM reaction as a function of temperature

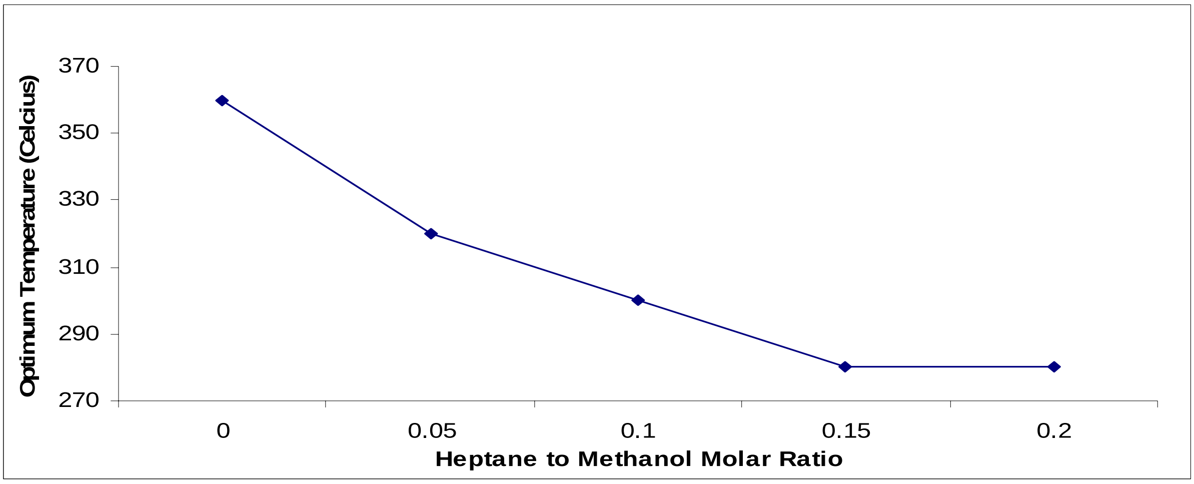

Figure 4: Effect of heptane to methanol molar ratio on the optimum operating temperature

CONCLUSION

Effects of water and FFA content in triglycerides/fats were investigated in SCM and heterogeneous catalytic reactions. It was concluded that SCM process has a high tolerance for water and FFA while solid catalyst suffer from adverse effect of deactivation when expose to triglcyerides/fats containing high water content. On the other hand, the potential of heptane as co-solvent to reduce the operating conditions in SCM reaction was investigated as well.

ACKNOWLEDGMENT

The authors would like to acknowledge Ministry of Science, Technology and Innovation (Malaysia) (ScienceFund-Project No: 03-01-05-SF0138) and Universiti Sains Malaysia for the financial support given.

REFERENCES

[1] Saka, S. and Kusdiana, D., Fuel, Vol. 80, **2001**, p. 225.

[2] Kusdiana, D. and Saka, S., Bioresource Technology, Vol. 91, **2004**, p. 289.

[3] Han, H., Cao, W. and Zhang, J., Process Biochemistry, Vol. 40, **2005**, p. 3148.

[4] Yin, J.-Z., Xiao, M. and Song, J.-B., Energy Conversion and Management, Vol. 49, **2008**, p. 908.

[5] Kansedo, J., Lee, K.T. and Bhatia, S., Biomass and Bioenergy, *In Press*.