

Kinetic studies of catalytic cracking of octanoic acid

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Abstract

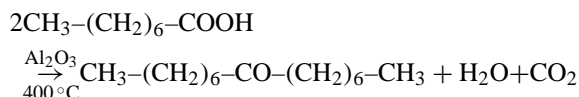
Catalytic cracking of octanoic acid was studied previously in our laboratory [J. Anal. Appl. Pyrolysis 58/59 (2001) 605]. The mechanism proposed by Leung et al. [Energy Fuel 9 (1995) 913] for carboxylic acids was checked and well validated by this parametric study with activated alumina (ALCAN) as catalyst. So, a kinetic study of catalytic cracking of octanoic acid was realized to determine the reaction order and the kinetic parameters. The experiments were carried on in changing the catalyst mass and the temperature (low values for obtaining low conversions). The aim of this study was to complete better the mechanism of catalytic cracking of fatty acids and to use it in the future for the catalytic cracking of oleic acid issued from vegetables oils.

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1. Introduction

In a recent study [1], a parametric study of catalytic cracking (effect of temperature and mass hourly space velocity (MMH)) was conducted in order to gain a clearer understanding of the reactions of which mechanism involves acids. Products of these experiments are well interpreted by the mechanism proposed by Leung et al. [2] which is described below:



Two acid molecules condensed on alumina, at 400 °C, to form the symmetrical ketone. The reaction

was described by March [3], but the mechanism is not yet fully understood. After, the symmetrical ketone is converted into methyl ketones and alphaolefins (+ paraffins) with two fewer carbon atoms, via a γ hydrogen transfer mechanism:

The main products obtained and detected by GC/MS are:

- olefins C6, C9, C15 and
- 8-pentadecanone (symmetrical ketone) and 2-nonanone (methyl ketone).

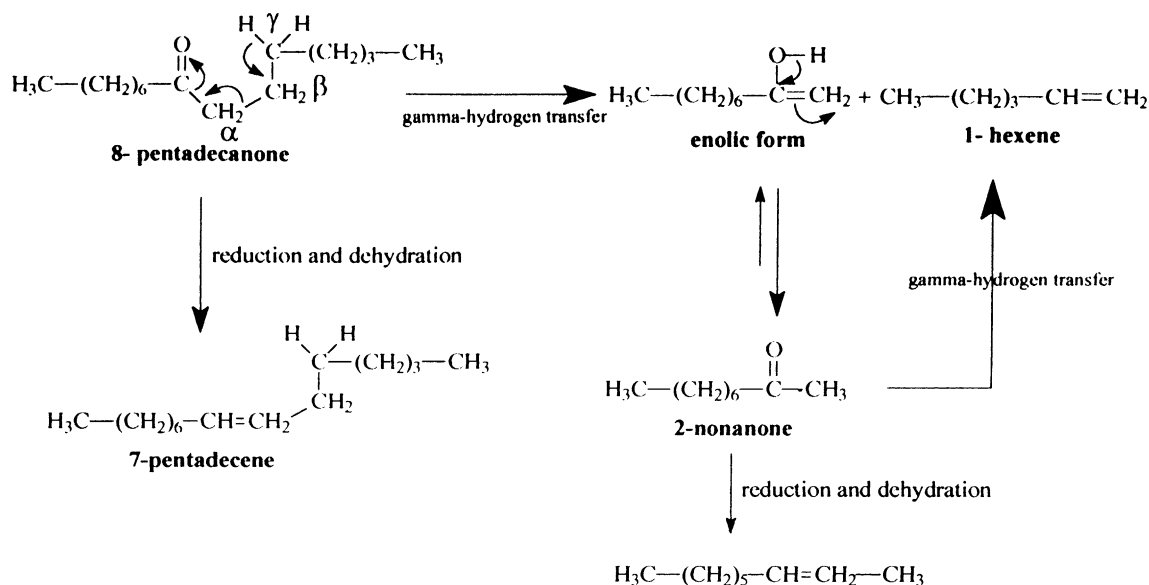
The results obtained by the parametric study of catalytic cracking were summarized briefly as follows.

- The conversion obtained at 450 °C without catalyst were low: 4%.
- At 450 °C, with 40 g of activated alumina, the octanoic acid was almost entirely converted; the 8-pentadecanone produced during the reaction was generally converted to other products and negligible

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quantities of 2-nonanone were produced; the formation of C9 and C15 hydrocarbons were favored, hence the reduction and dehydration reactions of the corresponding ketones (2-nonanone and 8-pentadecanone) to detriment of hydrogen reactions.

- At 350 °C, with 40 g of activated alumina, C8 acid was not very effectively converted to symmetrical ketones (Fig. 1), hence there were low proportions of C6–C7–C9–C15 hydrocarbons; there was still a high proportion of unconverted 8-pentadecanone (Fig. 2) in the liquid organic product (LOP).
- At 400 °C, with 40 g of activated alumina, the reduction and dehydration reaction were favored to the detriment of hydrogen transfer and cracking of heavy compounds into lights compounds.

- At 500 °C, with 40 g of activated alumina, the proportion of C15 compounds decreased substantially; the proportion of C6, C7 and C8 compounds was higher than that in reactions at lower temperatures.
- The temperature was fixed at 400 °C and the mass of catalysts varied from 40 to 10 g: reducing the mass of catalyst resulted in decreasing the conversion rate (Fig. 3) and increasing quantities of 8-pentadecanone (Fig. 4) except when working with 10 g of catalyst, since C8 acid was not effectively converted; in fact, when the catalyst mass decreased, the residence time decreased too, so the secondary reactions were weak.

Thanks to these results, it was possible to establish a kinetic study of decomposition of octanoic acid to 8-pentadecanone (ketonization). The choice of the

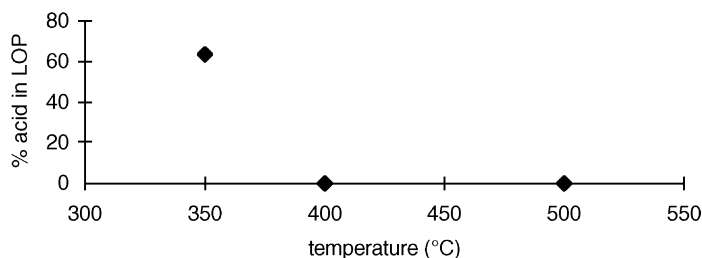


Fig. 1. Percentage of acid in LOP vs. temperature.

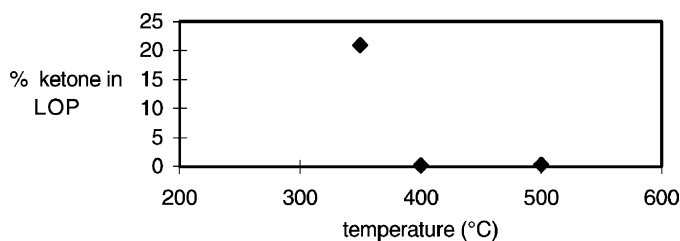


Fig. 2. Percentage of 8-pentadecanone in LOP vs. temperature.

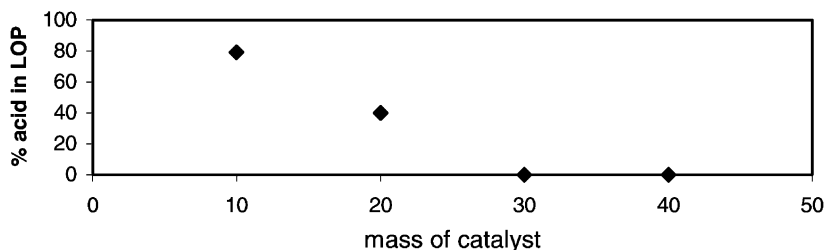


Fig. 3. Percentage of acid in LOP vs. mass of catalyst.

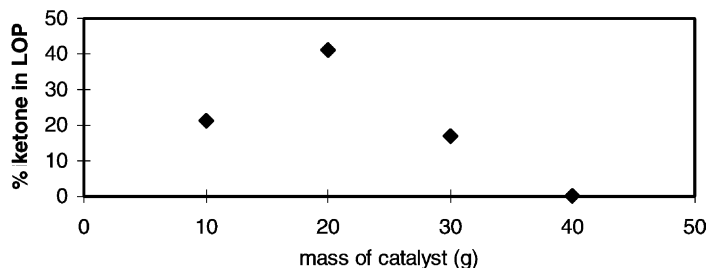


Fig. 4. Percentage of 8-pentadecanone in LOP vs. mass of catalyst.

activated alumina was done; the reaction temperature has to be low in order to minimize the conversion in ketone: between 350 and 400 °C; the mass of catalyst has to also be small (between 3 and 20 g) for the same reason.

Many authors have worked about the mechanism of ketonization of acetic acid [4–7] with catalyst such as TiO₂, Cr₂O₃ and Fe₂O₃, and have concluded that the carboxylate and carbonium acyl were the intermediates of this reaction without studying the kinetic parts.

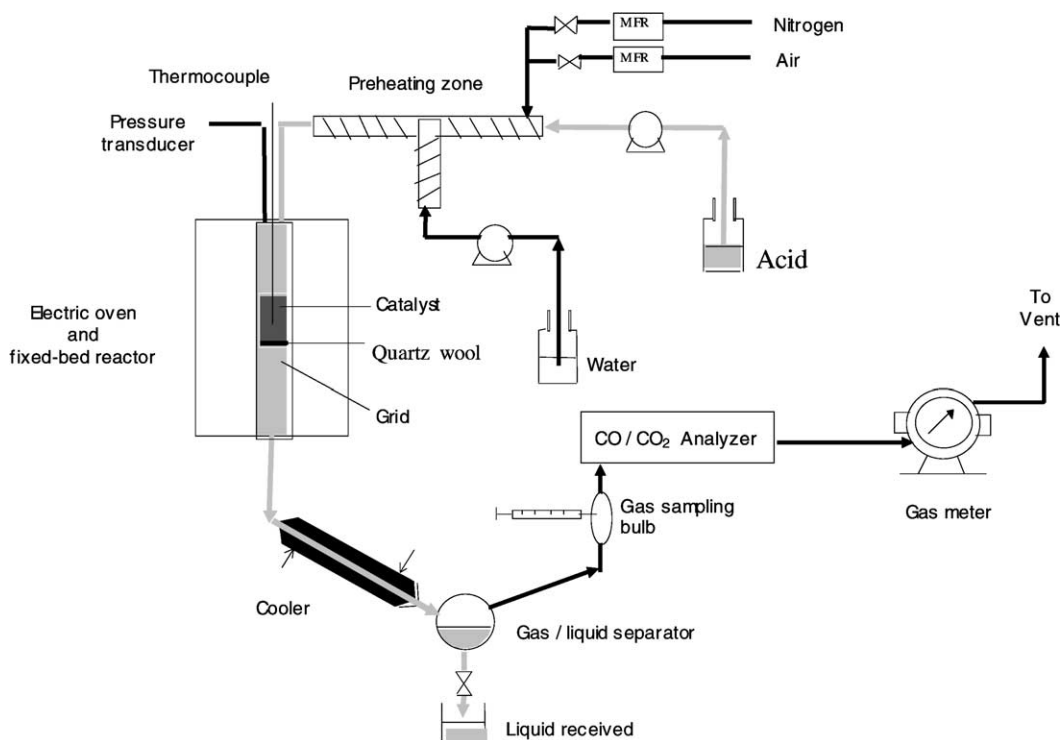
In the first part, the laboratory pilot and the experimental procedures are presented. In the second part, the experimental determination of kinetic parameters

is showed. At last, a summary and application of these results are given.

2. Experimental

The carboxylic acid used is octanoic acid, CH₃–(CH₂)₆–COOH; it is liquid at ambient temperature while acids C10 and over are solid, and is 99% pure.

The catalyst tested was the activated alumina from Alcan. Its characteristics are given below: its particle diameter is marbles 2.4 mm × 4.5 mm; it is composed of chi, eta and boehmites; its BET surface area is about 280–300 m² g⁻¹ and its pore size is equal to 4 nm.



Scheme 1. Catalytic cracking system.

The catalytic cracking system could be split into five parts (Scheme 1):

- injection of octanoic acid and the dilutant nitrogen; compressed air was used to eliminate the coke of the catalyst;
- preheating zone of charge and dilutant;
- the oven (thermolyne F 79300 type) in which the fixed-bed catalytic reactor was placed;
- product trapping and gas/liquid separation; and
- liquid and gaseous effluent analysis.

The acid was injected using a spectra physics SP 8810 pump with a flow range between 0.01 and $10 \text{ cm}^3 \text{ min}^{-1}$. Nitrogen was injected using a 31 l min^{-1} mass flow regulator (MFR). The MFR showed the flow rate under normal temperature and pressure conditions (20°C and 760 Torr). It was calibrated beforehand with a gas meter (fitted after the CO/CO₂ analyzer), which gave the gas volume flow rate at ambient temperature and pressure.

Before entering the reactor, the acid and dilutant were heated to 300°C (lower than the thermal crack-

ing temperature). This ensured that the thermal energy inside the reactor was not used to evaporate the acid.

A thermolyne F 79300 type oven ensured an almost isothermic zone ($\pm 0.6^\circ\text{C}$) within an 8-cm radius of the center. The oven had its own temperature regulation system.

The reactor comprised a stainless steel tube (length: 70 cm; external diameter: 25.4 mm; internal diameter: 22.1 mm). A fine mesh to hold the catalyst was welded in the center of the reactor. The total reactor volume was 169 cm^3 . A thermocouple placed in the catalytic bed indicated the temperature of the catalyst. In addition, a pressure sensor fitted to the reactor inlet indicated the internal pressure.

Before each experiment, the catalyst was heated at the temperature of the reaction during 2 h in a stream of N₂. At the end of each experiment, the reactor was heated to 600°C with a mixture of compressed air/N₂ to decoke the catalyst.

The flow rate of dilutant and charge were fitted at 0.05 l min^{-1} and $0.34 \text{ cm}^3 \text{ min}^{-1}$, respectively, during all experiments.

Gaseous and liquid effluent analyses were conducted as follows.

- Analysis of products in the gaseous and liquid products: hydrocarbons were determined by GC/MS and quantitatively analyzed by gas chromatography, using a Shimadzu GC 17A type chromatograph fitted with a capillary column (PONA Hewlett-Packard, Les Ulis, France) (apolar stationary phase: grafted methyl silicone, $e = 0.5$ mm, $L = 50$ m, i.d. = 0.21 mm) and a flame ionization detector (FID) at 300 °C. To determine the liquid fraction, slow temperature programming of the furnace is required to separate all the products (60 °C for 20 min, +2 °C min⁻¹ up to 300 °C). The programming temperature of the furnace for the gas detection is -60 °C for 4 min, 10 °C min⁻¹ up to 180 °C, 180 °C for 10 min, +10 °C min⁻¹ up to 300 °C.
- Analysis of CO/CO₂ in the gaseous effluent: a Cosma Cristal 300 infrared analyzer fitted in line to the gas circuit was used to measure the CO/CO₂ volume percentage.

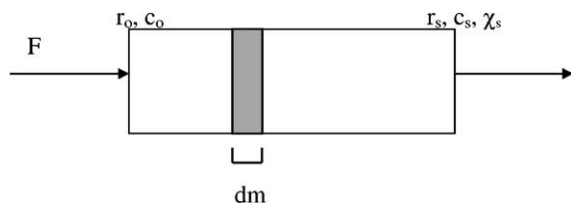
3. Results and discussion

3.1. Kinetic study

Catalytic cracking of octanoic acid was carried out in a fixed-bed reactor which could be represented by the following Scheme 2.

The following nomenclature is applied to the study:

c	concentration of acid
F_0	initial molar flow
k	reaction rate constant
m	mass of catalyst
n	reaction order
r	rate of reaction
χ	conversion



Scheme 2. A representation of the reactor.

The experimental parameters are:

- ambient temperature $T_a = 20$ °C;
- atmospheric pressure $P_a = 760$ mmHg;
- gaseous flow rate d (cm³ min⁻¹); and
- temperature of reactor T (°C).

The following hypothesis are accepted:

- atmospheric pressure in all reactor (loss of charges negligible);
- the reactor is isothermal at the temperature T ; and
- the reactor is considered like piston.

The grey part of the reactor (see Scheme 2) could be represented by the following Eq. (1):

$$F_0(1 - \chi)dt = F_0(1 - \chi - d\chi)dt + r dm dt \quad (1)$$

after simplification

$$F_0 d\chi = r dm \quad (2)$$

By hypothesis, if $n = 0$: $r = k$, so by using Eq. (2), Eq. (3) could be written:

$$F_0 d\chi = k dm \quad (3)$$

The integration of Eq. (3) between the entry and the exit of the reactor gives Eq. (4):

$$k = \frac{F_0}{m} \chi \quad (4)$$

$$\frac{r}{r_0} = \frac{c}{c_0} = (1 - \chi) \quad (5)$$

By hypothesis, if $n = 1$: $r = k \times c$, so by using Eq. (2) and the expression (5), Eq. (6) could be written:

$$F_0 d\chi = r_0(1 - \chi) dm \quad (6)$$

The integration of Eq. (6) between the entry and the exit of the reactor gives Eq. (7):

$$r_0 = -\frac{F_0}{m} \ln(1 - \chi_s) \quad (7)$$

with $k = r_0/c_0$ and χ_s = exit conversion.

By hypothesis, if $n = 2$: $r = k \times c^2$, so by using Eq. (2) and the expression (5), Eq. (8) could be written:

$$F_0 d\chi = r_0(1 - \chi)^2 dm \quad (8)$$

The integration of Eq. (8) between the entry and the exit of the reactor gives Eq. (9):

$$r_0 = \frac{F_0}{m} \frac{\chi_s}{1 - \chi_s} \quad (9)$$

Table 1

Results with 13.1, 10, 7.05, 3.01 and 0 g of activated alumina at 400 °C

	13.1 g	10 g	7.05 g	3.01 g	0 g
LOP (mass%)	31.1	21.3	17.6	10.1	–
Gas (mass%)	4.27	9.9	4.4	4.9	–
Coke (mass%)	0.6	0.5	0.6	0.2	–
Conversion (%)	49.9	40.3	31.3	35.91	4
m/F (mol ⁻¹ min)	6396.7	4666.8	3615	1470	0

For determining the reaction order of the ketonization, the conversion is varied by changing the mass of catalyst and the temperature of reaction. For example for $n = 0$, if we plotted the graph conversion versus m/F_0 and if we obtained a right line, the hypothesis is validated otherwise we checked for $n = 1$ by tracing the graph $\ln(1 - \chi)$ versus $m/F_0, \dots$

So, the experiments were conducted at three different temperatures (350, 375, 400 °C) with five different mass of catalysts (0, 3, 7, 10, 13 g) and are presented by Tables 1–3.

3.2. Experimental results at 400 °C

The following Fig. 5 allowed to determine the reaction order of the ketonization at 400 °C; the figure for $n = 1$ is only represented.

Table 2

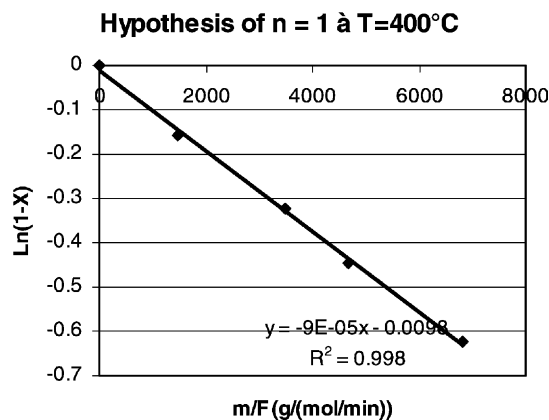
Results with 13.1, 10, 7.05, 3.01 and 0 g of activated alumina at 375 °C

	13.1 g	10 g	7.05 g	3.01 g	0 g
LOP (mass%)	16.5	15.7	9.7	5.6	1.3
Gas (mass%)	4.9	4.0	2.2	1.9	2.3
Coke (mass%)	0.7	0.5	0.7	2.4	0.1
Conversion (%)	37.5	31.4	24	14.3	3.5
m/F (mol ⁻¹ min)	6395	4956.4	3508	1546	0

Table 3

Results with 13.1, 10, 7.05, 3.01 and 0 g of activated alumina at 350 °C

	13.1 g	10 g	7.05 g	3.01 g	0 g
LOP (mass%)	8.5	6.5	4.2	2.5	2.4
Gas (mass%)	2.7	3.9	3	0.5	0.3
Coke (mass%)	0.6	0.5	0.4	0.5	0.1
Conversion (%)	23.1	21.6	14.9	11.4	3.8
m/F (mol ⁻¹ min)	6488.5	4830	3440	1470	0

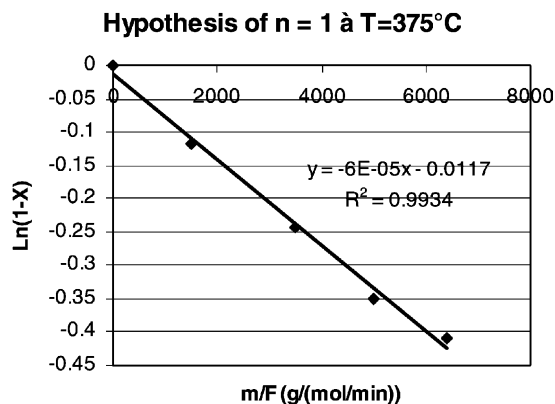
Fig. 5. Conversion vs. m/F at $T = 400$ °C ($n = 1$).

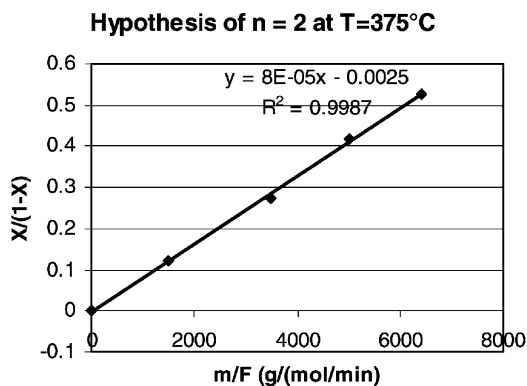
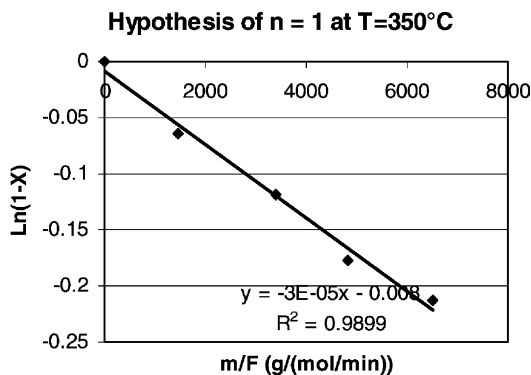
The hypothesis of a reaction order equal to 1 is validated at $T = 400$ °C: five points of the graph gave correctly a right line with a good regression constant ($r^2 = 0.998$).

3.3. Experimental results at 375 °C

The following Figs. 6 and 7 allowed to determine the reaction order of the ketonization at 375 °C; the figure for $n = 1$ and 2 is only represented.

At 375 °C, it seems more difficult to distinguish the order 1 or 2: five points of the graph gave correctly a right line for $n = 1$ and 2, but the regression constant is higher for $n = 2$.

Fig. 6. Conversion vs. m/F at $T = 375$ °C ($n = 1$).

Fig. 7. Conversion vs. m/F at $T = 375^\circ\text{C}$ ($n = 2$).Fig. 8. Conversion vs. m/F at $T = 350^\circ\text{C}$ ($n = 1$).Table 4
An r_0 and k at 350, 375 and 400°C

T ($^\circ\text{C}$)	r_0 ($\text{mol s}^{-1} \text{ g of cata}^{-1}$)	k ($\text{h}^{-1} \text{ g of cata}^{-1}$)
350	6.57×10^{-7}	0.11
375	1.17×10^{-6}	0.20
400	1.85×10^{-6}	0.31

3.4. Experimental results at 350°C

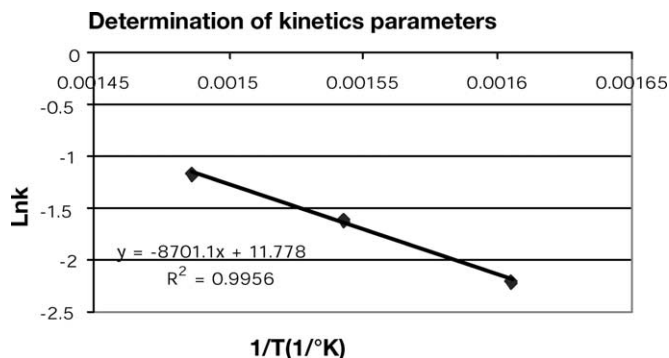
The following Fig. 8 allowed to determine the reaction order of the ketonization at 350°C ; the figure for $n = 1$ is only represented.

The hypothesis of a reaction order equal to 1 is validated at $T = 350^\circ\text{C}$: five points of the graph gave correctly a right line with a good regression constant. According to the general results, we can propose that the ketonization order is 1.

For determining the reaction rate constant at $T = 350, 375$ and 400°C , the initial rate of the reaction is firstly calculated by the slope of the right line obtained in the graph for $n = 1$. After, by the equation $k = r_0/c_0$ with $c_0 = 0.021 \text{ mol l}^{-1}$, k could be found. The results are presented in Table 4.

According to the equation $k = A \exp(-E_a/RT)$, the graph $\ln k$ versus $1/T$ could be traced (Fig. 9). So E_a , the activation energy could be obtained by the slope of the right line and also, A the pre-exponential factor. The values were:

$$E_a = 70943 \text{ J mol}^{-1}; \quad A = 98300 \text{ h}^{-1} \text{ g of cata}^{-1}$$

Fig. 9. $\ln k$ vs. $1/T$.

4. Conclusion

The reaction of ketonization was studied by using octanoic acid such as compound model. The parametric and kinetic conditions were defined in order to determine the reaction order and the kinetic parameters E_a and A . This method could be extrapolated to other study like the catalytic transformation of the 8-pentadecanone or 2-nonanone.

The aim of this study was to determine the mechanism of catalytic cracking of oleic acid which is issued from canola oil and methyl oleate. Our final objective was the non-alimentary upgrading of vegetable oils and their derivatives in molecules with high added value such as alphaolefins for the detergent and lubricant industries. Many lab's team worked about the catalytic transformation of biomass, vegetable oils without studying the kinetic conditions of the formation of products. So our work could be a future help in the determination of mechanisms.

Acknowledgements

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