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Research article

Refining of crude rubber seed oil as a feedstock for biofuel production

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ABSTRACT

Crude rubber seed oil is a potential source for biofuel production. However it contains undesirable impurities such as peroxides and high oxidative components that not only affect the oil stability, colour and shelf-life but promote insoluble gums formation with time that could cause deposition in the combustion engines. Therefore to overcome these problems the crude rubber seed oil is refined by undergoing degumming and bleaching process. The effect of bleaching earth dosage (15–40 wt %), phosphoric acid dosage (0.5–1.0 wt %) and reaction time (20–40 min) were studied over the reduction of the peroxide value in a refined crude rubber seed oil. The analysis of variance shows that bleaching earth dosage was the most influencing factor followed by reaction time and phosphoric acid dosage. A minimum peroxide value of 0.1 milliequivalents/gram was achieved under optimized conditions of 40 wt % of bleaching earth dosage, 1.0 wt % of phosphoric acid dosage and 20 min of reaction time using Response Surface Methodology design.

1. Introduction

Crude rubber seed oil is a prospect source for a renewable fuel production. Since it is a vegetable oil, it is tagged as an environmentally friendly source because it contained no sulphur compounds and does not add to environment's carbon dioxide level. Thus reducing the greenhouse gases impacts (Barnwal and Sharma, 2005). Furthermore being a non-edible oil source, food versus fuel conflicts will not arise especially in densely populated countries like India and China (Hassan et al., 2015).

Since rubber seeds are readily available throughout the year the sustainability of the feedstock supply is assured. The rich in oil seeds are found in the fruits bear by the rubber tree. Historically the tree originates from the tropical rainforest of the Amazon basin and Guianas. It was then distributed to the South East Asia regions that contributed to 95% of latex production (Heuzé and Tran, 2015). Malaysia, however, being one of the top rubber suppliers in the world has rubber plantation of approximately 1,021,540 ha reported in the year 2009 that yields above 120 ktons of rubber seeds yearly (Gimbun et al., 2012). About 40–50% of oil is found in the dried kernel which produces more than 20 million litres oil annually (Ramadhas et al., 2005). So far, these seeds are underutilized and had been disposed of as waste all this while. Therefore they are considered as cheap feedstock for renewable fuel. Selecting a cheap feedstock is beneficial because 75% of the overall production cost comes solely from the supply and price of the feedstock (Meng et al., 2009). Although being a very desirable feedstock for renewable fuel, the crude rubber seed oil is preferred to be refined first in order to remove non triglyceride materials that deteriorate the oil quality in terms of appearance, stability and shelf life (Ejikeme Ebere et al., 2013).

Past literature disclosed that various edible vegetable oils have been refined to improve the oil properties for consumption and industrial reasons (Egbuna et al., 2013). A number of researchers had also expanded their horizons on refining non-edible oils for biofuel production. The prevalent biodiesel production from non-edible oils started gaining attention ever since the intense debate on the food to fuel supply. Typically, refined oils are desired for biodiesel production. This is because refining improves the physicochemical properties of oils by removing impurities that impede the transesterification reaction due to soap formation (Wallace

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et al., 2017). If the reaction produced soap the catalyst will be consumed, thus reducing its catalytic efficiency (Fernández et al., 2010). The impurities removal also prevent the engine from corrosion and reduce oil susceptibility to peroxidation (Winfried et al., 2008). While some researchers like Onukwuli et al. (2016) and Sootchiewcharn et al. (2015) worked on converting refined oils to biodiesel, Adekunle et al. (2016) and Omorogbe et al. (2013), on the other hand, did a comparison study between unrefined oils and refined oils for biodiesel yield. Their findings proved that refined oils gave a higher biodiesel yield and better diesel properties compared to unrefined oils.

Apart from transesterification, refined oils had also been also been used by several researchers in the catalytic cracking reactions to produce petroleum like fractions such as gasoline, kerosene and diesel. This is the current preferred route for biofuel production because the fuel shows excellent compatibility with the conventional combustion engines. Recently Emori et al. (2017) had compared the influence of crude and refined soybean oil compositions on the product distribution of the cracking reaction. His results revealed that catalytic cracking of refined oil with hydrogen flow produced the highest gasoline yield while unrefined oil gave a higher yield of kerosene and diesel range hydrocarbons. The impurities present in the unrefined oil is the reason for the deactivation effect that reduces the catalyst cracking efficiency with time, resulting in heavy hydrocarbons production. Furthermore, the incomplete deoxygenation reaction occurs in unrefined oil are caused by sulphur and phosphorus compounds that are produced during the cracking of proteins and phosphatides present in the unrefined oil. These compounds poison the acid sites leading to undesirable oxygenated organic molecules formation.

The unrefined oil could be physically or chemically refined to remove the impurities like phosphatides, pigments, trace metal complexes and oxidative components such as peroxides. These undesirable impurities stimulate oil oxidation (Chew et al., 2016). Generally, the oil refining is done in four stages which include degumming, neutralization, bleaching and deodorizing. On that note, several optimization studies had been published on the effects of different refining stages on the oil quality. For an instance, the effect of degumming parameters was studied by Egbuna (2015) on the phosphatides removal. He concluded that optimum conditions for degumming were achieved at temperature 80°C, a phosphoric acid concentration of 1% and contact time of 40 min for palm oil. In terms of bleaching process, Egbuna et al. (2015) published that the optimal bleaching efficiency in respect of carotenoid adsorption was 83% which was achieved at 99.83°C for 40 min with 4% of clay dosage in palm oil refining. Alternatively Wei et al. (2015) studied the optimized refining temperatures of all the four refining stages so as to minimise the loss of bioactive compounds and essential fatty acids in tea seed oil while refining.

However, Chew et al. (2017) and Strieder et al. (2017) appear to be the few first who had studied the optimized conditions in minimizing the peroxides in kenaf seed oil and rice bran oil respectively. The former managed to reduce the peroxide value to 1.57 meq/kg. Similarly, the latter managed to remove 83% of peroxides in a bleaching process using a blend of 1% adsorbent and 8% of activated carbon. Despite both studies worked on optimizing peroxides, their common focus was to meet the peroxides level suitable for consumption purpose. Hence their target was to attain optimum conditions that prevent the removal of important bioactive compounds. This contradicts with biofuel production where the aim of refining was to remove all the impurities present leaving behind triglycerides and sometimes fatty acids (depending on the refining pathway chosen). Therefore after critically analysing the most recent state of the art refining process, none has actually optimized the peroxide value (PV) of refined rubber seed oil to make it suitable for biofuel production. Hence the present PV study is conducted.

Among the four treatments, oil that underwent degumming and bleaching process experienced a significant reduction in its PV (Chew et al., 2016). For that reason, rubber seed oil in this study is degummed and bleached only. PV is given utter importance because it measures the hydroperoxides present in an oil that is formed due to primary oxidation. The removal of these peroxides is essential because it preserves the oxidative stability of the oil preventing it from deteriorating during storage (Sánchez-Machado et al., 2015). The presence of hydroperoxides in oil induces polymerisation of olefins resulting in the formation of long insoluble gums (Speight, 2014). These unfavourable gums produced will block the filters and forms deposits on engines consequently affecting the engine's efficiency (Rashed et al., 2015). Moreover, rubber seed oil is rich in polyunsaturated fatty acids that decrease the oxidative stability because it tends to attract more oxygen molecules which increase the PV of oil, hence the need for refining.

Therefore in this investigation response surface methodology (RSM) had been used as a tool to design the experiment and further optimized the parametric conditions in respond to PV. This statistical tool evaluates the influence and interactions of various factors on the response variables. It profoundly reduces the number of experimental runs but still generates statistically reliable results (Chew et al., 2017). The effects of three parameters such as phosphoric acid dosage (0.5–1.0 wt%), bleaching earth dosage (15–40 wt%) and reaction time (20–40 min) were studied on the peroxide value of the refined oil following central composite design (CCD).

2. Materials and method

The materials used and the experimental procedures were explained in this section.

2.1. Reagents and chemicals

The crude rubber seed oil is acquired from Kinetics Chemicals (M) Sdn Bhd Malaysia. The analytical grade and HPLC chemicals used in this experiment were purchased in Malaysia. The analytical grade chemicals are phosphoric acid (85% concentrated) and starch puriss obtained from Sigma Aldrich, acetic acid and sodium thiosulphate from Biobasic and potassium iodide procured from Merck. While chloroform which is a HPLC type chemical is obtained from Biobasic. The bleaching earth is supplied by Lee Oil Mill Kapar, Malaysia.

2.2. Design of experiment (DOE)

In this experiment the DOE applied was central composite design (CCD) under Design Expert 10.0.1 Software. A set of specific experiment matrix was created first by CCD which composed of variables at different level of combinations that was performed experimentally in order to obtain their respective responses (Bezerra et al., 2008). The independent variables studied in the refining of crude rubber seed oil were phosphoric acid dosage, bleaching earth dosage and reaction time where the variables were coded as A, B and C accordingly.

They were kept in a space of minimum to maximum levels referring to the data provided in the literature. Typically each factor in CCD has five levels and they are grouped into three design points which are known as two level factorial points defined as 1 and −1, axial points defined as α and $-\alpha$, and center points defined as 0. The center points are basically repeated experimental arrays closer to the center of factor space to ensure superlative prediction potential.

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