



Thermal catalytic cracking of crude palm oil at pilot scale: Effect of the percentage of Na_2CO_3 on the quality of biofuels



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ABSTRACT

In this study, the influence of catalyst content on the physical–chemical properties, yield, and chemical composition of organic liquid products (OLP) obtained by thermal catalytic cracking of palm oil (*Elaeis guineensis*, Jacq.) was studied at a pilot scale. The experiments were carried out in a reactor of 143 L, running in batch mode at 450 °C and 1 atm, using 5%, 10%, 15%, and 20% (w/w) Na_2CO_3 as the catalyst. Physical–chemical characterization of OLP was conducted for acid value, saponification value, specific gravity, refractive index, kinematic viscosity, copper strip corrosion, and flash point. The chemical composition of OLP was determined by gas chromatography–mass spectrometry (GC–MS). As the catalyst content increased, the kinematic viscosity of OLP decreased from 6.59 to 3.63 mm² s^{−1} and the acid value from 51.56 to 1.26 mg KOH/g. The GC–MS analysis showed that OLP comprise hydrocarbons (normal paraffin, olefin, and naphthenic) and oxygenated compounds (carboxylic acids, alcohols, ketones, and esters), with a high dependency on the catalyst level. As the catalyst content increased, the concentration of hydrocarbons increased, whereas the concentration of oxygenates decreased. The optimal sodium carbonate catalyst level was found to be 15% (w/w). This gave the highest rate of conversion into biofuel, of which around 60% was OLP, and produced biofuels with the lowest acid values. The physical–chemical properties were within the limits fixed by ANP No. 65 (Diesel S10 specification) due to their high hydrocarbon content (92.84%) and low oxygenate content (7.16%). The hydrocarbons produced had characteristics similar to those of petroleum diesel, offering the potential to replace petroleum fuels without requiring deacidification or deoxygenation pretreatment.

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1. Introduction

There is a growing interest in research and development of alternative fuels to meet future energy needs (Taufiqurrahmi and Bhatia, 2011). Alternative fuels can be produced from a wide variety of renewable sources. Among these, triglycerides play an important role (Doronin et al., 2013; Yu et al., 2013), as they are the major

compounds present in vegetable oils and animal fats (Scrimgeour, 2005).

Several technical routes are available for the conversion of vegetable oils and animal fats into biofuels, and these have been extensively studied (Doronin et al., 2013; Yu et al., 2013). One of the most promising technical routes to the production of alternative fuels from vegetable oils and animal fats is pyrolysis. This is also known as cracking and can be subdivided into thermal cracking (Kozliak et al., 2013; Iha et al., 2014; Kubátová et al., 2011; Luo et al., 2010; Mangas et al., 2012; Şensöz and Kaynar, 2006) and thermal catalytic cracking (Chew and Bhatia, 2008; Dupain et al., 2007; Maher and Bressler, 2007; Ong and Bhatia, 2010; Xu et al., 2013).

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A wide variety of raw materials have been used for biofuel production using cracking. These include (a) carboxylic acids (Wang et al., 2012) and mixtures of fatty acids (Hengst et al., 2015; Ooi et al., 2004a); (b) crude vegetable oils such as palm oil (Leng et al., 1999; Tamunaidu and Bhatia, 2007), canola oil (Archambault and Billaud, 1998; Katikaneni et al., 1995), soybean oil (Buzetzkzi et al., 2011a; Yu et al., 2013), and sunflower oil (Chen et al., 2010; Yigezu and Muthukumar, 2014, 2015); (c) recycled cooking oil (Li et al., 2013); (d) industrial fatty wastes such as soybean soapstock, beef tallow, and poultry industry waste (Santos et al., 2010) and scum from grease traps (Almeida et al., 2016); and (e) nonedible oils such as jatropha oil (Biswas and Sharma, 2014) and camelina oils (Zhao et al., 2015). According to Melero et al. (2012), crude vegetable oils are the most significant in terms of global production. Industrial fatty wastes are more economical as their transformation into biofuels does not create competition with other users or have an adverse impact on the food supply chain.

The oil palm tree has the highest oil yield per hectare, making its oil an inexpensive feedstock (Kuss et al., 2015). It is a perennial crop, producing a harvest every month of the year, and has the highest oil production at around 4000–6000 kg/ha, compared with the 400–600 kg/ha of soybeans (Rodrigues et al., 2014) and 97–833 kg/ha of nonedible camelina oil (Moser, 2010).

Palm oil and palm kernel oil account for 36% of the world production of vegetable oils. In Brazil, the center of production is the state of Pará (Amazon region), which is responsible for 93% of the national palm oil production (Souza et al., 2010). To investigate the potential of palm oil as a raw material in thermal catalytic cracking, we conducted experiments in a pilot cracking unit located in the state of Pará.

Catalytic cracking has advantages over other triglyceride processing methods (Ong and Bhatia, 2010). First, the products from catalytic cracking include gas, organic liquid product (OLP), water, and coke (Taufiqurrahmi and Bhatia, 2011; Wiggers et al., 2009b). OLP comprise oxygen compounds (aldehydes, ketones, and carboxylic acids) and hydrocarbons (normal paraffin, naphthenic, and olefin) that match the boiling point ranges of gasoline, kerosene, and diesel (Wang et al., 2012; Wiggers et al., 2009a). Second, the reaction temperature is lower than that of pyrolysis, and large molecules are broken down into smaller compounds by dehydration, dehydrogenation, deoxygenation, and decarboxylation (Taufiqurrahmi and Bhatia, 2011). Third, catalytic cracking offers a cheaper route to energy consumption (Zhang et al., 2005).

Compared with transesterification, which converts triglycerides to biodiesel (methyl or ethyl esters of fatty acids), cracking has the following advantages: (a) lower processing cost; (b) production of standard engine fuels; (c) flexibility in raw materials, as a range of triglyceride biomass sources can be used (Stumborg et al., 1996; Zhang et al., 2005); (d) compatibility with existing infrastructure; (e) when using homogeneous catalysts, transesterification incurs high costs in energy consumption and the separation process (Chew and Bhatia, 2008); and (f) biodiesel from transesterification has drawbacks in its cold fuel properties and high acidity (Lovás et al., 2015). Therefore, cracking of biomass based on triglycerides avoids the many technical limits of transesterification. In addition, transesterification can only be used to produce biodiesel, whereas catalytic cracking can produce gasoline and kerosene, among other products as well as diesel fuel.

To increase the yield of OLP in thermal catalytic cracking and reduce the yield of unwanted reaction products such as gas, water, and coke, a wide variety of catalysts have been tested (Benson et al., 2009; Li et al., 2013; Ooi et al., 2003; Twaiq et al., 2003a, 2007; Vonghia et al., 1995). Among these catalysts, the zeolites have great potential because of their unique porous structure and thermal and hydrothermal stability (Yu et al., 2013). However, OLP obtained when using zeolites in thermal catalytic cracking have a high car-

boxylic acid content. Buzetzkzi et al. (2011a) obtained OLP with an acid value close to 120 mg KOH/g. Wiggers et al. (2009b) reported acid values higher than 120 mg KOH/g. Buzetzkzi et al. (2011b) produced OLP with acid values exceeding 141 mg KOH/g.

Alternative processes have been explored in an attempt to reduce the acid values and olefin concentration of OLP produced by cracking of triglycerides (Wiggers et al., 2013). One of these processes uses Na_2CO_3 (sodium carbonate) as a catalyst (Dandik and Aksoy, 1999; Dandik et al., 1998; Konwer et al., 1989).

The use of sodium carbonate as a catalyst in the cracking of sunflower oil has been investigated in experiments using a reactor coupled to a packed fractionation column (Dandik and Aksoy, 1998). In comparison with the results reported by Konwer et al. (1989), Dandik et al. (1998) found low concentrations of aromatic compounds in OLP. In addition, the conversion rates were lower than those obtained by Konwer et al. (1989), and almost the half of the feed material was converted to coke. The main products of the cracking reactions were liquid-phase hydrocarbons that had a lower acid value and a gas phase with water, H_2 , CO, and CO_2 .

Dandik and Aksoy (1999) investigated the catalytic cracking of residual sunflower oil using the catalysts sodium carbonate, silica–alumina, and HZSM-5. They found that the highest conversion of 73.17% (w/w) was obtained when using sodium carbonate. Sodium carbonate also gave higher yields of liquid products, consisting mainly of hydrocarbons with a similar temperature range to that of gasoline.

Chew and Bhatia (2008) reported that the temperature required for catalytic cracking (450 °C) was lower than that of pyrolysis (500–850 °C). A range of studies (Twaiq et al., 2003b, 2004; Ooi et al., 2004b,c) have investigated the catalytic cracking of palm oil using different catalysts at 450 °C and 1 atm in laboratory-scale reactors. The resulting products have resembled gasoline, kerosene, and diesel fuel, with the yield of gasoline dominant.

Idem et al. (1996) conducted thermal cracking of canola oil at temperatures in the range from 300 to 500 °C under atmospheric pressure and demonstrated hydrocarbon yields of 54% (w/w). Tamunaidu and Bhatia (2007) produced gasoline-rich OLP from thermal catalytic cracking of palm oil. Their results suggested an ideal reaction temperature of 450 °C. Li et al. (2009) carried out thermal catalytic cracking of cottonseed oil and studied the effect of temperature (400–500 °C) on the yield of gasoline and diesel fractions. A reaction temperature of 426.2 °C produced the highest yield of these fractions, and temperatures lower than 400 °C often resulted in low yields. In the range from 400 to 500 °C, the yield of hydrocarbons increased.

Investigations of the thermal catalytic cracking of biomass in pilot units using triglycerides have been carried out by Almeida et al. (2016), Mota et al. (2014), Weber et al. (2012), Wiggers et al. (2009a), Wiggers et al. (2009b), Wiggers et al. (2013) and Xu et al. (2013). Almeida et al. (2016) demonstrated pilot-scale thermal catalytic cracking of scum from grease traps. The cracking reactions were carried out in a 143 L stirred tank slurry reactor running in batch mode at 450 °C and 1.0 atm, using 5%, 10%, and 15% (w/w) activated red mud. The yield of OLP ranged from 62.34% to 75.92% (w/w), with acid values of between 84.65 and 109.55 mg KOH/g. OLP produced using 15% (w/w) activated red mud comprised 37.49% (w/w) hydrocarbons and 62.51% (w/w) oxygenates.

Mota et al. (2014) investigated the production of liquid fuels by thermal catalytic cracking of palm oil. The pilot-scale experiment was conducted at 450 °C, under atmospheric pressure and using 20% sodium carbonate as the catalyst. OLP yield was 65.86% (w/w) with an acid value of 1.02 mg KOH/g and comprised 30.24% (w/w) noncondensable gases, 2.5% (w/w) water, and 1.4% (w/w) coke.

Weber et al. (2012) performed thermal degradation of free fatty acids and animal fat in a pilot plant at temperatures between 410 and 450 °C using a moving bed of sodium carbonate as the catalyst

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