

BIOFUELS PRODUCTION BY THERMAL CRACKING OF SOAP FROM BROWN GREASE

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ABSTRACT

The transformation of waste oils and fats in biofuels has 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 particular, cracking of sodium soaps of fatty materials is a simple process which provides high quality liquid suitable for use, in pure form or in mixtures, in diesel engines. Yields above 60% and acidity below 0.5 mg KOH / g were obtained in this work.

Keywords: thermal cracking, soap, biofuel, fatty acid, brown grease

INTRODUCTION

Due to the increasing energy demand and environmental awareness, Brazil and many others countries have shown 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, as the only fuel or as a blend mixed with fossil fuel (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, such inputs. Waste oils and fats raw materials are quite recently referred to as being economically and environmentally advantageous.

The best-known process for producing biofuel from fatty materials is the 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 phenomenon. Due to the increase

production of biodiesel all over the world, there is today an overproduction of glycerin, and industries that use it as raw material in their processes are now saturated.

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

The 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, 2010). The cracking of fatty acids from animal and vegetable fats is a simple and efficient method for the production of biofuels since it is a relatively inexpensive and yields are shown very satisfactory.

The cracking of triglycerides is not applied on industrial scale. However, compared with the 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 greater (BUZETZKI et al., 2011).

The basic catalytic route has emerged as an interesting alternative to chemical reactions, especially for cracking and isomerization reactions, because they can provide less acidic liquids.

Junming et al (2009) evaluated the pyrolysis of refined soybean oil obtained from commercial sources and used without further purification. Well-known acid catalysts were used in the experiments of cracking reactions (Al_2O_3 and MCM-41) as well as carbonates of potassium and sodium. The experiments were performed at temperatures ranging from 623-673 K. The products were analyzed by pyrolysis GC-MS and FTIR showing the formation of olefins, paraffins, 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 found that products with higher acidity were not completely miscible with fossil diesel due to the hydrophobic character of the diesel. This behavior was not observed for products with lower acidity which showed good solubility in diesel even at low temperatures. The product of lower acidity presented physicochemical properties similar to fossil diesel.

NA et al (2009) investigated the production of hydrocarbons by decarboxylation of oleic acid. Hydrotalcites with three different amounts of MgO (30, 63 and 70% by weight) were used at different reaction temperatures between 573 and 673 K. The evaluation was made from conversion of oleic acid and the distribution of products obtained.

The literature reports that soaps made from vegetable oils or fats can be processed into products rich in hydrocarbons by pyrolysis reaction with high yields and temperatures not so high as expected (DEMIRBAS et al, 2006).

CHANG and WAN (1947) studied the formation of hydrocarbon, 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 tung 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 as raw material tung oil. 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%). In 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 olefin, 4.4% of aromatics, 24.8% of paraffins and 5.7% of waste. The distilled products from calcium soap of tung oil were olefins (56.3%), aromatics (25.8), paraffins (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.

In this context, the present study intends to develop a method of thermal cracking and / or catalytic cracking for the conversion of brown grease, a relatively abundant and inexpensive raw material, into hydrocarbons, especially in the diesel range.

EXPERIMENTAL

Materials. For the experiments of this study, the brown grease from EMI was collected, sodium hydroxide PA (Vetec) and calcium hydroxide (Vetec) were used to obtain the soap.

Treatment of the brown grease. The choice of the processing of the sample is based on the saponification number. Briefly, if the fatty material presents an index between 180 and 200 mg KOH / g of oil, sophisticated purification procedures such as extraction with hexane are unnecessary. Simple steps of filtration and drying are enough to treat the brown grease for biofuel production. The filtration step was performed with two steel sieve with holes of 0.5 and 2 mm, and steel wool for final filtration. Drying was performed by evaporation in an open bottle on a hot plate with magnetic stirring. The sample was heated at 403 K for 30 minutes.

Saponification. The sodium soap was obtained by slowly mixing 50.00 g of brown grease to an aqueous solution of sodium hydroxide at 12% (w / w). The amount of sodium hydroxide employed was stoichiometric. The material was stirred until it has reached a "firm" consistency. Then, the soap was taken to the stove to remove the present water. The calcium soap was prepared following the same procedure used to obtain the sodium soap employing calcium hydroxide instead of sodium hydroxide.

Reaction. In this study we used a stainless steel reactor with a volumetric capacity of 300 mL for the catalytic cracking reactions. The reactor was heated by a cylindrical oven placed on a magnetic stir plate. The rate of heating and the final temperature were controlled by a programmer and a thermocouple which was inside the reactor. With a T-joint mounted at the top of the reactor, a discharge pipe was connected tilted to facilitate the collection of the product to the Kitassato flask immersed in an ice bath (Figure 1).

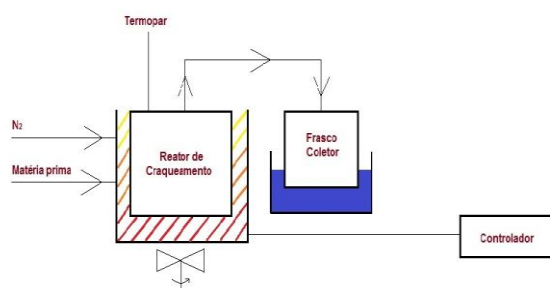


Figure 1. Scheme of the thermal cracking process

The reactor (with a magnetic agitation) and an empty flask were weighed before each cracking reaction (0.01 g precision). The feed - or soap residue - was weighed (50.00 g) and introduced into the reactor. The reactor was sealed with a gasket T and positioned in a heating furnace.

Tests were conducted with heating rates of 5 and 10 K.min⁻¹ until it reached the temperature of 723 K, this temperature was maintained for 30 min. Other testing rate of 10 K.min⁻¹ were scheduled to reach levels of 703 K and 753 K and stand for 30 min. The magnetic stirring was triggered when material melted at about 400 K. An inert gas (nitrogen) was fed during the whole process at a flow rate of 0.02 NI.min⁻¹.

The gaseous products were condensed in the flask immersed in an ice bath. After the reaction, the flask containing the liquid product and reactor were weighed again to calculate the material balance. The organic product was washed with hot distilled water (343 K) so the catalyst and water present in the product were removed from the organic phase by decantation in a separating funnel. The final product was packaged in a clean container with a lid and sent for analysis.

Saponification Value. The saponification value of the brown grease was determined according to the methodology described by MORETTO and FETT (1989). In an Erlenmeyer flask were added 2.00 g of residual grease and 20 ml of alcoholic KOH 4%. The flask was adapted with a reflux condenser and the sample was heated softly for a period of 30 min. The sample was cooled down and 3 drops of phenolphthalein were added. The mixture was titrated with 0.5 M HCl solution until disappearance of the pink color. This same procedure was done for the blank test. The difference between the volumes of HCl expended in the two titrations is equivalent to the amount of KOH spent in the sample saponification.

Acid Value. A weight of 0.300 g of the sample (brown grease or product), a volume of 30 to 50 mL of cyclohexane and 3 drops of phenolphthalein alcohol solution used as indicator were added in an Erlenmeyer flask. The cyclohexane was used as solvent to dilute and to facilitate visualization of indicator changes during the titration. The mixture was titrated with 0.1 M KOH solution properly standardized until the appearance of pink color.

Infrared. The absorption spectra in the region of infrared (IR) were obtained with a FTIR spectrometer from Shimadzu Prestige 21. Liquid samples of products and raw materials were added between KBr plates using pipettes to allow slight fluid pressure and in order to

ensure uniformity of the formed film. The chosen spectrum resolution was 16 cm^{-1} and the scanning range was $400\text{ to }4000\text{ cm}^{-1}$.

Gas chromatography–mass spectrometry (CG-MS). The products were analyzed on a Shimadzu 2010 gas chromatograph coupled to a mass spectrometer Shimadzu QP 2010 containing a capillary column Rtx-5MS with the measures of 30 m of length, 0.25 mm of diameter and 0.25 μm of thickness. The split ratio was 1:50 and purge flow of 3.0 mL / min. The conditions employed in the chromatograph were 563 K for injector temperature, 553 K for the detector temperature, 353 K for initial column temperature with a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ till the temperature of 573 K. The total run time was 26 min.

The scanning range of the mass spectra of the analyzed liquid products was 30 to 300 m / z.

Nuclear Magnetic Resonance. The ^1H and ^{13}C NMR spectra were recorded on a Bruker spectrometer brand BioSpin, Topspin version 1.3. Deuterated chloroform was used as a solvent. Tetramethyl silane (TMS) was used as internal reference. The spectra were obtained using 30° pulses, with an acquisition time of 2.6 to 3.0 s, a recycle time (d1) of 1.3 to 2.0 with 32 transients for ^1H NMR and 2048 for the NMR ^{13}C .

Thermogravimetric analysis (TGA). TGA analyzes were performed on a thermal analyzer Shimadzu TA-50WSI. The sample was heated at a heating rate of $10\text{ K} / \text{min}$ till the temperature of 873 K. The tests were conducted under nitrogen flow of $20\text{ ml} / \text{min}$.

RESULTS AND DISCUSSION

The saponification number of the fatty material was $194\text{ mg KOH} / \text{g}$ of sample, indicating that the material is mostly composed of fatty acids. By presenting a high index of saponification, this material offers a great potential of grease-soap transformation to use it in a thermal cracking. Also, sophisticated purification procedures such as extraction with hexane, are unnecessary in cases like this where saponification numbers are in range of $180\text{-}200\text{ mg KOH} / \text{g}$ of oil.

Table 1 shows the physical-chemical analysis results and shows the liquid product yield of the thermal cracking reaction of soap made of brown grease.

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Table 1. Summary of the physico-chemical results from the thermal cracking of brown grease and soap made of brown grease

Feed	Temperature	Rate Kmin ⁻¹	Acid Value	Yield	Gas	Solid	Loss of weight (solid- TGA)	TGA – Loss of organic weight
Sodium soap	450°C	10	0,41	63,40%	15,60%	21,00%	2,82%	98,12%
Sodium soap	450°C	10	0,40	62,90%	16,10%	21,00%	2,82%	98,12%
Sodium soap	450°C	10	0,41	50,00%	31,00%	19,00%	2,82%	98,12%
Calcium soap	450°C	10	7,95	54,83%	19,24%	25,93%	8,31%	91,69%
Sodium soap	480°C	10	0,40	61,70%	13,80%	24,50%	2,54%	97,09%
Sodium soap	430°C	10	0,38	62,25%	14,11%	23,65%	3,36%	96,64%
Brown grease	450°C	10	140,52	76,70%	19,00%	4,30%	-	97,73%
Sodium soap	450°C	5	0,39	62,81%	12,50%	24,70%	-	-

The yield of liquid product achieved was approximately 60% when it comes to the thermal cracking of sodium soap. There were no significant differences in this cases when parameters such as temperature and heating rate were changed from 20-30 K and 5 K.min⁻¹ respectively.

The yield obtained by the cracking of brown grease was higher, 76.7%. However, the acidity of the liquid product of cracked soap are very low, on the order of 0.4 mg KOH / g of acid (for sodium soaps) in comparison with the acidity of the cracked brown grease which was 140.5 mg KOH / g. This proves the occurrence of the decarboxylation of the fatty acids present in the feedstock. This assertion is supported by the infrared graphics (Figure 2) and nuclear magnetic resonance graphics (Figure 3).

In the infrared graph (IR) of the cracked brown grease there is a signal at approximately 1710 cm⁻¹ typical of a carbonyl of a fatty acid that practically disappears in the spectrum of the liquid product obtained from the cracking soap.

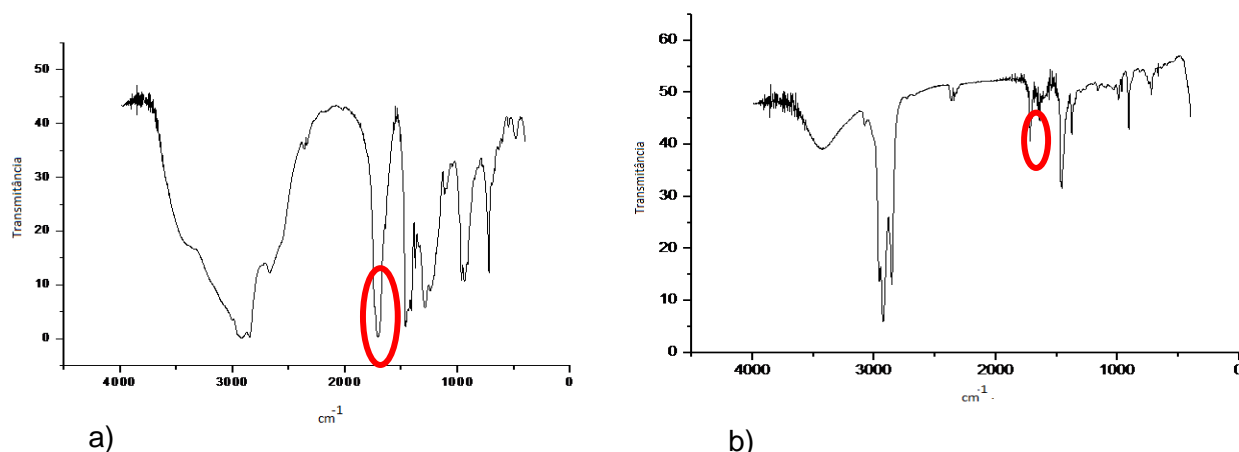
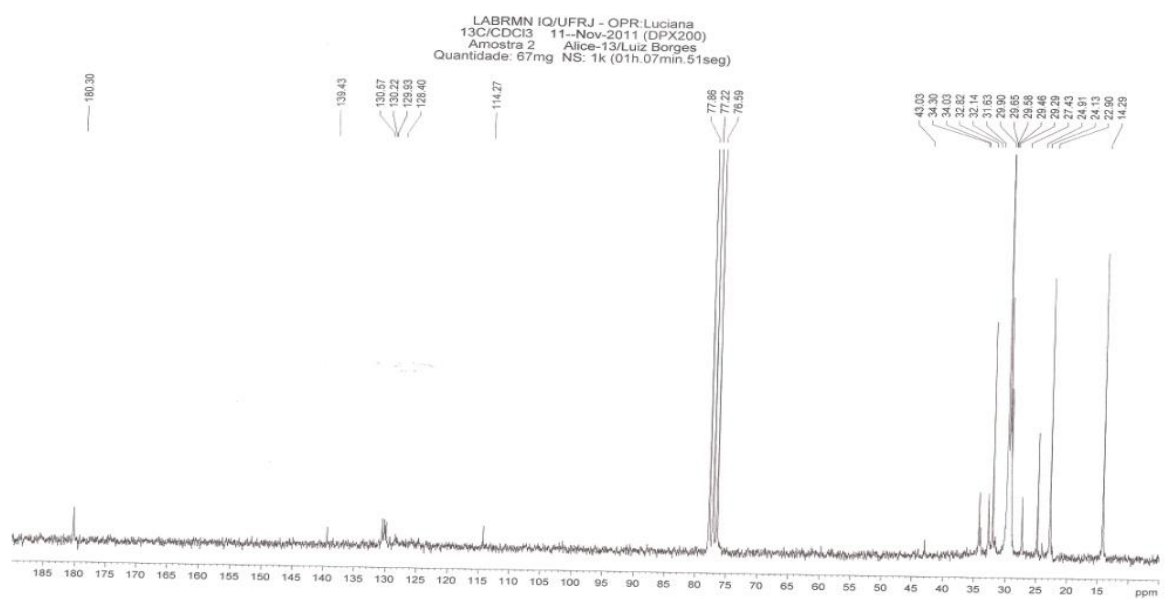


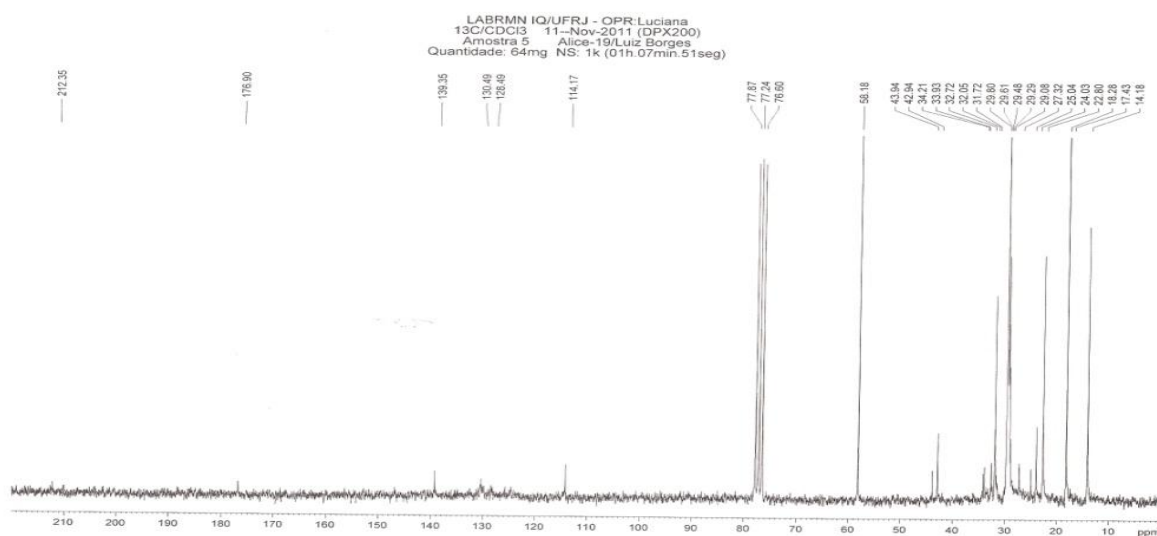
Figure 2. Infrared spectra of a) cracked brown grease and b) cracked sodium soap.

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The decarboxylation of the carbonyl is also confirmed by the ^{13}C NMR spectrum. At approximately 180 ppm the signal that appears in the spectrum of cracked brown grease, disappears in the spectrum of the cracked soap from brown grease.



a)



b)

Figure 3. ^{13}C NMR spectra of a) the cracked brown grease and b) cracked sodium soap

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The series of spectras also indicates the presence of unsaturated compounds, seen by the signals in the region of 1610-1680 cm^{-1} in IR, the peaks between 100-140 ppm in the carbon NMR and the peaks at 5.0 ppm region of the ^1H NMR (Figure 4).

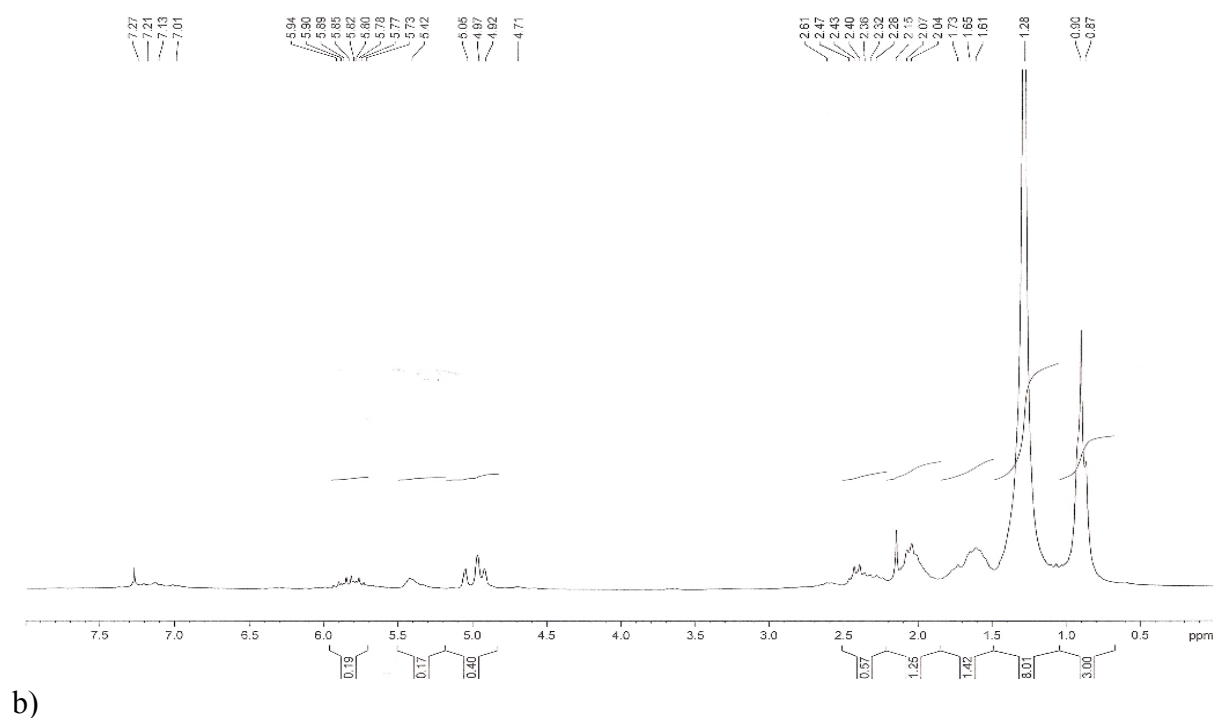
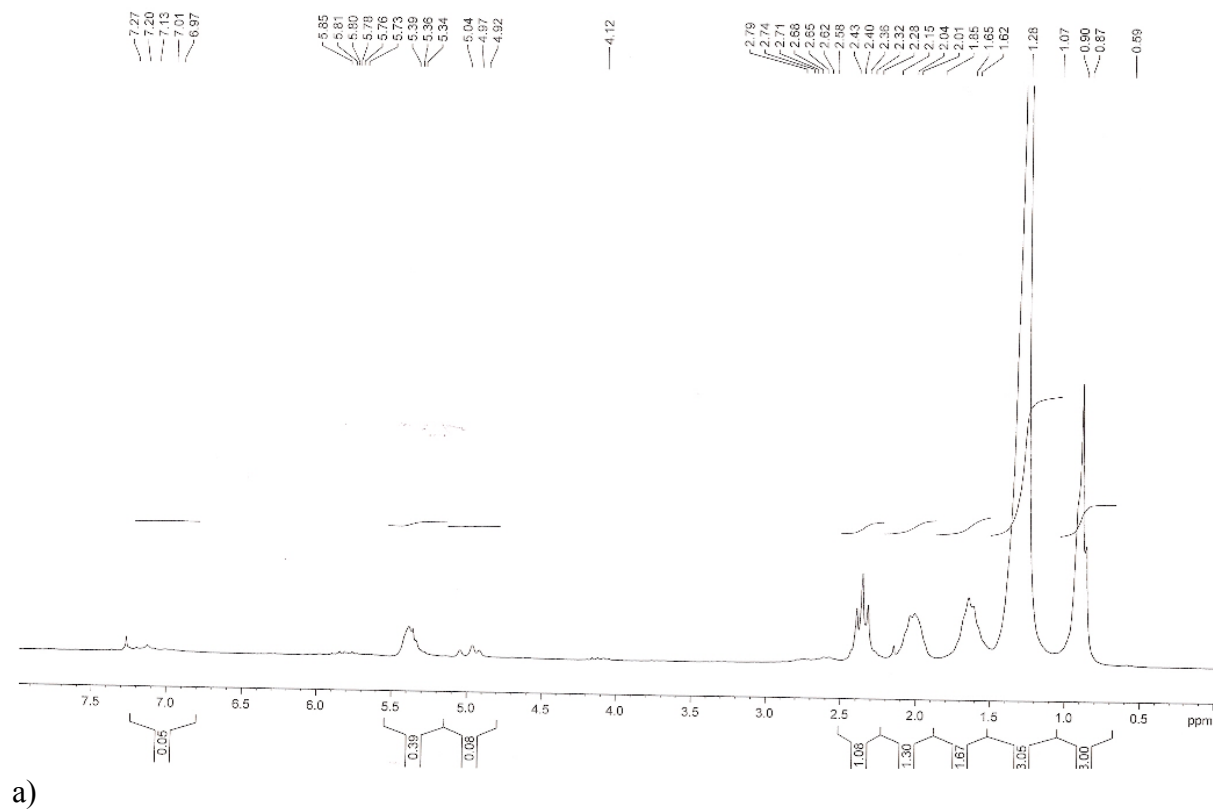


Figure 4. ^1H NMR spectra of a) the cracked brown grease and b) the cracked sodium soap

The analysis by gas chromatography coupled with mass spectrometry shows the presence of long chain of hydrocarbons in the liquid product (Figure 5).

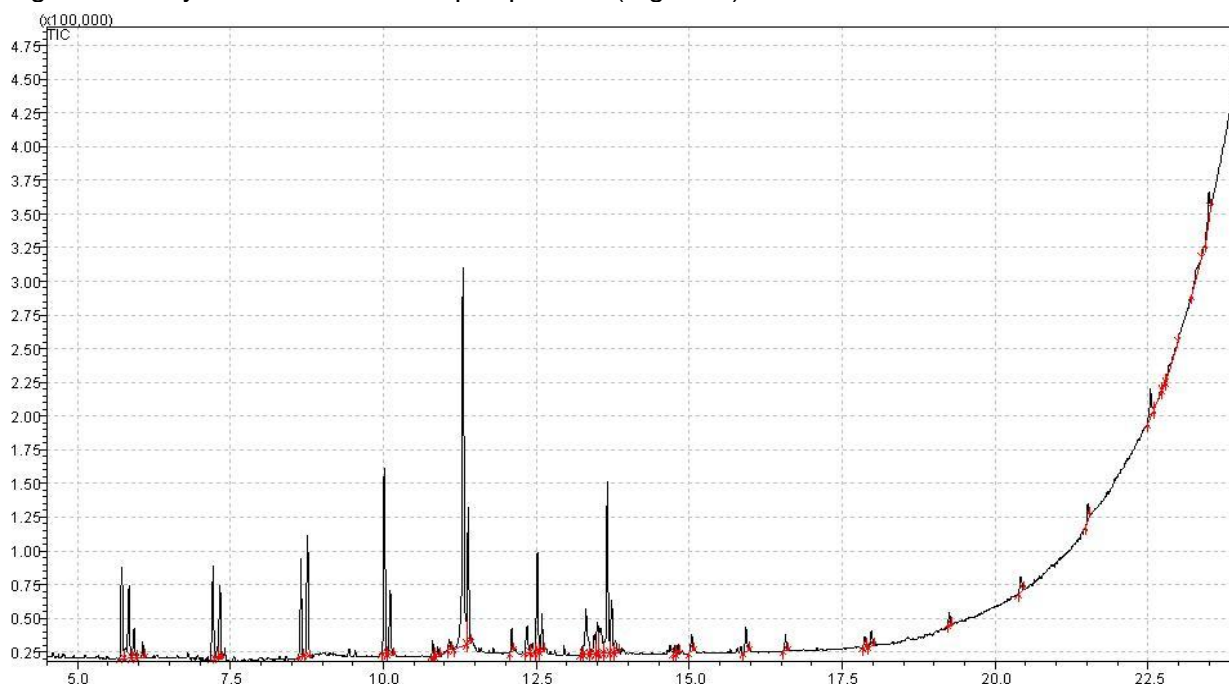


Figure 5. Chromatogram of liquid product derived from the cracked sodium soap

The liquid products were also subjected to thermogravimetric analysis and it was found that the cracked brown grease began to evaporate at 473 K while the cracked sodium soap from grown grease began before at 423 K. The mass loss is nearly complete reaching 98% at 593 K for those two samples. This result indicates that the structure of the hydrocarbon chain remains the same.

CONCLUSION

The cracking of soap from brown grease is an efficient and simple process for the production of long-chain hydrocarbons with similar characteristics to fossil diesel. The results yield still can be optimized, however the liquid products exhibit very low levels of acidity, which fit, for example, the rules established by ANP for biodiesel.

REFERENCES

CHANG, C.C., e WAN, S.W. **China's Motor Fuels from Tung Oil**. *Industrial and Engineering Chemistry* 1947;39:1543-1548

- BUZETZKI, E., SIDOROVÁ, K., CVENGROSOVÁ, Z., KASZONYI, A., e CVENGROS, J.,
The Influence of Zeolite Catalyst on the Products of Rapeseed Oil Cracking, Fuel
Processing Technology 2011, 92: 1623-1631
- DEMIRBAS, A., e KARA, H., **New Options for Conversion of Vegetable Oils to
Alternative Fuels**, Energy Sources 2006, part A 28 :619-626
- HSU, H.L., OSBURN, J.O., e GROVE, C.S. **Pyrolysis of the Salts of Fatty Calcium Acids**.
Industrial and Engineering Chemistry 1950;42:2141-2145
- JUNMING, X ., JIANCHUN, J ., YANJU, LU e JIE, C .**Liquid hydrocarbon fuels obtained
by the pyrolysis of soybean oils**. Bioresource Technology 2009; 100, 4867-4870
- MORETTO, E.; FETT, R. **Tecnologia de Óleos e Gorduras Vegetais na Indústria de
Alimentos**, Editora: Livraria Varela. São Paulo, 1998. 150 p.
- NA, J.G., YI, B.E., KIM, J.N., YI, K.B., PARK, S.Y., PARK, J.H., KIM, J.N., KO, C.H. **Hydrocarbon
Production from Decarboxylation of Fatty Acid Without Hydrogen**. Catalysis Today
2009
- SANTOS, F.R., FERREIRA, J.C.N., e da COSTA S.R.R.. **Decomposição Catalítica de
Óleo de Soja em Presença de Diferentes Zeólitas**. Química Nova 1998; 21:560-563.