Application of limestone as based catalyst in transesterification of rubber seed oil in biodiesel production

M.M. Zamberi[1,2,3], I.A.K.M. Safari[1,2], N.H. Razak[1,2], F.N. Ani[3,*], M.F.B. Abdollah[1,2]

[1)] Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[2)] Centre for Advanced Research on Energy, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[3)] Department of Thermodynamics and Fluid Mechanics, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

[*]Corresponding e-mail: farid@mail.fkm.utm.my

Keywords: Limestone; rubber seed oil; biodiesel

ABSTRACT – The effect of using natural limestone as heterogeneous catalyst on the transesterification of high free fatty acid rubber seed oil with methanol was carried out to produce a quality biodiesel. Affecting variables such as methanol to oil molar ratio and catalyst concentration were investigated. The catalyst was calcined at 900ºC and were characterized using XRD, SEM and XRF. The results revealed that the CaO catalyst derived from limestone was very clean, easy to used and can maintain a good catalytic activity after being used for several times and can reached up to 88.06% biodiesel yield.

1. INTRODUCTION

Biodiesel feedstock from non-edible plants is now gaining much attention due to the great concern of food demand when opting edible plants as raw feedstock especially in the developing countries. The option of non-edible oil over edible oils can overcome the problems of environmental, economic issues and high cost feedstock related to edible vegetables [1]. Calcium oxide (CaO) catalyst is one among the most promising heterogeneous catalyst that can be classified having an eco-friendly characteristic and value added to the green biodiesel process [2]. Natural limestone is one of the good CaO resources where its major component, calcium carbonate ($CaCO_3$) will convert into calcium oxide and carbon dioxide under very high temperature.

This study was undertaken to investigate the performances of the heterogeneous catalyst derived from natural limestone on the production of biodiesel from high free fatty acid (FFA) rubber seed oil (RSO) with methanol to boost up the process performances.

2. METHODOLOGY

2.1 Material selection and catalyst preparation

Crude rubber seed oil (RSO) was purchased from Kinetics Chemical (M) Sdn Bhd, Malaysia. The physical characteristics of the RSO were conducted and the test result was tabulated as in Table 1. The limestones were purchased from Damai Kuari, Sdn Bhd, Kelantan, Malaysia. The limestones were later crushed and grounded using pestle and mortar and sieves into different particles sizes (2 mm- 4mm). Then it was calcined in a furnace at 900ºC with a heating rate of 10ºC/min for 4 hours to convert calcium carbonate, $CaCO_3$ into calcium oxide, CaO. The calcined samples were then kept in desiccators to prevent from any contamination.

Table 1 Properties of methyl ester of crude RSO.

Test	Unit	Method	Results
Acid Value	mg KOH/g	ASTM D664	78.9
Iodine Value	(g I_2/100 g)	AOCS Id 3-92	129.8
Water Content	%wt	EN ISO 12937	0.44
Kinematic viscosity @ 40ºC	mm^2/s	ASTM D7042	32.96
Density@ 15˚C	kg/L	ASTM D4052	0.9248

The chemical composition of cockle was observed using X-ray fluorescence in- build XRD (ARL 8660S) and scanning electron microscopy with energy dispersive X-ray detector (SEM-EDS) technique. The SEM-EDS technique was used to obtain the information of the morphology and elemental composition of the samples.

3.1 Esterification and transesterification

The esterification process is needed in order to reduce the high FFA content of the crude RSO. The process is prepared in the presence of 10 wt% sulphuric acid (H_2SO_4) in reference to the mass of oil and methanol. The treated oil was separated and collected and the amount of FFA content remaining is determined before conducting the transesterification process.

The acid value of crude RSO reduced from 78.9 mg KOH/g to 1.45 mg KOH/g after conducting the esterification process. Transesterification process is carried out by heating 50g of rubber seed oil to ±64ºC on a constant temperature with magnetic stirrer. At the same time, methanol and the catalyst were added, mixed and heated up to 60°C and was stirred at all-time throughout the transesterification process. Upon the reaction completion, the catalyst is filtered out and the end product was poured into a separation funnel and was left overnight for separation process. The lower layer which is glycerol is drawn out and the excessive

amount of methanol was evaporated. The product obtained which is the biodiesel was taken out for further properties analysis. The yield obtained was calculated using the formula shown below:

$$\text{FAME Yield (\%)} = \frac{\text{Total weight of FAME}}{\text{Total weight of oil}} \text{x100} \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1 Characterization of calcined limestones

The elemental composition analysis of the calcined sample with XRF spectroscopy was tabulated as shown in Table-2. XRF analysis showed that the sample was composed mainly of calcium oxide with 58.41wt.%. These results indicated that all calcium carbonate ($CaCO_3$) in the samples was completely transformed to CaO. Typically, plenty of Calcium (Ca) and Oxygen (O_2) were observed.

Figure 1 show the surface morphologies of the calcined heterogeneous catalyst which gave an irregular in shape and some of them bonded together as aggregate. Spot of analyzed (EDS) consists plenty of calcium and oxygen.

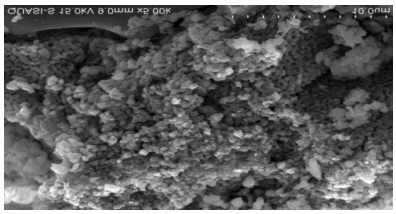

Figure 1 SEM images of the heterogeneous limestones calcined at 900°C for 4 h.

Table 2 Chemical composition of calcined limestone with XRF-XRD.

Formula	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	SO_3
Concentration (%)	58.41	21.81	0.21	1.43	1.04	0.64

3.2 Effect of variables on transesterification process

As shown in Figure 2, the yield conversion was increased from 66.82% at 6:1 molar ratio to 88.06% at 16:1 molar ratio. This result is consistent with previous findings [3] which found that the amount of molar ratio of methanol to oil at the ratio of 10 or lower than that is not sufficient enough to dissolve the oil and catalyst phase.

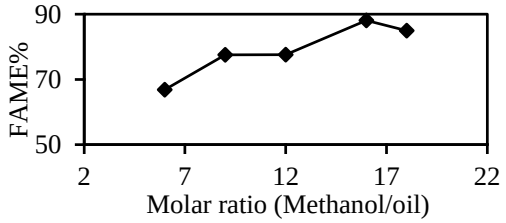

Figure 2 Effect of methanol to oil molar ratio on the biodiesel yield.

Figure 3 show the effects of catalyst loading. The highest yield of 88.06% was obtained within 3h reaction time by using 9 wt.% of catalyst. However, the yield conversion was decreased to 64.22% after amount of the catalyst increased up to 25 wt.%. This is in line with previous study [4] which reported that the catalyst concentration levels greater than 9 wt% may not able to promote the reaction to form more products because it is already achieved the equilibrium state. The fuel properties of the biodiesel produced from heterogeneous RSO methyl esters are compared with biodiesel and petro diesel standards and most of the physico-chemical properties of RSO methyl ester are comparable to those of biodiesel standard and petro-diesel.

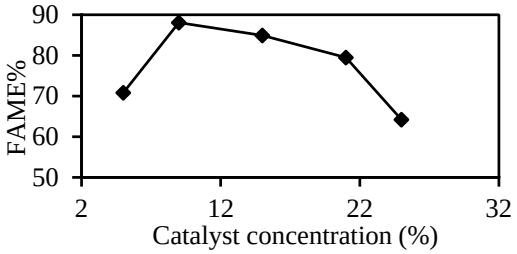

Figure 3 Effect of catalyst concentration on the biodiesel yield.

4. CONCLUSIONS

Overall biodiesel yield conversion was found as high as 88.06%. Molar ratio of methanol to oil and catalyst loading played major role in the production process. Using ratio of 16:1 methanol/oil, catalyst percentage about 9 wt.% and about 3 h reaction time the optimum yield was achieved. Limestones was found had high potential to be commercialized as a green low cost heterogeneous catalyst.

ACKNOWLEDGEMENT

The authors wish to acknowledge the Ministry of Higher Education Malaysia, UTM for the award of UTM-Research University Grant 4F600 and UTeM for the financial support during the course of this study.

REFERENCES

[1] M.M. Gui, K.T. Lee and S. Bhatia, "Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock, "*Energy,* vol. 33, pp.1646-1653, 2008.

[2] F.N.Ani and A.E. Bakheit, "Heterogeneous Microwave Irradiation Biodiesel Processing of Jatropha Oil," *Applied Mechanics and Materials,* vol.554, pp. 500-504, 2014.

[3] C. Ngamcharussrivichai, W. Wiwatnimit and S.Wangnoi, "Modified dolomites as catalysts for palm kernel oil transesterification," *Journal of Molecular Catalysis A: Chemical*, vol. 276(1-2), pp.24-33, 2007.

[4] J.Gimbun, S.Ali, C.C.S. Charan Kanwal, C.C.S., L. Amer Shah, N.H.M.Ghazali, K.C. Chin and S. Nurdin, "Biodiesel Production from Rubber Seed Oil Using Activated Cement Clinker as Catalyst,"*Procedia Engineering*, vol. 53, pp. 13-19, 2013.