



## Performance of thermochemical conversion of fat, oils, and grease into kerosene-like hydrocarbons in different production scales



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### ABSTRACT

This work aims to investigate the effect of catalytic cracking of residual fat, oils, and grease (FOG) from grease traps in different production scales (bench, laboratory, and pilot) on the reaction products yields and OLP properties and the feasibility to produce kerosene-like hydrocarbons. The cracking experiments were carried out in batch mode at 450 °C and 1.0 atmosphere, with 10% (wt.) Na<sub>2</sub>CO<sub>3</sub> using a laboratory scale cylindrical borosilicate-glass reactor of 143 mL, a bench scale stirred tank slurry reactor of 1.5 L, and a pilot scale stirred tank slurry reactor of 143 L (≈1:10:1000). The reaction liquid products were physical and chemical analyzed for acid and saponification values, density, kinematic viscosity, refractive index, and copper strip corrosion. FT-IR analysis provided the qualitative chemical composition of OLP obtained in bench, laboratory, and pilot scales, as well as kerosene, light and heavy diesel-like hydrocarbons fractions obtained by distillation of OLP produced in pilot scale with 10% (wt.) Na<sub>2</sub>CO<sub>3</sub>. The chemical compositions of OLP and kerosene-like hydrocarbons fraction obtained in pilot scale determined by NMR and GC–MS. The results showed an OLP yield ranging from 62.90 to 66.57% (wt.), a coke yield ranging between 7.02 and 9.79% (wt.), and a gas yield ranging from 16.32 to 22.40% (wt.), showing a mean absolute percentage deviation of 2.12%, 11.88%, and 14.91% for OLP, gas, and coke yields respectively, obtained in different production scales (≈10:1000). The OLP acid values varied from 19.08 to 10.45 mg KOH/g, the density between 0.820 and 0.835 g/cm<sup>3</sup>, and the kinematic viscosity from 3.28 to 4.21 mm<sup>2</sup> s<sup>-1</sup>. The yield of kerosene-like hydrocarbons fraction average 14.90% (wt.) with an acid value of 5.43 mg KOH/g, density of 0.740 g/cm<sup>3</sup>, and kinematic viscosity of 0.66 mm<sup>2</sup> s<sup>-1</sup>, while those of light and heavy diesel-like hydrocarbons fractions average 32.01% (wt.) and 19.35% (wt.) respectively. FT-IR and NMR analysis of OLP and kerosene-like hydrocarbons fraction confirms the presence of functional groups characteristic of hydrocarbons (alkenes, alkanes, ring-containing alkenes, and ring-containing alkanes, and cycloalkanes) and oxygenates (carboxylic acids, ketones, fatty alcohols, and dienes). The GC–MS analysis of OLP and kerosene-like hydrocarbons fraction obtained in pilot scale with 10% (wt.) Na<sub>2</sub>CO<sub>3</sub> identified in OLP 76.97% hydrocarbons (39.44% alkenes, 31.91% alkanes, 4.12% ring-containing alkenes, and 1.50% ring-containing alkenes) and 23.03% oxygenates (12.14% carboxylic acids, 6.98% ketones, 1.90% fatty alcohols, and 2.01% dienes).

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The kerosene-like hydrocarbons fraction is composed by 94.62% (area) hydrocarbon (44.99% alkenes, 29.61% alkanes, 7.58% ring-containing alkenes, 6.15% ring-containing alkanes, 4.31% cycloalkanes, and 1.98% aromatics) and 5.38% (area) oxygenates (5.38% carboxylic acids), showing that catalytic cracking of scum from grease traps with 10% (wt.)  $\text{Na}_2\text{CO}_3$  is technically feasible.

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## 1. Introduction

Food services (restaurants, fast-food restaurants, industrial restaurants, etc.) generates wastewaters streams containing fats, oils, and greases (FOG) and suspended solids (SS) [1–7]. The discharge of fats, oils, and grease-containing wastewaters into public sewers may cause not only a reduction of sanitary sewers performance and flowing capacity [5,7], but also clogging in drain pipes and sewer lines, because of formation of hard deposits [2,7]. In addition, corrosion of sewer lines due to anaerobic reactions may occur [2], posing a waste management challenge for environmental-public policies, particularly in developing countries [2,5,7].

The most common pre-treatment process for fats, oils, and greases removal from grease-containing wastewater, prior to discharge into public sewers, is a grease trap [5,7]. However, other processes and/or devices for removal of fats, oils, and greases from grease-containing wastewater streams have been reported in the literature [8,7], including grease trap filters [1,5], ultrafiltration processes [9], and the use of microorganism [10]. In this context, processes have been proposed for the treatment of fats, oils, and grease-containing wastewaters streams, including aerobic removal of FOG by microorganism [10], production of biodiesel [4,6,11–14], and the anaerobic co-digestion of FOG to improve biogas production from anaerobic digesters at wastewater treatment units [7,15,16].

The residual fat material from grease trap, a lipid base material of low quality, consists of fatty acids, frying oils (soybean, sunflower, etc.), animal fats, hydrogenated fats, fatty alcohols, and other compounds [4,8,14,17]. A process that makes it possible the use of lipid base materials of low quality for producing liquid and gaseous fuels is pyrolysis [18–26], and/or catalytic-cracking [17,27–43].

Conversion of low quality lipid materials to produce renewable liquid and gaseous fuels can be either achieved by pyrolysis such as soybean cake [18], safflower seed press cake [19], olive oil residue [20], used sunflower oil [21], waste fish oil [22,23], waste frying oil [24,25], and until industrial fatty wastes (soybean soap stock, beef tallow, and poultry waste) [26], or by thermal-catalytic cracking including fat, oils, and grease (FOG) [17], frying oils [27], used sunflower oil [28], used palm oil and palm oil-based fatty acid mixture [29–34], used vegetable oil [35], fatty acids and animals fat [36–40], animal fat and meat and bone meal [41], and until residues of rendering plants [42]. Most studies on the pyrolysis and catalytic cracking of lipid base material have been carry out in micro [29–33,35,43–48], laboratory [18–21,26–28,34,39,40,49], bench scales [23,26,42,50], and semi-pilot scales [22,24,25,51], a only a few in pilot and/or technical scale [17,36–38,41,52].

Ooi et al. [29–33] studied the catalytic conversion of palm oil-based fatty acid mixture, fatty acids mixture, palm oil fatty acids, and used palm oil, using a fixed bed micro scale reactor (ID = 10 mm, L = 155 mm,  $V_R$  = 12.17 mL), over HZSM-5 at 400 and 450 °C, 1.0 atm, fatty acid-to-catalyst ratios between 6 and 10, and WHSV between 2.5 and 4.5  $\text{h}^{-1}$ , obtaining at 450 °C and 2.5  $\text{h}^{-1}$ , and OLP yield of 55.8% (wt.) and 40.9% (wt.) gasoline-like fraction [29]; composite MCM-41/ $\beta$  zeolite and a mixture of zeolite  $\beta$  and MCM-41 [30], mesoporous materials (AIMCM-41 and LPMM-41) at 450 °C, 1.0 atm, WHSV of 2.5  $\text{h}^{-1}$ , obtaining OLP, gas, coke, and water yields

between 48.5 and 63.1%, 6.7 and 25.7%, 1.4 and 11.7%, and 3.2 and 8.8% (wt.), respectively, and gasoline fractions up to 43.0% (wt.), obtained with LPMM-41 [31], over composite catalysts (HZSM-5 and MCM-41/ZSM-5) at 400, 425 and 450 °C, 1.0 atm, and WHSV between 2.5 and 4.5  $\text{h}^{-1}$ , obtaining gasoline fractions up to 52 and 43.0% (wt.) for HZSM-5 and MCM-41/ZSM-5, respectively [32], over composite catalysts composed of microporous HZSM-5 and mesoporous MCM-41/SBA-15 molecular sieve at 450 °C and weight hourly space velocity of 2.5  $\text{h}^{-1}$ , obtaining conversion up 98% (wt.) and gasoline yield 44% (wt.) with HZSM-5 composite catalyst [33]. Ooi Yean Sang [43] investigated the catalytic-cracking of palm oil at 450 °C and 1.0 atm, with HZSM-5 as catalyst, using the apparatus described elsewhere [29], obtaining a OLP composed by hydrocarbons (gasoline, kerosene, and diesel) with a gasoline yield of 48% (wt.). Twaiq et al. [44–47] investigated the catalytic cracking of palm oil, using the apparatus described elsewhere [29], using different catalysts such as MCM-41 with different Si/Al ratios, at 450 °C and 1.0 atm, obtaining conversions between 80 and 90% (wt.), with high selectivity to liquid hydrocarbons [44], zeolites (HZSM-5, K-HZSM-5, zeolite  $\beta$ , and USY), at temperatures between 350 and 450 °C and 1.0 atm, producing mainly OLP, gas, and water, with conversions up to 99% (wt.) and gasoline yield of 28% (wt.) at 350 °C [45], composite zeolite ZSM-5/mesoporous molecular sieve, at 450 °C and 1.0 atm, obtaining conversions of 80–100% (wt.) and gasoline yields between 38 and 47% (wt.) [46], MCM-41, at 450 °C and 1.0 atm, obtaining linear hydrocarbons ( $\text{C}_{13}$ ). The yield of OLP decreased with increasing specific catalyst surface area, and the gasoline selectivity increased, while that of diesel decreased with increasing conversion of palm oil [47]. Siswanto et al. [48] investigated the catalytic cracking of palm oil to produce gasoline, at 450 °C and 1.0 atm, using a fixed bed micro reactor (150 mm  $\times$  25 mm ID,  $V_R$  = 73.63 mL), over MCM-41, and oil-to-catalyst ratios between 30 and 50, obtaining an OLP yields up to 60.73% (wt.) and gasoline yield up to 43.63% (wt.). The yield of OLP decreases with increasing oil/catalyst ratio. Witchakorn Charusiri and Tharapong Vitidsant [35], studied the conversion of used vegetable oil into liquid fuels, at the temperature interval of 400–430 °C, reaction time between 30 and 90 min, and  $\text{H}_2$  pressure between 10 and 30 bar, over sulfated zirconia, using a 70 mL batch micro scale reactor. The optimum conditions obtained at 430 °C, 90 min, 10 bar, producing the highest conversion of gasoline-like hydrocarbons (~24.38%), as well as kerosene, light gas oil, gas oil, residues, hydrocarbon gases, and small amounts of solids (~11.98%, 24.35%, 5.70%, 13.86%, 19.07%, and 0.65%), respectively. The drawbacks of catalytic cracking investigations in micro scale reactors is the small quantities of feed used, producing liquid hydrocarbons only for GC-MS analysis, thus making it not possible to collect enough quantities of OLP necessary to carry out complete physicochemical characterization [29–33,35,43–48].

Pütün et al. [18,20] investigate the pyrolysis of soybean cake (slow) and olive oil residue (fast) using a 316 stainless steel fixed bed laboratory scale reactor (ID = 70 mm, L = 104 mm,  $V_R$  = 400 mL), heated by an electric furnace, connected to a water-cooled condenser, coupled to a set of traps (collectors) and a gas flow meter. Pütün et al. [18] studied the slow pyrolysis of soybean cake under static,  $\text{N}_2$ , and steam atmosphere to investigate the

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