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Rubber seed oil as potential non-edible feedstock for biodiesel production using heterogeneous catalyst in Thailand

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ABSTRACT

This research present an alternative raw material of rubber seed which is non-edible crops as a source to produce oil for biodiesel production in Thailand. The rubber seed powder was extracted with hexane at room temperature to give rubber seed oil with the yield of 24 wt%. The composition and key properties of the extracted oil were analyzed including fatty acid compositions, density, kinematic viscosity, flash point, water content and acid value. This high FFAs oil (5.20 wt%) was successfully transesterified by various heterogeneous catalysts such as CaO-based waste coral fragment, sodium metasilicate and CaO-based eggshell to biodiesel in high yield and high %FAME of >97% in single step. Thermal stability of biodiesel obtained from rubber seed oil was evaluated by using thermogravimetric analysis and compared with petrol-diesel fuels. The biodiesel obtained from rubber seed oil was examined and found to meet the EN 14214 standard for bio-auto fuel.

1. Introduction

Biodiesel is an important alternative renewable energy source because it is environmental friendly, non-toxic, and has lower emission gases when used for the combustion [1]. Biodiesel is produced from direct transesterification of vegetable oils or animal fat, where the corresponding triglycerides react with small molecule alcohol such as methyl alcohol in the presence of a catalyst [2,3]. Currently, more than 95% of biodiesel is produced from edible oils which are easily available on large scale from the agricultural industry. However, continuous and large-scale production of biodiesel from edible oils has recently been of great concern because they compete with food materials – the food versus fuel dispute. There are concerns that biodiesel feedstock may compete with food supply in the long-term. Therefore, non-edible plant oils have been found to be promising crude oils for the production of biodiesel. The use of non-edible oils is very significant in developing countries because of the tremendous demand for edible oils as food and that they are far too expensive to be used as fuel at present [4–6].

In Thailand, palm oil is an important raw material for biodiesel production. However, palm oil has been used for essential consumption and food industry. Thus, using palm oil as raw material to produce biodiesel has caused the shortages edible oil consumption and raised palm oil price in the country. At this point, research for non-edible oils or new non-edible crops is crucial for biodiesel production industry in Thailand. Likewise, *Jatropha curcas* plants is promoted as raw material for biodiesel because it plants easily, grows rapidly and offers high yield of oil [7–9]. However, due to the limited plantation area for *Jatropha curcas* plants, they are insufficient to be a feedstock in biodiesel production.

In the recent years, there are several works reported on biodiesel production using rubber seed oil which has higher potential to be used as alternative diesel fuel because it is a non-edible oil that can produce sufficient amount of oil for the industry [10,11]. Ramadhas et al. [12] reported that rubber seed kernels contain between 40 and 50 wt% oil. Yusup and Khan [13] investigated the

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blend of crude rubber seed oil and crude palm oil as a potential feedstock for biodiesel production and the obtained product were in the acceptable range of the international standards. Gimbun et al. [14], applied limestone based catalyst for transesterification of high free fatty acid (FFA) rubber seed oil and they found that the produced biodiesel was within the limits of specifications described by ASTM D6751. Ahmad et al. [15] reported the study of fuel properties of rubber seed oil based biodiesel and found that all the properties of biodiesel were within the range of both the ASTM D6751 and EN14214.

According to the office of agricultural economics and rubber authority of Thailand, in 2014, rubber trees cover around 35,482.7 square kilometers (3,548,274 ha) in Thailand and this number is increasing each year [16]. According to the rubber seed production in India which is about 150 kg per hectare, the production of rubber seed in Thailand is expected at 0.532 million tons per year [12,13]. Therefore, using rubber seed as a high potential oil feedstock for biodiesel would increase the value of rubber trees in Thailand. In fact, the use of rubber seeds originated from Thailand in biodiesel production is reported [11]. Moreover, many researchers have reported to convert rubber seed kernel as non-edible sources to bio-oil using pyrolysis process [17]. Chaiya and Reubroycharoen [18] found that rubber seed shell and residue give the highest yield of bio-oil which is 34.35–38.22%. Hence, rubber seed shell is a good raw material for liquid bio-fuel production because the extracted oil can be used to produce biodiesel through transesterification reaction, while the residue of rubber seed after extraction oil can be converted to bio-oil by pyrolysis process [18,19].

In this work, we report the possibility of using rubber seed collected in Northeastern provinces of Thailand as oil source for biodiesel production. The rubber seed oil was extracted using simple solvent extraction technique. The composition and properties of the extracted rubber seed oil were analyzed. The effect of stored time on free fatty acid (FFAs) content of the rubber seed oil was studied. Single step transesterification of the extracted oil using heterogeneous catalysts was examined and the fuel properties of the obtained biodiesel were evaluated.

2. Material and methods

2.1. Material

Disodium metasilicate (Na_2SiO_3) was purchased from Aldrich and the calcium oxide (CaO) AR grade was purchased from Acros. Potassium hydroxide (KOH) used in this work was purchased from Lab-scan. The analytical grade methanol, hexane, acetone, dichloromethane and ethyl acetate were purchased from Fluka. Waste coral fragments collected from Krabi province, Thailand were crushed into small size (0.5–1.0 cm^3) and transformed to CaO-based coral fragment catalyst according to the reported procedure [20]. Eggshell was collected from the local restaurant and cleaned by washing with deionized water. After that it was dried at 100 °C for 6 h and transformed to CaO-based eggshell catalyst according to the reported procedure [21,22]. Palm oil was obtained from commercial sources in local market. The rubber seed was collected from the Northeastern provinces of Thailand.

2.2. Extraction and characterization of rubber seed oil

Rubber seed has brown color, hard shell, white flesh and oval shape as depicted in Fig. 1A. After cleaning with water and air dry, the seed were ground by blender to get rubber seed powder. The powder (1 kg) was added into the solvent, shaked for 30 min, filtered through filter cloth, centrifuged at 2000 rpm for 10 min to obtain a clear liquid, dried with anhydrous Na_2SO_4 and filtered. The solvent was removed to give a rubber seed oil. Various kinds of solvent were used including hexane, acetone, dichloromethane and ethyl acetate. The solvent to seed powder ratio (v/wt.) was optimized and the total oil content (wt.%) was calculated from weight of extracted oil divided by weight of rubber seed. FFAs content in oil was determined by the reported method [7,23]. The fatty acids component in oil was determined by a gas chromatograph (GC-2010, Shimadzu) equipped with capillary column, DB-WAX (30 m × 0.15 mm) and a flame ionization detector. The methyl-heptadecanoate was used as the internal standard for quantification, according to EN14103 standard method [24].

2.3. Transesterification of rubber seed oil

The transesterification was performed in a batch reactor. Rubber seed oil, methanol and catalyst were mixed in a 250 ml 3-neck round bottom flask equipped with a reflux condenser. The reaction mixture was heated at a controlled temperature and stirring rate. The heterogeneous catalysts used for the transesterification of the rubber seed oil were waste coral fragment, sodium silicate granule, CaO-based eggshell and CaO. The optimized conditions for each catalyst are listed in Table 3. To monitor the reaction progress, the mixed solution of 0.5 ml was sampled, and then the excessive amount of methanol was evaporated in an oven before the analysis of biodiesel yield. The conversion of rubber seed oil to biodiesel was determined in terms of percent fatty acid methyl ester (%FAME) as a function of time. The %FAME was determined using nuclear magnetic resonance (NMR) technique [25–27]. The %FAME was calculated according the following equation:

$$\%FAME = \frac{2A_{CH_3}}{3A_{CH_2}} \times 100$$

where A_{CH_3} is an integration of the methoxy protons (CH_3–O) at chemical shift of 3.66 ppm (singlet peak) and A_{CH_2} is an integration of the methylene protons (–CH_2–) at chemical shift of 2.30 ppm (triplet peak). The factors 3 and 2 were derived from the number of attached protons at the methoxy and methylene carbons, respectively. It should be noted that the triplicate experiments are carried out for each combination of reactants and processing conditions, and the errors of %FAME value were typically within 0.5%. %FAME value in biodiesel was finally analyzed again by gas chromatography [24,28].

3. Results and discussion

3.1. Oil extraction

Many kinds of solvents were used to extract triglycerides (oil) from the rubber seed powder including hexane, acetone, dichloromethane and ethyl acetate. The results are summarized in Table 1. Since higher percentage of FFAs in the oil reduces the yield of the esterification process, this data suggests that hexane is the best solvent for extraction of oil from rubber seed as it gives high yield of oil and less FFAs content. Moreover, hexane is cheaper than others and can be recovered from the process and reused.

The obtained oil and FFAs contents were varied and seem to correlate with the polarity of the extracted solvents which are in the order of hexane << ethyl acetate < acetone ≈ dichloromethane. Less polar solvent can extract high amount of non-polar oil (triglyceride) and less amount of high polar FAAs, and a vice versa. By this method, hexane gives the highest extracted oil content of 24 wt % (FFAs = 5.2 wt%) at a solvent to seed ratio of 0.5 v/wt (Fig. 2). Further increase in the solvent amount does not have any impact on oil yield. Ethyl acetate gives lower oil content of 20 wt%