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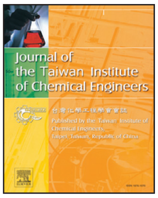

Gasoline-like hydrocarbons by catalytic cracking of soap phase residue of neutralization process of palm oil (*Elaeis guineensis* Jacq)

M.C. Santos[a,b], R.M. Lourenço[a], D.H. de Abreu[a,b], A.M. Pereira[a,b], D.A.R. de Castro[a,b], M.S. Pereira[a,b,f], H.S. Almeida[a,b], A.A. Mâncio[a,b], D.E.L. Lhamas[a,d], S.A.P. da Mota[b,c], J.A. da Silva Souza[a,b], S.D. Júnior[e], M.E. Araújo[a,b], L.E.P. Borges[f], N.T. Machado[a,b,*]

[a] *Laboratory of Separation Processes and Applied Thermodynamic (TERM@), Faculty of Chemical Engineering-UFPA, Rua Augusto Corrêia N°. 1, CEP: 66075-900, CP. 8619 Belém, Pará, Brazil*
[b] *Graduate Program of Natural Resource Engineering-UFPA, Rua Augusto Corrêia N°. 1, CEP: 66075-900, CP. 8619 Belém, Pará, Brazil*
[c] *Faculty of Materials Engineering-UNIFESSPA, Quadra 17, Bloco 4, Lote Especial, Nova Marabá, CEP: 68505-080 Marabá, Pará, Brazil*
[d] *Faculty of Mining and Chemical Engineering-UNIFESSPA, Quadra 17, Bloco 4, Lote Especial, Nova Marabá, CEP: 68505-080 Marabá, Pará, Brazil*
[e] *Faculty of Chemical Engineering-UEAM, Avenida Darcy Vargas N°. 1200, CEP: 69050-020 Manaus, Amazonas, Brazil*
[f] *Laboratory of Catalyst Preparation and Catalytic Cracking, Section of Chemical Engineering-IME, Praça General Tibúrcio N°. 80, CEP: 22290-270 Rio de Janeiro, RJ, Brazil*

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ABSTRACT

In this work, the soap phase residue of neutralization process of palm oil (*Elaeis guineensis* Jacq) submitted to catalytic cracking to produce gasoline-like hydrocarbons fuels. The cracking reaction carried out in a stirred tank reactor of 143 L, operating in batch mode at 440 °C and 1.0 atmosphere, using 15% (wt.) Na_2CO_3 as catalyst. The organic liquid products (OLP) yield 71.34% (wt.) with an acid value of 1.07 mg KOH/g and kinematic viscosity of 1.90 mm^2s^{-1}, matching sulfur content, copper strip corrosion, flash point, viscosity and density of ANP (Brazilian Petroleum Agency) N° 65 for diesel S10. The distillation of OLP carried out in laboratory scale according to the boiling temperature range of fossil fuels, yielding 6.69% (wt.) gasoline, 12.77% (wt.) kerosene, 15.52% (wt.) light diesel, and 38.02% heavy diesel-like hydrocarbons fuels, showing that Na_2CO_3 was more selective to convert salts of carboxylic acids into diesel-like hydrocarbons fuels. The GC–MS analysis showed that OLP is composed by 91.59% (wt.) hydrocarbons and 8.41% (wt.) oxygenates. The gasoline-like hydrocarbons fraction composed by 100% hydrocarbons with an acid value of 1.69 mg KOH/g and kinematic viscosity of 0.83 mm^2s^{-1}, matches many physicochemical parameters of ANP N° 40 for gasoline A, proving the technical feasibility of catalytic cracking process.

1. Introduction

During the refining (chemical and physical) process of vegetable oils, a complex mixture of mono-, di-, and triglycerides and minor fat-soluble compounds (carotenes, tocopherols, squalene, sterols, fatty alcohols, waxes, etc.), the minor compounds are removed [1–4]. The removal of fat-soluble compounds from vegetable oils to produce refined edible oils is necessary, as most of these compounds may be detrimental to the flavor, oxidative stability, and physical appearance of refined oil [1–4]. Thus, significant amounts of salts of carboxylic acids (soap) [5–9], fatty acid deodorizer distillates [10–12], and acid process water are generated as by-products of vegetable oils refining process [6,13]. Among these by-products, the soap phase residue of the neutralization process, a complex mixture consisting of salts of carboxylic acids, non-reacted palm oil, neutralized oil, and water [5–9], and fatty acid deodorizer distillates are rich renewable sources of fat materials [10–12]. Fatty acids deodorizer distillates and soap stock are the major by-products from vegetable oil refining, and both have little commercial value, been sold at a fraction of the oil cost [10]. Biodiesel industry is another source for obtaining soap phase residue, since the traditional transesterification process requires the removal of carboxylic acids, as well as compounds present in minor concentrations [4,10,14,15].

By considering that global production of oilseeds, oils & fats, and biodiesel for the 2014/2015, crop years reached 520.0, 202.0, and 28.9 million metric tons, respectively [16], as well as the fact that soap stock accounts for 5 to 10% (wt.) of crude vegetable oil mass after chemical refining processes [6], large amounts of soap stocks are generated yearly [17]. Estimates of process-streams

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* Corresponding author at: Fax: 0055-9132017291.
E-mail addresses: marceloenqui@bol.com.br, machado@ufpa.br (N.T. Machado).

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refining by-products of soybean, rapeseed, and sunflower oils production for the 2007 year, accounts for 0.35–0.60 million metric tons of soap stock produced [17], as well as 1-25-2.50 million metric tons of soap stock produced as by-products of biodiesel processing for the 2014/2015 year [16], based on stoichiometric relations.

In the neutralization process of vegetable oils, an alkali (sodium or potassium hydroxide) solution reacts with free fatty acids to form the *soap phase residue*, separated from neutralized oil by decanting or centrifugation to yield soap stock (SS). In addition, sediments of soap stock (OS) are separated by sedimentation. Thus, the major by-products of neutralization step of chemical refining process of vegetable oil are soap stock (SS) and the sediments of soap stock (OS), forming the (OS–SS) mixture [14]. The soap stock (SS) consists of approximately 30–50% (wt.) water and 70–50% (wt.) of fatty material (neutralized oil, non-reacted oil, salts of carboxylic acids, etc.), as well as phospholipids, degradation products and others non lipid base materials dissolved into the soap [7–9,14,15], and until proteins and carbohydrates [18]. In general, most of the fatty material, 60–70% (wt.) in soap stock is present in the form of sodium soaps of carboxylic acids [6]. The volume/mass of soap stock generated during the neutralization process depends on the acid value of vegetable oils and fats, a determinant factor of oils quality [7–9]. The volume of soap stock generated average 6% (vol.) the volume of refined oil and its commercial value is about one-fifth the price of crude oil [19].

In this context, the use of industrial waste derived from oils and fats refining process to produce renewable biofuels has remarkable economic and environmental appeals, as it may be a direct or indirect way to improve the energy balance by reducing the consumption of non-renewable energy resources [20]. In addition, it improves the sustainability of agribusiness by recycling agricultural-industrial wastes [20]. One alternative to use soap stocks to produce biofuels is trans-esterification [14,15,19–28]. The chemical transformation of soap stock into biodiesel (FAME) can be either achieved by acid-catalyzed trans-esterification including soybean [14,15,19,22,23,25–27], hazelnut [21], cottonseed [24], or enzyme-catalyzed trans-esterification of rapeseed soap stock with immobilized *Candida Rugosa* [28]. In addition, a few studies reported the use of soap stocks as substrate for lipase production [7,9].

The drawbacks of acid-catalyzed trans-esterification of soap stocks remains on the fact that it contains considerable amounts of water, producing emulsions, which are difficult to remove and/or separate [19]. In addition, water inhibits the trans-esterification reactions as it competes with the reactant (e.g. methanol), transforming the ester reaction into ester hydrolysis, generating free fatty acids, and may inhibits the acid-catalyzed esterification reaction [19]. A technology with a considerable potential to overcome the drawbacks of acid-catalyze esterification of soap stocks and great promise to produce hydrocarbons-like fuels using fat rich by-products of the refining process of edible oils is pyrolysis [20,29–33], or catalytic cracking [34–43], particularly the by-products of the refining process of palm oil such as palm oil-based fatty acid mixture [35–38]. Despite a few studies on the application of pyrolysis to produce hydrocarbons from soap stocks including calcium soaps of Macauba (*Acrocomia sclerocarpa M.*) pulp and nut oil [29], soaps of vegetable oils (sunflower, corn, cottonseed and soybean) [30], soybean soap stock [31], sodium soaps of palm oil [32], and sodium salts of carboxylic acids [33], until the moment, only one study reported the application of catalytic cracking to produce gasoline-like fuel from soap stocks [34], but no study reported and/or investigated the catalytic cracking of soap phase residue of neutralization process of palm oil, a complex multicomponent mixture containing soap-salts of carboxylic acids, non-reacted oil, neutralized oil, and water, in pilot scale.

This work aims to investigate systematically the technical feasibility to produce gasoline-like hydrocarbons fuels by catalytic cracking of soap phase residue of palm oil neutralization process at 440 °C and 1.0 atmosphere, with 15% (wt.) Na_2CO_3 in pilot scale and batch mode.

2. Materials and methods

2.1. Materials

Crude Palm Oil (CPO) was provided by Dentáua S/A (Santo Antônio do Tauá-Pará-Brazil). The Biodiesel Pilot Plant (LEQ/FEQ/UFPA) provided the soap phase residue (soap-salts of carboxylic acids + non-reacted palm oil + neutralized palm oil + water) of the neutralization process of palm oil. The catalyst Na_2CO_3, commercial soda ASH Light (D50), with purity of 98.0% (wt.) was supplied by Solvay Chemicals International SA (Brussels, Belgium).

2.2. Neutralization process of crude palm oil

2.2.1. Experimental apparatus and procedures

The neutralization process of palm oil was carried out in the Biodiesel Pilot Plant illustrated schematically in Fig. 1. The Pilot Plant is composed by the following units/systems: (1). Feed, Reagents (Alcohol) and Products (Biodiesel, Glycerin) Tanks, (2). Neutralization Unit (Reactor R01, Tank T01), (3). Transesterification Unit (Reactor R02, Tank T01), (4). Vacuum System (Tank SV01, Pump BV01), (5). Condensation System (Shell and Tube Condenser TC), (6). Water Cooling System (Tanks H_2O, Pumps H_2O), (7). Ethanol Recovery System (Tank VC01, Evaporator VCE01, Adsorption/Desorption Column CAD), (8). Vapor Generator System, (9). Dry Air Compression System (Air Compressor, Water Condenser), and (10). LCP (Logical Computer Programming) Control Unit.

The neutralization unit has a cylindrical jacket carbon stainless steel (ASTM 409) reactor (R01) of 1250 L, with a mechanical impeller system, concentrically surrounded by a thermal insulation of refractory material. The unit designed to operate at pressures up to 4 atmospheres and temperatures up to 150 °C, connected to the cylindrical Tank (T01) of MDPE and 100 L. Fig. 2 illustrates the lateral view of Biodiesel Pilot Plant (Faculty of Chemical Engineering-UFPA, Belém-Pará-Brazil).

600 L of crude palm oil was transferred from a carbon stainless steel (ASTM 409) reservoir tank of 2500 L, into the neutralization tank (R01) by using a pump (DANCOR; Model: CHS-17 1 hp). The reservoir tank has an internal heating system of 3000 W to better aid the flow of viscous vegetable oils, as well as to liquefy the solid stearin sediment at bottoms. Afterwards, a sodium hydroxide solution was prepared in tank (T01) by dissolving 4.0 kg of NaOH in 40 L of distilled water under vigorous agitation by means of an impeller system (WEG; Model: OE. 0.97 hp). The neutralization jacket reactor (R01) was heated up to 65 °C using saturated steam provided by the Steam Generator System (GERAMATIC; Model: GV.1, 75 kg/h) and the mechanical impeller velocity was set at 95 rpm. Then, the vacuum system (SV01) was turned-on and the pressure inside the reactor (R01) was set at 500 mbar. Afterwards, the valve connecting the reactor (R01) to the tank (T01) was open, transferring the NaOH solution to the reactor (R01). The reaction time was 30 min. Then, a 10% (wt.) NaCl solution has been prepared in tank (T01) by dissolving 7.0 kg NaCl in 70 L distilled water in order to aid the separation of neutralized palm oil and the soap phase residue (soap-salts of carboxylic acids + non-reacted oil + neutralized oil + water). The vacuum system (SV01) was turned-on and the pressure inside the neutralization reactor (R01) was set at 500 mbar in order to transfer the NaCl solution to the neutralization reactor (R01). Afterwards, the heating system was turned-off

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