PRODUCTION OF GREEN DIESEL BY HYDROCRACKING OF CANOLA OIL ON Ni-Mo/γ- Al_2O_3 AND Pt-ZEOLITIC BASED CATALYSTS

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Abstract

As an alternative way to produce biodiesel, the hydrocracking of canola oil was studied on different types of catalysts. Experiments were carried out in a batch reactor over a temperature range of 300 to 400°C, initial hydrogen pressure of 5 to 11MPa, and reaction times 1 to 6 hours. Three types of bifunctional catalysts were developed and used: Pt/H-Y zeolite, Pt/HZSM-5 and sulfided NiMo/γ- Al_2O_3. At the conditions studied, the hydrocracking on Ni-Mo/γ- Al_2O_3 catalyst gave the highest conversion to liquid hydrocarbons in the boiling range of diesel fraction. The Pt-zeolite catalysts revealed a strong catalytic activity for both cracking and hydrogenation reactions, and therefore initial high hydrogen pressures were found to be required to reach a good conversion. The time of reaction was limited in observance of the rates of reaction for both hydrogenation and cracking reactions, which strongly depended on the type of catalyst. In most cases, the GC analysis of the gaseous phase revealed the presence of mainly CO_2, CO, propane, and hydrogen. Oxygen was not present. The hydrocracking of canola oil on a NiMo/Al_2O_3 catalyst produced a diesel fraction mainly composed of normal paraffins from C_{15} to C_{18}. Traces of unconverted fatty acids and a very low amount of water were also detected. After evaluation of the composition and physical properties of the liquid product, they were found to be very similar to those of petro diesel, but with the advantage that the former contains a higher percentage of C_{17} and C_{18} hydrocarbons, and therefore a higher cetane number.

Keywords: *Hydrocracking, hydrotreating, vegetable oil, canola, NiMo/Al_2O_3 catalyst.*

1. Introduction

The efficient utilization of biomass for the production of transportation fuels such as biodiesel and bioethanol is becoming increasingly important. Biofuels have the potential to replace a large amount of the current gasoline and diesel used worldwide. The use of biofuels can help to slow down the consumption of petroleum while preserving the oil reserves. An important characteristic in the use of biofuels is that during their combustion there is a neutral carbon dioxide balance, which has a reduced effect on global warming. The use of transportation biofuels can also improve rural environment, generate jobs, and reduce the dependency of imported fuels.

Biodiesel as a prospective important transportation fuel is mainly produced by transesterification. A large production of biodiesel involves a large usage of water and the byproduct glycerol needs to be treated to be reused. In addition, the oxidation stability of the biodiesel is poor, and the engine may need some modifications or special maintenance when methyl esters are used. Moreover new plants are required to be built.

The above drawbacks can be overcome by using the current technology found in refinery plants in which vacuum gas oil (VGO) is hydrotreated. The basic idea is to mix the VGO stream with vegetable oil and by effect of a high pressure, high temperature and a bifunctional catalyst the triglycerides in the oil are transformed into hydrocarbons in the diesel boiling range. The metal function of the catalyst and a high hydrogen pressure contribute to the saturation of the side chains of the triglycerides. The acid function of the catalyst contributes to the cracking of the C-O bound and to the isomerization of the n-olefins formed, which are then transformed in isoparaffins. A high enough temperature is important to increase the cracking activity. However at temperatures higher than 380 °C cracking of the hydrocarbons increases and hence the yield of diesel decreases. Though more gasoline and propane can be obtained in this way, and depending of the refiner requirements, they may also be desirable products.

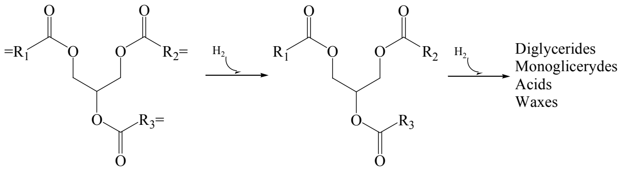
The hydrocarbon mixture produced from the hydrocracking of vegetable oil is commonly called green diesel, as it is indeed diesel but produced from a green plant. Green diesel is mainly composed of n-heptadecane and n-octadecane. As both of them contain a high cetane number, green diesel can also be used as a cetane additive. A green diesel with high content of isoparaffins is desirable as they have lower pour point than those of the corresponding n-paraffins. The yield of isoparaffins depends on the acid sites of the catalyst. Thus, it becomes important to study different operative conditions and different catalysts to elucidate the operative range than allows obtaining a high yield of high quality green diesel.

A number of papers[1-3] and patents[4-7] related with hydroconversion of vegetable oils have been previously published. Most efforts have focused on experiments with sulfided NiMo/γ-Al_2O_3 catalysts. This catalyst is commonly used at petroleum refineries for the hydroprocessing of middle distillates. The high hydrogenation activity and mild acidity make this catalyst appropriate for the hydroconversion of vegetable oils. More acid-supported catalysts such as Pt/H-ZSM-5 and Pt/USY zeolite, Pt/SAPO11, Pt/HZSM-22 have also been used for the same purpose[7]. The oils that have been commonly used are sunflower, rapeseed and some others like babacu oil. Huber and Corma[2] have previously shown the effects of mixing VGO with sunflower oil.

In this study, NiMo/γ-Al_2O_3 catalysts and Pt/zeolite catalyst are used for the hydrocracking of canola oil. Several reaction temperatures and hydrogen pressures and three types of catalysts have been studied to provide insights that allow for a future optimal operation.

2. Chemistry of the hydroconversion of vegetable oils

Based on their analytical results, several authors have tried to elucidate the mechanism of the hydrocracking of vegetable oils into diesel. It is generally acknowledged that the triglycerides are first saturated on their side chain, which is then followed by scission of the C-O bound, leading to the formation of diglycerides, monoglycerides, carboxylic acids and waxes[2]:



Then, these are transformed into hydrocarbons by three different paths, i.e. hydrodeoxygenation, decarbonylation and dehydration:

a. Decarboxylation:

$$C_{17}H_{35}COOH \longrightarrow C_{17}H_{36} + CO_2$$

b. Decarbonylation:

$$C_{17}H_{35}COOH + H_2 \longrightarrow C_{17}H_{36} + H_2O + CO \qquad \text{(Catalytic reaction)}$$

$$C_{17}H_{35}COOH \longrightarrow C_{15}H_{31}CH{=}CH_2 + H_2O + CO \qquad \text{(Thermal reaction)}$$

c. Reduction (hydrodeoxygenation):

$$C_{17}H_{35}COOH + 3H_2 \longrightarrow C_{18}H_{38} + 2H_2O$$

The predominant hydroconverted products are n-heptadecane and n-octadecane. As byproducts, carbon monoxide, carbon dioxide, and water are obtained. Due to the acid function of the catalyst, isomerization and cyclization of the olefin intermediates can occur, leading to the production of isoparaffins, naphthenes and in case there is not enough hydrogenation, aromatics can be formed. Dehydrogenation is favored at high temperature and low pressure.

3. Methods

3.1 Materials

The canola oil used in the experiments corresponds to a commercial type sold in Japan. Table 1 shows the total fatty acid composition of the oil. This was determined by derivation of the corresponding fatty acid methyl esters (FAME). A modified method AOAC 969.33 by Lee et al.[8] was used to obtain the FAME. A GC-2014 Shimadzu was used. Table 2 shows some physical properties of the oil. The CHNS composition was determined by using an elemental analyzer (CE instruments EA1110), the oxygen content was obtained in an approximated way by balance.

The density was determined at 20 °C using a density/specific gravity meter (Kyoto Electronics DA-130N). The viscosity of the oil was determined at 20 and 40 °C using a vibro viscometer (A&D Co. Lim. Japan, SV-10). The acid value of canola oil was obtained by titration with a KOH solution (0.1 M).

Table 1. Fatty acid composition of canola oil.

Fatty acid	Structure*	Wt%
Miristic	C14:0	0.00
Palmitic	C16:0	3.65
Palmitoleic	C16:1	0.18
Stearic	C18:0	1.65
Oleic	C18:1	63.72
Linoleic	C18:2	15.42
Linolenic	C18:3	14.28
Cis-11-eicosenoic	C20:1	1.11

*Cx:y, where x: number of carbon atoms; y: number of double bonds

Table 2. Physicochemical properties of canola oil

Property	
Elemental composition (%)	
C	77.903
H	11.689
N	0.041
S	0.000
O*	10.367
Density at 20 °C , g cm^{-3}	0.89
Viscosity at 25 °C, mPa-s	63.0
Viscosity at 40 °C, mPa-s	28.1
Acid value	0.55
FFA content, wt%	0.28

*By balance

3.2. Catalysts

NiMo/γ-alumina

The catalyst precursor consisting in a mixture of NiO and MoO supported in γ-alumina corresponded to a commercial type (CDS-R25NQ) and was supplied by Catalyst and Chemicals Ind. Co. This catalyst is used in refining operations for hydrotreating of gas oil and atmospheric residue. It contains a high desulfurization activity. The activation of the catalyst was carried out by two methods: A) in situ activation with elemental sulphur: a ratio of 0.8 g S/g catalyst was used. B) Presulfidation in a tube reactor in which the catalyst was sulfided with H_2S (10 vol. %)/H_2 gas mixture at 400 °C for 8 hours and a hydrogen flow rate of 50 mL (STP)/min. The final catalyst was crushed in particles of about 0.3 mm of diameter either before method A or after method B.

Pt/HZSM5 catalyst (2 wt% Pt)

The precursor NH4-HZSM-5 was obtained by ionic exchange between Na-ZSM-5 and ammonium chloride (NH_4Cl). This precursor was dried for 24 hours at 110 °C and then calcined at 550 °C in air for three hours to form HZSM-5. The HZSM-5 particle was then impregnated with a 1 wt% $H_2PtCl_6 \cdot 6\ H_2O$ solution by incipient wetness method. The solution was added dropwise to the particle. For a catalyst containing 2% of platinum, 1.5 g of HZSM-5 powder and 7.95 g of $H_2PtCl_6 \cdot 6\ H_2O$ solution were used. About 20 mL of water were also added. The mixture then was heated at 30 °C and stirred for one hour so the platinum was absorbed into the zeolite pores. The solution was then dried at 95 °C for 24 hours. Subsequently, the particle was calcined at 400 °C in air for three hours. Finally, the catalyst sample was reduced at 350 °C, for two hours, in a reactor tube with an internal diameter of 1 cm, and a hydrogen flow rate of 50 mL (STP)/min.

Pt/H-Y zeolite catalyst (2 wt% Pt)

This catalyst corresponded to a synthetic HS-320 catalyst and was purchased from Waco Chemicals Co. (I.D. 325-27765). The SiO_2/Al_2O_3 molar ratio is 5.5.

3.3. Experimental procedure

Experiments were conducted in an 80 mL-batch reactor with an internal diameter of 20 mm, and equipped with a mechanical stirrer. The operative limits of the reactor were 30 MPa and 900 °C. For all experiments, the stirrer speed was kept constant at 350 rpm, and the temperature control was ± 2 °C.

The feed consisted in canola oil and catalyst in a ratio of 3 wt % cat/wt. oil. The reaction conditions for hydrotreating experiments were in a temperature range of 300 to 400°C, initial hydrogen pressures between 5 and 11 MPa. to reaction, the reactor was purged several times with nitrogen and then with hydrogen at room temperature. The reactor was maintained at the final temperature for 3 hours (reaction time).

After cooling down the reactor, the gas and liquid products were recovered. The liquid phase containing the catalyst was filtered. When solid product was obtained this was diluted prior to its analysis with 1,2,3,4-tetra hydro naphthalene. Both gas and liquid phases were analyzed by gas chromatography. To verify the presence in the liquid product of important compounds, such as remaining carboxylic acids, isoparaffins, cyclic paraffins and aromatics, a detailed analysis by mass spectrometry was performed. A small amount of water (ca. 4 wt%/wt oil) was also observed in the liquid phase. The produced gases were analyzed by a GC 323 (GL Sciences) equipped with a thermal conductivity detector and two columns, one being a Pora-Q capillary column (30 m, 0.53 mm I.D.) for determination of CO_2, and the other one a packed column (MS-5A) for determination of H_2,O_2, N_2 and CO. The hydrocarbon fraction C_4- was determined by a FID GC-353B (GL Sciences).

4. Results and discussion

4.1. Canola oil composition

The composition of canola oil in Table 1, reveals a high content of unsaturated carboxylic acids, i.e. oleic, linoleic and linolenic acids. Conversely, the content of saturated acids is very low. A high content of unsaturated acids implies a high consumption of hydrogen during hydrocracking process.

In Table 2 it is also possible to notice that this commercial canola oil does not contain a significant amount of free fatty acids (FFA), as it is given by the acid value. This low content of FFA is characteristic of commercial oils.

The low content of FFA is desirable since the higher this value the higher the consumption of hydrogen required and therefore the higher the operative cost.

4.2. Product composition

Figure 1 shows a typical composition of the liquid product. This case corresponds to the liquid obtained at an initial pressure of 9 MPa, final temperature of 350 °C and using $NiMo/Al_2O_3$ as catalyst. With this catalyst, the hydrocracking of canola oil produces mainly normal paraffins from C_{15} to C_{20}, which are in the interval of the diesel fraction obtained from distillation of petroleum. At this relatively low temperature, a non-significant amount of gasoline (C_5-C_{12} hydrocarbons) is produced.

The green diesel mainly contains C_{17} and C_{18} normal paraffins. The content of isoparaffins (viz. Fig. 2) is very low. The main isoparaffins observed by GC-MS analysis were single-branched paraffins, e.g. 1-methyl and 2-methyl paraffins.

As the cetane number of these normal paraffins is higher than 100, the cetane number of the green diesel will be very high, and probably much higher than that of biodiesel or that of petrodiesel.

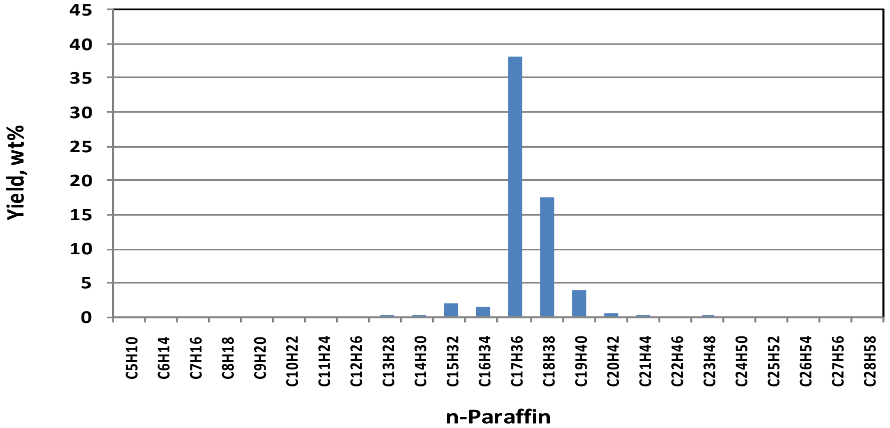


Figure 1. Yields of the C_5-C_{20} n-paraffins in the liquid fraction obtained with $NiMo/Al_2O_3$ as catalyst.

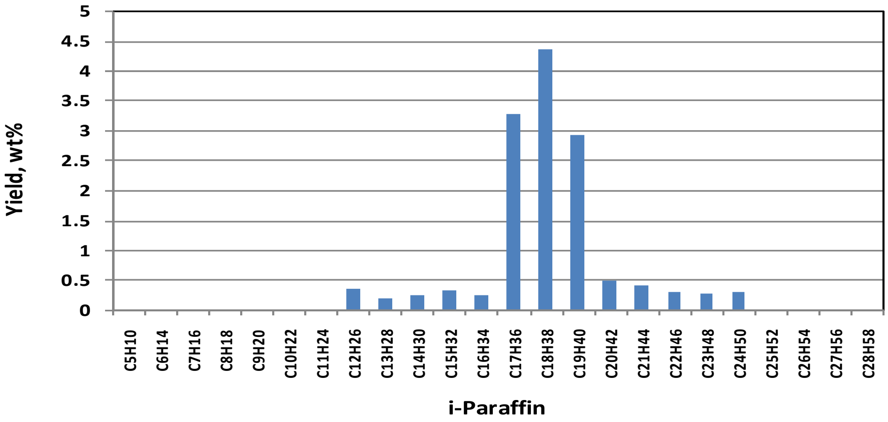


Figure 2. Yields of the C_5-C_{28} i-paraffins in the liquid fraction obtained with NiMo/Al_2O_3 as catalyst.

To increase the production of gasoline, temperatures higher than 350 °C can be used. Cracking of the formed paraffins is thus increased and the yield of gasoline increases as well, although the yield of diesel will be reduced.

By GC-MS analysis it was also detected the presence of cycloalkanes and aromatics. The latter ones were more predominant in the products obtained with zeolitic catalysts. This may be due to the strong acids sites in the zeolites that promote isomerization and cyclization.

Figure 3 shows the components in the gas phase (excluding the remaining hydrogen (ca. 40% mol). The yield of CO_2 predominates over CO, which indicates that decarboxylation is favored over decarbonylation. The latter reaction requires more hydrogen than the former one. As can be observed in Figure 3, propane is also produced, which in a large scale operation it will be very beneficial.

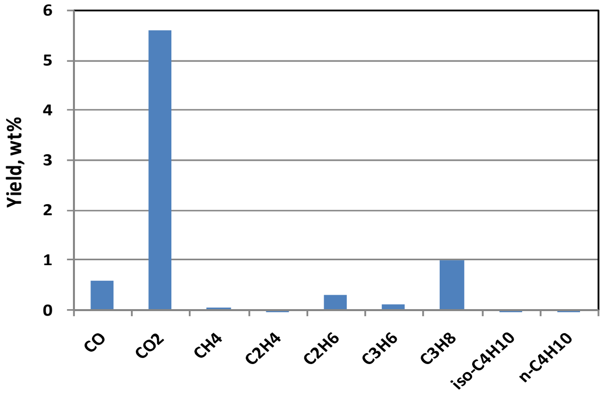


Figure 3. Yields of the components in the gas phase recovered after three-hour reaction at 350 °C with NiMo/Al_2O_3 as catalyst.

4.3. Effect of initial hydrogen pressure

As the hydrogen consumption is one of the important limiting economical factors in hydrotreating, the effect of the initial hydrogen pressure was studied. To evaluate this effect several experiments were performed in an interval of 5 to 11 MPa. When using NiMo/Al_2O_3 as catalyst, initial hydrogen pressures of 8 to 10 were found to be more appropriate. At pressures below 8 MPa the product was mostly solid and a high content of carboxylic acids were detected. They were mainly palmitic, stearic and oleic acids. With zeolitic catalysts, even higher pressures were required. In this section, only the results with NiMo/Al_2O_3 as catalyst are shown. In section 4.5, the results with zeolitic catalyst are described.

Figures 4, 5 and 7 show the global yields for the different fractions obtained when using NiMo/Al_2O_3, a reaction time of three hours at 350 °C, and different initial hydrogen pressures. The main effect of the initial pressure is on the yield of the wax fraction and on the yield of fatty acids. The global yield of green diesel is not affected significantly by the pressure. Figure 6 shows the yields of the two main components in the green diesel, i.e. n-heptadecane and n-octadecane. The higher yield of the former and the high content of CO_2 in the gas phase indicate that the main reaction path is decarboxylation.

The effect on increasing the initial hydrogen pressure is slightly more pronounced on the yield of n-octadecane than on the yield of n-heptadecane. Thus, it is posssible to argue that hydrodeoxygenation is favored at higher pressures This however produces more water as well, which may deactivate the catalyst and reduce the yield of green diesel. Figure 7 shows the global yield of carboxylic acids obtained at different initial hydrogen pressures. Even at 10 MPa, there fatty acids, mainly saturated ones, are not totally converted into hydrocarbons. To achive that, it is necessary to increase the temperature as described in the next section.

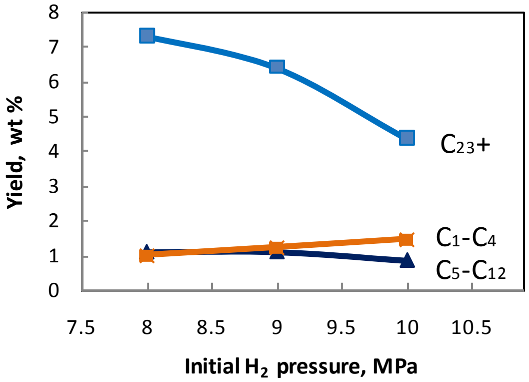


Figure 4. Influence of initial hydrogen pressure on the production of the global yields of the main fractions: gas (C_1-C_4), gasoline (C_5-C_{12}), and wax (C_{23}^{+}). T = 350 °C on NiMo/Al_2O_3.

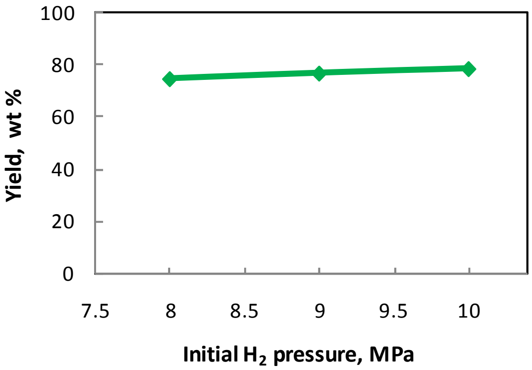


Figure 5. Influence of initial hydrogen pressure on the production of the global yields of the main fraction: green diesel (C_{12}-C_{22})

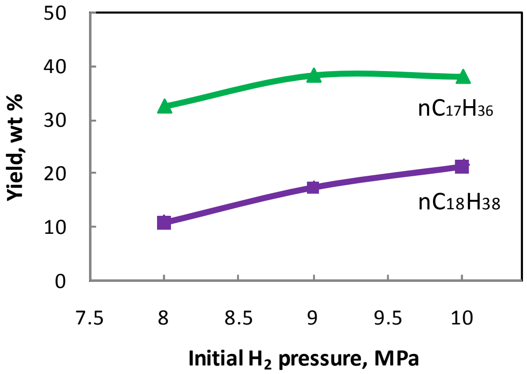


Figure 6 Influence of initial hydrogen pressure for the major products: n-heptadecane and n-octadecane. T = 350 °C on NiMo/Al_2O_3.

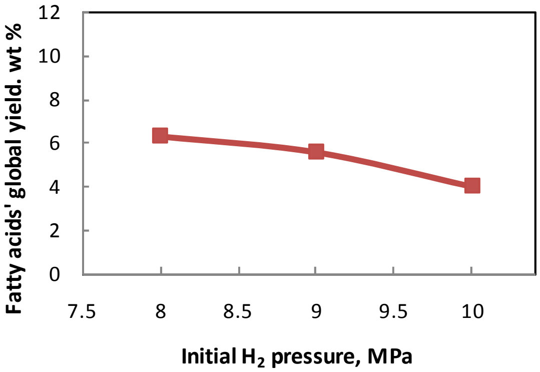


Figure 7. Influence of initial hydrogen pressure for the major products: n-heptadecane and n-octadecane. T = 350 °C on NiMo/Al_2O_3.

4.4. Effect of temperature

The temperature plays an important role in cracking the C=O bound. The effect of temperature on the hydrocracking of canola oil on NiMo/Al_2O_3 was studied by performing experiments from 300 to 400 °C , and fixing the initial hydrogen pressure at 9 MPa. The reaction time was three hours. Initial experiments from 1 to 6 hours at

350 °C were carried out to determine the optimal reaction time. Three hours were found to be appropriate. Higher reaction time did not increase the yield of the main components; conversely they were slightly reduced as cracking occurred.

Global yields of the different fractions obtained at different temperatures can be observed in Figures 8 and 9. The yields of the main products are shown in Figure 10. At temperatures below 350 °C the product was mostly solid. Only a small amount of liquid was obtained. Therefore only those results obtained at temperatures at 350 °C and above are presented here. At temperatures above 350 °C there is an increase in the degree of cracking of n-paraffins and isoparaffins in the boiling range of diesel fraction, and therefore the yield of C_5 to C_{12} (gasoline fraction) increases..

The highest yield of the C_{13}-C_{22} fraction is observed at 350 °C. The global yield of fatty acids in the product obtained at differet temperatures is also observed in Fig. 11. These results indicate that an enough high temperature (375 °C) is required to hydrocrack the carboxylic acids. The transformation of carboxylic acids can be considered therefore as the most important step for the production of diesel or gasoline hydrocarbons from the hydrocracking of vegetable oils.

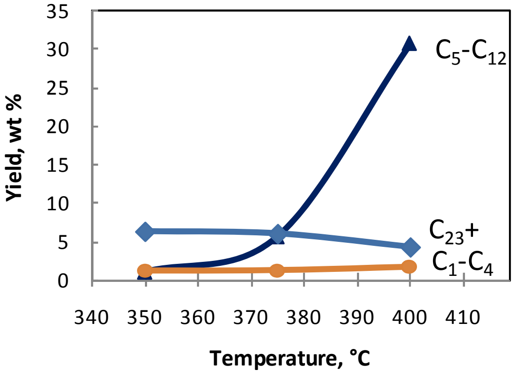


Figure 8. Influence of temperature on the production of the main fractions: gas (C_1-C_4), gasoline (C_5-C_{12}), and wax ($C_{23}^{+)}$. Initial P_{H2} = 9 MPa. NiMo/Al_2O_3 as catalyst.

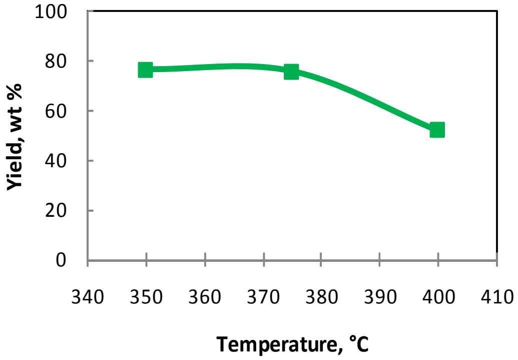


Figure 9. Influence of temperature on the production of green diesel (C_{13}-C_{22}) Initial P_{H2} = 9 MPa. NiMo/Al_2O_3 as catalyst.

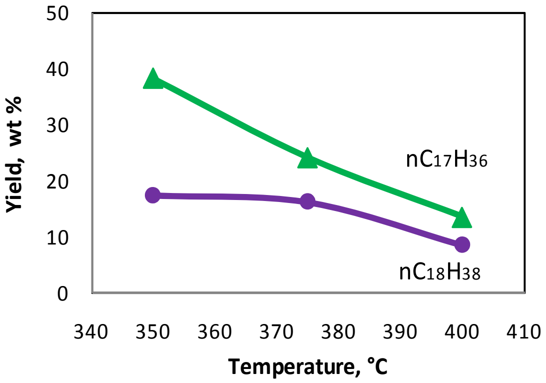


Figure 10. Influence of temperature on the production of major products. Initial P_{H2} = 9 MPa. NiMo/Al_2O_3 as catalyst.

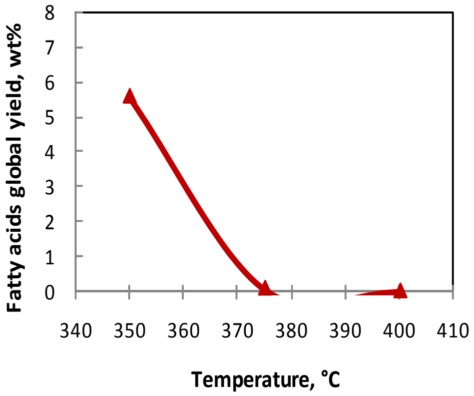


Figure 11. Influence of temperature on the global yield of fatty acids. Initial P_{H2} = 9 MPa. NiMo/Al_2O_3 as catalyst.

4.5. Zeolitic catalyst performance

The high content of C_{15} toC_{18} n-paraffins assures that the green diesel obtained with NiMo/Al_2O_3 as catalyst has a very high cetane number. However the pour point of these n-paraffins is relatively high and therefore the use of pure green diesel might not be recommendable for inter season. The best option is to transformed these n-paraffins into their corresponding isoparaffins, which have a lower pour point. As the isomerization reaction is promoted by the acids sites of the catalyst, the use of strong acid catalyst, such as zeolites can be appropriate.

Two types of Pt/zeolite catalysts were used, i.e. Pt/HZSM5 and Pt/H-Y. Figure 12 compares the yields of the major fractions obtained with both catalyst when operating with an initial hydrogen pressure of 11 MPa and 380 °C . These conditions were the ones that gave the highest yield of diesel from both catalysts. Pt/HZSM5 is observed to have more cracking activity than Pt/H-Y as it produces more gasoline and gas fractions. Pt-HY presents a lower cracking activity and the yield of diesel obtained with it is higher than that obtained with Pt-HZSM5. However, compared with the yield of diesel obtained with $NiMo/Al_2O_3$ (ca. 80%), the yield with Pt-HY is very low (ca. 35%). The ratio of isoparaffins to n-paraffins to with zeolitic catalyst is larger than that of the product obtained with $NiMo/Al_2O_3$. Which has the benefit of a lower pour point.

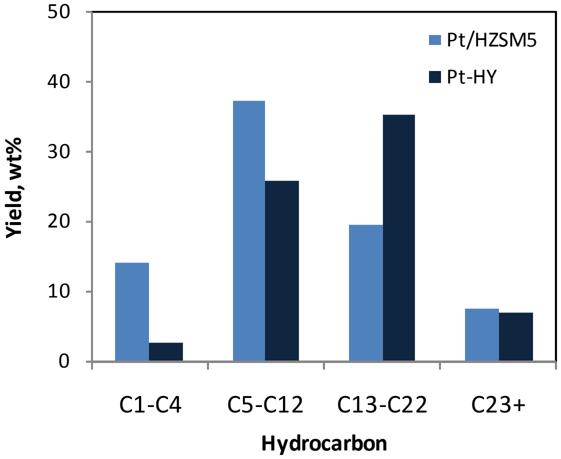


Figure 12. Global yields obtained with the operation of the two zeolitic catalyst used in the experiments. Initial P_{H2} = 11 MPa. Final T= 380 °C .

The results obtained with this study indicate that both pressure and temperature play an important role in the transformation of triglycerides and mainly carboxylic acids. An enough high pressure is needed to hydrogenate the unsaturated chains in the triglycerides and in the carboxylic acids as well as those of the olefins formed by cracking. Increasing temperature favors the cracking of the double bond C=O in the carboxylic acids, thus favoring the production of n-paraffins.

5. Conclusions

The hydrotreating of vegetable oils on bifunctional catalysts makes possible the production of liquid hydrocarbons known as “green” diesel containing mostly n-heptadecane and n-octadecane, which are mainly formed by decarbonylation and hydrodeoxygenation reactions, respectively. Green diesel can be used directly as transportation fuel or used as an excellent additive for increasing the cetane number of the petro diesel.

Due to their strong acid sites, the Pt/zeolites-supported catalysts have a high cracking activity. The hydrogenation activity is also very high and therefore the hydrogen is very fast consumed with these catalysts. In consequence, the yield of diesel is lower than that obtained when using $NiMo/Al_2O_3$ as catalyst. The process to produce diesel with the former requires higher severity, and therefore a higher cost than the latter. However, due to their strong acid sites, the use of zeolite catalyst favors the production of isoparaffins, which are desirable for the diesel to have a low pour point. It is therefore necessary to moderate the acidity of the zeolite catalysts to increase the isomerization activity while keeping a moderate cracking. Thus a large amount of isoparaffins could be obtained.

The transformation of carboxylic acids is the most important step for the production of diesel hydrocarbons from canola oil and similar oils. The quality of the diesel product depends mainly on the pressure, temperature and in the catalyst used. NiMo catalyst effectively catalyzes the hydrocracking of triglycerides and carboxylic acids lower temperature and pressure, however the moderate acidity of the alumina support does not largely contribute to the production of isoparaffins, which are also important due to their lower melting point than their corresponding n-paraffins.

Due to its large concentration of nC_{17} and nC_{18} hydrocarbons, the green diesel has a high cetane number even larger than that of the typical biodiesel composed by FAME. It can therefore be used as an excellent additive for improving the ignition properties of the petro diesel.

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References

1. Da Rocha Filho, G. N.; Brodzki, D.; Djega-Mariadassou, G. Formation of Alkanes, Alkylcycloalkanes and Alkylbenzenes During Catalytic Hydrocracking of Vegetable Oils. *Fuel* **1993,** *72*, 543-549.

2. Huber, G. W.; O'Connor, P.; Corma, A. Processing Biomass in Conventional Oil Refineries: Production of High Quality Diesel by Hydrotreating Vegetable Oils in Heavy Vaccum Oil Mixtures. *Applied Catalysis A: General* **2007**, 120-129.

3. Gusmao, J.; Brodzki, D.; Djega-Mariadassou, G.; Frety, R. Utilization of Vegetable Oils as an Alternative Source for Diesel-Type Fuel: Hydrocracking on Reduced Ni/Sio2 and Sulphided Nimo/Al2O3. *Catalysis Today* **1989**, 533-544.

4. Craig, W. K.; Soveran, D. W. Production of Hydrocarbons with a Relatively High Cetane Rating. 4992605, Feb. 12, 1991, 1991.

5. Herskowitz, M.; Landau, M.; Reizner, I.; Kaliya, M. Production of Diesel from Vegetable and Animal Oils. US 2006/0207166 A1, Sep. 21, 2006, 2006.

6. Gomes, J. R. Vegetable Oil Hydroconversion Process. US 2006/0186020 A1, Aug. 24, 2006, 2006.

7. Duarte, F. A.; Soares, W.; Ferreira, A. E.; Ximenes, L. M.; Gomes, J. R. Process to Obtain N-Paraffins from Vegetable Oil. US 2007/0260102 A1, Nov. 8, 2007, 2007.

8. Lee, D. S.; Noh, B. S.; Bae, S. Y.; Kim, K. Characterization of Fatty Acids Composition in Vegetable Oils by Gas Chromatography and Chemometrics. *Analytica Chimica Acta* **1998**, 163-175.