ENHANCEMENT OF BIODIESEL YIELD FROM HIGH FFA MALAYSIAN RUBBER SEED OIL WITH SODIUM METHOXIDE TREATED LIMESTONE

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ABSTRACT

This paper presents the potential of high free fatty acid (FFA) Malaysian rubber seed oil (MRSO) as feedstock for biodiesel production. Pre-calcinated limestone known as clinker was activated using either methanol or sodium methoxide and transesterification was performed under reflux at constant stirring. Mineral composition of the catalyst was analysed using x-ray fluorescence (XRF) with in build x-ray diffraction (XRD) indicates about 66% of CaO content. The rubber seed oil was obtained using both microwave and soxhlet extraction using hexane as solvent. FFA content and fatty acid methyl ester content were determined using gas chromatography mass spectrometry (GC-MS). The methanol activated limestone based catalyst derived from cement clinker showed an efficient conversion (up to 96.7%) of high FFA rubber seed oil to biodiesel, and the biodiesel yield was 75%. The yield of biodiesel improved significantly (up to 88%) when sodium methoxide loaded clinker was used. The results suggest that the sodium methoxide activated catalyst employed in this work was less likely to be negatively affected by moisture and free fatty acids as compared to the methanol activated catalyst. The biodiesel produced in this work is within the limits of specification described by ASTM D6751.

***KEYWORDS**: Biodiesel, cement cinker, Rubber seed oil, Yield enhancement*

1.0 INTRODUCTION

Biodiesel has been for some time considered as the most viable petrodiesel substitute because it can be used in any compression ignition engine without the need for modification. Moreover, biodiesel can alleviate the environmental concern and sustainability issue commonly associated with the traditional petroleum-derived fuels. There are several sources of vegetable oil suitable for production of biodiesel such as palm oil, rapeseed, soy bean, etc. However, these

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sources are also consumed as food;hence banned by the European Union. Subsequently a new avenue of producing biodiesel using a non-edible sources such as the oil-seed from the rubber tree (Hevea Brasiliensis) is explored. Malaysia is rubber producing country with an estimated plantation acreage of 1,021,540 hectares in 2009 (Malaysian Rubber Board, 2011) producing an estimated average of more than 120 thousand tons of rubber seeds annually, and this project aims to utilize these unused seeds to produce biodiesel. The rubber seed contains approximately 40% kernel with 20-25% moisture. The dried kernel contains 40-50% of oil (Ramadhas et al., 2005) which translates into a potential production of over 20 million litres of oil per year. Nonetheles, the rubber seed oil has a high free fatty acid content, which means the use of alkaline catalysts such as sodium hydroxide to produce biodiesel is unfavourable(Ramadhas et al., 2005)due to the formation of relatively large amounts of soaps. Consequently this cause production loss and separation difficulty in purification of the biodiesel produced (Kouzu et al., 2008). Therefore, the current work aims to overcome this issue by using a limestone-based heterogeneous catalyst.

Heterogeneous catalysts have advantages of being reusable, noncorrosive, show greater tolerance to water and free fatty acids (FFAs) in feedstock, improve biodiesel yield and purity, have a simpler purification process for glycerol and are easy to separate from the biodiesel product (Kawashima et al., 2008; Liu et al., 2008; Hsiao et al., 2011). Calcium oxide (CaO) is one of the most common employed heterogeneous catalysts for the transesterification of vegetable oil. In fact, producing biodiesel using CaO as a solid base catalyst has many advantages such as higher activity, mild reaction conditions, reusable and low cost. Liu et al. (2008) showed that CaO powder can yield 95% conversion of soybean oil to biodiesel in the presence of excess methanol (12:1) at temperature of 60 °C and reaction time of 3 h. Hsiao et al. (2011) has achieved 96.6% of conversion of soybean oil to biodiesel using a microwave assisted transesterification with 3% wt. of nanopowder CaO catalyst, methanol/oil ratio of 7:1, reaction temperature of 65°C and residence time of 1 h. However, the use of nanopowder CaO has several drawbacks as the nanopowder is not readily available and hence require a high energy to manufacture.Furthermore, catalyst recovery or separation will be challenging. This work aims to prepare a cheaper catalyst from limestone that is easy to recover apart from providing an efficient conversion of vegetable oil to biodiesel.

Our recent work (Gimbun et al., 2013) on rubber seed oil transesterification using cement clinker based catalyst showed almost perfect conversion (close to 100%); however, yield of biodiesel remain lower than 80%. This is attributed to the glycerol and soap formation especially when using high FFA oil. Recently, Chen et al. (2012) reported significant increases in yield of biodiesel from waste cooking oil using sodium methoxide. Thus, this work aims to study the effect of sodium methoxide to the yield of biodiesel from MRSO.

2.0 MATERIALS AND METHODS

2.1 Chemicals

Chemicals were obtained from various sources, namely Merck Malaysia (dried methanol 99.9%, KOH pellets, hexane HPLC grade), R&M chemicals (diethyl ether), John Kollin Chemicals (ethanol, 99.9%), and Sigma-Aldrich (fuller earth, phenolphthalein, methyl heptadecanoate GC grade, n-hexane, acetone).

2.1 Rubber Seeds and Extraction

Rubber seeds were collected during the maturation period from the rubber tree plantation area located near Kampung Pandan, Kuantan, Pahang, Malaysia. They were washed to remove dirt and stored at 4°C until extraction. Rubber seeds were first de-shelled and dried at 60°C for 3 h. The dried seeds were finely crushed using Waring 800S Commercial Lab Blender and then oven-dried at 45°C overnight. Subsequently 250 g of crushed seed was weighed into a glass jar, and the oil was extracted with 500 ml of n-hexane for 30 min at 64°C and power of 200 W using the Milestone Micro synth ATC-FO 300. The solvent, n-hexane was then separated from the crude rubber seed oil using a rotary evaporator.

2.3 Analysis of MRSO and Biodiesel

The extracted MRSO and biodiesel was being analyzed for its lipid and ester content respectively. Standard ASTM D6751 methods were employed in determining, acid value (ASTM D664), calorific value (ASTM D240), kinematic viscosity (ASTM D445), moisture content (ASTM D2709), flash point (ASTM D93), specific gravity (ASTM D287) and cetane number (ASTM D613).

2.4 Catalyst Activation

Cement clinker, a limestone-based cement intermediate, was obtained from Pahang Cement, Malaysia. Detail chemical composition of the clinker obtained from X-ray florescence with in-build XRD (ARL 8660S) is shown in Table 1 which indicates a significant CaO content (66.6%) useful for transesterification process. Clinker was crushed and ground to reduce the particle size around 200 μm to ensure a large surface area per unit mass. The catalyst activation was performed by soaking with methanol followed by calcination at 700°C for 7 hours in the furnace (Carbolite, CWF1215).

Table 1. Clinker analysis with XRF-XRD

Element	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	P_2O_5	TiO_2
Wt. %	66.61	21.92	6.33	4.00	0.73	0.46	0.92	0.12	0.03	0.30

As the issue on the yield of biodiesel using the methanol treated limestone catalyst become apparent, another catalyst was prepared using sodium methoxide. The pre-calcinated limestone (clinker) was treated with various concentrations of sodium methoxide ranged from 0.2 wt% to 0.5 wt% by dissolving the mixture in methanol and 6 wt% of clinker. Methanol was recovered by heating up the mixture at 60°C, followed by calcination at 700°C for 5 hours.

2.5 MRSO and FAME Analysis

Oil and FAME composition of seed oil was determined using gas chromatography mass spectroscopy (GC-MS) according to ASTM D6584. Samples from the extraction and biodiesel production process were taken and dissolved in HPLC grade hexane before being injected into the GC-MS. Tri-acylglycerides (TAG) analysis was performed on Agilent 7890A GC System equipped with Agilent 7683B Series Injector, 5975C Inert MSD and a DB-1 column (30 m × 0.25 mm × 0.25 μm films), with a temperature range of 60 – 340°C, while the FAME produced were analyzed on HP-5 column (30 m × 0.25 mm × 0.25 μm) with a temperature range of 60°C to 325°C. Identification of the peaks was performed by comparing retention times with those of library standards analyzed under the same conditions. FAME and fatty acid composition was determined as in Table 2. The most abundant fatty acids in RSO were linoleic, stearic, and palmitic acids. While the FAME is mainly of methyl linolelaidate and methyl vaccinate.

Table 2. FAME and Fatty Acid composition of RSO

Properties	This work	Ramadhas et al. (2005)
Fatty acid composition (%)		
Palmitic acid C16:0	10.29	10.2
Stearic acid C18:0	8.68	8.7
Oleic acid C18:1	20.07	24.6
Linoleic acid C18:2	58.5	39.6
Linolenic acid C18:3	0.8	16.3
FAME content (%)		
Methyl palmitate	7.7	
Methyl stearate	3.9	
Methyl linolelaidate	43.2	
Methyl vaccenate	45.1	
Others	3.1	
Specific gravity	0.92	0.91
Calorific value (MJ/kg)	38.96	37.5
Acid value (mg KOH/g)	35.14	34
Moisture content (%)	0.26	
FFA (as palmitic wt%)	3.4	

2.6 Transesterification and Purification of Rubber Seed Oil

The catalyst of various amounts ranging from 3 to 7 wt% was dispersed in methanol at temperatures from 50 to 70°C for a period of time prior to contact with the preheated feedstock, providing a robust transesterification catalyst system. Transesterification was performed at various residence times ranged from 0.5 to 4 h with aid of agitation. Water soluble methanol and glycerol were removed by washing intensely with water. The biodiesel produced was filtered to remove the catalyst and residual methanol was vacuum evaporated. Fuller earth was used to reduce the moisture content of the product. Eppendorf 5810R centrifuge was used to remove the fuller earth, residual catalyst and glycerol followed by analysis of its properties according to ASTM D6751 standard. All experiments were repeated three times, and the value reported in this paper was the average value.

3.0 RESULTS AND DISCUSSION

3.1 Factors Affecting MRSO Conversion

Theoretically, the stoichiometry of transesterification reactions requires 3 moles of alcohol for every mole of triglyceride in order to produce 3 moles of methyl ester and 1 mole of glycerol as a by-product. However, it is not always possible to achieve an optimum transesterification using a 3:1 ratio since yield of glycerol and conversion is not always perfect. Results in Fig. 1 show the increasing trend of the conversion rate with the methanol/oil molar ratio ranging from 2:1 to 4:1, but afterwards shows a slight decline in conversion rate with the methanol/

oil molar ratio going from 5:1 to 6:1. At first, excess methanol increases the solubility of the by-product (glycerol) which then may initiate the reversible reaction to reduce the conversion (Hsiao et al., 2011). The optimum methanol/oil molar ratio was observed at 4:1. Excess methanol can be removed easily by washing with water, and its residual may be removed using rotary evaporator.

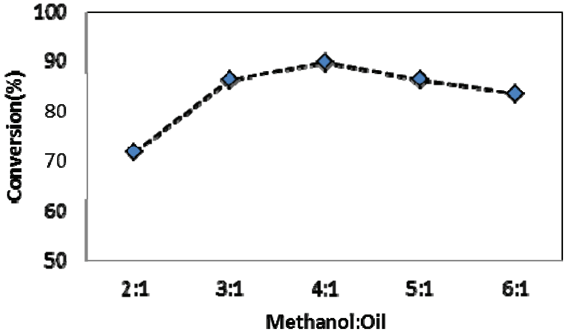

Figure 1. Effect of methanol to oil ratio (4 wt.% catalyst, 55°C)

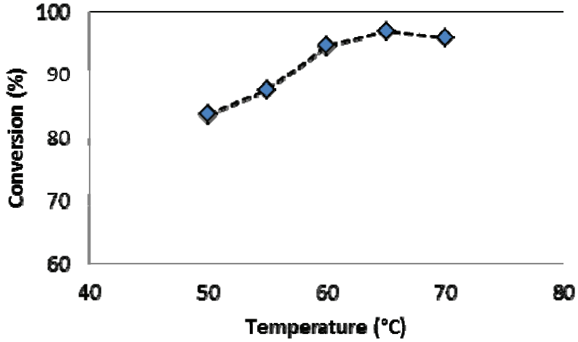

Figure 2. Effect of temperature
(methanol: oil 4:1, catalyst loading 5% wt.)

Generally, as the reaction temperature increases, the rate of reaction increases as they are affected by temperature through the Arrhenius equation. Fig. 2 shows the conversion increases from 65.4% to 96.9% when the temperature increased from 40°C to 60°C. Higher temperature improves the efficiency of transesterification, which in turn enhances the RSO conversion. However, increasing the temperature above 60°C does not significantly affect the RSO conversion; in fact, conversion reduces slightly to 95.8% when temperature increases to 70°C. This is due to methanol evaporation at temperature higher than 64.7°C (methanol boiling point) and hence oil to methanol ratio cannot be maintained to achieve a desirable reaction. Optimum temperature for RSO transesterification with limestone based catalyst is around 60°C.

Fig. 3 shows the conversion of RSO to biodiesel increases when the amount of catalysts increased from 0.5 to 3.5 wt.% with the methanol to oil ratio of 6:1, agitation speed of 400 rpm and temperature of 60°C, but decreased when the amount of catalysts exceeded 4 wt.%. This is due to reversible nature of the transesterification process (Darnoko, 1999) whereby the catalyst concentration levels greater than 5 % may have favoured the backward reaction. The results suggest that optimum catalyst loading for RSO transesterification is 3.5 wt.% with conversion of 96.7%.

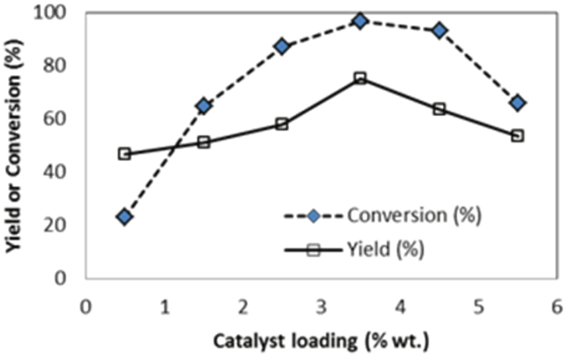

Figure 3. Effect of catalyst loading (Methanol:Oil 6:1, 60°C)

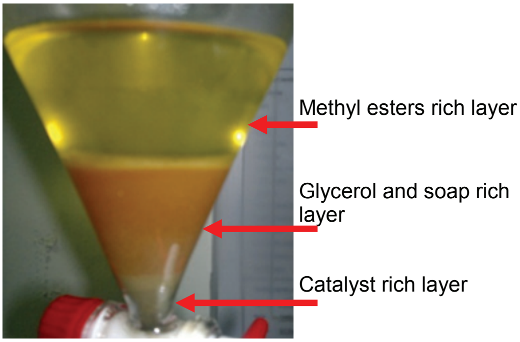

Figure 4. Commonly observed three distinguished layers after MRSO transesterification

It is also interesting to observe from Fig. 4 that the yield of biodiesel (FAME) is actually quite low (≤ 75%) even though the conversion is at maximum 96.7%. This is because some portion of the oil is converted to glycerol instead of methyl esters. A distinctive three layers of methyl ester, glycerol and soap, and the solid catalyst can be observed from Fig. 4, which shows the typical product of a MRSO transesterification with heterogeneous catalyst. A considerable amount of glycerol is produced since one mole of glycerol is produced for every three moles of methyl esters. Furthermore, high FFAs oil such as MRSO tends to produce soap with base catalyst. Sodium methoxide has been reported recently (Chen et al., 2012) to significantly increase the yield of biodiesel from waste cooking oil. Further assessment of their effectiveness on MRSO is reported in the next section.

3.2 Enhancement of Biodiesel Yield with Methoxide Loaded Catalyst

A fixed amount of clinker (0.6 wt%) with various loading of sodium methoxide ranged from 0 to 0.6 wt%, was used for MRSO transesterification with methanol to oil ratio of 7:1 at a temperature of 60°C for 4 hours. As shown in Fig. 5, the yield increased with increasing amount of sodium methoxide loading from 0.20 wt% to 0.5 wt%, and then decreased from 0.5 wt% to 0.6 wt%. The best yield (88%) was obtained with clinker loaded with 0.5 wt% of sodium methoxide. In contrast similar process without sodium methoxide only yielded 61.5% of biodiesel. These results indicate that although excess catalyst might increase the biodiesel yield, the amount of glycerin produced is also increased due to saponification, causing a reduction of biodiesel yields (Chen et al., 2012). A further increase in catalyst concentration did not increase the conversion and led to extra costs due to its removal from the reaction medium at the end of the process Dorado et al., 2004). In this study, the best yields were achieved with 0.6 wt% of clinker loaded with 0.5 wt% of sodium methoxide for MRSO. The yields of biodiesel with sodium methoxide loaded catalyst were higher than those for methanol activated catalyst.

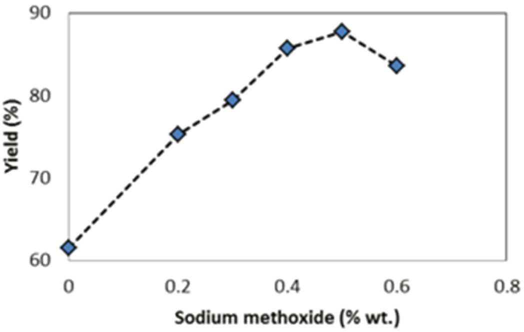

Figure 5.Effect of sodium methoxide to biodiesel yield

Table 3. Properties of MRSO Biodiesel

Properties	**ASTM**	**Limits**	**This work**	**Ramadhas et al. (2005)**
Kinematic Viscosity, 40°C (mm^2/s)	D445	1.9 - 6.0	4.64	5.81
Flash point (°C)	D93	> 130	154.6	130
Specific Gravity	D287	0.82 - 0.9	0.87	0.87
Acid value (mg KOH/g)	D664	< 0.50	0.07	0.8
Cetane number	D613	> 47	66.2	43
Calorific value (MJ/Kg)	D240	--	39.37	36.5

3.3 Properties of Methyl Esters from Rubber Seed Oil

The fuel properties of FAME produced in this work is compared with Ramadhas et al. (2005), who studied rubber seed oil transesterification using a homogeneous catalyst (NaOH). Their work requires a two-step method of acid esterification followed by base transesterification. This work is a single step method which involved only the transesterification process. As shown in Table 3, all the properties are within the biodiesel specification described by ASTM D6751. The calorific value of in this work seems to be slightly higher than the previous work by Ramadhas et al. (2005); furthermore, the kinematic viscosity and acid value are very much lower in comparison. The cetane number of 66.2 for biodiesel produced in this work is better than the previous work byRamadhas et al. (2005) and compliance to the ASTM standard. The good biodiesel property in this work is attributed to extensive the purification step undertaken to the FAME which includes among other washing, centrifugation and bleaching.

4.0 CONCLUSIONS

The methanol activated limestone based catalyst derived from cement clinker showed an efficient conversion (up to 96.7%) of high FFA rubber seed oil to biodiesel, and the biodiesel yield is 75%. The yield of biodiesel improved significantly (up to 88%) when sodium methoxide loaded clinker was used. The results suggest that the sodium methoxide activated catalyst employed in this work is less likely to be negatively affected by moisture and free fatty acids as compared to the methanol activated catalyst. The biodiesel produced in this work is within the limits of specification described by ASTM D6751.

5.0 ACKNOWLEDGEMENT

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