



Process analysis of physicochemical properties and chemical composition of organic liquid products obtained by thermochemical conversion of palm oil

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ABSTRACT

In this work, the influence of catalyst content on the physicochemical properties (acid value, saponification value, specific gravity, kinematic viscosity, and flash point), yield and chemical composition (hydrocarbons and oxygenates) of organic liquid products (OLP) obtained by thermal-catalytic cracking of palm oil (*Elaeis guineensis*, Jacq.) has been systematically investigated in technical scale. The pilot experiments were carry out in a stirred tank slurry reactor of 143 L, operating in batch mode at 450 °C and 1.0 atm, using 5, 10, 15, and 20% (wt.) Na₂CO₃ as catalyst. The catalyst has been characterized by XRF and SEM techniques. The organic liquid products have been physicochemical characterized for acid and saponification values, specific gravity, refractive index, kinematics viscosity, copper strip corrosion, and flash point. The chemical composition of organic liquid products was determined by GC–MS. The experimental results indicate that initial cracking temperature, as well as specific gravity, kinematic viscosity, acid value, and saponification value of OLP show a tendency to decrease with increasing catalyst content. Hydrocarbons and oxygenates were the major chemical compounds present in OLP, with chemical composition strongly dependent on the catalyst content. The major hydrocarbons present in the organic liquid products have carbon chain length ranging from C₁₂ to C₁₅ and its summation shows a tendency to increase with increasing catalyst content, while the summation of oxygenate compounds shows a tendency to decrease. In addition, the distribution of hydrocarbons classes (normal paraffins, olefins, and naphthenics) present in OLP shows a maximum concentration for normal paraffins and naphthenics and a minimum concentration for olefins using 10% (wt.) Na₂CO₃ as catalyst.

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1. Introduction

Energy is essential to the modern global society not only to ensure the quality of life but also as it provides a key element of

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our economy [1], consequently, the global energy consumption has dramatically increased in the last years [2]. In addition, as most of energy still comes from fossil fuels [2], the continue and extensive use of fossil fuels is set to face future challenges including depletion of fossil fuel reserves, global warming, environmental issues, geopolitical conflicts, with great reflexes on oil price instabilities [3].

Renewable energy offers not only the promise of clean and abundant energy but also a solution to the growing energy challenges in the future [2,3]. Despite the complex synergy (biodiversity, soil

and nature conservation, carbon sequestration, and climate change mitigation) between large-scale bioenergy production, future land-use and biomass management, the contribution of bioenergy in the global energy supply chain, particularly liquid biofuels, tends to increase [4].

Biofuels can be produced from a wide variety of renewable sources [5–7], including triglycerides [8], the major compounds present in vegetable oils and animal fats [9,10]. Among the processes and technologies for conversion of oils and fats into liquid biofuels [8,11–13], one of the most promising is thermal cracking (pyrolysis) and/or thermal-catalytic cracking, and the literature reports several studies on the subject [8,14–46,49–54,56–61]. Both have the purpose of obtaining hydrocarbons suitable for use as fuels [16,21,30,32,60,61]. However, the chemical composition of reaction liquid products shows a significant difference. This is due to the complex cracking mechanism of triglycerides [21,30]. Besides the type of cracking mode (thermal cracking and thermal-catalytic cracking), other factors that significantly affect the liquid fuel composition are the characteristics of raw material, reaction temperature, residence time, mode of operation (fluidized bed reactor, sludge bed reactor, etc.) and the presence of water in the raw material and/or in the catalyst [30].

The products obtained by the thermal cracking (pyrolysis) and thermal-catalytic cracking of oils, fats, and fatty acids include gaseous fuels, liquid fuels referred as organic liquid products (OLP), water and coke [22,27,30,32,39,60,61]. The physicochemical properties and chemical composition of OLP depends on the selectivity of catalyst used [27,39]. The liquid fuel (OLP) is a product of great interest, and consists of hydrocarbons (linear paraffins, cyclic paraffins, naphthenics, aromatics, and olefins) corresponding to the boiling point range of gasoline, kerosene and diesel, as well as oxygenate compounds (aldehydes, ketones and carboxylic acids) [18,22,23,27,32,40,41,60,61].

The advantages of thermal-catalytic cracking of fats and oils include high tolerance to the quality of raw lipid-base materials, compatibility of liquid reaction products with combustion engines, as well as compositional similarities to fossil fuels [19]. The products obtained by thermal-catalytic cracking presents lower amounts of carboxylic acids, compared to pyrolysis, due to the catalyst activity in the secondary cracking step, where the carboxylic acids are broken up to form hydrocarbons [21]. The OLP can be not only easily stored and transported, but also refined and/or upgraded by applying physical (filtration, decantation, and centrifugation) and thermal separation processes (distillation, liquid-liquid extraction, and adsorption) to produce high quality green fuel-like fractions (gasoline, kerosene, light and heavy diesel) with potential to substitute partially fossil fuels [22,27,32]. The disadvantages and/or drawbacks of liquid biofuels obtained by thermal-catalytic cracking of fats and oils remains on the high acid value and high concentrations of olefins, making it a corrosive and unstable fuel [30].

In order to increase the yield of OLP and reduce the yield of undesired reaction products, such as gas, water and coke, as well as the content of oxygenate compounds, a wide variety of catalysts have been tested in thermal-catalytic cracking [14,16–18,23,25,26,28,31,32–38,43,45,46,60,61]. Among these catalysts, the zeolites have been the most applied due to their unique porous structure and thermal and hydrothermal stability [17,25,28]. However, the OLP obtained by thermal-catalytic cracking using zeolites and mesoporous catalysts still has a high carboxylic acid content [17,25,26,28,31].

Buzetzi et al. [25] investigated the catalytic cracking of rapeseed, sunflower, soybean, jatropha, and used frying oils in the presence of zeolite catalysts (NaY and Clinoptilolite-CL) in batch mode, obtaining OLP with acid values between 98 and 122 mg KOH/g and between 99 and 118 mg KOH/g for NaY and CL respec-

tively. Buzetzi et al. [26] investigated the influence of zeolites (NaY, HY, NH₄Y, Na-ZMS5, H-ZMS5) content on the yields of reaction products (OLP, Coke, and Gas) and physicochemical properties (viscosity, density, and acid value) of rapeseed oil cracking, obtaining OLP with acid values between 77 and 141 mg KOH/g. Lu Li et al. [31] investigated the cracking of waste cooking oil using mesoporous molecular sieves K₂O/Ba-MCM-41 that exhibited higher performance than alkali catalysts such as Na₂CO₃ and K₂CO₃. This might be due to the relatively larger pores sizes [28,31], closer to the molecular size of hydrocarbons, making it possible to improve the quality of liquid fuels [28]. Nevertheless, its higher catalytic performance, the production of those alkali zeolites, prepared under hydrothermal conditions, makes its production costs high expensive.

Ooi Yean Sang [33] investigated the catalytic cracking of palm oil at 450 °C and 1.0 atm in a fixed bed micro reactor using HZSM-5 as catalyst, and the OLP composed by hydrocarbons (gasoline, kerosene, and diesel) with a gasoline yield of 48% (wt.). Twaiq et al. [34] studied the catalytic cracking of palm oil at 450 °C and 1.0 atm in a fixed bed micro reactor (155 mm × 10 mm ID, V_R = 12.17 mL) using MCM-41 with different Si/Al ratios, obtaining conversions between 80 and 90% (wt.) with high selectivity to liquid hydrocarbons. Twaiq et al. [35] investigated the catalytic cracking of palm oil at 350–450 °C and 1.0 atm in a fixed bed micro reactor of (155 mm × 10 mm ID, V_R = 12.17 mL) using different zeolites (HZSM-5, K-HZSM-5, zeolite β, and USY), obtaining mainly OLP, gas, and water, conversions up to 99% (wt.) and gasoline yield of 28% (wt.) at 350 °C. Twaiq et al. [36] studied the catalytic cracking of palm oil using composite zeolite ZSM-5/mesoporous molecular sieve at 450 °C and 1.0 atm in a fixed bed micro reactor of (155 mm × 10 mm ID, V_R = 12.17 mL), obtaining conversions of 80–100% (wt.) and gasoline yields between 38 and 47% (wt.). In addition, the catalysts were selective to formation of aromatics in OLP. Twaiq et al. [37] investigated the catalytic cracking of palm oil using at 450 °C and 1.0 atm in a fixed bed micro reactor of (155 mm × 10 mm ID, V_R = 12.17 mL) using MCM-41, showing the catalyst was selective for the formation of linear hydrocarbons (C₁₃). In addition, the yield of OLP decreased with increasing specific catalyst surface area, and gasoline selectivity increased while that of diesel decreased with conversion of palm oil. Siswanto et al. [38] investigated the production of gasoline by catalytic cracking of palm oil at 450 °C and 1.0 atm in a fixed bed micro reactor with MCM-41 and oil/catalyst ratios between 30 and 50, obtaining OLP yields up to 60.73% (wt.) and a maximum gasoline yield of 43.63% (wt.). The yield of OLP decreases with increasing oil/catalyst ratio. The studies of thermal-catalytic cracking of palm in micro reactor scale used small quantities of feed, producing liquid fuels only for GC-MS analysis, thus making it not possible to collect enough quantities of OLP necessary to carry out complete physicochemical characterization [33–38].

In this context, processes have been investigated to minimize the high acid value and high concentration of olefins in OLP produced by catalytic cracking of fats and oils [30], including the application of simple and cheap chemical compounds as catalysts such as Na₂CO₃ to reduce the acid value of liquid biofuels [16,17,32,43,44].

Konwer et al. [43] used Na₂CO₃ as catalyst to produce liquid fuels from pyrolysis of *Mesua ferrea* L. seed oil and their pure primary fatty acids. The results showed that pyrolysis of *Mesua ferrea* L. seed oil in the presence of 1% (wt.) sodium carbonate and at 500 °C produced black pyrolytic oil similar to crude oil and their fractions could be suitable for various applications, including gasoline and diesel.

Dandik et al. [16] investigated the catalytic cracking of sunflower oil using Na₂CO₃ as catalyst in a reactor coupled to a fractionation column packed. In comparison to the results obtained by Konwer

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