5[th] World Conference on
Applied Sciences, Engineering & Technology
02-04 June 2016, HCMUT, Vietnam

Studies of Biodiesel Production from Rubber Seed Oil and Testing of Performance Characteristics in a Diesel Engine

NGUYEN THI THANH XUAN[1], DUONG VIET DUNG[2]
[1]Faculty of Chemical Engineering, University of Science and Technology – The University of Danang, Viet Nam
[2]Faculty of Transportation Mechanical Engineering, University of Science and Technology – The University of Danang, Viet Nam
Email: nttxuan@dut.udn.vn, dvdung@dut.udn.vn

Abstract: The results of various researchers support the use of biodiesel as a viable alternative to conventional petroleum fuel for use in diesel engines. However biodiesel production from refined edible type oils such as sunflower, soybean and palm oil causes the risk of competition with food and land. This increases the overall production cost of the biodiesel as well which is not economical. Hence, it is better to use the non-edible type of oil for biodiesel production. The aim of this paper is to study the suitability of locally available rubber seed oil in Vietnam as substitutes to conventional diesel fuel in diesel engines. The significant properties of rubber seed oil include oil content, water content, acid value, saponification numbers, density, viscosity are found out during this investigation. The acid value for rubber seed oil is high (around of 50 mg KOH/g oil). A two-step transesterification method is developed to produce biodiesel from rubber seed oil possessing very high free fatty acid (FFAs). The first step, acid catalysed esterification reduces the FFA content of the oil to less than 2%. The second step, alkaline catalysed transesterification process converts the products of the first step to its mono-esters and glycerol. The major factors affect the conversion efficiency of the process such as molar ratio, amount of catalyst, reaction temperature and reaction duration is analysed. The blends of pure rubber seed oil as well as biodiesel from rubber seed oil via transesterification with conventional diesel were used as fuels in the CI engine and the performance and emission characteristics of the engine were analysed. The experimental results proved that the use of biodiesel produced from unrefined rubber seed oil is a viable alternative to the diesel fuel.

Keywords: *Rubber Seed oil, Biodiesel, Tranesterification method, Engine performance, Exhaust Emissions*

Introduction:

World's energy crisis, global warming, diminishing fossil fuel reserves are raising concerns and inevitability to find more economic and more environmentally friendly solutions to satisfy the current energy consumption. Biodiesel has become more attractive recently because of its environmental benefits [1] and the fact that it is made from renewable resources such as vegetable oils or animal fat. As a substitute fuel, biodiesel can be used in efficient form or in mixed form with petroleum-based diesel without the need for diesel engine modification [2]. The cost of biodiesel, however, is the main hurdle to commercialization of the product. The major cost of production of biodiesel is feedstock and therefore, choosing the paramount feedstock is essential to ensure low production cost. Most previous studies focused on edible oil such as sunflower [3], soybean [4], [5], rapeseed oil [6] coconut, and palm oil [7]. The prices of these edible vegetable oils are higher than diesel fuel. This increases the overall production cost of the biodiesel as well which is not economical. Therefore waste vegetable oils and non-edible vegetable oils prefer in place of edible vegetable oils for production of biodiesel. It has also been found that the continuity in transesterification process is another choice to minimize the production cost. Biodiesel is currently not economically feasible, and more research and technological development are needed. Thus supporting policies are important to promote biodiesel research and make their prices competitive with other conventional sources of energy. Currently, biodiesel can be more effective if used as a complement to other energy sources [8].

Using non-edible oils for the production of biodiesel over edible oil sources has many advantages, of which is minimizing the economical and food sacristy impacts resulted from using edible oils, added value to the relevant agricultural industry, contribution to the gross domestic product (GDP) while reducing expenditure over imported fuels, reduction in deforestation rate, diminution in the amount of carbon dioxide and more efficient, productive utilization for the current plantation. Despite the previously instated facts, the current amount of non-edible oils available does not meet the required quantities for industrial production. However the potential exists, especially in tropical countries where such plantation grows abundantly. In Vietnam, rubber seed is currently a waste and lack of utilization whereas the potential of rubber seed oil is abundant. By the end of 2012, the country's rubber plantation area accounted for 910,500 ha. This total continues to expand, not only domestically but also due to expansion of Vietnamese rubber companies in neighboring countries such as the Laos PDR and Cambodia [9]. Rubber plant is one of the producers of vegetable oils obtained from seeds, with 42% yield of oil [10]. Therefore, rubber seed selected as raw materials in this study because it has not been utilized and there are plentiful numbers.

The aim of this paper is to study the suitability of locally available rubber seed oil in Vietnam as substitutes to conventional diesel fuel in diesel engines. The significant properties of rubber seed oil include oil content, water content, acid value, saponification numbers, density, viscosity are found out during this investigation. The acid value for rubber seed oil is high (around of 50 mg KOH/g oil). A two-step transesterification method is developed to produce biodiesel from rubber seed oil possessing very high free fatty acid (FFAs). The first step, acid catalyzed esterification reduces the FFA content of the oil to less than 2%. The second step, alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and glycerol. The major factors affect the conversion efficiency of the process such as molar ratio, amount of catalyst, reaction temperature and reaction duration is analyzed. The blends of pure rubber seed oil as well as biodiesel from rubber seed oil via transesterification with conventional diesel were used as fuels in the CI engine and the performance and emission characteristics of the engine were analysed.

Materials and Methods:

Oil Extraction

Dried rubber seeds obtained from Kontum province of Vietnam were decorticated manually to separate the kernels from the shells. The kernels were crushed up to size of about 2mm to allow for faster and more oil extraction [11]. The kernels that have crushed up, treated by cooking with steamed in different time (20, 40, 60 and 80 minutes), then pressed with mechanical press. The oil obtained after removing residue and water by filtration and vacuum evaporators system will be weighed and measured in volume and tested characteristics.

In order to evaluate the effectiveness of the above method we used also a soxhlet extractor with n-hexane as the solvent and operated at 60ºC to extract oil.

The percentage oil yield was calculated using equation (1)

$$\text{Oil yield } \% = \frac{\text{Weight of oil extracted}}{\text{Weight of seed kernels used}} \times 100 \quad (1)$$

Characterization of the Oil:

Characterization includes the analysis of rubber seed viscosity, acid number or free fatty acid levels. and triglyceride. Types of free fatty acids and triglyceride oils analyzed by means of GCMS (Thermo Scientific™ ISQ™ LT Single Quadrupole).

Free Fatty Acids (FFA) are the result of the breakdown of oil or biodiesel. FFA% is usually used to describe the FFA content of oils, while Acid Number (AN) is commonly used to describe the FFA content of finished biodiesel. Acid number is the number that expresses, in milligrams the quantity of potassium hydroxide required to neutralize the free acids present in 1 g of the substance.

Free Fatty Acid (FFA) value of the oil was calculated from Acid Number by equation (2)

$$\%FFA = AN \times 0.503 \quad (2)$$

This value aims to determine if pretreatment was necessary or not before alkaline transesterification.

The acid number of rubber seed oil was found to be 37 mg KOH/g (FFA of 18.5%) which was too high for direct alkaline transesterification. This value must be reduced to 2 mg KOH/g in order to yield maximum biodiesel, otherwise alkaline catalyst reacts with FFAs forming soap instead of ester that reduces the biodiesel production [12].

Transesterification Procedure:

Transesterification is the chemical reaction between triglyceride (rubber seed oil) and alcohol to produce monoester and glycerin. This monoester which is biodiesel can be separated and blend with diesel or used directly with no major modification in IC engines. In the case of rubber seed oil the transesterification consists of acid and alkaline transestrification process.

Acid esterification

One liter of crude rubber seed oil requires 200 ml of methanol (equivalent to the alcohol to oil molar ratio of 6:1) for the acid esterification process to achieve the maximum conversion efficiency [13]. The rubber seed oil is poured into the flask and heated to about 50^oC. The methanol is added with the preheated rubber seed oil and stirred for a few minutes. 0.5% of sulphuric acid is also added with the mixture. Heating and stirring is continued for 60 min at atmospheric pressure. On completion of this reaction, the product is poured into a separating funnel for separating the excess alcohol. The excess alcohol, with sulphuric acid and impurities moves to the top surface and is removed. The lower layer is separated for further processing (alkaline esterification).

Alkaline esterification

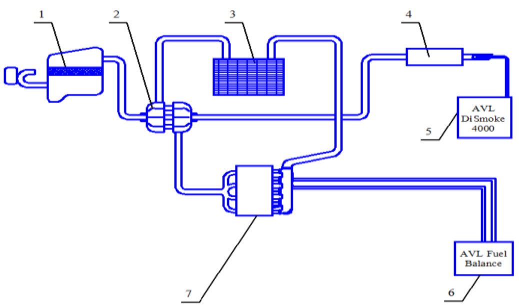
Alkaline catalyzed esterification process uses the experimental setup of acid catalyzed pretreatment process. The products of first step are preheated to the required reaction temperature of 60^oC in the flask. Meanwhile, 5gm of NaOH is dissolved in 300 ml methanol and is poured into the flask. The mixture is heated and stirred for 30 min. The reaction is stopped, and the products are allowed to separate into two layers. The lower layer, which contained impurities and glycerol, is drawn off. The ester remains in the upper layer. Lower layer is discarded and yellow color upper layer known as biodiesel is separated. Methyl esters are then washed to remove the entrained impurities and glycerol and again heated to about 85°C for 15 minutes to remove the moisture content in the biodiesel.

HPLC was used to analyze mono-, di- and triglycerides composition in crude rubber seed oil (CRSO) and in biodiesel from rubber seed oil (BRSO) after the first and second step in order to evaluate the conversion of rubber seed oil.

Engine details and testing:

Experimental engine is Mazda WL – Turbo engine 4-stroke 4 –cylinder with the parameters: Capacity of 2499 cm^3; Maximum torque of 280 Nm/2000rpm; Maximum capacity of 85 kW/3500rpm. The engine were fully mounted sensors to record the parameters of the engine during working such as fuel pump pressure, intake air pressure, exhaust gas pressure, the pressure in the cylinder,…

The engine is linked behind the APA dynamometer , by shaft which is described in scheme below:



1. Air purifiers 2. Turbo 3. Cooling box 4. Catalytic three function 5. Exhaust gas Measuring 6. Fuel consumption Measuring 7. Engines

Figure 1. Laboratory layout

Results and Discussion:

Oil Extraction

A number of rubber seed samples were collected from different locations. The seed kernel was separated and weighted to measure the seed to kernel ratio. A good rubber seed which is not flat, not empty bears a kernel with average wt.% is about 48.33%. However among of collected rubber seed samples, the ratio of the bad seeds is relatively high (14.4%) due to process of gathering, transporting, storing in a long time which reduce the quality of grain. Therefore the seed to kernel ratio is about 42%.

Two methods were used to extract oil from the seed. Table 1 shows the results of rubber seeds oil content obtained by press method in different time of steamed rubber seed kernels.

These results indicate the content of rubber seed oil is in approximately 22-24% and the change of time steamed does not affect strongly the oil content obtained.

Soxhlet method which was carried out base on n-hexane as solvent brought a maximum 38% of the oil extracted. The results was similar with literature [14, 15]. This indicate that by mechanical press method oil is still trapped in the rubber seed meat and must be processed to obtain maximum rubber seed oil content.

Table 1: Measuring of oil content obtained by press method in different time steamed kernels rubber seed

Samples	1	2	3	4
Weight of Seed kernel (g)	300	300	300	300
Time steamed (min)	20	40	60	80
Crude oil vol. (ml)	77	78	78	83
Crude oil weight (g)	69	70.3	71	75.1
Water and residue (%)	2.46	2.77	3.83	5.26
Oil yield (%)	22.43	22.79	22.8	23.72

Synthesis of biodiesel:

The oil collected from all these methods is stored for biodiesel production. The physiochemical properties of the rubber seed oil are investigated and the results are presented in Table 2.

Table 2: Physico-chemical properties of rubber seed oil

Properties	*Experimental value*
Physical state	Liquid
Moisture content, wt.%	0.7–1.0
Specific gravity at 30°C	0.89 – 0.91
Viscosity, mm^2/s at 40°C	33 – 39
Acid Number (mgKOH/g)	32 – 41
FFA, wt.%	16 - 21
*Molecular wt of the oil, g/mole**	875.36

*Calculated from the oil composition reported by Ramadhas et al. [13].

Biodiesel was prepared from the RSO by a two-step method: acid and alkaline esterification. After the first step the acid number must be determined to assure the FFA below of 2%. Effect of reaction time on acid value reduction in the 1st step (initial acid value: 41 mg KOH/g) were investigated and the results showed that just only for at least 1h reaction time with the methanol–oil ratio of 0.2v/v there was a reduction of about 95% in acid value to get the optimum FFA below 2%. This was confirmed in the research of Satyanarayana and Muraleedharan [16].

The transesterification process was optimized for methanol–oil ratio of 0.3v/v and 0.5%w NaOH as alkaline catalyst and reaction temperature at 60°C during half an hour as reaction time. The products are allowed to separate into two layers of glycerin and rubber seed methyl ester.

Table 3 summarizes the results of viscosity, acid number and conversion rate of the converted oil after the first and the second esterification step.

Table 3: Analysis results of viscosity, acid number and conversion rate of the crude rubber seed oil and the converted oil after the first and the second esterification step

Samples	*1*	*2*	*3*	*4*
AN of CRSO (mgKOH/g oil)	33.26	35.9	40.15	32
Viscosity of CRSO (cSt)	33.44	34.32	39.32	35.47
1st conversion (%)	96.67	95.71	91.55	97.14
AN of 1st-step BRSO (mgKOH/g)	3.2	4.6	4.9	3.2
Viscosity of 1st-step BRSO (cSt)	17.93	18.57	19.04	18.92
2nd conversion (%)	94.59	94.42	92.59	95.34
AN of 2nd-step BRSO (mgKOH/g)	0.05	0.08	0.12	0.05
Viscosity of 2nd-step BRSO (cSt)	4.39	4.42	4.62	4.49
Overall conversion (%)	91.44	90.37	84.77	92.61

The results indicate that the two-step transesterification is suitable for biodiesel production from rubber seed oil with high conversion efficiency, above 90% depending on the FFA content in the raw material and the biodiesel properties satisfy the Biodiesel standard ASTM 6751-02. This has been confirmed in the figure 2, 3, 4 which results from HPLC analysis carried out on crude rubber seed oil (CRSO) and the products obtained after the 1st (1st_step BRSO) and the 2nd (2nd_step BRSO) of esterification.

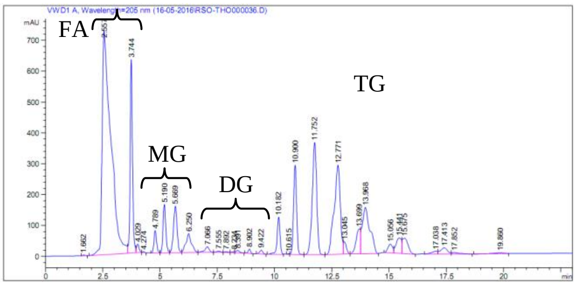


Figure 2: Sample HPLC plot showing peaks for fatty acid (FA), monoglycerides (MG), di (DG) and triglycerides (TG) of CRSO.

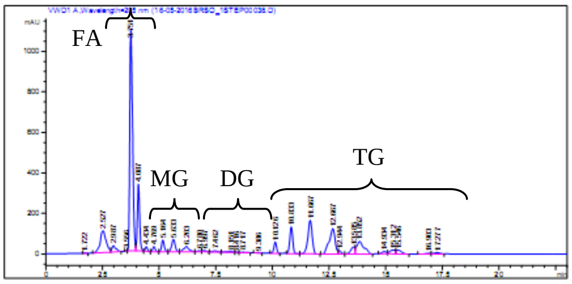


Figure 3: Sample HPLC plot showing peaks for fatty acid (FA), monoglycerides (MG), di (DG) and triglycerides (TG) of 1st_step BRSO

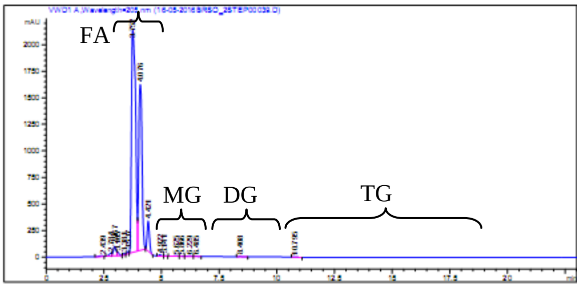


Figure 3: Sample HPLC plot showing peaks for fatty acid (FA), monoglycerides (MG), di (DG) and triglycerides (TG) of 2st_step BRSO

Figure 4 shows the analysis result with GCMS, with the residence time is shown in Table 4.

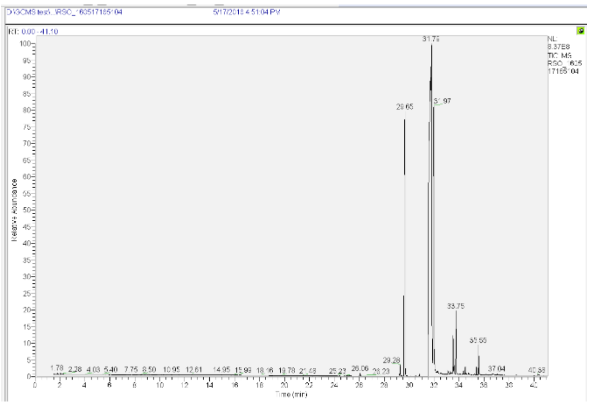


Figure 4: Chromatogram of free fatty oil analysis

Number of free fatty acids is calculated by multiplying the percentage of area with content of oil free fatty acid.

Table 4: Summary of GCMS analysis results of free fatty acids in oils

No	Residence time	Percent (%)	Acid	
1	29.28	0.583	Palmitoleic	C16:1
2	29.65	29.849	Palmitic	C16:0
3	31.78	37.212	Linoleic	C18:2
4	31.97	26.593	Stearic	C18:0
5	32.29	0.160		
6	33.1	0.302	Arachidonic	C20:4
7	33.75	3.298	Ecosenoic	C20:0
8	34.5	0.430		
9	35.55	1.448	Docosanoic	C22:0

Engine testing:

Performance test was conducted on a Mazda WL engine running under steady state operating conditions using ordinary diesel and biodiesel blends (B20, B25, B30). During the experiment the incylinder pressure and the specific fuel consumption were measured.

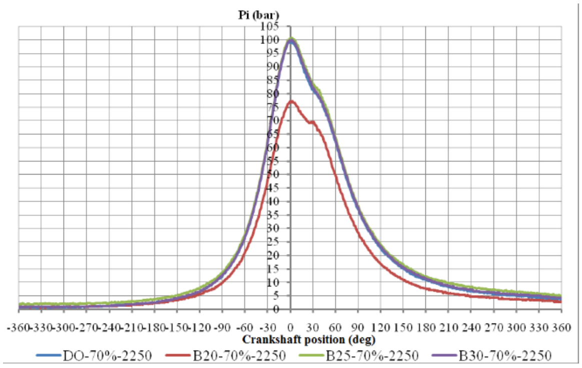


Figure 5: Changes in combustion pressure at 70% - 2250rpm using different fuel (DO, B20, B25, B30)

The results on figure 5 shows that Pi of B25, B30 is roughly equivalent to the one of DO while Pi of B20 is smaller. From this graph we see at 70% loading mode and 2250 rpm, engine power and torque of motor are higher when using biodiesel blends (B20, B25, B30) than using ordinary diesel DO.

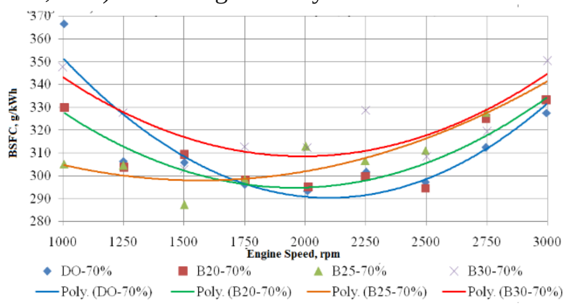


Figure 6: The variation in BSFC using biodiesel blends (B20, B25, B30) and diesel at 70% engine loading mode belong with engine speed

Figure 6 shows the variation in Brake specific fuel consumption (BSFC) using biodiesel blends and diesel at 70% engine loading mode. We can see that BSFC decreases with the increase in engine speed and reaches a minimum (in the maximum torque region) and then increases again. The BSFCs for three of the biodiesel blends were higher than that of diesel fuel in range of engine speed of above 1750 rpm. At the engine speed below this value, the BSFCs for the biodiesel blends were smaller. This results were similar to the experimental survey of Sehmus Altun [17].

Conclusion:

Rubber seed oil is extracted from the seed by different methods which are found to be a promising alternative fuel source. The combine of pressing machine and solvent extraction can get the high yield of oil is 40%. The properties of the rubber seed oil are analyzed. FFA content in the oil is found as high. So that a two-step esterification process comprises acid and alkaline esterification is studied to prepare biodiesel from the oil. Overall yield of FFA from RSO is found to be around 96%. At optimum conditions above 90% conversion of the oil to FAME is obtained. HPLC spectrum of the RSO and biodiesel samples are analyzed which confirms the conversion of RSO to biodiesel. Biodiesel properties are evaluated by standard methods. A significant reduction of viscosity and acid value is found.

An experimental investigation has been carried out on the combustion and performance characteristics of a Mazda WL engine running with biodiesel under steady state operating conditions using different biodiesel blends and conventional diesel fuel. The brake torque with diesel fuel was higher than those with the biodiesel blends. The BSFCs for al of the biodiesels were higher than that of diesel fuel at high engine speed but smaller at low engine speed. This can be explained by the reason that biodiesel fuels have lower heating values than petroleum diesel fuel, and this results in higher BSFC, as affirmed by most studies.

This study revealed that methyl ester of rubber seed oil (Biodiesel) is a suitable substitute to diesel. But still further research work is needed, such as additional property measures, tribological studies, and long-term engine testing, in order to recommend for a full-fledged alternative fuel.

References:

[1] Balat M., (2006), “Fuel characteristics and the use of biodiesel as a transportation fuel”, Energy Sources Part A (28), 2006b, pp 855–864.

[2] Demirbas A.,(2002) “Biodiesel from vegetable oils via transesterification in supercritical methanol”, Energy Convers. Mgmt. (43), 2002, pp 2349–2356

[3] Harrington, K.J., Catherine, D.V., (1985), “A comparison of conventional and in situ methods of transesterification of seed oil from a series of sunflower cultivars”. Journal of the American Oil Chemists' Society (JAOCS) 62, 1009-1013.

[4] Goering C.E., Fry B., (1984) “Engine durability screening test of a diesel oil/soy oil/alcohol microemulsion fuel:, JAOCS 61, 1627-1632

[5] Freedman B., Butterfield R.O., Pryde E.H., (1986), “Transesterification kinetics of soybean oil”, JAOCS 63, 1375-1380.

[6] Strayer R.C., Blake J.A., Craig W.K., (1983), “Canola and high erucic rapeseed oil as substitutes for diesel fuel: Preliminary tests”, JAOCS 60, 1587-1592.

[7] Ooi C.K., Bhaskar, A., Yener, M.S., Tuan, D.Q., Hsu, J., Rizvi S.S.H., (1996). “Continuous supercritical carbon dioxide processing of palm oil”, JAOCS 73, 233-237

[8] Atabania A.E., Silitonga A.S., Irfan Anjum Badruddina, Mahliaa T.M.I., Masjukia H.H., Mekhilefd S., (2012) “A comprehensive review on biodiesel as an alternative energy resource and its characteristics”, Renewable and Sustainable Energy Reviews, Vol. 16, (4) 2012, pp 2070–2093

[9] To Xuan Phuc and Tran Huu Nghi, (2014), “Rubber Expansion and Forest Protection in Vietnam”, Tropenbos International Viet Nam

[10] Mahbub Morshed, Kaniz Ferdous, Maksudur R. Khan, M.S.I. Mazumder, M.A. Islam, Md.T. Uddin, (2011), “Rubber seed oil as a potential source for biodiesel production in Bangladesh”, Fuel 90 (2011) 2981–2986

[11] Sayyar S, Abidin SS, Yunus R, Muhammed A., “Extraction of oil from jatropha seeds optimization and kinematics”, Am. J. App. Sci. 2008;6(7):1390-1395.

[12] Srivastava A., and Prasad R. (2000), “Triglycerides-based diesel fuels”, Renew. & Sustain. Energy Rev. 4:111–133

[13] Ramadhas A.S., Jayaraj S., Muraleedharan C., “Biodiesel production from high FFA rubber seed oil”, Fuel 84 (2005) 335–340

[14] Widayat W. and S. Suherman, “Biodiesel Production from Rubber Seed Oil via Esterification Process”, Int. Journal of Renewable Energy Development 1 (2) 2012: 57-60

[15] Achmad Wildan, Devina Ingrid, Indah Hartati, “Oil Extraction Process from Solid Waste Rubber Seed by Soxhletation and Extraction Solvent by Stirring Methods”, International Conference on Chemical and Material Engineering 2012 ISBN : 978-602-097-281-7

[16] Satyanarayana, Muraleedharan, “Methyl Ester Production from Rubber Seed oil Using Two-Step Pretreatment Process”, International Journal of Green Energy, 7: 84–90, 2010, ISSN: 1543-5075

[17] Sehmus Altun, “Performance and exhaust emissions of a DI diesel engine fueled with waste cooking oil and inedible animal tallow methyl esters”, Turkish J. Eng. Env. Sci. 35 (2011) , 107 – 114