Utilization of Crude Rubber Seed Oil (CRSO) for the Production of Biogasoline: Physicochemical Studies

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Abstract

The main objective of this paper is to investigate crude rubber seed oil (CRSO), a non-edible type of vegetable oil, hence that can be considered as a potential alternative fuel in Malaysia. The rubber seed production in Malaysia is about 150-200 kg/ha per annum. The estimated availability of rubber seed is about 30,000 MT/year. At present, rubber seed oil has not been found to be utilized in any major application. The challenge of the present study is to analyze the suitability and feasibility of rubber seed oil applied as biofuel, specifically in biogasoline range. Standard procedures of American Oil Chemists Society and ASTM Standard were used to determine the physicochemical properties of crude rubber seed oil (CRSO). Using standard techniques the specific properties data were obtained for this bio-oil namely for the following parameters: pH, specific gravity, refractive index, water content, peroxide value, acid value, kinematic viscosity, calorific value, density, molecular weight, flash point, cloud point, pour point, CHNS contents, saponification value, iodine value, and oxidative stability. Properties of rubber seed oil in comparison with standard biodiesel and other source of oils were also given. The observed values of this study were in agreement with the CRSO values of previous literature. The characteristic features of CRSO from this study show that CRSO can be exploited as an environmentally friendly alternative biofuel.

Keywords: rubber seed oil, biogasoline, physicochemical

1. Introduction

Using non-edible oil for the production of biogasoline over edible oil sources have proven to have many advantages, of which is minimizing the economical and food shortage impacts resulted from using edible oils, added value to the relevant agricultural industry, and contribution to the gross domestic product (GDP) while reducing expenditure over imported fuels [1]. It is also leads to the reduction in deforestation rate, decreasing in the amount of carbon dioxide, and more efficient in productive utilization for the current plantation [3]. Bio-oils are promising alternative to crude petroleum [2].

Despite the previously 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 plantations grow abundantly. In Malaysia, palm oil is widely produced and the country is considered among the world top producers with 20 MT/year. But this was challenged by the increasing palm oil prices [4].

Other abundant tree plantation in Malaysia is rubber trees which cover more than 1.2 million hectare all over the country and each hectare can give an approximate amount of 150 kg of seeds [5]. It had been found that the seeds yield good amount of oil (between 30 and 40 wt%) that may be used for bio-oil synthesis. Up until now, no major application could be found for rubber seed oil and the industry remains underrated [6]. Thus, the current study focuses on establishing properties for crude rubber seed oil as a possible source for biogasoline production to reduce the utilization of the edible raw material without the need for major modification in the production technology. In fact, the modification in engine should be anticipated the gum development because of high viscosity, formation of deposit and ring sticking.

Therefore, reduction in viscosity is one of utmost challenge to make this bio-oil a suitable alternative fuel. Solution to the problem of high viscosity of vegetable oils has been approached in several ways, such as preheating the bio-oil from crude fossil, blending or dilution with other fuels, transesterification and thermal hydrocracking [7].

In addition, potential for direct substitution of rubber seed oil for bio-fuel may be limited due to high oxygen content and thermal instability of bio-oil. Consequently, upgrading of the bio-oil before use is desirable to produce a liquid product that can be used in a wider variety of applications [8]. Furthermore, upgrading process which is necessary to improve the quality of bio-oil through reduction of oxygenates normally involved process such as catalytic cracking, hydrogenation, and steam reforming [9].

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In a few literature reviews, the crude rubber seed oil (CRSO) measurements for characterization process gave different readings from different geographical origin [10]. It becomes important to obtain the specific data for sample of oil from a particular area because there is a range of variation in the physicochemical parameters of the oil due to environmental factors such as rain, soil fertility, agronomic practices, maturation period, and genetic substitution.

In this paper, crude rubber seed oil (CRSO) was used since it can be extracted and produced locally in Malaysia from their abundant resources. The CRSO was characterized for density, kinematic viscosity, heating value, acid value, refractive index, and other physicochemical parameters.

2. Materials and Methods

Acid value test was carried out based on AOAC official method (Cd, 3d-63) [11]. The acid value was determined the free fatty acids (FFA) content and was done through titration of potassium hydroxide (KOH) for low acid values, as shown in Figure 1. Meanwhile, the kinematic viscosity was determined using Bohlin Gemini dual rotational rheometer (AD-100 Malvern Manufacturing, Germany). A Bomb calorimeter (C5000, IKA Werke, Germany) equipped with water bath and oxygen controller was used to obtain the heating value. Refractive index test was conducted using a temperature controlled refractometer (RX5000, Atago, Japan).

Figure 1 Acid Value

For density measurement, it was carried out using Anton Paar DMA 4500 M Density meter. 2 ml sample is prepared and injected into density meter nozzle with density meter temperature set to be 20 oC. The readings are displayed on the panel, and the measurement was taken for few reading so that the average value density and specify gravity can be measured as shown in Figure 2.

Figure 2 Density meter

Physical properties such as colour, water content, density, and calorific value of the oil were determined by following standard process ASTM D1500, ASTM D 1744 (Karl Fisher method), ASTM D 1480/81 and ASTM D 240 respectively [12-14]. For water content, it was determined using MetroOhm 831 KF Coulometer. The sample is prepared in a syringe and injected into a titrator and, then weight difference was measured. This method is based on water reaction with iodine in the presence of lower alcohol whereas the amount of iodine consumed is used to measure the water content of the sample. An average value of the water content is measured by repeating the procedure.

The viscosity, flash point, pour point and cloud point were determined by standards ASTM D445, ASTM D 93, ASTM D 2500 and ASTM D97 respectively [15-16]. The flash point of the sample was determined by using Petrotest Cleveland Open Cup Instrument (CLA 5) automated flash point analyzer, as shown in Figure 3.

Figure 3 Flash point

3. Results and Discussion

Rubber seed oil was characterized experimentally along the following physicochemical parameters and the results are shown in Table 1.

Table 1 Properties of Crude Rubber Seed Oil (CRSO)

Property	Unit	Testing Method	Experimental Value
pH	-	-	6
Specific gravity	-	ASTM D4052	0.92
Refractive index	-	ASTM D2500	1.46
Water content	wt.%	ASTM D2709	0.40
Peroxide value	mg/g	-	3.30
Acid value	mg KOH/g	Cd 3d-63	85.07
Kinematic viscosity	mm^2/s	ASTM D445	41.05
Calorific value	MJ/kg	ASTM D240	40.25
Density (at 20ºC)	g/cm^3	ASTM D5002	0.91
Molecular weight	g/mol	-	844.20
Flash point (open cup)	ºC	ASTM D93	247
Cloud point	ºC	ASTM D97	3.1
Pour point	ºC	ASTM D2500	1.2
CHNS analysis	wt. %	-	C: 76.52 H: 10.40 N: 0.30 S:12.83
Saponification value	mg KOH /g	ASTM D664	202.05
Iodine value	G I_2/100g	ASTM D5291	140.20
FFA	wt.%	-	41.74
Oxidative stability	h	ASTM D240	5.14

The pH value (6) obtained for CRSO was favour with those obtained for its similar group like castor seed oil (6.8) and kapok seed oil (6.6)[17]. This value is an indication of the presence of reasonable amount of free fatty acid (FFA). High acidity is not favoured because it will bring difficulties during storage as it will cause corrosion and instability. On the other hand, the specific gravity of CRSO was found to be 0.92 indicating that the oil is less dense than water. High specific gravity is caused by the presence of hydroxyl groups. The value observed indicate that there is no heavy element presence in the oil. The specific gravity obtained for CRSO in this study is similar to most all bio-oils [18].

Refractive index is an indication of the level of saturation of the oil. In this experiment, the refractive index of 1.46 obtained fall within the standard value for refractive index of organic vegetable oil which is between 1.3–1.6. The value is also in the range found for common bio-oils such as castor seed (1.47) and shear butter oil (1.60).

The percentage water content of 0.40% obtained for CRSO in this study is lower than castor seed oil (8%). and shear butter oil (10%) [19]. Low water content is an indication of good shelf life for the oil. Meanwhile, peroxide value is an indication of deterioration of oil. Oil with higher peroxide values is more unsaturated than those with lower peroxide value. More unsaturated oils are known to absorb more oxygen and develop higher peroxide value, and oil with higher peroxide values is prone to rancidity. In this experiment, good peroxide value of 3.30 was found because of the oxidation of unsaturated esters.

It was polymerised with other free radicals to form insoluble sediments and gums. For application, antioxidant additives might be added if the fuel could not meet the specification.

The acid value (85.07) obtained in this study is quite higher than those reported in previous literature. Acid value measures the degree of unsaturation of oil. It corresponds to the amount of potassium hydroxide needed to neutralize the free fatty acids. The lower the acid value of oil, the fewer free fatty acids it contains which make it less exposed to the phenomenon of rancidification. The acid value may increase with time due to the contact with water and air, which can lead to corrosion and water present in fuel.

One of the important properties of the oil is the viscosity since it must meet the criteria of international standard. The degree of saturation has a strong relation with viscosity because the degree of saturation in oil increases with viscosity. Viscosity of the hydrocarbon increases with the chain length (number of carbon atoms) and degree of saturation. Factor like double bond configuration affects viscosity where cis double bond configuration giving a lower viscosity than trans [19]. The double bond position affects the viscosity least. High viscosity states that polymerization occurs and size of molecules been larger. Therefore, lower viscosity is preferred.

The kinematic viscosity (41.05 mm²/s) obtained for CRSO is slightly higher than those of other similar bio-oils and several times higher than that of diesel oil (7.50 mm²/s) at 40 ºC. For application, the combination of high viscosity and low volatility of rubber seed oil causes poor cold engine start-up, missfired, and ignition delayed. Calorific value is another fuel property indicating the economic efficiency of fuel. Calorific value of the CRSO (40.25) is lower than diesel, which is another shortage of the CRSO as a renewable fuel. It will be improved noticeably during the thermal cracking. Rubber seed oil has about 15% less calorific value than that of diesel oil due to the oxygen content in their molecules. It is recommended to remove the water content through heating process or centrifugation at higher speed to separate both miscible layers.

The flash point (FP) is the most important properties from storage point of view, because higher FP thus reduces the chances of blazing. High FP will bring burning issues of the fuel and very low flash point on contrary brings less safety of fuel storage. In this experiment, the flash point (247) decreased near to the borderline of standard amount. Therefore, lower FP is more preferred.

The cold flow properties of biogasoline are generally determined by three general parameters; cloud point, pour point, and cold filter plugging point. The cold flow properties are related to the composition of the fatty acids, chain length of carbon, degree of saturation and un-saturation, and the orientation of double bonds. Meanwhile, biomass materials with high ash content are not a good source of burning material because ash acts as catalyst in cracking of the liquid product to form gases. The low nitrogen and sulphur contents indicated that this bio-oil is an environmental-friendly source.

Last but not least, the Rancimate method described in ASTM D240 is to determine the oxidation stability, which the most important factor with respect to storage and performance of the fuel. The increase in viscosity, gumming, and deposition of unwanted particle during the storage resulted in poor oxidation stability. The oxidation stability was 5.14 for this work and is lower than that reported in other studies for the rubber seed oil. Therefore, higher oxidation stability is preferred. However, this value meets both the standard values of ASTM D6751 and EN 14214.

Table 2 Comparison of result with other articles of CRSO and international biodiesel standard

Property	Unit	Experimental Value	Other articles [20] [21]	Biodiesel Standard ASTM [22]
pH	-	6	-	-
Specific gravity	-	0.92	0.88	0.83
Refractive index	-	1.46	1.50	292.20
Water content	wt. %	0.40	0.90	Max 0.05
Peroxide value	Mg/g	3.30	14.4	-
Acid value	mg KOH/g	85.07	75.38	0.80
Kinematic viscosity	mm²/s	41.05	35	1.90-7.50
Calorific value	MJ/kg	40.25	37.5	42.25
Density (at 20 ºC)	g/cm³	0.91	0.92	0.87-0.90
Molecular weight	g/mol	844.20	875.36	292.20
Flash point (open cup)	ºC	247	180	More than 130
Cloud point	ºC	3.1	3.2	-13 to 12
Pour point	ºC	1.2	1.0	-15 to 10
CHNS analysis	wt. %	C: 76.52 H: 10.40 N: 0.30 O:12.83	-	-
Saponification value	mg KOH /g	202.05	192	-
Iodine value	G I2/100g	140.20	134.51	-
FFA	%	41.74	45	-
Oxidative Stability	h	5.14	8.54	-

The physicochemical properties of the rubber seed oil are investigated and the results are compared with previous work. The properties of the CRSO in this work is quite similar and within the range from the report by Ramadash et al (2005) and Kyari, M (2008) as shown in the Table II. The present study showed affirmative results than earlier reported studies. The comparison with international biodiesel standard is also shown in the same table.

4. Conclusion

One of the best potential options for replacement the fuel in tackling the food-for-fuel and land-use change issues is through biogasoline production from non-edible feedstock. Accordingly, the future of biogasoline production from RSO looks bright and promising based on its properties. Rubber seed oil (RSO) oils have been found to be promising crude oils for the production of biogasoline. The physicochemical properties of CRSO have been examined successfully and showed good prospect of using non-edible rubber seed oil as an alternate crude oil fuel for transportation vehicle, with improvement of its bio-oil properties.

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