Utilization of Kapok Seed as Potential Feedstock for Biodiesel Production

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Abstract: - The huge development in industry and growth in population resulted in increase the demand of fuel. Now the fossil fuel depletion grabs the world's attention towards renewable energy sources. Biodiesel is one of the alternatives due to environment friendly, free from sulfur and reduced carbon dioxide emission. The researcher explored a new non edible feedstock for the biodiesel production known as Kapok seed oil (*Ceiba pentadra*). The Kapok seed contains 22-25% wt/wt oil contents. The experimental design consists of two steps. The first is the reduction of the free fatty acid (FFA) of oil to 1.37 KOH/g, by using sulfuric acid as the catalyst, and the another step is the treated oil is converted into fatty acid methyl ester (FAME) by transesterification with potassium hydroxide (KOH) as the catalyst. The fuel properties of the biodiesel were analyzed and compared to ASTM D6751 and EN14214 standards.

Key-Words: Kapok seed oil, free fatty acid, transesterification, fatty acid methyl ester, Biodiesel

1 Introduction

Recent growth in population along with industrial development is important factors towards the depletion of fossil fuel reserve of the world. Currently, researchers are looking for new sources of renewable sustainable energy due to insufficient fossil fuel to world's fuel requirements and increasing prices of fossil fuels. Ethanol, bio-methanol, and methyl ester from vegetable oils and animals fats are the alternative sources to fossil fuel [1]. Different type of energy sources such as water, solar, wind and biofuels have the potential to replace the fossil fuels. These fuels are largely utilized as transportation fuel [2]. At present, the biofuels such as biodiesel and bio-ethanol are used as the energy sources in different countries especially in Brazil, Germany, Malaysia, Indonesia, USA, Spain, and Argentina. Utilization of biofuels has gained wide attention worldwide [3]. In previous studies, it was clear that the feedstock containing high free fatty acids was not suitable to be converted into the biodiesel by using only an alkaline catalyst. Reduction of free fatty acids value of the feedstock by using acid catalyst, prior using the alkaline catalyst is essential to reduce problems associated with biodiesel production [4-5]. Biodiesel is defined as the mono alkyl ester of long chain fatty acid derived from the vegetable oil and animal fat. Vegetable oils are also used as an alternative fossil fuel as they are renewable, environmental friendly and free from sulfur. Direct utilization of vegetable oil is not recommended due to viscosity problem [6]. Due to this problem, the researchers explore new energy and renewable energy sources. Thus, conversion to biodiesel from different type of edible and non edible oils is explored. Utilizing edible oil as biodiesel feedstock will cause fuel versus food controversy. In current study, non-edible oil is used as biodiesel feedstock. Biodiesel is also called a green diesel because it is renewable, biodegradable and eco-friendly non toxic fuel for diesel engine. Different methods have been used to produce biodiesel but transesterification is the most preferred because of higher yield obtained. Basically, the transesterification is the reaction of triglycerides (vegetable oil or animal fat) with alcohol to produce ester and glycerin as by product [7-8]. Different feedstock are used for biodiesel production around the world, such as soybean oil, canola oil, palm oil, but they are from edible oil sources and its utilization will increase the cooking oil prices. Thus, new and non edible feedstock for the biodiesel

production has been researched such as *Moringa oleifera* seed oil, Tobacco seed oil and Castor seed oil [9-11].

Biodiesel that will be used in diesel engine must meet some standards such as ASTM D6751 and EN 14214 [12]. The properties of biodiesel depend mainly on two factors, which are the quality of feedstock and the technique used for the biodiesel production. Fatty acid profile, cetane number, oxidative stability, low temperature properties, and viscosity are related to the nature of the feedstock [13].

Kapok (*Ceiba pentandra*) which is locally known as Kekabu is a native in America and West Africa [14]. The seeds were introduced to Southeast Asia via India. The availability of Kapok seed in Southeast Asia is scarce except for in Western India, Malaysia, Vietnam, Indonesia and Philippines. *Ceiba Pentandra* is a humid tree of the order Malvales and a family of Malvaceae. The kapok tree produces between 500 to 4000 fruits at one time, with each fruit containing 200 seeds. The seed of Kapok are very striking with pointed capsule shape and the woody pods hanging on tree like cucumber in which the flashy silky fiber black color seeds are present [15]. The fiber contains almost 64% cellulose are elastic in nature and use in cushion, pillow, mattresses, life jackets etc [16]. The seed are brownish black in color and surrounded in the lint fiber. The seed contain 25-28% oil contents same as cotton seed. The main objective of the current study is to explore the utilization of Kapok seed oil which is non edible oil as potential feed stock for higher quality of biodiesel.

Transesterification is a chemical reaction in which triglyceride reacts with alcohol in the presence of catalyst. During this reaction, mono-ester is produced. The long chain and branched chain fatty acid molecules are converted to mono-ester by transesterification [6]. The transesterification reaction consists of three consecutive reversible steps; firstly conversion of triglycerides to diglycerides, followed by diglycerides to mono-glycerides. The glycerides are converted into glycerol and one ester molecule in each step. The properties of the ester produced during this reaction are similar to that of diesel. The reaction is as shown in Fig. 1. [17].
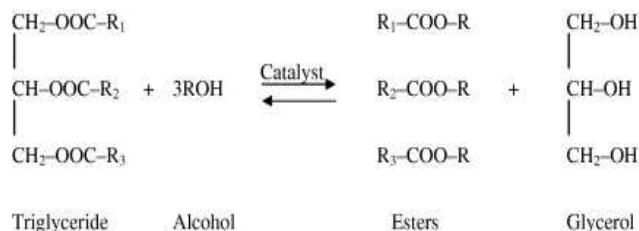

Fig.1: Transesterification of triglycerides with alcohol [17]

Theoretically, three moles of alcohol are required for one mole of triglyceride, but in actual practice a higher molar ratio of methanol is required to establish the equilibrium and to obtain higher percentage yield of ester. Commonly, short chain alcohol such as methanol, ethanol and propanol are used as the solvent. The yield of ester is independent of the type of alcohol. Mostly methanol is used as a solvent because it is the cheapest among others. Both types of acidic and basic catalyst are used for feedstock having high content of free fatty acid and most common basic catalysts are potassium hydroxide.

2 Material and Methods
2.1 Materials
Kapok seed was obtained from Bota, Perak, Malaysia. The analytical grade methanol, sulfuric acid and potassium hydroxide used for esterification and transesterification were supplied by Merck Chemical Company (Darmstadt, Germany). Pure standard of FAME was purchased from Sigma Chemical Company (St. Louis, USA).

2.2 Extraction of Kapok seeds
1500 g of Kapok seeds were crushed using a grinder. The extraction of Kapok seed oil was carried out in soxhlet extractor using n-hexane as the solvent at 60°C for 6 hr. The solvent was then distilled off at 45°C under vacuum using lab scale rotary evaporator. The extracted oil was reheated at 45°C to eliminate the excess solvent.

2.3 Analysis of raw material

The acid value for Kapok seeds oil (KSO) was determined using AOCS method and it was shown that the acid value of KSO used in this study was 72.05 mg KOH/ g oil which correspond to 36.03% of free fatty acid (FFA) content in the oil. Higher FFA content (> 1%) can lead to soap formation during transesterification reaction. Therefore, the FFA content of KSO was reduced below 1% using acid catalyzed esterification as the pre-treatment of the feedstock.

2.4 Acid Esterification (pretreatment)

The acid esterification reaction of KSO was carried out at 65°C for 3 hr using 6 to 1 methanol to oil ratio and 0.5 wt/wt of sulfuric acid as catalyst. This process was repeated until the acid value of the sample was less than 2 mg KOH/ g of oil or below 1% of FFA content before proceeded to transesterification reaction.

2.5 Transesterification of Kapok oil

100 g of KSO was heated in a round bottom flask at desired temperature using heating plate. The methanol-KOH solution at specific amount was then added into the round bottom flask and stirred for 3 hr. Once the transesterification reaction was completed, the mixture was left overnight inside the separating funnel for complete separation. Two layers of immiscible phase were obtained. The upper layer consisted of fatty acid methyl esters (FAME) and the lower layer contained glycerol, excess methanol, and unreacted catalyst. The FAME was purified with warm deionized water to remove the residual catalyst and anhydrous sodium sulphate (Na_2SO_4) was then added to the methyl esters to absorb the residual water.

3 Results and discussions

3.1 Fatty acid methyl ester (FAME) profile by GC-MS

Kapok seed oil methyl esters (KOME) were analyzed using Gas Chromatography Mass Spectroscopy (GC-MS) from Agilent-Technologies. GC system equipped with a Triple Axis inert XL EI/CI mass selective detector and Agilent-technologies capillary column RT-2500 (100 x 0.25 mm; film thickness 0.20 μmeter). 1.0 μL of sample was injected to the column using the split mode (split ratio 1:100). Helium was used as a carrier gas at 1.2 ml/min. Column oven temperature was adjusted from 150°C to 250°C at a linear ramp rate of 4°C/min. The initial and final hold up time was 1 and 5 min respectively. For GC/MS detection, an electron ionization method was used with the ionization energy of 70 eV. The determination of KOME on GC/MS was analysed in quantitative and qualitative analysis. The identification of the unknown KOME was compared with the standards of FAME based on their relative retention times. The fatty acids composition was shown in Table 1.

Table 1: Fatty acid profile of KOME

KOME	Percentage (%)
Palmatic acid	23.17
Capric acid	9.42
Linoleic acid	30.00
Oleic acid	22.88
Stearic acid	4.73
Sterculic acid	8.64
Arachidic Acid	1.18

4 Fuel Properties

The fuels properties of the KOME such as cetane number, density and oxidative stability were analyzed and compared with ASTM D6751 and EN14214 standard methods as shown in Table 2.

Table 2: Properties of KOME in comparison to ASTM D6751 and EN 14214 standards

Property	KOME	ASTM D6751	EN 14214
Cetane number	57.52	47 min	51 min
Density (25°C) kg m^{-3}	0.86	-	-
Oxidative stability (hr)	0.22	0.05	0.1
Cloud point (^{o}C)	4	5	[a]
Pour point (^{o}C)	4.4	-15	[b]
Cloud filter plugging point (^{o}C)	1	-	[b]
Flash point (^{o}C)	148	93 min	120 min
Kinematic Viscosity (mm^{2}s^{-1} at 40°C)	1.8	1.9-6	3.5-5.0
Sulphur content (wt %)	0.024	0.05 max	-
Moisture content (%)	0.03	-	-
Higher heating value (MJ kg^{-1})	39.4	-	-
Acid value (mg KOH g^{-1})	1.37	0.5 max	0.5 max

[a] Not specified

[b] Not specified. EN14214 use time-and location dependant values for the cold filter plugging point (CFPP) instead.

4.1 Cetane Number

The cetane number expresses the ignition property of biodiesel similar to cetane number in fossil base diesel. The cetane number decreases with decreasing chain length and increasing degree of un-saturation and branching. Cetane number measures the biodiesel ignition delay with higher cetane number indicates shorter time between initiation of fuel injection and ignition.

4.2 Flow properties of biodiesel

The flow of biodiesel consists of cloud point (CP), pour point (PP) and cloud filter plugging point (CFPP). These properties are temperature dependant and the limits of cloud point are not specified in both the ASTM and EN standards since the value is associated with the weather condition and the place where the test is conducted. Table 2 showed that the CP, PP and CFPP values of KOME were 4, 4.4 and 1°C respectively. Rapeseed biodiesel have lower values of CP and PP which were CP -3°C and PP -9°C [14]. The low temperature properties of KOME can be improved by using different type of additives.

4.3 Oxidative stability

The oxidative stability of biodiesel was analyzed by biodiesel rancimat method EN 14112. The oxidation of biodiesel contributes to major problem during storage. The presence of unsaturated bonds influenced this property largely. The oxidation occurs due to presence of air, eminent temperature and presence of metals content which promote the oxidation of the unsaturated bonds. The induction time of KOME was determined to be 12.3 hr which was beyond the standard values in both ASTM D6751 (3 hr) and EN14214 (6 hr).

4.4 Higher heating value (HHV) and sulphur contents

HHV is the measurement of the energy produced during biodiesel burning. This property is related to the stability of biodiesel. In this analysis, HHV of KOME was 39.4 MJ/kg. The sulphur content of KOME was analyzed by LECO CHNS-932 USA model and the value was 0.024 wt% which was less than the standard value.

5 Conclusions

The biodiesel production from high FFA feedstock in one step is difficult because if it is not treated prior to transesterification, the high FFA creates problem and large amount of oil are converted into soap. In this study, esterification followed by transesterificaion was followed. Initially the FFA composition was decreased by using acid catalyst followed by utilization of base catalyst. The low temperature properties and the oxidative stability of the KOME biodiesel were higher than that of the standards values. The Kapok seed oil is a potential feedstock for biodiesel production because its abundance cultivation, high oil content ratio and is a

non-edible sources. Nevertheless further research and development is required to improve its fuel properties.

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