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# Biofuels production by thermal cracking of soap from brown grease

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ABSTRACT

The transformation of waste oils and fats into biofuels attracts great interest due to the low cost of these materials. The thermal and/or catalytic cracking of oils and fats is an alternative route to the classic transesterification process of biodiesel production when the raw material has low quality. In this work, thermal cracking of sodium soaps of residual fatty materials from Brazilian restaurants (brown grease mainly composed of fatty acids of soybean oil) was tested to assess the feasibility of yielding a high quality diesel-like product. The reactions occurred in a single stirred steel reactor of 300 ml at high temperatures (723 °K) at atmospheric pressure for 1h45 min. The organic liquid product was analyzed for acid and saponification value, thermogravimetric characteristics. The chemical composition of the liquid product diesel-like fractions was determined by FT-IR, Nuclear Magnetic Resonance Spectroscopy (NMR $^1$H and $^{13}$C) and GC–MS. The hydrocarbons obtained were very similar to diesel oil and suitable for use, in pure form or in mixtures, in diesel oil engines. Yields above 60% and very low acidity (0.5 mg KOH/g) were obtained, meeting the requirements of ANP (Brazilian National Petroleum Agency) Resolution N° 51 de 25/11/15.

## 1. Introduction

Due to the increasing energy demand and environmental awareness, Brazil and many other countries have developed a great interest in alternative and sustainable technologies.

Biofuels are renewable energy sources derived from any material of biological origin. They can be obtained from sugar cane, corn, soybean, castor oil, forest biomass, livestock manure, as well as waste. They may be used in engines either directly as fuel or as a blend mixed with fossil fuels (Demirbas et al., 2006).

However, society has been increasingly resistant to the idea of using agricultural materials as feedstock for biofuels rather than food. In this context, residues have proven to be a promising option to replace, at least partially, agricultural biomass. Raw materials such as waste oils and fats are recently referred to as being economically and environmentally advantageous for this purpose.

The best-known process for producing biofuel from fatty materials is transesterification, in which the triglycerides from vegetable oils and animal fats react with a short chain alcohol in the presence of basic catalyst to form a mixture of esters, called biodiesel and glycerin. The generation of a byproduct glycerin is a negative feature of the process. Due to the increased production of biodiesel all over the world, there is today an overproduction of glycerin, and industries that use it as a raw material in their processes are saturated (Santos et al., 1998).

The search for alternative processes capable of utilizing lower quality feed has gained importance and various technologies have been proposed, such as esterification/hydroesterification, pyrolysis and hydrocracking.

Cracking, or pyrolysis, is a decomposition of molecules present in oils and fats leading to the formation of a mixture of chemical compounds with properties very similar to fossil fuels and it can be used directly in conventional engines. Such reactions occur in the absence of oxygen, under high temperatures (above 623 °K), in the presence or absence of catalysts (Santos et al., 1998). Cracking of fatty acids from animal and vegetable fats is a simple and efficient method for production of biofuels since it is relatively inexpensive and yields are shown to be satisfactory.

The cracking of triglycerides is not yet applied on industrial scale. However, compared with transesterification, pyrolysis has some important advantages: the technology is simple, has greater flexibility in the use of raw materials, the costs of investment and operation are smaller and engines compatibility with fossil fuels is higher (Buzetzki et al., 2011).

According to Chang et al. (1947), Alencar et al. (1983) and Idem et al. (1996), the deoxygenation of oxygenated organic molecules such as carboxylic acids, ketones, aldehydes, and esters is the key step for

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triglyceride conversion into fuel through pyrolysis reaction.

The molecular structure of the unsaturated triglyceride has great influence on the yield and a selectivity of the thermal cracking. For instance, the radical that intervenes in the reaction that produces C1–C5 hydrocarbons can be obtained by the decomposition of weighed oxygenated compounds by different routes. A decarboxylation and decarbonylation may occur before or after the C—C bond breakage. If the triglyceride is unsaturated, a breakdown of the C—C bond generally occurs prior to decarboxylation and decarbonylation. Such breaks, depending on the unsaturation of the compound, result in different final products (Maher et al., 2006).

The thermal cracking of fatty materials leads to the production of carboxylic acids which result in acidic products. Decarboxylation and/or deoxygenation through a catalytic process is the most commonly used strategy to neutralize such products and to use them as fuels.

Regarding soybean oil pyrolysis, well-known acid catalysts were used in Junming's et al. (2009) experiments of cracking reactions ($Al_2O_3$ and MCM-41) as well as potassium and sodium carbonates. The experiments were performed at temperatures ranging within 623–673 °K and the products were analyzed by pyrolysis GC–MS and FTIR showing the formation of alkenes, alkanes, carboxylic acids and aldehydes. The authors found that the amount of carboxylic acids and aldehydes significantly decreased with the use of basic catalysts. The acidity ranged from 120 mg KOH/g for the product obtained using alumina and 21 mg KOH/g for the product using sodium carbonate. The authors also showed that products with higher acidity were not completely miscible with fossil diesel oil due to their hydrophobic character. This behavior was not observed for products with lower acidity which presented good solubility in diesel oil even at low temperatures. The product of lower acidity presented physicochemical properties similar to fossil diesel oil.

The saponification of triglycerides prior to pyrolysis offers a way to yield pyrolysates with a composition similar to that of diesel fuel (Lappi and Alén, 2009). For instance, using sodium or calcium hydroxide, this treatment also facilitates, to some extent, the pyrolytic process, since the thermal cracking of vegetable oils (i.e., not as soap), compared to that of metal fatty acid salts, is much more difficult to control. It should be pointed out that pyrolysis of unsaponified vegetable oils produces not only the desirable linear or cyclic alkanes and alkenes but also indesirable oxygenated compounds such as aldehydes, ketones, and carboxylic acids. In contrast, pyrolysates of saponified vegetable oils compared, for example, to neat triglycerides seem to contain less chemically bound oxygen. Inorganic metal cations produce the corresponding metal carbonates in pyrolysis, which can then further decompose to metal oxides and carbon dioxide depending on the treatment temperature and metal (Lappi and Alén, 2009).

The literature reports that soaps made from vegetable oils or fats can be processed into products rich in hydrocarbons by pyrolysis reaction achieving high yields and applying lower temperatures (Demirbas et al., 2006). Chang et al. (1947) studied the formation of hydrocarbons, similar to oil fractions, obtained from catalytic and thermal cracking of vegetable oils and soaps. The experimental methods used were: (1) distillation of vegetable oils and subsequent cracking of their vapors, (2) liquid phase cracking of vegetable oils in the presence or absence of catalysts, and (3) pyrolysis of soaps from vegetable oils. The three processes were effective in producing hydrocarbons having physicochemical properties similar to the specifications of oil fractions. The yields obtained from decarboxylation of soap from rapeseed oil, groundnut oil and tunge oil at 610 K were 74%, 72% and 72%, respectively. Measurements of the acidity of the liquid varied between 0.2 and 1.5 mg KOH/g (Chang et al., 1947).

Hsu et al. (1950) continued to study the pyrolysis of soaps of fatty acids using tung oil as raw material. The authors obtained a high yield of residual coke (48.6%) and low yield of liquids (41.5%), which contained large quantities of aromatics (25.8%). On the other hand, the pyrolysis of calcium salts of stearic acid had low residual coke yield (17.3%) and high yield of liquid product (76.0%) containing 65.1% of alkenes, 4.4% of aromatics, 24.8% of alkanes and 5.7% of waste. The distilled products from calcium soap of tung oil were alkenes (56.3%), aromatics (25.8), alkanes (11.7%) and waste (6.2%). In either case, the analyzes showed that 10% of total gaseous products obtained was carbon monoxide potentially formed by thermal decomposition of ketones.

Lappi and Alén (2011) proceeded the investigation conducting pyrolysis of vegetable oil soaps, focusing on chemical behavior of sodium soap from palm oil, castor oil, olive oil and rapeseed oil. The thermal cracking resulted in volatile products similar to those found in gasoline and diesel fuel boiling range fractions of petroleum.

A small but relevant fact is that according to the original oleaginous plant and even with its cultivation place, each type of oil has a specific fatty acid distribution and physicochemical properties. Balat and Balat (2008) showed that soybean oil is mainly composed by linoleic acid representing 64% of its composition, 20% made of oleic acid, 11% palmitic acid, 2% stearic acid and 3% other acids.

In Lappi's (2009) research, the main products in the pyrolysis experiments with sodium linolate were small compounds (C3–C7), aromatics, and oxygen-containing compounds together with alkenes and alkanes. The relative proportion of oxygen-containing compounds increased with the decreasing pyrolysis temperature. The highest relative proportions of various alkenes and alkanes were obtained from the saturated sodium stearate. In contrast, the lowest relative proportions of these products, but the highest proportion of aromatics and oxygen-containing compounds, were detected in unsaturated sodium linolete. These findings reinforce that the formation of products clearly depends on the unsaturation of the fatty acid carbon chain and follows the typical reaction pathways generally outlined for pyrolysis.

In Bressler's (2014) work the organic liquid product obtained by the pyrolysis of brown grease showed fuel proprieties as flash point, density, pour point and heat combustion very similar to regular diesel oil and gasoline. However, acid number was still very distinct and high (41 mg KOH/g).

In this context, the present study intended to develop a method of thermal cracking and/or catalytic cracking for the conversion of brown grease soap (mainly from soybean oil), and to analyze the obtained product from this relatively abundant and inexpensive raw material into hydrocarbons, especially those of the diesel oil range. It was assumed that the raw material used for thermal cracking is mainly made of soybean oil because of the brown grease collected from Brazilian cuisines. In Brazil, soybean oil is the one most used in restaurants and residences (USDA, 2017). Thence, in this research, besides its main goal of demonstrating the viability of using soap of brown grease feedstock pyrolysis conversion technology, the paper investigated the product acidity. Acidity analysis are very rare in the literature on biofuel production, and was one of the most expected results in this study. Laboratory-scale batch experiments were conducted using brown grease from Brazilian restaurants. Chemical characterization of the pyrolysis products were conducted using a combination of analytical techniques. These properties were correlated with the fuel properties of the liquid pyrolysis product and compared with hydrocarbon diesel-like fuels.

## 2. Materials and methods

### 2.1. Materials

For the experiments of this study, brown grease from IME (*Instituto Militar de Engenharia* – Military Engineering Institute) cuisine was collected, sodium hydroxide PA (Vetec) and calcium hydroxide (Vetec) were used to obtain the soap.