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Review on methyl ester production from inedible rubber seed oil under various catalysts

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ABSTRACT

The outcomes of the United Nations Climate Change Conference in Paris Convention (COP 21), the steady escalating of global carbon dioxide (CO_2) concentration and the declaration of 2015 as the warmest year ever, demanding solutions to keep the earth fit for human habitation for years to come. One of such solutions is the use of biodiesel as an energy supply for diesel engines, that is regarded as a less environment-damaging fuel. As such, this review presents the possibility of utilizing non-edible rubber seed *(Hevea brasiliensis)* oil as a potential feedstock in biodiesel preparation via both homogeneous and heterogeneous acid and alkali catalysts. It deliberates the one-step and two-step routes of methyl ester production with various reaction conditions that to be weighted in order to achieve environment-responsibility yet cost-effective renewable fuel.

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1. Introduction

The very recent, though tough, outcomes of the United Nations Climate Change Conference in Paris Convention (COP 21) demands all countries report their emission profile and their mitigation efforts on a regular basis to be reviewed internationally. It commits all countries to do their ablest to alleviate the climate change. While the convention reiterates the below 2 °C limit on global temperature increase, it advocates actions to limit it to 1.5 °C. On the other hand, in agreement with the urgent need for such actions, global CO_2 concentration is escalated to 403 mg/L this year from 380 mg/L (2013), in addition to the reports of 2015 to be the warmest year ever recorded on the planet (da Rosa, 2013; Embong et al., 2016; NOAA, 2016). This scenario mandates drastic yet effectual actions to be taken to make the earth fit for living things.

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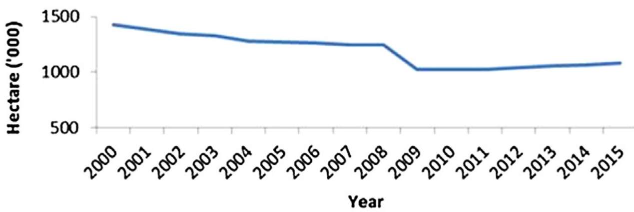

Fig. 1. Malaysia's rubber tree planted hectarage between 2000 and 2015 (MRB, 2016).

One of the ways to lessen the deterioration of the environment is to use energy from renewable sources as to feed the energy call of the globe. In this context, biodiesel can play its global role in minimizing greenhouse gasses emission. The usage of this renewable fuel around the world indicates the need of an unceasing supply of biodiesel in the near future. While the US uses 44 million tonnes of biodiesel, the EU is at 6.1 million tonnes and the UK at 265 million litres (EIA, 2016; EBB, 2016). In terms of sources of triglycerides, edible oils dominate the feedstock. A course must be set as the next direction whereby researchers all around should extensively focus their research on inedible and waste oils.

Rubber seed oil (RSO) is a promising feedstock for biodiesel in Malaysia. The combination of harvested area from three largest natural rubber production countries such as Indonesia, Thailand, and Malaysia cover two-thirds of world's harvested area (Widyarani et al., 2014). Rubber tree (*Hevea brasiliensis)* belongs to the Euphorbiaceae family and is the dominant species in Malaysia plantations since 1888 (Aravind et al., 2015; MRB, 2016). Being the second largest plantation in Malaysia, rubber plantation stands at 1078.63×10^3 ha in 2015 with approximately 540 million trees that produces 1 078 630 t of seeds annually (Ahmad et al., 2014; RISDA, 2016). Although there was a declining trend of planted area from 2000 to 2010, a gradual increase is seen from 2010 onwards which recorded a value of almost 1.1 million ha in 2015 (Fig. 1).

The seeds are variable in size that is 2.5–3 cm long, typically weighing 2–4 g, consists of 42–51% shell and 49–58% kernel and mottled brown in appearance (Widyarani et al., 2014). Rubber seed oil is extracted from the crushed and filtered kernel with 50–60 wt.% of oil content. In a ratio of 7:3 for usable seeds to waste, it accounted for about 330 000 t of waste seeds which in turn translates to 161 800 t of discarded rubber seed oil in 2015, at the 50 wt.% oil content basis. This source is an excellent supply for biodiesel production and as to counter the high feedstock cost of edible oils for the purpose. As for the socio-economy, utilization of this source for fuel value adds to the sustainability of rubber plantation by stabilizing the economy of the sector. Meanwhile, rubber seed cake, treated residue from the extracted oil will be beneficial for cattle farming for its protein and carbohydrates (Takase et al., 2015).

2. Characteristics of RSO

The typical properties and composition of the RSO are reported in Table 1. RSO contains 55.9−58.5% of poly-unsaturated fatty acids (linoleic and linolenic), 20.1−24.6% of mono-unsaturated fatty acid (oleic) and 18.9% of saturated fatty acids (palmitic and stearic). The dominance of poly-unsaturated fatty acid in this species may contribute to the improvement of cold flow properties and the cetane number (Shang et al., 2010; Silitonga et al., 2016). Recognized as a non-edible oil, composition of fatty acid in RSO may not be suitable for human consumption because of the toxic compound contained in the oil. Rubber seed is capable of producing cyanogenic glucoside which contains poisonous prussic acid from the reaction of the enzyme (Gui et al., 2008; Salimon et al., 2012). During 2000−2015, Malaysia produced almost 2 million tonnes of latex but still had to import about 5 million tonnes because of the high demand. In 2015 alone, Malaysia produced 45 862 t latex, while the usage was nearly nine-fold, 406 930 t, translating the high demand for latex (The Sun Daily, 2016; MRB, 2016). As this scenario gives a brighter outlook on rubber plantation hectarage in Malaysia, it too confirms the continuous supply of RSO. Another characteristic of RSO to be noted is its high acid value. RSO contains higher free fatty acid (FFA) as high as 91.4 mg-KOH/g compared with the natural edible oil (Uemura et al., 2013). High FFA forms soap through saponification which in turn complicates product separation and eventually resulted in lower biodiesel yield.

3. Various oil extraction methods

RSO is reported to be extracted from the seed kernels by several methods except for the case of in situ transesterification where ground rubber seed is directly being used (Abdulkadir et al., 2015). Extraction methods have been classified into two types: mechanical and chemical (solvent) extraction, the favored method is mechanical press technique or screw pressing which involves a simple procedure to drain out the oil through squeezy the kernels by the mean of pressure. However, most of the researchers have not reported the yield of the oil extraction obtained by this method. (Ramadhas et al., 2005a; Jose et al., 2011; Ahmad et al., 2014; Karnjanakom et al., 2016) A study by Morshed et al. (2011) reported only 5.35% of oil yield from laboratory scale mechanical press, but with a combination method, using hexane in mechanical press technique, interestingly a maximum oil yield of 49% is obtained.

Meanwhile, for chemical extraction, Soxhlet and microwave assisted extraction (MAE) are the methods of choice to extract the rubber seed oil. Ikwuagwu et al. (2000) reported that approximately 45.63% of oil yield was obtained by using Soxhlet extractor with petroleum ether (40–60 °C). Similarly, in Soxhlet extraction, Ong et al. (2014) employed hexane as an extraction solvent at 70 °C, for 6 h per cycles using 1:3 (w/v). As a comparison to Soxhlet method, Gimbun et al. (2013) achieved more effective extraction of 40% oil yield in 15 min through MAE. As compared to conventional Soxhlet when 36% is achieved in 6 h. Evidently, MAE performed better than Soxhlet in term of percent yield and extraction time.

4. Esterification and transesterification

Fatty acid methyl ester (FAME) can be produced by a single reaction of transesterification or by a 2-step reaction involving esterification and transesterification. A single esterification reaction can also produce FAME when utilizing free fatty acid (FFA) as a feedstock. Acid value varies from 1.7 to 84 mg-KOH/g and both homogeneous and heterogeneous catalysts are capable to catalyze the reaction either functionalised by acid or basic active site. Notified the variation of acid value in RSO, other than, the used esterification step, pretreatment like bleaching reduces the acidity. It is worth to note that longer storage time (exceeding 2 months) possibly increases the acid value of the oil (Ikwuagwu et al., 2000; Morshed et al., 2011). In practise, the pH value from 0.5 mmol/g to 3.0 mmol/g is usualy employed for a succeed esterification using acidic catalyst. Meanwhile, for basic catalyst in the range of 9.3 mmol/g to 18.4 mmol/g.

Esterification and transesterification are the simplest methods to transform oils or fats into biodiesel. In transesterification reactions, the triglyceride molecules present in oils/fat are responsible for reacting with a short chain alcohol in the presence of a catalyst to form alkyl esters and glycerol. Stoichiometrically, a mol of methanol required for each mol of FFA to produce methyl ester and water in the esterification reaction. Meanwhile, in the transesterification reaction, a mol of triglyceride reacts with 3 mol of methanol