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Preparation of Biodiesel from *Hibiscus sabdariffa* Seeds Oil using Calcium Oxide Catalyst from Waste Egg Shells

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Abstract – *The aim of this study is to optimize the transesterification process for conversion of Hibiscus sabdariffa seed oils (HSO) into biodiesel. Conversion of HSO into biodiesel were obtained at optimum parameters of methanol to oil ratio 6:1, temperature 67.5ºC, 1% calcium oxide (CaO) catalyst derived from waste egg shells and agitation speed of 750 rpm. The yield achieved was 95.01%. The results showed that all of the fuel properties such as kinematic viscosity 4.55 mm^2/s acid value 0.027 mg KOH/g, cloud point 3ºC, pour point 1ºC, flash point 161ºC, cetane index 49 min and density 856 kg/m^3 of the Hibiscus sabdariffa methyl esters (HSME), are in compliance within the range of ASTM D6751 and EN 14214 standard specifications except for oxidation stability which was at 3.48 hours. The results suggested that Hibiscus sabdariffa seed oil could be a potential feedstock for biodiesel.*

Keywords: *Hibiscus sabdariffa*, egg shells, plant seed oils, biodiesel

1.0 INTRODUCTION

Fossil fuel resources are diminishing rapidly and also cause problems such as toxic compound emission and global warming (Balat & Balat, 2009). This may lead to a serious problem as most countries depends on fossil fuels to run the transportation industry (Jayed et al., 2011). As such the world is in search for alternative fuel sources such as biofuel. Biofuel is gaining more and more importance as it is a bio-based product produced from agricultural and plant bio-products, fats and animal wastes. The reusability, renewability and non-toxic nature of biofuel especially biodiesel makes it a favourable fuel to be produced from biological products. Various feedstocks such as soybean (Samart et al., 2010), palm kernel (Awalludin et al., 2015), tobacco (Usta et al., 2011), palm (Nur et al., 2014), cotton (Qian et al., 2010) and canola oil (Kai et al., 2014) have been used for biodiesel production.

However, animal fats, wastes cooking oils and plant seeds oils are also transesterified and biodiesel is produced as the output product (Hincapié et al., 2011). Non-edible oils such as tobacco, macaúba, hochst, linseed oil, rubber seed oil, Chinese tallow, soapnut, milk bush, polanga and nahor oil have been used as feedstocks (Demirbas, 2007). Therefore, more emphasis is now given to non-edible seed oils as a source for biodiesel.

Hibiscus sabdariffa is a Hibiscus species, commonly known as Roselle (family Malvaceae). Its calyx is widely used for various pharmaceutical and industrial usages in many countries. The research during 2000 to 2015 showed its usage in industrial and medicinal properties (Padmaja et al., 2014). However, the seeds are normally left unused as waste. In this work, *Hibiscus sabdariffa* seeds oil is used as an alternative feedstock for biodiesel production. In addition, a heterogeneous CaO catalyst prepared from waste egg shell was also used in this study for biodiesel transesterification.

2.0 METHODOLOGY

2.1 Materials Preparation

A 500-ml soxhlet apparatus was used with hexane as solvent for oil extraction. A known amount of powder (grinded) seeds of *Hibiscus sabdariffa* was put in thimble placed in condenser. A flask containing known volume of hexane was stationed to the end of the soxhlet apparatus and a condenser was fixed tightly at the bottom end. The whole set up was heated up in a heating mantle at a constant temperature of 70ºC and the *Hibiscus sabdariffa* oils was collected in the flask. The yield was calculated according to the equation given below:

$$Oil\ Yield = \frac{Weight\ of\ oil\ produced}{Weight\ of\ oil\ used} \times 100 \qquad (1)$$

2.2 Synthesis of CaO Nano-catalyst from Waste Egg Shells

As much as 6.0 g of waste egg shells powder was stirred with 1% hydrochloric acid solution for 10 hours at room temperature. Then the solution was filtered with Whatman filter paper and collected. Meanwhile, 20 ml of 2N solution of Na_2CO_3 was added dropwise to the 20 ml residual solution collected, while stirring. The solution was stirred for more than 30 min to obtain a homogeneous solution. Then, the solution was transferred to an auto clave and maintained at a temperature of about 200ºC overnight. Next, the collected white powder was washed with distilled water several times over the Whatman filter paper via vacuum pump filtration process and dried at 50ºC. Finally, the obtained $CaCO_3$ powder was calcinated at 900ºC for 2-3 hours to obtain nano-CaO powder.

2.3 Pre-esterification and Transesterification

Esterification process was applied as pre-treatment by using 1% H_2SO_4 (v/v) to reduce the free fatty acid content to less than 2% and followed by base catalyst transesterification using sodium hydroxide (Dwivedi & Sharma, 2015). After the completion of the reaction, alcohol-catalyst was separated from upper layer. Next, the esterified oil is washed with distilled water to remove the remaining catalyst and heated to remove water content.

The transesterification process was conducted in a 500 mL three-neck round bottom flask. An oil quantity of 40 to 50 g was used for each experimental run. For each experiment, oil was carefully transferred into the reaction flask and preheated in an oil bath up to its reaction temperature. The CaO catalyst prepared from waste egg shells beforehand was used. Catalyst and methanol solution were prepared and added to the preheated oil, and the mixture was agitated. At the completion of the transesterification process, the mixture undergoes gravity settling in a separating flask for 6 to 8 h to separate the methanol-water and the biodiesel phases. The top phase containing the biodiesel was collected and mixed with distilled water at 40ºC to remove residual impurities. Methanol and water were removed using rotary evaporator at 70ºC.

2.4 Fuel Properties Testing

Karl Fischer moisture titrator MKC-520 (Kyoto Electronics MFG. Co. Ltd.) was used to check the water content and Automatic Kinematic Viscosity Measuring System AKV-201 was used to test the kinematic viscosity at 40ºC. Iodine value was measured according to Wijs method while density was determined using I-type hydrometer. Oxidation stability was determined by Rancimat 743 (Metrohm, Herisau, Switzerland). Tocopherol, iodine value, water content, kinematic viscosity, and anacid value was determined using AOCS Official Method AOCS Cd 3d-63 (AOCS, 1976). The pour point and cloud point tests were done on a Mini Pour/Cloud Point Tester MPC-102. Automated Cold Filter Plugging Point Tester AFP-102 was used to determine cold filter plugging point while Pensky-Martens Closed Cup Automated Flash Point Tester APM-7 was used to determine the flash point.

3.0 RESULTS AND DISCUSSION

3.1 *Hibiscus sabdariffa* Oil Properties

Hibiscus sabdariffa seeds used in this study contain 17.5 wt% oil. Physio-chemical properties are the most important criteria to check the quality of oils. The physio-chemical properties were evaluated and the result obtained are shown in the Table 1. The oil was yellowish in colour at room temperature with a refractive index of 2.16 and an ultrasonic speed of 1.52 ms^{-1}. The acid value of the oil was 5.486 mg KOH/g showing the presence of free fatty acids in the oil. Oxidative stability of the HSO was tested on rancimat which was 2.8 h and the kinematic viscosity of the oil was 14.228 mm^2/s.

Table 1: Physico-chemical properties of *Hibiscus sabdariffa* seed oil

Properties	Unit	Seed Oil
Oil yield	wt%	17.5
Refractive index	ms^{-1}	2.16
Acid value	mgKOH/g	5.48
Ultrasonic	ppm	1468
Iodine value speed	ms^{-1}	1.52
Oxidative stability	h	2.8
Water content	ppm	55
Kinematic viscosity, 40ºC	mm^2s^{-1}	14.228

3.2 Cao Characterization

The FT-IR results as shown in Figure 1(A1) and Figure 1(A2) correspond to the spectrums of $CaCO_3$ and CaO nano-crystal powders. The spectrums were collected in the range between 4000-500 nm. The sharp peaks of (C-O str.) at 714 cm^{-1}, (C-O bending) at 873 cm^{-1} were seen for $CaCO_3$ and weak peaks of (C=O str.) at 1799 cm-1 corresponding to HCO_3 along the peak at 3450 cm^{-1} due to (OH str.) vibrations conforms the presence of $CaCO_3$ Figure 1(A1). While, after calcination at 900°C the presence of wide and intense band 1482 cm^{-1} and week band at 877 cm^{-1} shows the presence of Ca – O bond.

However, at 3657 cm^{-1} the presence of peak shows the absorption of -OH groups on the surface of CaO Figure 1(A2). The nano-crystal with cubic shape was conformed from the XRD patterns. It was seen the diffraction peaks at at 32.02, 37.12, 53.80, 64.17 and 67.26, are belongs to the (hkl) indices (111) (200) (202) (311) and (222) respectively, of crystal planes with cubic shapes Figure 1(B1). Moreover, the morphological shape of CaO nano-crystals of cubic shape is illustrated by TEM images at 100 nm and 200 nm dimensions as per Figure 1(C1) and Figure 1(C2), respectively.

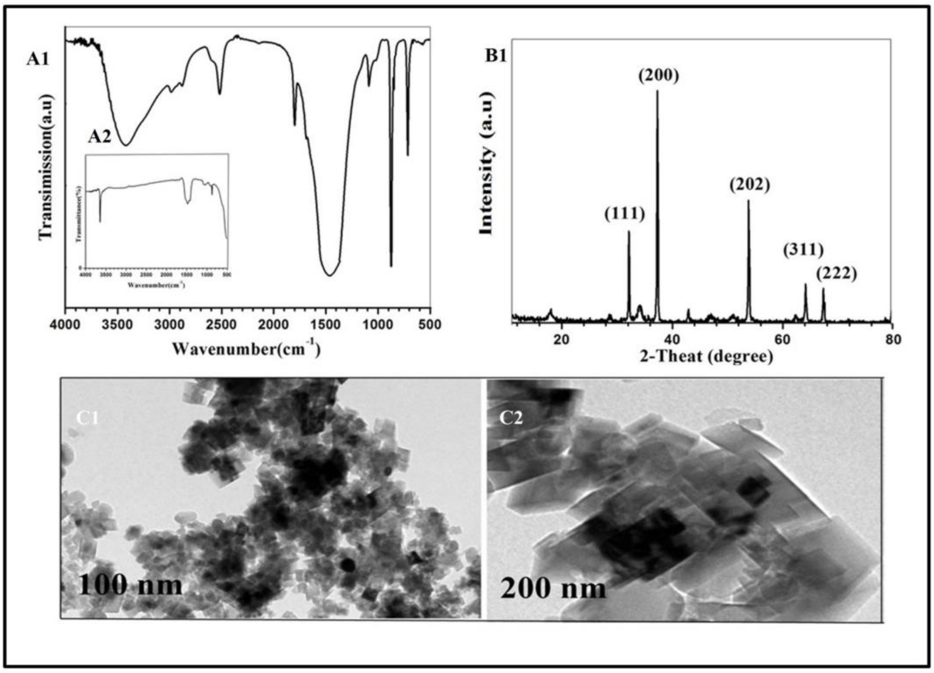

Figure 1: A1 and A2 show the FT-IR peaks of $CaCO_3$ and CaO; B1 shows the XRD peaks of CaO; and C1 and C2 show the TEM images of CaO at 100 nm and 200 nm, respectively

3.3 Gas Chromatography Analysis

Gas chromatography was used to determine the fatty acid composition of HSME, *Hibiscus sabdariffa* biodiesel which is shown in Table 2. The dominant fatty acids were methyl palmitate (6.57%), methyl oleate (10.0%), methyl stearate (49.74%), linoleic (25.37%), Methyl arachidate (2.21%), Methyl erucate (2.94%) and others (3.24%). The results are in agreement of previous findings on *Hibiscus sabdariffa* methyl esters.

Table 2: FAME composition of *Hibiscus sabdariffa* biodiesel

FAME		wt%
Methyl palmitic	16:0	6.57
Methyl steareate	18:0	49.74
Methyl arachidate	20:0	2.21
Methyl oleate	18:1	10.0
Methyl Linoleate	18:2	25.3
Methyl erucate	--	2.94
Others	--	3.24
Total	-	100

3.4 Biodiesel Fuel Properties

The EN 14214 and ASTM D6751 are the international standards used to compare fuel properties. HSME physicochemical are shown in Table 5. The kinematic viscosity of HSME biodiesel which is 4.55 mm^2/s falls within international standards (ASTM D6751 and EN 14214 are 1.9-6.0 mm^2/s and 3.5-5.0 mm^2/s correspondingly). The density of biodiesel depends on its purity and the composition of fatty acid in it. The injection system of fuel could be affected if the density is increased and in turn the fuel can become more viscous (Demirbas, 2008). The HSME density found was 856 kg/m^3.

This follows the range of specifications (Martínez et al., 2014). The acid value measured for HSME biodiesel which was 0.054 KOH/g also falls within range of international standards. Usually, fuels with high acid values is not considered as a good fuel because corrosion can occur severely in the fuel system which indirectly disturb internal engine. The oxidative stability is the property which shows the strength of fuel to be stored longer. The oxidative stability for HSME was found to be 2.47 h which should be a minimum of 2.47 hours according to ASTM and 6 hours for EN 14214.

Though, the HSME oxidative stability was found to be far from diesel which has an oxidative stability of 15.2 h, the flash point was 161°C, cloud point 3°C and cetane number 49 min. But, still was within the range of specified standards. The results displayed in Table 3, suggests that most HSME physicochemical properties were fall in the range of EN14214 and ASTM standards.

Table 3: *Hibiscus sabdariffa* (Roselle) biodiesel properties

Plant Seed Oils	Density (mg KOH/g)	Cloud Point (°C)	Flash Point (°C)	Oxidative Stability (hour)	Viscosity (mm^2/s)	Cetane Number (min)
Roselle	856	3	161	3.48	4.55	49
Neem	884	14.4	–	7.1	5.21	57.83
Mahua	850	–	208	–	3.98	–
Castor	899	-13.4	–	1.1	15.25	–
Jatropha	880	2.7	135	2.3	4.80	52.31
Karanja	–	–	150	–	4.80	55.84
Malada Pahit	871	2	164	3.0	3.55	51
EN14214	900	–	120	6	5	55
ASTM	–	-3 to 12	170	3	6	47

4.0 CONCLUSIONS

This study discusses the production of biodiesel from non-edible *Hibiscus sabdariffa* seed oils and the optimization of its transesterification parameters. The optimum operating parameters for converting *Hibiscus sabdariffa* oil into biodiesel are methanol to oil ratio 6:1, temperature 67.5ºC, catalyst 1% and 750 rpm. The yield achieved was 95.01%. The results showed that, except for oxidation stability which is 3.48 hours, other HSME fuel properties such as kinematic viscosity 4.55 mm^2/s, acid value 0.027 mg KOH/g, cloud point 3ºC, pour point 1ºC, flash Point 161ºC, cetane index 49 min and density 856 kg/m^3 conformed within the range of ASTM D6751 and EN 14214 standard specifications. The results indicated some suitable fuel properties of HSME biodiesel and satisfactory yield by using CaO catalyst derived from waste egg shells.

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