

Journal of the Brazilian Chemical Society



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REFERÊNCIA

RODRIGUES, Juliana Petrocchi et al. Comparing thermal-cracking and catalytic hydrocracking in the presence of Rh and Ru catalysts to produce liquid hydrocarbons from vegetable oils. **Journal of the Brazilian Chemical Society**, São Paulo, v. 25, n. 12, p. 2364-2369, dez. 2014. DOI: <http://dx.doi.org/10.5935/0103-5053.20140249>. Disponível em: https://www.scielo.br/scielo.php?script=sci_arttext&pid=S0103-50532014001202364&lng=en&nr_m=iso&tlng=en. Acesso em: 13 jul. 2020.

Comparing Thermal-Cracking and Catalytic Hydrocracking in the Presence of Rh and Ru Catalysts to Produce Liquid Hydrocarbons from Vegetable Oils

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Neste trabalho descrevemos a obtenção de hidrocarbonetos líquidos por meio do hidrocrackeamento catalítico de óleo de soja, dendê e mamona, na presença e ausência de catalisadores nanoparticulados de rutênio e ródio. A reação realizada a 200 °C leva somente à hidrogenação de ligações duplas C=C. No entanto, a 400 °C, foi observada a decomposição dos triacilglicerídeos, levando a hidrocarbonetos e compostos oxigenados. O hidrocrackeamento catalítico de óleos vegetais na presença de Rh e Ru levou a um aumento da quantidade de produtos desoxigenados e à formação de hidrocarbonetos lineares de cadeia longa, que são adequados para utilização como combustível para motores diesel, quando comparado com o da reação de pirólise na ausência de catalisadores. O catalisador de Ru é mais eficaz do que o catalisador de Rh, especialmente no caso do óleo de mamona, provavelmente devido à sua maior oxofilicidade quando comparado com Rh.

We describe herein the production of liquid hydrocarbons through the catalytic hydrocracking of soybean, palm tree and castor oils, in the presence and absence of ruthenium and rhodium nanoparticle catalysts. The reaction at 200 °C leads to the hydrogenation of C=C double bonds only. However, at 400 °C, the decomposition of the triacylglycerides was observed, leading to hydrocarbons and oxygenated compounds. The catalyzed hydrocracking of vegetable oils in the presence of Rh and Ru strongly increased the amount of deoxygenated products and the formation of long-chain linear hydrocarbons, which are suitable for use as diesel fuel, when compared with pyrolysis reaction in the absence of the catalysts. The Ru catalyst is more effective than Rh, especially in the case of castor oil, probably due to its higher oxophilicity when compared to Rh.

Keywords: hydrocracking, vegetable oil, rhodium, ruthenium, bio-oil, biomass

Introduction

As a consequence of the oil supply crisis and the increasing demand for liquid fuels, as well as enhanced environmental awareness, the study of the use of biomass to provide alternative energy sources has intensified in recent decades. Given its wide availability, renewability and biodegradability, biomass has been highlighted as an

elegant solution to substitute raw fossil materials. Because of their labor intensive characteristic, in developing countries like Brazil, biomass-derived fuels have also been highlighted as a way to promote social and economic development in depressed rural areas.¹

In this context, several alternative liquid fuels have been proposed for diesel engines, such as the direct use of fats and oils, the use of methyl or ethyl fatty acid esters (biodiesel) and hydrocarbons produced from thermal cracking of fatty materials (renewable diesel). Note that the

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renewable diesel obtained from thermal cracking, as well as biodiesel, matches international specifications required for transport fuel when blended with diesel fuel in up to 20 vol%.²⁻⁵ However, the production of renewable diesel by thermal cracking is associated with several negative issues due to incomplete deoxygenation of the fuel, leading to a mixture containing not only the desired hydrocarbons but also a wide variety of oxygenated compounds, such as fatty acids, aldehydes and ketones.^{6,7} In order to address this issue, different approaches have been proposed, such as performing the cracking reaction in the presence of steam,⁸ employing solid catalysts (catalytic cracking)⁹ and the use of catalysts under hydrogen pressure (hydrocracking).¹⁰

The processing of diesel streams by hydrocracking is already used in refineries for the stabilization and desulphurization of hydrocarbons. The reaction, widely known as hydrodesulfurization (HDS), which is performed under high hydrogen pressures in the presence of a heterogeneous catalyst, consists of the hydrogenation of double bonds and the breaking of sulfur-carbon bonds affording low-sulfur stabilized diesel.¹¹ Oils and fats can also be processed by hydrocracking in order to deoxygenate triacylglycerides and hydrogenate the alkyl chains, producing linear hydrocarbons in the range of diesel fuel. Thus, the hydrocracking of oils and fats, known as hydrodeoxygenation (HDO), may provide a mixture of hydrocarbons with appropriate physical-chemical properties to substitute petroleum diesel.¹²

It is well accepted that HDO occurs in several steps. Firstly, the alkyl chain double bonds are hydrogenated and the triglycerides are then broken into fatty acids and, finally, deoxygenated into hydrocarbons.¹³ This final process occurs via hydrocracking, deoxygenation or hydrogenolysis, in sequence or concurrently. Recently, Donniss *et al.*¹⁴ studied the mechanism involved in the HDO of oils and fats by running reactions of oxygenated molecules and also modeling mixed diesel-rape seed oil. They concluded that there are two possible routes for the deoxygenation reaction products. Besides decarboxylation at high temperature, there may be a route where there is a keto-enol equilibrium, forming water and alkanes. However, there are few reports available in the open literature regarding the production of hydrocarbons from fats and oils by HDO. The majority of these studies were carried out by petroleum companies, aiming to use the knowledge acquired directly in their refineries. Some of the few academic studies available in the open literature describe the use of HDS catalysts for the HDO of fats and oils.^{10,14} The most common catalysts used in the HDS process applied to petroleum-based fuels, and usually studied in relation to the HDO of fats and oils, are based

on sulfides, particularly WS₂ and MoS₂ supported on alumina (γ -Al₂O₃),¹⁵ commonly doped with Ni and Co to increase their activity.

One of the pioneering studies involved the HDO of vegetable oils using Ni/SiO₂ and NiMo/Al₂O₃ under different temperatures and hydrogen pressures.¹⁶ The authors claim they achieved the complete deoxygenation of triglycerides leading to a mixture of aliphatic saturated hydrocarbon.¹⁶ This pioneering work was revisited, confirming the potential use of fats and oils to produce hydrocarbons in the range of diesel directly in the HDS process in petroleum refineries.¹⁰ Also, Huber *et al.*¹³ have studied the HDO, promoted by the traditional catalysts NiMo/Al₂O₃ under standard HDS conditions, of pure sunflower oil and mixtures with residue from the vacuum distillation of petroleum to compare the products obtained. They concluded that the mixture is converted into alkanes and, thus, the process may be applied directly using HDS plants available in the oil refineries, without the need for modifications.

It is well established in the literature that the activity and selectivity of catalytic systems can be finely tuned through the appropriate choice of the catalyst. In this respect, based on studies reported in the literature, it can be noted that the metals widely used for catalytic hydrogenation of C=C and C=O bonds are: Pd, Pt, Ni, Rh and Ru.^{16,17} In heterogeneous catalytic systems, these metals are usually supported on activated carbon, silica and alumina¹⁸ in order to increase their surface area and thus their activity. This strategy provides high catalytic activity towards the target reaction using small amounts of noble metal catalysts.

In this study, we investigated the catalytic properties of Rh and Ru in the HDO of soybean oil, palm tree oil and castor oil. Our approach involved the use of catalysts based on rhodium and ruthenium nanoparticles immobilized on a magnetic responsive solid support (magnetite nanoparticles spherically coated with silica, Fe₃O₄@SiO₂). Our main goal was to perform a qualitative study on the potential use of these two noble metals in HDO and to compare their activities. The magnetic properties are an additional attribute of these materials, facilitating the catalyst separation after completion of the reactions, and avoiding filtration, centrifugation or any other time-, solvent- and energy-consuming step.

Experimental

Materials

Refined soybean oil, castor oil and palm tree oil were obtained from commercial sources and used without further treatment.

Preparation of rhodium and ruthenium catalysts

The magnetically-recoverable catalyst support, comprised of silica-coated magnetite nanoparticles ($\text{Fe}_3\text{O}_4@\text{SiO}_2$), was prepared following the described-previously procedure.¹⁹

The Rh catalyst¹⁹ was prepared by adding 100 mg of the amino-functionalized magnetic support, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$, to 20 mL of an aqueous solution of rhodium chloride (210 mg L⁻¹). The mixture was stirred for 2 h at room temperature and then the solid was magnetically collected from the solution and washed twice with acetone followed by drying at 100 °C for 3 h. The Rh³⁺-loaded solid was reduced to Rh nanoparticles by molecular hydrogen in a Fischer-Porter glass reactor (cyclohexene, 6 atm H₂, 75 °C, ca. 20 min), as previously reported. The Rh content in the final solid was analyzed by inductively coupled plasma/optical emission spectrometry (ICP OES): 1.5 wt.%.

The Ru catalyst²⁰ was prepared by adding 100 mg of the amino-functionalized magnetic support, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$, to 20 mL of an aqueous solution of ruthenium chloride (500 mg L⁻¹). The mixture was stirred for 2 h at room temperature and then the solid was magnetically collected from the solution and washed twice with distilled water and acetone followed by drying at 100 °C for 3 h. The Ru³⁺-loaded solid was reduced by NaBH₄ in ethanol to produce Ru nanoparticles. The dried solid obtained above was added to 20 mL of ethanol containing 10 mg of NaBH₄. Thereafter, the material was washed twice with distilled water and acetone and dried under vacuum. The Ru content in the final solid was analyzed by ICP OES: 1.4 wt.%.

Hydrocracking reaction

Hydrocracking experiments were carried out at different temperatures using a home-made stainless steel autoclave. The vegetable oil (10 g) and the catalyst ($\text{Fe}_3\text{O}_4@\text{SiO}_2\text{NH}_2\text{Rh}$ or $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{NH}_2\text{Ru}$, 0.1 g) were introduced into the reactor and then the system was pressurized with the desired hydrogen pressure and heated by an external electric resistance. The temperature was monitored by a thermocouple in contact with the reaction-bulk. After 1 h, the reaction was stopped and the reactor was cooled down, depressurized and opened. The catalyst was magnetically separated from the products.

Characterization methods

The products were analyzed by gas chromatography-mass spectrometer (GC-MS), infrared (FT-IR) and

acid number (AN). The GC-MS analysis was carried out with a Shimadzu chromatograph equipped with a mass spectrometer (GCMS-QP5050), with a 50-m polydimethylsiloxane column of 0.25 mm i.d. and film thickness of 0.2 μm (CBPI PONAM50- 042), operating between 50 and 250 °C applying a heating rate of 10 °C min⁻¹. The FT-IR spectra were obtained in triplicate on a Bruker Equinox 55 spectrometer using a horizontal ATR cell of 7 cm length (10 reflections), which covers the regions 650–4000 cm⁻¹. The FT-IR spectrum corresponds to the sum of 32 scans with a spectral resolution of 4 cm⁻¹. The spectra were normalized using the 1459 cm⁻¹ signal (CH₃ bending) as internal standard. The AN is a direct evaluation of the presence of carboxylic acid and was determined by the titration of the products with a methanol/KOH solution, according to standard method ASTM D465-9. The titration of each sample was conducted in triplicate with a negligible error of ± 0.3 mL for Vf.

Results and Discussion

We investigated the catalytic hydrocracking of vegetable oils by Rh and Ru nanoparticle catalysts supported on a magnetic solid support comprised of magnetite nanoparticles spherically coated with silica ($\text{Fe}_3\text{O}_4@\text{SiO}_2$). The synthesis and complete description of these catalysts have been recently published by some of the authors.^{19,20} The catalysts exhibit magnetic properties due to the presence of superparamagnetic Fe_3O_4 cores (ca. 10 nm), which were spherically coated with a layer of silica by means of a reverse microemulsion. The main features of the support material are: controlled morphology (ca. 60 nm silica spheres), BET surface area of ca. 62 m² g⁻¹, and saturation magnetization of ca. 69 emu g⁻¹ of Fe_3O_4 at 70 kOe.^{19,21} The uptake of metal ions in the magnetic silica spheres ($\text{Fe}_3\text{O}_4@\text{SiO}_2$) was improved by the surface functionalization with the silane coupling reagent 3-(aminopropyl)-triethoxysilane. After functionalization, the magnetic solid could be loaded with metal ions when stirred with metal chloride aqueous solutions and recovered by applying a magnetic field. The Rh³⁺ and Ru³⁺-loaded solids were reduced by H₂ and NaBH₄, respectively, to give well dispersed Rh and Ru nanoparticles deposited on the solid surface. The preparation of the catalysts was optimized in such a way that they all contained ca. 1.4–1.6 wt.% of metal, as determined by ICP OES. The two solids were previously characterized by high-resolution transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS) analysis, and the Rh and Ru nanoparticles were found to be of controlled size < 5 nm. Previous catalytic studies on both supported Ru²⁰

and Rh¹⁹ catalysts have shown very interesting results in the hydrogenation of either olefins or aromatics.

In Table 1, the main results of the catalytic hydrocracking of vegetable oils obtained using Fe₃O₄@SiO₂NH₂Rh (**1**) are summarized. The results obtained in the absence of catalyst (pyrolysis) are given for comparison. The catalyst was recovered magnetically by transferring the reaction mixture to a beaker and placing a small magnet (4000 G) on the glass wall. This caused a quick migration of the catalyst to one side of the glassware, allowing the product (hydrocarbon and oxygenated compounds) to be removed with a syringe. It is reasonable to assume that the silica layer is protecting the magnetic core, but it is important to highlight that if magnetite is reduced to metallic iron under the reaction conditions (400 °C and hydrogen pressure), it will not compromise the magnetic separation and catalyst recovery after reaction. Note that some coke (less than 0.01% of the starting mass) was deposited on the catalyst. As can be seen in Table 1 (entries 1-6), the presence of the Rh catalyst **1** increases the deoxygenation of the products. Indeed, the AN, a direct measurement of carboxylic acids content (main oxygenated product of the cracking of triglycerides), indicates deoxygenation of around 50%.

Table 1. Hydrocracking of vegetable oils in the presence of Fe₃O₄@SiO₂NH₂Rh using different conditions^a

entry	Oil	Catalyst mass ^b / %	p H ₂ / atm	AN ^c / (mg _{KOH} g _{sample} ⁻¹)
1	Palm tree	1.0	25.0	53.70
2	Palm tree	0	25.0	117.70
3	Castor	1.0	25.0	83.20
4	Castor	0	25.0	95.00
5	Soybean	1.0	25.0	42.90
6	Soybean	0	25.0	88.90
7	Soybean	1.0	25.0	3.10
8	Soybean	1.0	12.5	41.90
9	Soybean	1.0	6	71.86

^aReaction temperature = 400 °C (except entry 7, T = 200 °C); ^b10 g of oil and 0.1 g catalyst (1.5 mg Rh); ^cAN = acid number.

The FT-IR spectra of final products obtained in the hydrocracking reactions detailed in Table 1 are shown in Figure 1. For entries 1 to 6, 8 and 9, the C=O stretching band with a maximum at 1710 cm⁻¹ is attributed to the carboxylic acid formed during the reaction. For entry 7, in contrast to the experiments where the triacylglyceride decomposed, the C=O stretching band appears with a maximum at 1745 cm⁻¹ attributed to the ester carboxylic group of the triacylglyceride, indicating that it was not converted in the presence of catalyst at 25 atm H₂ and 200 °C. The band at 1745 cm⁻¹

also appears in the spectrum of entry 8, meaning that the decomposition of the triacylglyceride was not complete at 6 atm of H₂ and 400 °C. The products were also analyzed by gas chromatography [GC-flame ionization detector (FID) and GC-MS]. As an example, the chromatograms (GC-FID) for the mixtures obtained after catalytic hydrocracking of castor, soybean and palm tree oils in the presence of the Rh nanoparticle catalyst are shown in Figure 2.

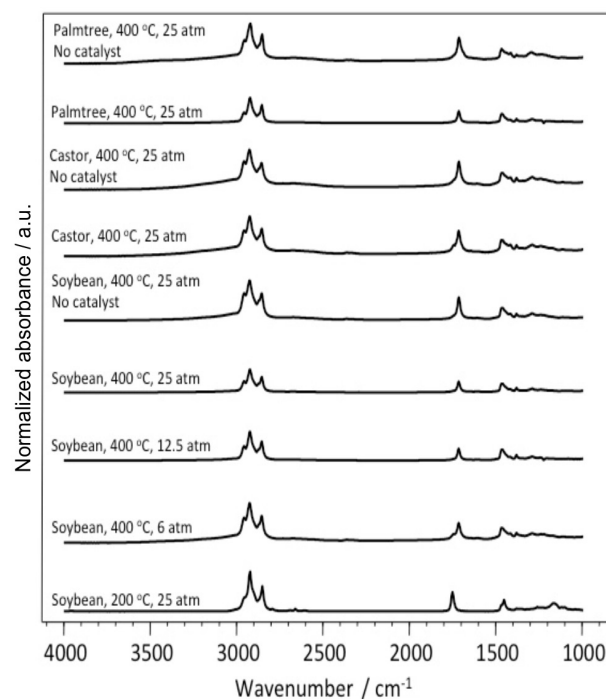


Figure 1. FT-IR of the products obtained from hydrocracking of palm tree, castor and soybean oils in the presence of Rh catalyst **1**.

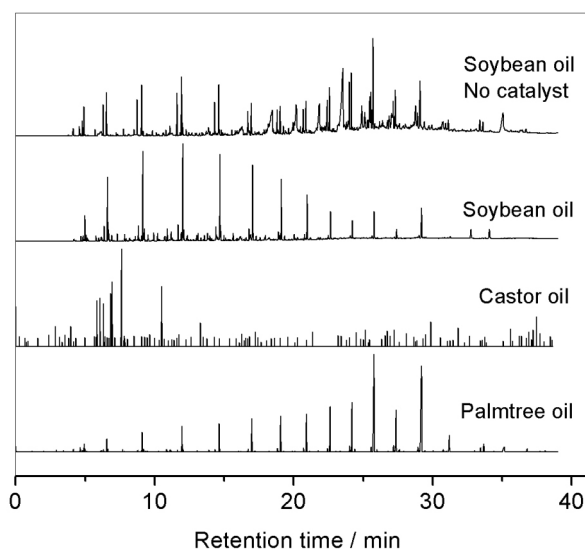


Figure 2. GC-FID of the products obtained from hydrocracking of palm tree, castor and soybean oils in the presence of Rh catalyst **1** and the products obtained from pyrolysis of soybean oil in the absence of catalyst (400 °C and 25 atm H₂).

As can be depicted from these chromatograms, it is really complicated to identify and quantify all peaks. However, comparing GC-MS with the Wiley Library CLASS-5000 (6th edition), it was possible to determine, with more than 95% similarity, that the pyrolysis results in a mixture of hydrocarbons with linear and saturated or unsaturated chains and oxygenated products, such as linear carboxylic acids, aldehydes and ketones. It is still the case that most of the molecules identified after cracking in the absence of catalyst are carboxylic acids and long-chain hydrocarbons, such as docosane (C₂₂H₄₆), but in smaller amounts. When using castor oil, a low level of deoxygenation took place and it was possible to identify a wide variety of oxygenated products, such as alcohols, carboxylic acids, esters, and some hydrocarbons. On comparing the results for the different fats and oils (Table 1, entries 1 to 6), it is clear that the activity of the catalytic system increases in the order: castor oil < palm tree oil < soybean oil. The presence of catalyst, in the case of castor oil, did not improve the deoxygenation to the same extent as observed for soybean and palm tree oils. This can be evidenced by comparing the AN of the reaction without catalyst (Table 1, entry 4) and in the presence of catalyst (Table 1, entry 3), and also the results obtained for the other oils. Further evidence that the product obtained from castor oil is rich in oxygenated compounds is the increased baseline between 2500 and 3500 cm⁻¹, attributed to the C–O–H···O=C of dimerized carboxylic acids, in the FT-IR spectrum (Figure 1). This result is probably due to competition between the oxygen from the hydroxyl group and those from the acyl group present in castor oil.

As can be seen in Table 1, the lowest AN using soybean oil was obtained at 400 °C and pressures of 12.5 and 25 atm (entries 5 and 8). In fact, in the chromatographic analysis the prevalence of normal alkanes, mainly undecane, pentane and docosane, was observed. The fact that the deoxygenation was almost the same for 12.5 and 25 atm, can be explained by the saturation of hydrogen in the bulk reaction, and probably the diffusion of this reagent towards the catalytic center does not limit the reaction under such conditions. However, when the pressure is lowered to 6 atm (entry 9), the AN increases considerably, being close to the non-catalyzed thermal cracking, which strongly suggests a diffusion control of the reaction under this pressure condition. Also, a shoulder in the band related to the carboxyl group in the FT-IR spectrum (νC=O at 1745 and 1710 cm⁻¹ in Figure 1) suggests that the conversion was not complete. At lower temperature (200 °C, entry 7), an AN close to that of the initial soybean oil (2.04 mg_{KOH} g_{sample}⁻¹) was obtained, which confirms the information given in the literature²² that there is no

cracking of triglycerides at this temperature, and that the sole final product is the hydrogenated soybean oil. Indeed, the FT-IR spectrum corresponding to the reaction at 200 °C differs from the FT-IR spectra of the reactions at 400 °C, and exhibits the C=O stretching band characteristic of the ester carboxylic group at 1745 cm⁻¹, with the absence of the band corresponding to carboxylic acid (see Figure 1). It is also not possible to identify the broad band related to O–H as observed during the decomposition of triacylglycerides. Unsaturated fats and oils have a well-known band at 3000-3100 cm⁻¹, corresponding to the stretching of olefinic C–H bonds. This band is not present in the FT-IR of all samples shown in Figure 1, further indicating the reduction of the olefinic bonds.

In Table 2, the main results of the catalytic hydrocracking of vegetable oils obtained using a ruthenium catalyst, Fe₃O₄@SiO₂NH₂Ru (**2**), are summarized. The presence of the Ru catalyst **2** also increases the deoxygenation of the products when compared to non-catalyzed reactions. The Ru catalyst **2** resulted in products with a lower AN value than the products obtained with the Rh catalyst **1**, under similar reaction conditions. This is probably due to the higher oxophilicity of ruthenium compared to rhodium. The results of the gas chromatography analysis showed the prevalence of normal alkanes, such as undecane, pentane and docosane, in the products of soybean oil hydrocracking. In the case of castor oil, some oxygenated compounds were observed, but in smaller amounts than when using Fe₃O₄@SiO₂NH₂Rh (**1**) as the catalyst. The FT-IR analysis also confirmed the decomposition of triglycerides, except for the reaction at 200 °C, which exhibits the C=O stretching band of the ester carboxylic group at 1745 cm⁻¹ and does not exhibit the band corresponding to carboxylic acid (Figure 3).

Table 2. Hydrocracking of vegetable oils in the presence of Fe₃O₄@SiO₂NH₂Ru using different conditions^a

entry	Oil	Catalyst mass ^b / %	p H ₂ / atm	AN ^c / (mg _{KOH} g _{sample} ⁻¹)
10	Soybean	1.0	6	78.63
11	Soybean	1.0	12.5	46.90
12	Soybean	1.0	25	42.41
13	Soybean	1.0	25	3.44
14	Palm tree	1.0	25	42.16
15	Castor	1.0	25	70.07

^aReaction temperature = 400 °C (except entry 13, T = 200 °C); ^b10 g of oil and 0.1 g catalyst (1.4 mg Ru); ^cAN = acid number.

Conclusions

Rh and Ru nanoparticles immobilized on silica were effective catalysts for the deoxygenation of soybean and

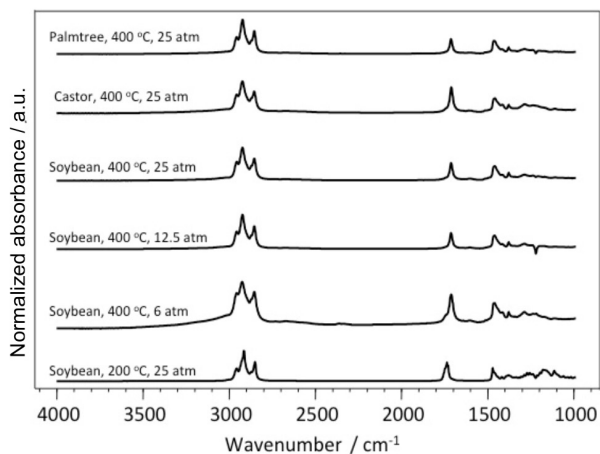


Figure 3. FT-IR spectra of the products obtained from hydrocracking of palm tree, castor and soybean oils in the presence of Ru catalyst 2.

palm tree oils at 400 °C and the Ru nanoparticles were also active for castor oil. These catalysts are also active in the hydrogenation of soybean oil at 200 °C. The hydrocracking of vegetable oils leads to the preferential formation of long-chain linear hydrocarbons, which are suitable for use as diesel fuel. However, their acid number are still high and future studies are needed before an optimized process can be developed for industrial production of fuels that match specification for commercial diesel fuel. Due to the presence of a magnetic-responsive catalyst support, the product (hydrocarbon) could be collected after the catalyst was magnetically separated and other separation techniques, such as filtration and centrifugation, are unnecessary.

Acknowledgments

The financial support of CNPq, FAPDF, and FAPESP is gratefully acknowledged. The authors also express their gratitude for the research fellowship granted by CNPq.

The authors would like to dedicate this paper to the memory of Roberto F. de Souza, a great human being, teacher and researcher. PAZS and LMR had the great opportunity to start their research career with him and Yeda Pinheiro-Dick, and recognize them as their mentors in catalysis research.

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Submitted on: July 21, 2014

Published online: October 28, 2014

FAPESP has sponsored the publication of this article.