

UTILIZATION OF VEGETABLE OILS AS AN ALTERNATIVE SOURCE FOR DIESEL-TYPE FUEL:
HYDROCRACKING ON REDUCED Ni/SiO₂ AND SULPHIDED Ni-Mo/γ-Al₂O₃

J. GUSMÃO¹, D. BRODZKI¹, G. DJÉGA-MARIADASSOU¹ and R. FRET²

¹Laboratoire de Cinétique Chimique, Université Pierre et Marie Curie, 1, rue Guy de la Brosse, 75005 Paris, France

²Institut de Recherches sur la Catalyse, CNRS, 2, av. Albert Einstein, 69626 Villeurbanne, France

ABSTRACT

Vegetable oil hydrocracking was studied in a batch reactor under high hydrogen partial pressure (10-200 bars) at 623-673 K, catalyzed by either reduced Ni/SiO₂ or sulphided Ni-Mo/γ-Al₂O₃. We have established the sequence of reactions which transform a vegetable oil into a diesel-type fuel. We have demonstrated the role of the catalyst in each of these reactions, and the occurrence of thermodynamic equilibria restricting the completion of the transformation. The displacement of these equilibria was achieved by an increase in hydrogen pressure, where molar yields close to 100% were attained. The corresponding product is a mixture of hydrocarbons (essentially normal alkanes in the diesel fraction).

INTRODUCTION

Vegetable oils have recently been investigated as raw material from which hydrocarbon fuel can be obtained. For example, a "vegetable gasoline" can be produced with yields of about 50 wt% when solid acids - H-ZSM5 (1,2) or SiO₂-Al₂O₃ (3,4) - are used as catalysts at 643-673 K and atmospheric pressure. However, published results (5-11) concerning the production of a "vegetable diesel" are still inadequate: yields reach 30-40 wt%, the liquid obtained frequently being a mixture of carboxylic acids and hydrocarbons. Some of the published work shows the advantages in prehydrogenating vegetable oils before the catalytic cracking (5,6), in the utilisation of hydrogenating catalysts (7,10,11) and in operating at high hydrogen pressure (10). These ideas are carefully analysed and developed below.

Our purpose was to optimize the yield in diesel-type hydrocarbons (C₁₂ to C₂₀ alkanes) obtained from vegetable oils. Some basic questions have been formulated in order to attain our objective:

- 1) How is the triglyceride molecule (which represents more than 95% by weight of a vegetable oil) transformed, under high hydrogen pressure in the presence of hydrogenating catalysts?

- ii) How can the operating conditions be modified in order to convert the primary products of this transformation into diesel-type hydrocarbons?
- iii) What is the role of the catalyst in these transformations?

EXPERIMENTAL

Hydrocracking Experiment

Vegetable oil hydrocracking experiments were conducted in two batch reactors (0,25 and 0,30 l), whose working limits were 723 K (450°C) and 150 and 300 bars, respectively.

A beaker containing measured amounts of vegetable oil and catalyst (catalyst/oil weight ratio between 0,01 and 0,06) was introduced into the reactor, the pressure set, and the heating programmed to a chosen final temperature. The reactor was maintained at this temperature for a certain time; lastly, the system was cooled to room temperature and the products analysed.

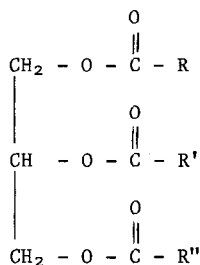
The gases (CO , CO_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , C_4H_{10}) were analysed chromatographically using a Poropak-R column (2m x 1/8"), at 343 K (70°C) and a thermal conductivity detector.

The remaining products were dissolved in chloroform, if the mixture was solid at room temperature and the catalyst removed by centrifugation. The final solution was qualitatively and quantitatively analysed by gas chromatography (Hewlett-Packard 5790A) in a 50 m capillary column (cross-linked methylsilicone). The most important peaks were identified as carboxylic acids and normal alkanes.

Carboxylic acids in solution were quantified by titration with a 0,1 N KOH/EtOH solution.

Composition of Vegetable Oils

Vegetable oils are essentially mixtures of triglycerides having the following general formula:



Where the groups R, R' and R'' are aliphatic, containing from 7 to 19 carbon atoms, and from 0 to 3 double bonds.

The analysis of these triglycerides involves a transesterification of the vegetable oil with methanol followed by separation and quantification of the resultant methyl esters by chromatography. The composition of vegetable oils is given in terms of fatty acids to soybean and "babaçu" oils used in this investigation (table 1).

TABLE 1

Babaçu and soybean oil composition in terms of fatty acids.

Notation: ACI.J = linear chain aliphatic carboxylic acid having I carbon atoms and J double bonds.

Fatty Acid	AC8.0	AC10.0	AC12.0	AC14.0	AC16.0	AC18.0	AC18.1	AC18.2	AC18.3
Babaçu Oil molar %	4,6	6,0	42,5	16,1	9,7	3,6	14,0	3,5	-
Soybean Oil molar %	-	-	-	-	15,0	3,5	21,7	54,0	5,8

These oils contain some impurities, e.g. sulphided compounds, which may act as poisons to metallic catalysts. The babaçu oil used contained 4,5 ppm of sulphur, whereas the soybean oil contained 5,0 ppm.

Preparation and Characterization of Catalysts

Reduced Ni/SiO₂, containing 8,3% by weight of Ni, was prepared by wet impregnation of an aqueous solution of Ni (NO₃)₂·6 H₂O on a SiO₂ (aerosil 380 - Degussa; BET area = 380 m²/g) support. The total volume to be impregnated was calculated so that preparation was carried out in three impregnation steps, distributing the active phase in a uniform way. After each step, the precursor so obtained was reduced in a fixed bed reactor at 673 K (400°C) during 20 hours (hydrogen flow = 2 l for an amount of 2 g), then passivated under helium flow (1 l/h) during 15 hours at room temperature.

The characterization of this catalyst was performed by the magnetic method of axial extraction (12). This method is based on the superparamagnetism of ferromagnetic metals (Fe, Co, Ni, ...) whose particles possess equivalent diameters of the order of a few nanometers. The degree of reduction of nickel was 57% and the mean diameter of these metallic particles was 7,5 nm.

The industrial catalyst - Sulphided Ni-Mo/γ-Al₂O₃ - was provided by PROCATALYSE and by the IFP ("Institut Français du Pétrole") in the oxide form, its composition being:

$$\text{MoO}_3 \text{ (\% by weight)} = 14,0; \text{NiO (\% by weight)} = 3,0; \frac{\text{Ni}}{\text{Mo+Ni}} = 0,29$$

The oxide precursor was activated by treatment with a gaseous mixture containing 15% $\text{H}_2\text{S}/\text{H}_2$ (flow = 2,4 l/h). The temperature of this treatment was programmed from 300 to 673 K, at a heating rate of 4 K/min, and kept for 4 hours at 673 K (400°C). After cooling the reactor, the gaseous mixture $\text{H}_2\text{S}/\text{H}_2$ was replaced by nitrogen. The sulphided supported Ni-Mo catalyst was maintained in n-hexane, under an argon atmosphere, in a closed flask.

A detailed study on the characterization of this kind of industrial catalyst has been presented by Topsoe et al-(13).

RESULTS AND DISCUSSION

Sequence of Soybean Oil Transformation Reaction in the Presence of Ni/SiO₂

Reduced Ni/SiO₂ is a classic vegetable oil hydrogenation catalyst, being employed commercially at temperatures near 423 K (150°C) and operating at a hydrogen pressure in the range 5-10 bars (14).

Fig. 1 shows the change of temperature and pressure during soybean oil hydrocracking at a final temperature of 663 K. In the chosen operational condition, the oil is completely hydrogenated between 415 and 465 K (142 and 192°C) - segment AB in Fig. 1. At point B, the reaction mixture may be considered as formed by triglycerides of stearic (85% molar) and palmitic (15% molar) acids.

Between points B (T=465 K) and C (T=568 K) the increase of pressure essentially corresponds to the increase in temperature: there is no appreciable chemical transformation in the reaction mixture. From point C onwards (T=568 K) we note a second hydrogenation, connected to the degradation of triglycerides and to the hydrogenation of the resultant insaturated compounds.

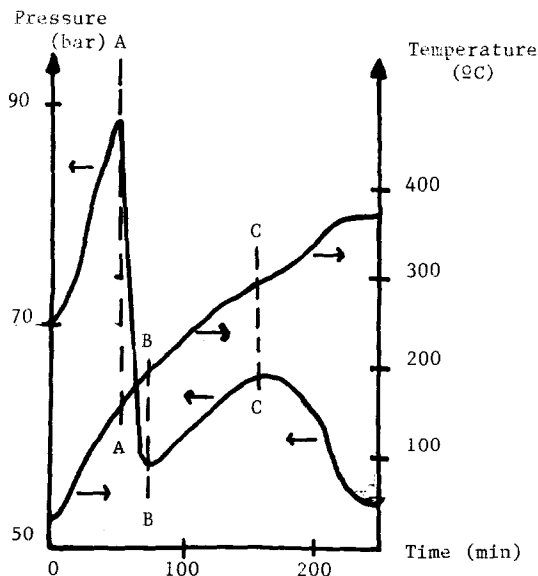
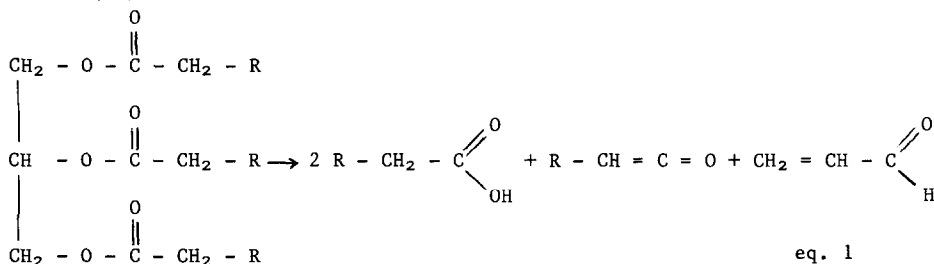


Fig. 1 - Evolution, with time, of pressure and temperature during soybean oil (45 g) hydrocracking in the presence of reduced Ni/SiO₂ (0,50 g).

Overall, the degradation of triglycerides can be represented by the following reaction scheme, first proposed by Chang and Wan (15) and confirmed by Gusmão (16):

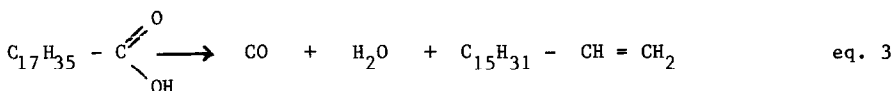


At the chosen operational conditions, ketenes and acrolein are very reactive. Gusmão (16) has shown that the primary products of this degradation are quickly transformed into carboxylic acids, n-propyl esters and C_2 , C_3 , R-CH_3 and $\text{R-C}_2\text{H}_5$ hydrocarbons.

After the degradation of triglycerides, the carboxylic acids are the most abundant chemical species in the reaction mixture, being stabler than ketenes and acrolein. Therefore, the capacity of the vegetable oils to be converted into hydrocarbons depends greatly on the reactivity of carboxylic acids. Consequently they have been studied as model compounds.

Carboxylic Acids as Model Compounds for Vegetable Oil Hydrocracking

Thermally, the main reactions which transform carboxylic acids are decarboxylation and decarbonylation:



For instance, the thermal cracking of stearic acid at 668 K (395°C) for 30 minutes (initial $P_{H_2} = 10$ bar) contributes to the following balance on carboxylic-origin carbon, in relation to 100 mmoles of acid:

Carboxylic acid function (titration)	=	96,5 mmoles
CO	=	1,0 mmoles
CO ₂	=	2,9 mmoles
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Sum	=	100,4 mmoles

In the presence of reduced Ni/SiO₂ another reaction intervenes: the acid function reduction. Fig. 2 shows the time evolution of pressure and temperature for stearic acid hydrocracking. We note that acid hydrogenation begins about 573 K (300°C). All products of partial and total acid function hydrogenation were detected and quantified by chromatography.

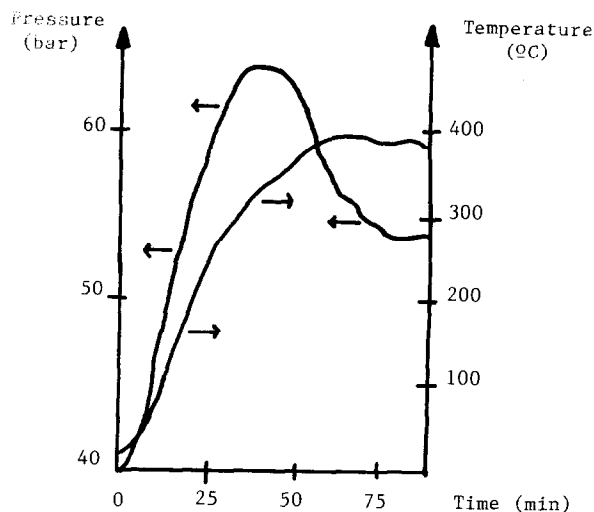


Fig. 2 - Time evolution of pressure and temperature (with a 30 min. plateau at 668 K) for stearic acid hydrocracking (43 g) in the presence of reduced Ni/SiO₂ (0,43 g).

Decarboxylation and decarbonylation are catalysed by reduced Ni/SiO₂. As this solid is active in methanation, CO formed is converted to CH₄. Therefore, the balance carboxylic-origin carbon for stearic acid hydrocracking is composed of the following terms (at 668 K for 30 min, initial $P_{H_2} = 40$ bar), in relation to 100 mmoles of acid:

Carboxylic acid function (titration)	=	47,9	mmoles	
Stearic alcohol (acid function partial hydrogenation)	=	0,1	mmoles	
Stearic aldehyde (acid function partial hydrogenation)	=	0,5	mmoles	
C18 hydrocarbons (acid function total hydrogenation)	=	16,0	mmoles	
decarbonylation	CO	=	2,7	mmoles
+				
decarboxylation	CO ₂	=	4,1	mmoles
+				
methanation	CH ₄	=	33,5	mmoles
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	Sum	=	104,5	mmoles

Once the reactions which transform fatty acids into hydrocarbons are known and quantified, we can investigate a way of increasing the overall yield.

Fig. 2 shows that after 75 minutes there is no more variation of pressure with time, although the reaction mixture still contains 47,9 mmoles of carboxylic acid and the hydrogen partial pressure is about 15 bars. Two hypotheses were formulated to explain this:

- i) the catalyst is completely deactivated by impurities present in the oil or occasionally produced in the course of the transformation;
- ii) the system attains a state of thermodynamic equilibrium.

Occurrence of Thermodynamic Equilibrium in the Fatty Acids to Hydrocarbons Transformation

If the catalyst is deactivated by impurities present in the oil, some of the active sites would be ineffective when a great quantity of catalyst is used. However, there would be enough sites to increase the yield of acid to hydrocarbon transformation. Therefore, the final acidity would decrease.

If the second hypothesis is correct, the addition of a great quantity of catalyst should not modify the yield. In this case, the final acidity would not change.

Table 2 presents the results for stearic acid hydrocracking (668 K for 30 min) in the presence of 0,5 and 2,5 g of reduced Ni/SiO₂. We note that the increase in the quantity of catalyst does not alter the final acidity of the product, provided that the initial pressure is kept constant. In view of the facts observed above, the second hypothesis (thermodynamic equilibrium) is the most plausible one. The thermodynamic equilibrium is confirmed by the estimate of the equilibrium constants of decarbonylation, decarboxylation and carboxylic acid reduction.

In our experimental conditions, this state of equilibrium can be shifted by an increase in hydrogen pressure (Table 2).

TABLE 2

Number of millimoles of carboxylic acid produced by hydrocracking of 100 mmoles of stearic acid at 668 K (395°C) during 30 min, in the presence of variable quantities of reduced Ni/SiO₂.

Hydrogen initial pressure (bar)	40	40	70
Mass of catalyst (g)	0,428	2,513	3,235
Acidity (mmoles)	47,9	48,3	22,0

Vegetable Oil Hydrocracking under Severe Hydrogen Pressures (200 bars)

Having demonstrated that H₂ partial pressure is an important parameter in the transformation of carboxylic acids into hydrocarbons, we have tried to obtain the highest possible conversion operating in the same reactor. Soybean oil hydrocracking was carried out at 643 K (370°C) in the presence of Ni/SiO₂ (2,57 g) and under a hydrogen partial pressure of 110 bars at equilibrium. The molar yields so obtained were 12% of carboxylic acids and 88% of hydrocarbons (essentially n-C₁₅H₃₂, n-C₁₆H₃₄, n-C₁₇H₃₆ and n-C₁₈H₃₈). The target of a molar yield close to 100% of hydrocarbons demands the utilization of a reactor which allows the use of high pressures.

We, therefore, moved to a second reactor, whose volume was 0,30 l and whose working limits were 300 bars and 723 K (450°C). However, this reactor had been used in coal hydroliquefaction in the presence of sulphided catalysts, which implies contamination of the reactor by traces of sulphur, which is a poison to nickel based catalysts.

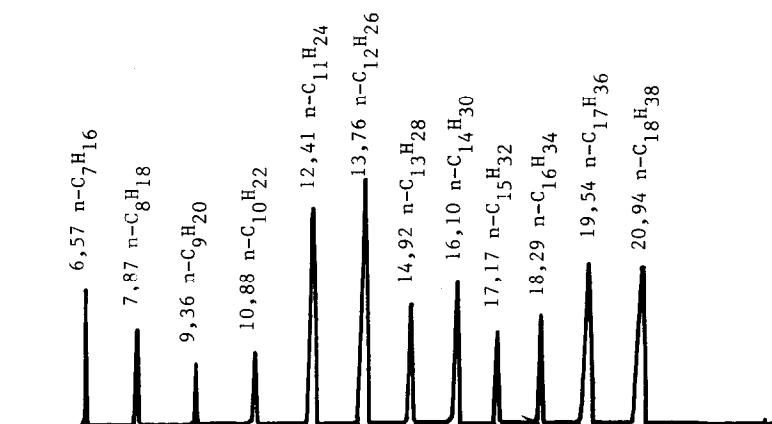


Fig. 3 - Chromatogram of babaçu oil hydrocracking products, at 633 K (360°C), final P_{H_2} = 200 bar approximately, in the presence of sulphided Ni-Mo/ γ -Al₂O₃.

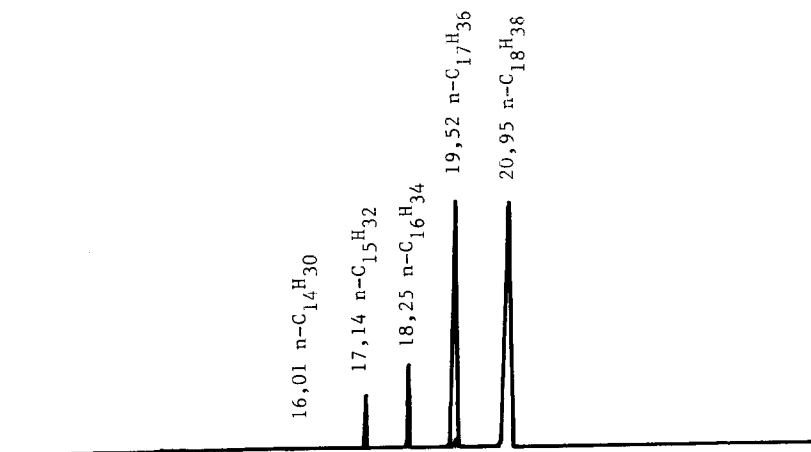


Fig. 4 - Chromatogram of soybean oil hydrocracking products, at 633 K (360°C), final P_{H_2} = 200 bar approximately in the presence of sulphided Ni-Mo/ γ -Al₂O₃.

In view of this limitation we have chosen sulphided Ni-Mo/ γ -Al₂O₃, which combines hydrogenation activity with sulfur poisoning resistance. When this catalyst is employed, soybean oil is hydrogenated between 498 and 553 K (225 and 280°C). The second hydrogenation, related to the triglyceride degradation and to the reduction of the resultant products, begins about 573 K (300°C), as in the case of reduced Ni/SiO₂.

The plateau temperature chosen for this transformation was 633 K (360°C). After 30 minutes at this temperature, the pressure did not vary any more, indicating that a state of equilibrium had been reached. We maintained the system at these conditions for a further 90 minutes, without observing any variation in pressure or in temperature.

The products were separated from the catalyst by decantation and found to contain some water (about 3,5 ml for 75 ml of soybean oil) and a transparent organic phase, the hydrocarbons. Table 3 presents the analysis of this organic phase. The chromatograms of these products are supplied by Figs. 3 and 4.

TABLE 3

Hydrocarbons molar percentages and carboxylic acid millimoles number obtained by hydrocracking of 33,3 mmoles of vegetable oils, at 633 K (360°C) for 2 hours, under 200 bars, final pressure in the presence of sulphided Ni-Mo/ γ -Al₂O₃. Experiments were undertaken using 75 ml of soybean oil, but the quantities of acids and hydrocarbons are all normalized to 33,3 mmoles of reagent oil.

P R O D U C T	WEIGHT OF CAT. (g)	2,185	2,972
	Oil	soja (a)	babaçu (a)
C ₅ H ₁₂		0,06	0,3
C ₆ H ₁₄		-	0,5
C ₇ H ₁₆		0,14	5,6
C ₈ H ₁₈		0,19	4,6
C ₉ H ₂₀		0,15	2,4
C ₁₀ H ₂₂		0,15	3,3
C ₁₁ H ₂₄		0,16	18
C ₁₂ H ₂₆		0,15	21
C ₁₃ H ₂₈		0,16	6,0
C ₁₄ H ₃₀		0,19	7,6
C ₁₅ H ₃₂		4,1	3,7
C ₁₆ H ₃₄		6,8	4,7
C ₁₇ H ₃₆		34	9,3
C ₁₈ H ₃₈		51	11
% normal alkanes		97	98
TOTAL ACIDITY, DETERMINED BY TITRATION (mmoles)		0,50	0, 08

The examination of Table 3 and Figs. 3 and 4 allows to draw the following conclusions:

- i) The absence of peaks corresponding to carboxylic acids on the chromatograms, and the acidity of the products close to zero indicate that the transformations of carboxylic acids into hydrocarbons are complete.
- ii) High concentrations in normal alkanes. For example, soybean oil hydrocracking products are formed by a 96% molar mixture of $n\text{-C}_{15}\text{H}_{32}$, $n\text{-C}_{16}\text{H}_{34}$, $n\text{-C}_{17}\text{H}_{36}$ and $n\text{-C}_{18}\text{H}_{38}$. These hydrocarbons are obtained from palmitic and stearic acids through decarbonylation, decarboxylation and hydrogenation. Thus, the transformation of carboxylic acids into hydrocarbons at the chosen operational conditions are not accompanied by either isomerization or hydrogenolysis to any appreciable extent.
- iii) The conversion of carboxylic acids being undertaken with the minimal chain breaking, hydrocarbon distributions are close to acid distributions in the original triglycerides. Consequently, hydrocarbon distribution can be modified by a judicious choice of the reagent oil or of a mixture of oils.

CONCLUSIONS

We have established the sequence of reactions which transform a vegetable oil into "diesel-type" hydrocarbons, under severe hydrogen pressure and in the presence of hydrogenating catalysts. We have shown that a thermodynamic limitation restricted the carboxylic acid transformation. The thermodynamic equilibrium was shifted by an increase in hydrogen pressure, which lead us to a molar yield close to 100% on "diesel-type" hydrocarbons.

The hydrocracking of vegetable oils having been understood from a chemical point of view, future studies should be concentrated on the improvement of the "diesel" so obtained, the ultimate aim being substitution or complementation of petroleum-derived diesel.

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