BIODIESEL PRODUCTION FROM RUBBER SEED OIL

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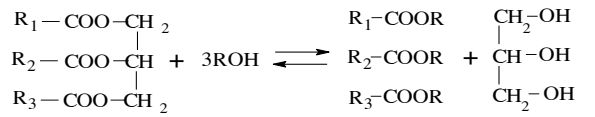
Abstract - World's energy crisis, global warming, diminishing fossil fuel reserves are raising concerns and inevitability to find more economic and more environmentally friendly solutions to satisfy the current energy consumption. The results of various researchers support the use of biodiesel as a viable alternative to conventional petroleum fuel. However, biodiesel production from refined edible oil types such as sunflower, soybean or palm oil causes the risk of competition with food and land that increases the overall production cost of the biodiesel which is not economical. Hence, it is better to use the non-edible types 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, density, viscosity which are found out during this investigation. Rubber seed oil possesses a very high free fatty acid (FFAs), which results in developing a two-step transesterification method to produce biodiesel from rubber seed oil: (1) acid catalyzed esterification reduces the FFA content of the oil to less than 2%;(2) alkaline catalyzed transesterification process converts the products of the first step to its mono-esters and glycerol.

Key words - Rubber Seed oil; Biodiesel; Rubber Seed oil Properties; Tranesterification method; Biodiesel Production

1. Introduction

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats which conform to ASTM D6751 specifications for use in diesel engines. Biodiesel is biodegradable, nontoxic, less harmful to environment, and locally available because it is made from renewable resources and has lower emissions compared to petroleum diesel. Furthermore, it is found to be a good alternative to petroleum products.

Transesterification (alcoholysis) is the chemical reaction between triglycerides and alcohol in the presence of different types of catalyst (acid, base) to produce mono-esters. The long and branched chain triglyceride molecules are transformed to monoesters and glycerin. Transesterification process consists of a sequence of three consecutive reversible reactions. That is, conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides. The glycerides are converted into glycerol and yielding one ester molecule in each step. The properties of these esters are comparable to that of diesel. The overall transesterification reaction can be represented by the following reaction scheme:



Triglycerides Methanol Esters Glycerol

There are different sources of raw materials for biodiesel production. The first generation of biodiesel feedstock come from edible oil sources such as palm oil [1], coconut oil [2]. These oil sources are of significant importance for human nutrition needs specially with increasing food demand worldwide. Various non-edible vegetable oil has developed as a raw material of second generation in production of biodiesel, such as castor oil, jatrophacurcas and rubber seed oil [3]. Jatropha seems to be a promising source of biodiesel as well, especially in case of tropical country like Viet Nam [4]. Research has shown that biodiesel can be obtained from their oil and further analysis on the fuel obtained has concluded that it meets the standards [5]. The Ministry of Agriculture and Rural Development in Viet Nam approved Decision No. 177/2007/QD-TTg as "Approval of National Program on jatrophacurcas research, development in Vietnam for the period 2008 – 2015, with an outlook up to 2025". It has been decided that tested plantation and production of jatropha and its products in different geographical regions throughout the country should be implemented during the period 2008 – 2010 with the set targeted area of tested jatropha plantation and production of 30000 ha by 2010 and of 300000 ha by 2015 and 500000 ha by 2025. However, as survey by Agrinergy [6], due to both technical and financial difficulties caused by the economic crisis, a number of jatropha projects have been cancelled, reducing the number of on-going projects from more than 30 projects in 2010 to only 07 projects in 2012. On the contrary, rubber seed is a waste and lacks utilization, currently. The potential of rubber seed oil in Viet Nam is abundant. By the end of 2012, the country's rubber plantation area accounted for 910,500 ha [7]. This total continues to expand, not only domestically but also due to expansion of Vietnamese rubber companies in neighboring countries such as the Laos and Cambodia.

Rubber plant is one of the producers of vegetable oils obtained from seeds, with 42% yield of oil [8]. Therefore, rubber seed selected as raw materials in this study because it has not been utilized and there are plentiful numbers.

2. Materials and methods

2.1. Oil Extraction

Dried rubber seeds obtained from Kontum province of Vietnam are decorticated manually to separate the kernels from the shells. The kernels are crushed up to size of about 2mm to allow for faster and more oil extraction [9]. The kernels that have crushed up are treated by cooking with steamed in different times (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 also use a Soxhlet extractor with n-hexane as the solvent and operated at 60ºC to extract oil.

The percentage oil yield is calculated using equation:

$$\text{Oil yield \%} = \frac{\text{Weight of oil extracted}}{\text{Weight of seed kernels used}} \text{x100 (1)}$$

2.2. Characterization of the Oil

Characterization includes the analysis of rubber seed oil viscosity, density, acid number or free fatty acid levels and triglyceride.

The kinematic viscosity of rubber seed oil is measured by using the capillary tube viscometer (Figure 1). In this method, the oil sample is placed into a glass capillary U-tube and the sample is drawn through the tube using suction until it reaches the start position indicated on the tube's side. The suction is then released, allowing the sample to flow back through the tube under gravity. The narrow capillary section of the tube controls the oil's flow rate; more viscous grades of oil take longer to flow than thinner grades of oil. This procedure is described in ASTM D445 and ISO 3104.

The density of rubber seed oil is determined by pycnometer. This value is measured at ambient temperature and then adjusted to 30°C to calculate the specific gravity.

Free Fatty Acids (FFAs) 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 is calculated from Acid Number by equation (2)

$$\%FFA = AN \times 0.503 \text{ (2)}$$

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 from 37 to 50 mg KOH/g depending on its storage time. This value corresponds to the content of FFAs around 18.5% which is 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 [11].

2.3. FAME analysis

Types of free fatty acids and triglyceride oils analyzed by means of GCMS (Thermo Scientific™ ISQ™ LT Single Quadrupole). The column used was Thermo Scientific™ Trace GOLD TG-5MS with dimension 0.25µm thickness – 0.25mm ID – 30m length). The oven temperature is initially held at 35°C for 10 min, increases to 200°C at 10°C/min and held for 10 min, increases continuously to 280°C at 10°C/min and then held for 5 min. The injector, transfer and source temperatures are 250°C, 260°C and 240°C respectively. Carrier gas is helium and total scan time 45 min. EI mode of ionization is applied and mass scan rang was from 50 to 450 m/z. GCMS solution Xalibur software is used for data processing. For identification of FAME library search is carried out using NIST, NBS and Wiley GC-MS library.

2.4. Transesterification Procedure

Figure 1. *Viscometer*

Transesterification is the chemical reaction between triglyceride (rubber seed oil) and alcohol to produce monoester and glycerin with the presence of catalysts. Alkaline hydroxides are the most effective transesterification catalysts as compared to acid catalysts. Potassium hydroxide and sodium hydroxide are the commonly used alkaline catalysts. Alkaline catalyzed transesterification of vegetable oils is possible only if the acid value of oil is less than 4 [3]. Higher percentage of FFA in the oil reduces the yield of the esterification process. In the case of rubber seed oil, the transesterification consists of acid and alkaline transestrification process.

2.4.1. 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 [12]. The rubber seed oil is poured into the flask and heated to about 50°C. The methanol is added with the preheated rubber seed oil and stirred for a few minutes. 0.5% of sulphuric acid is also added to 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).

2.4.2. 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°C in the flask. Meanwhile, 5gram of NaOH is dissolved in 300 ml methanol and is poured into the flask. The mixture is heated and stirred for30 min. The reaction is stopped, and the products are allowed to separate into two layers. The lower layer, which contains 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 is 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.

3. Results and Discussion:

3.1. Oil Extraction

A number of rubber seed samples were collected from different locations. The seed kernel is separated and weighed to measure the seed to kernel ratio. A good rubber seed which is not flat, not empty bears a kernel with average wt.% of about 48.33%. However among 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 are used to extract oil from the seed. Table 1 shows the results of rubber seeds oil content obtained by press method in different times of steamed rubber seed kernels.

Table 1. *Measuring of oil content obtained by press method in different times 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

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

Soxhlet method which is carried out based on n-hexane as solvent brought a maximum 38% of the oil extracted. The results are similar with literature [13, 14]. This indicates 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.

3.2. Rubber seed oil properties

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, mm²/s at 40°C	33 – 39
Acid Number (mgKOH/g)	32 – 51
FFA, wt.%	16 - 21
*Molecular wt of the oil, g/mole**	875.36

*Calculated from the oil composition reported by Ramadhas et al. [11].

The similar results are reported in the research of Suzana et al. [15]. Crude rubber seed oil exhibits high acid value, corresponds to high content of FFAs. Extracted rubber seed oil is of a distinct yellow color. When the oil is cooled down to room temperature and stored for several days, the color changes to darker brown and the acid number becomes higher. The acidity is one of the factors that have great importance in deciding the route of biodiesel production since the acid number is related to the free fatty acid present in the oils. High content of free fatty acid in the vegetable oil will yield significant amount of soap if base transesterification is solely used to produce methyl esters.

The rubber seed oil also possesses high density and viscosity (table 2). Viscosity can lead to engine mal-function and high densities are not recommended by the international standards. Transesterification of the oil has shown to rectify these properties to match the acceptable range.

3.3. Synthesis of biodiesel

The oil collected from all these methods is stored for biodiesel production.

Biodiesel is 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 2%. Effect of reaction time on acid value reduction in the 1st step (initial acid value: 41 mg KOH/g) are investigated and the results show that just only for at least 1h reaction time with the methanol–oil ratio of 0.2v/v there is a reduction of about 95% in acid value to get the optimum FFA below 2%. This is confirmed in the research of Satyanarayana and Muraleedharan [14].

The transesterification process is 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 trans-esterification 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.

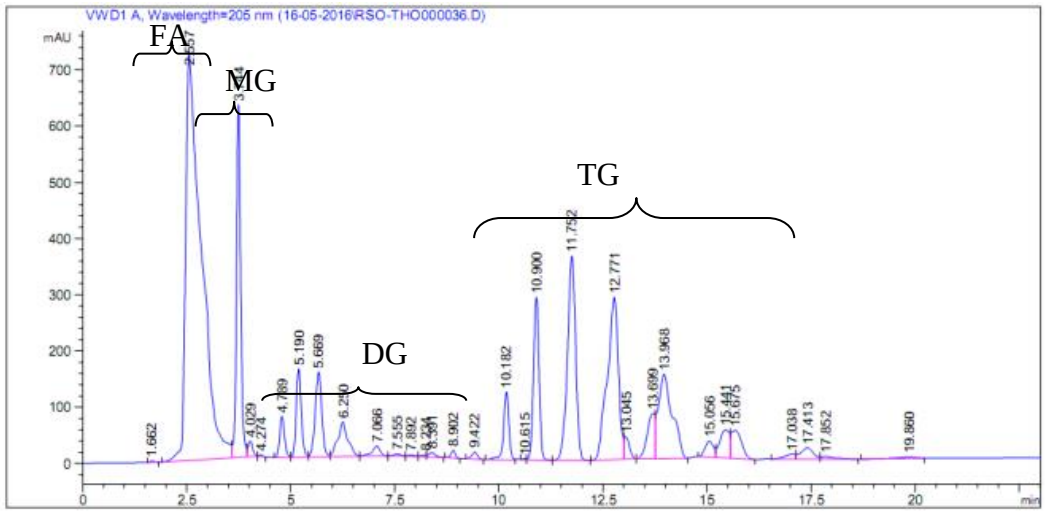


Figure 2. *Sample HPLC plot showing peaks for fatty acid (FA), monoglycerides (MG), di (DG) and triglycerides (TG) of CRSO*

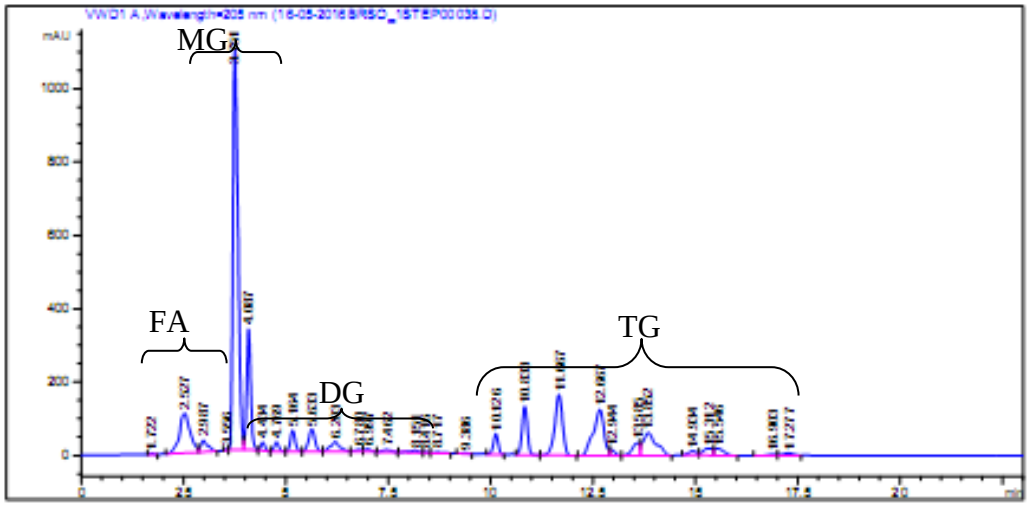


Figure 3. *Sample HPLC plot showing peaks for fatty acid (FA), monoglycerides (MG), di (DG) and triglycerides (TG) of 1st_step BRSO*

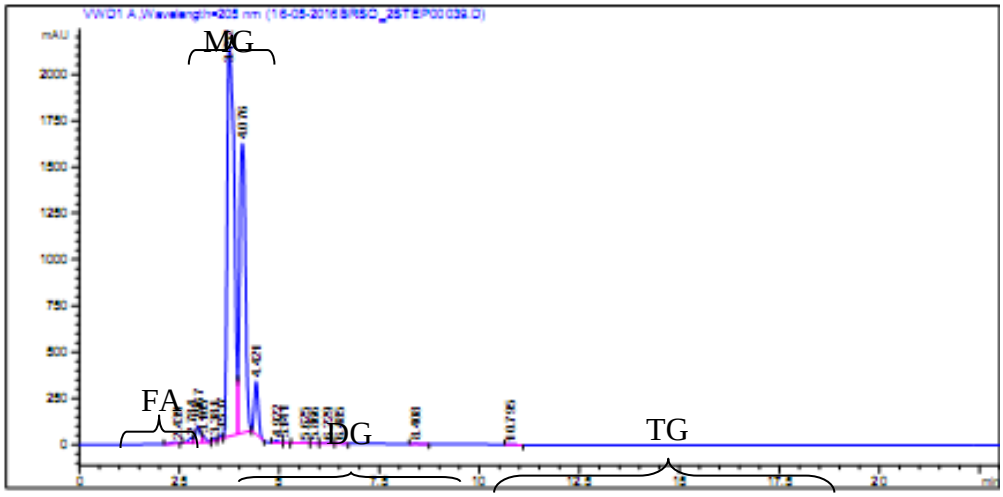


Figure 4. *Sample HPLC plot showing peaks for fatty acid (FA), monoglycerides (MG), di (DG) and triglycerides (TG) of 2st_step BRSO*

Figure 5 shows the analysis result with GCMS, with the residence time is shown in Table 4.

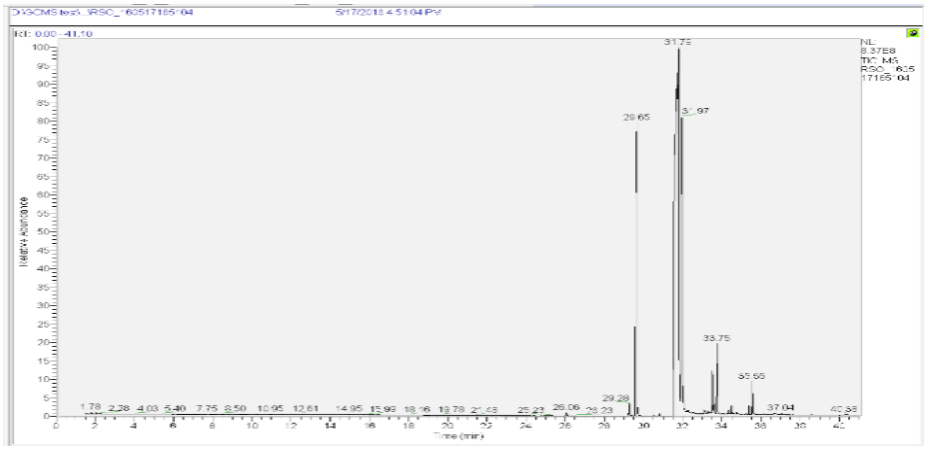


Figure 5. *Chromatogram of free fatty oil analysis*

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

4. Conclusions

Rubber seed oil is extracted from the seed by different methods which are found to be a promising alternative fuel source. The combination of pressing machine and solvent extraction can get the high yield of oil of 40%. The properties of the rubber seed oil are analyzed. FFA content in the oil is found as high. So 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. The present analysis reveals that biodiesel from unrefined rubber seed oil is quite suitable as an alternative to diesel. However, further research and development on additional fuel property measures, long-term run and wear analysis of biodiesel-fueled engine is also necessary.

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(The Board of Editors received the paper on 18/05/2017, its review was completed on 13/06/2017)