Production of Hydrocarbons by Pyrolysis of Methyl Esters from Rapeseed Oil

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ABSTRACT: The pyrolysis of a mixture of methyl esters from rapeseed oil has been studied in a tubular reactor between 550 and 850°C and in dilution with nitrogen. A specific device for the condensation of cracking effluents was used for the fractionated recovery of liquid and gaseous effluents, which were analyzed on-line by an infrared analyzer and by gas chromatography. The cracking products in the liquid effluent were identified by gas chromatography/mass spectrometry coupling. The effects of temperature on the cracking reaction were studied for a constant residence time of 320 ms and a constant dilution rate of 13 moles of nitrogen/mole of feedstock. The principal products observed were linear 1-olefins, *n*-paraffins, and unsaturated methyl esters. The gas fraction also contained CO, CO_2, and H_2. The middle-chain olefins (C_{10}–C_{14} cut) and short-chain unsaturated esters, produced with a high added value, had an optimum yield at a cracking temperature of 700°C.

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KEY WORDS: Fatty methyl esters, pyrolysis, rapeseed oil, thermal decomposition.

A great deal of research was done on the energy upgrading of vegetable oils or their derivatives between 1920 and 1950, then again during the oil crises in 1973 and 1978, so as to minimize oil imports, especially in tropical countries (South America) or in developing countries. Several authors studied the pyrolysis of vegetable and animal oils (1–12) and the pyrolysis of natural fatty acids (13–17). In each case, they obtained a mixture of hydrocarbons with a composition close to that of petroleum derivatives. The pyrolysis of esters from fatty acids, easily obtained by the transesterification of oils with a light alcohol (18–20), was used much less often because such esters are not natural products. The transesterification operation is inexpensive, and the esters are easier to use than oils (lower viscosity and boiling point). Research on the catalytic and noncatalytic pyrolysis of esters from fatty acids (20–24) determined the decomposition mechanisms as a function of the operating conditions and produced the hydrocarbons normally produced by petrochemistry, as for oils.

Currently, methyl esters from rapeseed oil, produced by the transesterification of rapeseed oil with methanol, are used as a diesel fuel with the addition of gas oil (19,25). In this work, we propose to use these esters as raw materials in the chemical industry for producing high added-value molecules: linear 1-olefins (C_{10}–C_{14} cut) and unsaturated linear methyl esters ($C_{6:1}$–$C_{12:1}$ cut). More interesting outlets for these molecules can mainly be found in the detergent and lubricant sectors. From C_{10}–C_{14} olefins, it is effectively possible to manufacture linear alkylbenzenesulfonates (base stocks for biodegradable detergents), linear low-density polyethylene, and biodegradable lubricants. Unsaturated esters can be used to produce biodegradable synthetic oils for engines or nylon monomers.

Mainly based on the research by Nawar (23) and Moulton *et al.* (21) on pyrolysis, in the presence of nitrogen, of methyl oleate and methyl palmitate, and on recent research on decomposition of vegetable oils (12) or fatty acids at high temperature (16,17), we undertook a study of the pyrolysis of a mixture of methyl esters issuing from rapeseed oil, called methyl colzate (Table 1). This was a mixture of eight saturated and unsaturated methyl esters, in which the majority ester was methyl oleate ($C_{18:1}$).

The operating conditions chosen were close to industrial conditions (high temperature, residence time less than one second, high dilution of the feedstock) so as to assess the import of the heavy-ester cracking process with a view to its industrialization. To diminish the partial pressure of the mixture of esters inside the reactor, nitrogen was used as the diluent. Nitrogen was chosen in preference to steam to limit the

TABLE 1
Composition of the Mixture of Methyl Esters from Rapeseed Oil (methyl colzate)

Ester	Formula	Mass%
Methyl palmitate	$C_{16:0}$	5.3
Methyl palmitoleate	$C_{16:1}$, Δ8	0.2
Methyl stearate	$C_{18:0}$	1.9
Methyl oleate	$C_{18:1}$, Δ9	61.6
Methyl linoleate	$C_{18:2}$, Δ9, Δ12	20.4
Methyl linolenate	$C_{18:3}$, Δ9, Δ12, Δ15	8.7
Methyl arachidate	$C_{20:0}$	0.6
Methyl gadoleate	$C_{20:1}$, Δ10	1.3

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study to high-temperature pyrolysis radical phenomena. For steam cracking, the hydrolysis reaction of the esters must also be taken into consideration (26).

We start by describing the experimental pyrolysis device designed for the cracking of heavy hydrocarbons. Then, to better understand the decomposition of this mixture of esters, we propose to determine the conversion of methyl colzate and the selectivities in products as a function of the reaction temperature (550–850°C). We will also specify the operating parameters chosen for the optimization of yields of the middle-chain olefins and esters.

EXPERIMENTAL PROCEDURES

Description of the micropilot cracking plant. The micropilot cracking plant is shown in Figure 1. For the gas injection and preheating parts and the reaction zone, we used the same technology as Billaud *et al.* (27) during the cracking of *n*-decane. For the feedstock injection and product trapping part, we based our device on the one used by Graille *et al.* (10) during the steam cracking of solid wastes from a palm-oil plant.

Gas injection. Gases (nitrogen and air) were injected separately by mass flow regulators. Nitrogen was used as the diluent during the pyrolysis of esters, and air was used at the end of each experiment to oxidize the coke formed during the pyrolysis reaction. A gas meter, situated after the effluent reaction and condensation zones, gave the flow rates of the nitrogen and gaseous effluents produced during cracking [or the flow rates of the air and coke's oxidation products (CO and CO_2)]. By subtraction, we determined the actual nitrogen or air flow rate at room pressure and temperature.

Feedstock injection. The feedstock (methyl colzate) was liquid at room temperature, and its viscosity was close to that of a C_{10} alkane. It was injected by a piston pump whose head, separate from its body and motor, was integrated into a thermostated container at a temperature of 70°C. The flow rates of the pump were between 0.3 and 10 cm^3/min. The use of heating cords along the feedstock injection lines served to maintain a temperature of 70°C up to the preheating zone.

Preheating. The feedstock (or the air after cracking reaction) and the diluent (nitrogen) were preheated separately in stainless-steel tubes (316, 18–8) surrounded by a roll of heating resistors. The diluent was preheated to 500°C, and the feedstock (or the air) to 400°C. At these temperatures, the feedstock was prevented from cracking before entering the reactor.

Reactor. The reactor (Fig. 2) is composed of a steel tube (316, 18–8) 190-mm long and 10-mm inside diameter. The presence of baffles (2 transverse tubes 1-mm diameter) over 10 mm, situated 12 mm from the reactor inlet, increases the turbulence and makes for good homogeneity of the gaseous mixture inside the reactor. This reactor is capable of operating with short residence times (200–500 ms) and is as near as possible to industrial crackers (the chemical industry mainly uses tubular reactors for thermal decompositions of chemical reagents). However, there are a few disadvantages when such a reactor is used:

Poor definition of time zero. Because the feedstock and diluent are preheated to a temperature lower than the reaction temperature (measured by a thermocouple in the middle of the reactor), it is difficult to know whether the reaction begins at the inlet of the reactor.

Nonuniformity of the temperature of the reactor. The temperature profile (Fig. 3) shows that, under our operating conditions, the temperature inside the reactor is isothermal only over a small portion of its length (3–4 cm). Likewise, over the last few centimeters of the reactor, the temperature is too low for any conversion of the ester to take place. Hence, it is im-

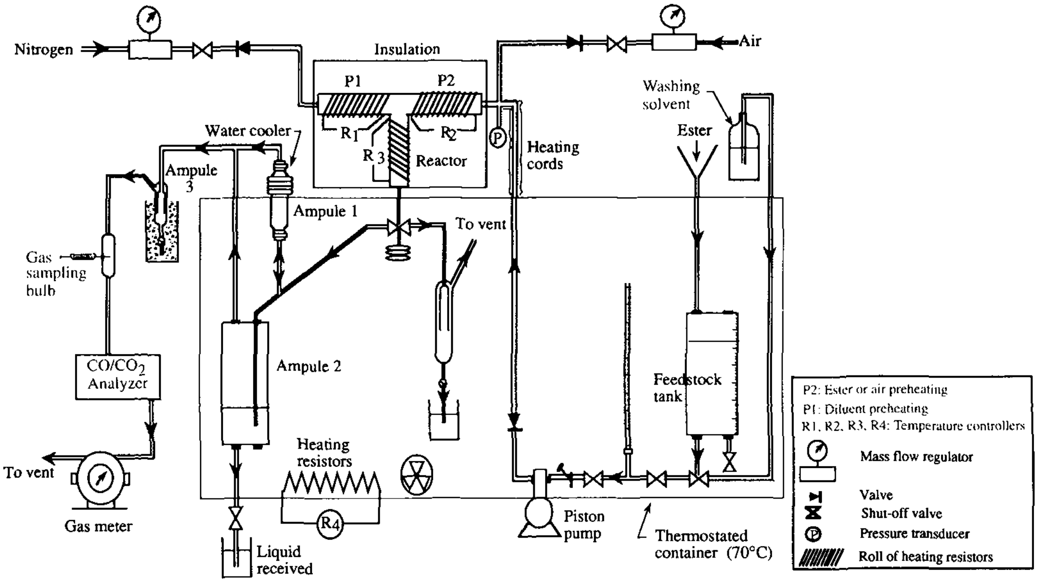

FIG. 1. Micropilot pyrolysis plant for methyl esters from rapeseed oil.

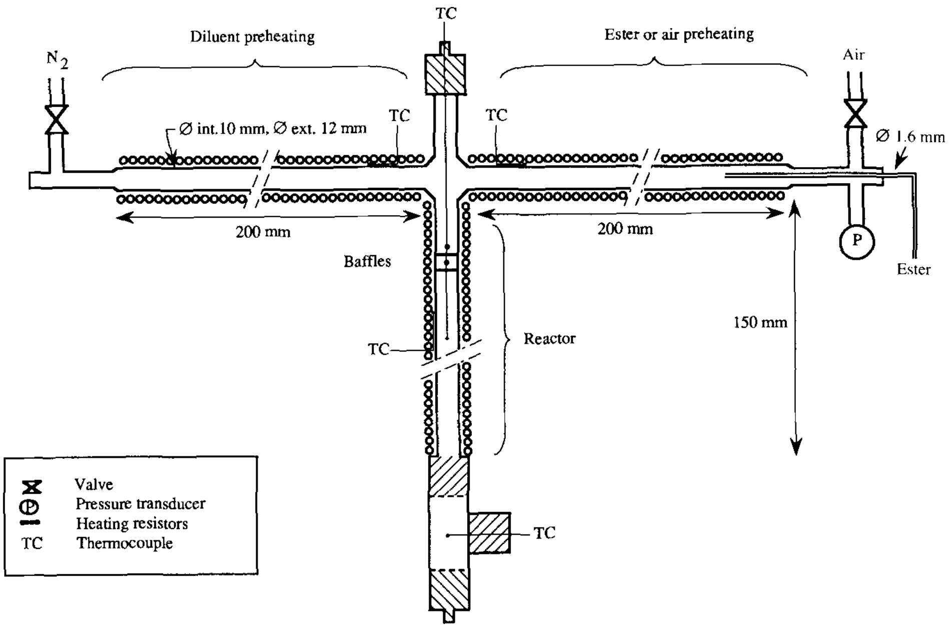

FIG. 2. Cross-section of the pyrolysis reactor and preheating zones.

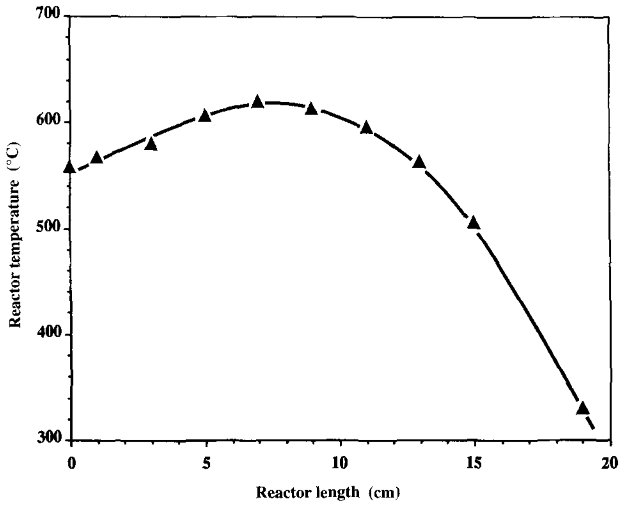

FIG. 3. Temperature profile inside the reactor (reaction temperature = 630°C, residence time = 320 ms, dilution = 13 moles of nitrogen/mole of ester).

possible to consider the reactor as a whole (i.e., 19 cm) as being useful for the reaction. To make a parametric study at a constant residence time in the temperature range used (550–850°C), we determined a mean working volume to be equal to 12 cm^3.

Trapping of products. At the reactor outlet, a set of three ampules (i.d. = 15 cm), maintained at different temperatures (70, 20, and 0°C), served to condense all liquid cracking products, i.e., light (C_5–C_{10}), middle (C_{10}–C_{15}), and heavy (C_{16}–C_{20}) hydrocarbons. The liquid fraction was weighed and analyzed at the end of the experiment. The noncondensable cracking fraction (C_1–C_4 gaseous hydrocarbons, H_2, CO, CO_2, and dilution nitrogen) was fed to an analysis circuit and then to a gas meter, placed on-line, so that the gaseous volume could be measured during the time of assessment.

Measurement of coke. The amount of coke formed during the reaction was determined by oxidation in air, at 850°C, at the end of each experiment.

Operating conditions. The experiments were performed at atmospheric pressure. Dilution was constant (13 moles of nitrogen per mole of feedstock), as was the residence time (320 ms). We made the reaction temperature vary from 550 to 850°C. Likewise, a "warm-up" time, lasting for 15 min, preceded each experiment and enabled the steady state to be obtained. It was also used for conditioning the reactor by depositing a pyrolytic carbon layer on the inside wall of the reactor.

Analysis and nature of cracking products. The liquid fraction, containing nonoxygenated hydrocarbons (olefins, paraffins, aromatics, etc.) and oxygenated hydrocarbons (esters), was analyzed by gas chromatography. A Delsi chromatograph of the DI200 type (Suresnes, France) was used, equipped with a PONA capillary column (Hewlett-Packard, Les Ulis Cedex, France) (apolar stationary phase = grafted methyl silicone, e = 0.5 mm, L = 50 m, i.d. = 0.21 mm). Slow temperature programming of the furnace is required to separate all the products (80°C for 20 min, +2°C/min up to 300°C). The injector (with 1:100 split) and flame-ionization detector (FID) was at 300°C, and the carrier gas was nitrogen. The sample was analyzed quantitatively by gas chromatography/mass spectrometry coupling. For quantitative analysis, an integrator (Chromjet; Spectra Physics, Les Ulis Cedex, France) linked to a chromatograph gave us the area of the peaks and the mass percent of each body.

The cracking gaseous fraction contained hydrogen (determined by catharometer chromatograph equipped with a silica-gel filled column, L = 5 m, i.d. = 6 mm, carrier gas = nitrogen), CO and CO_2 [determined by a Cosma Cristal 300 analyzer with nondispersive infrared absorption (Igny, France)], oxygenated and nonoxygenated hydrocarbons, determined by FID-detection gas chromatography (programming of the furnace = –60°C for 4 min, +10°C/min up to 180°C, 180°C for 10 min, +10°C/min up to 300°C).

The products analyzed can be classified as follows: H_2; CO, CO_2; C_1–C_4 cut (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8, C_4H_{10}, and traces of acetylene); C_5–C_9 cut (linear 1-olefins and *n*-paraffins); C_{10}–C_{14} cut (linear 1-olefins and *n*-paraffins); C_{15}–C_{18} cut (linear 1-olefins and *n*-paraffins); aromatics (benzene and toluene); $C_{3:1}$–$C_{8:1}$ esters cut [from CH_2=CH-$COOCH_3$ to CH_2=CH-$(CH_2)_5$-$COOCH_3$)]; $C_{9:1}$–$C_{16:1}$ esters cut [from CH_2=CH-$(CH_2)_6$-$COOCH_3$ to CH_2=CH-$(CH_2)_{13}$-$COOCH_3$)]; saturated methyl esters (methyl acetate and methyl propanoate); initial methyl esters (colzate), unconverted; other products (diolefins, polyunsaturated esters); coke. No acids or saturated methyl esters higher than $C_2H_5COOCH_3$ were observed.

RESULTS AND DISCUSSION

All the analyses performed on the liquid and gaseous effluents, the liquid mass received, the volume of gas formed, and the mass of coke determined at the end of each run were thus used to compile a complete balance between the inlet and outlet of the reactor (carbon, hydrogen, oxygen balances, and the overall balance). The micropilot cracking plant and the analysis system described above served for the condensation and analysis of all products from the pyrolysis of methyl colzate. We succeeded in reproducibly determining the balances in which all the carbonated, hydrogenated, and oxygenated matter is quantitated. The experiments with errors greater than five percent in the carbon, hydrogen, and overall balances were not retained.

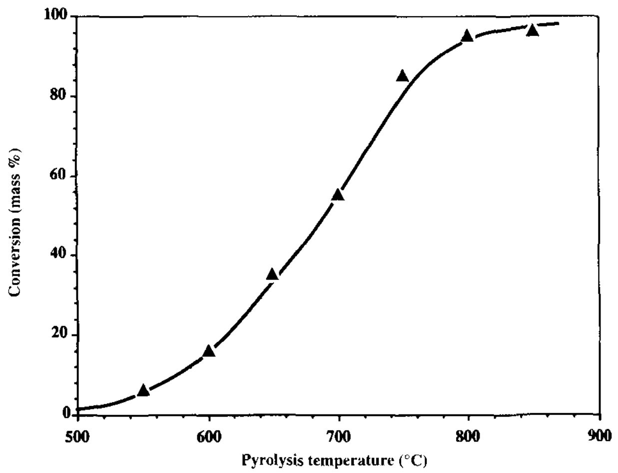

FIG. 4. Conversion of methyl colzate as a function of pyrolysis temperature.

The transformation rate of methyl colzate, in mass%, was defined in terms of conversion (X_t = 100 – mass% unconverted colzate). Figure 4 illustrates the increase in methyl colzate conversion with the pyrolysis temperature. The amount of colzate converted at 550°C is small (6%) and increases nonlinearly up to 850°C. Starting at 750°C, conversion increases more slowly as it approaches 100% (96.6% conversion at 850°C).

To illustrate the distribution of cracking products as a function of the pyrolysis temperature, Table 2 gives the selectivities of the cracking products (hydrocarbons, CO, CO_2, and H_2) obtained between 550 and 850°C. The selectivity of product *j* is defined as the molar percent of colzate converted, which has been transformed into this compound. For components *j* that contain one or several carbon atoms, a selectivity is calculated in molar percent of carbon cracked, *Sj* (*C*), and for compounds

TABLE 2
Selectivities (in molar percent of carbon atoms or hydrogen atoms cracked) of Cracking Products as a Function of Pyrolysis Temperature

	Selectivity (molar % of carbon atoms cracked)						
	550°C	600°C	650°C	700°C	750°C	800°C	850°C
C_1–C_4 cut	10.0	18.6	28.2	38.7	35.1	45.1	66.1
C_5–C_9 cut	36.0	19.6	17.6	13.2	17.5	12.6	3.6
C_{10}–C_{14} cut	3.0	3.5	3.5	2.7	1.7	1.0	0.3
C_{15}–C_{18} cut	0.9	0.7	1.3	1.1	0.3	0.2	0.3
Aromatics	5.2	2.0	2.7	3.9	7.2	11.6	8.9
$C_{3:1}$–$C_{8:1}$ esters	8.5	16.6	10.3	7.2	5.9	4.1	0.9
$C_{9:1}$–$C_{16:1}$ esters	2.3	3.2	3.4	2.3	0.9	0.5	0.3
Saturated esters	2.0	1.2	1.6	2.4	3.7	3.1	2.6
CO	0.5	1.2	1.3	2.3	2.7	3.8	5.3
CO_2	0.3	0.6	0.6	1.1	1.5	1.6	2.1
Coke	6.1	3.8	4.2	4.7	2.2	3.1	4.5
Other products	25.2	29.0	25.3	20.4	21.3	13.3	5.1
	Selectivity (molar % of hydrogen atoms cracked)						
H_2	0.3	0.9	1.7	2.7	3.6	4.6	5.9

j that do not contain any molar percent of cracked carbon, a selectivity is calculated in molar percent of hydrogen cracked, $Sj\ (H)$:

$$Sj\ (C) = (NbCj \times nj)/[NbC_{\text{colzate}}\ (n_{\text{colzate}}\ \text{inlet} - n_{\text{colzate}}\ \text{outlet})] \qquad [1]$$

$$Sj\ (H) = (NbHj \times nj)/[NbH_{\text{colzate}}\ \text{inlet} - n_{\text{colzate}}\ \text{outlet})] \qquad [2]$$

where n = number of moles, NbC = number of carbon atoms in the molecule considered, and NbH = number of hydrogen atoms in the molecule considered.

The selectivities of CO, CO_2, C_1–C_4 cut and H_2 increase with the temperature. In the C_1–C_4 cut, ethylene (C_2H_4) is the majority product at 850°C with 30% selectivity. Acetylene (C_2H_2) appears only starting at 700°C and remains at low levels (<0.5%). The C_5–C_9 hydrocarbon selectivity is great at low temperature (16% of C_5–C_9 olefins and 20% of C_5–C_9 paraffins at 550°C). It diminishes as temperature rises. Concerning C_{10}–C_{14} and C_{15}–C_{18} hydrocarbons (olefins and paraffins), the selectivity is better at low temperature. At around 650°C, a maximum of 3.5% is obtained for C_{10}–C_{14} cut (3% for olefins and 0.5% for paraffins), and 1.3% is obtained for C_{15}–C_{18} cut. When the temperature increases, these cut selectivities decrease because they transform into light secondary products. Aromatic (benzene and toluene) selectivities increase with the temperature (from 2% at 600°C to 9% at 850°C). It may be supposed that the formation of benzene rings is favored by the unsaturation present in colzate because benzene, quite probably a secondary product, is formed, according to Schwab *et al.* (12), by a Diels-Alder reaction between ethylene and 1,3-butadiene, followed by a dehydrogenation. It may also stem from cyclization of 1-hexene. The selectivity of light methyl esters (from $C_{3:1}$ to $C_{8:1}$) increases between 550 and 600°C (where it reaches 16.6%), and then diminished considerably as the temperature rises (less than 1% at 850°C). Heavier esters (from $C_{9:1}$ to $C_{16:1}$) are present in smaller amounts (2–3% at low temperature and 0.3% at high temperature), but their selectivity evolves in the same way as that of light esters. It may thus be supposed that heavy esters undergo "secondary" decompositions starting at 650°C, which would explain the decrease in their selectivity. The amount of coke formed during cracking of methyl colzate seems to be independent of the temperature, for it varies little between 550 and 850°C (between 6% and 3%). These variations may be due to errors in the balances and to experimental uncertainties. During the pyrolysis of hydrocarbons, coke is formed from $-CH_2-$ groups from the reactant molecules. The reaction is complex and is catalyzed by nickel and iron oxides present on the walls of the steel reactor (28):

$$-CH_2 - \xrightarrow{NiO,Fe_2O_3} \text{coke} \qquad [3]$$

It is probable that coke formation occurs during the first minutes of the reaction, and that this is true no matter what the reaction temperature is. When the reactor wall is entirely covered by this layer of coke, metal oxides are made inactive and can no longer catalyze any additional formation of coke.

Because methyl colzate contains more than 60% methyl oleate, its cracking products include those obtained by Nawar (23) during the decomposition of methyl oleate at 280°C. However, in the temperature range we chose, cracking is more severe and leads to more light olefins (C_1–C_4) and secondary products (including aromatics). To qualitatively explain the formation of linear 1-olefins and unsaturated esters, we can base ourselves on the mechanisms proposed by Nawar (23). It is a radical chain mechanism initiated by carbon-carbon (C-C) cleavages into β of the double bonds. In an unsaturated ester molecule, these bonds are effectively weakened (between 600 and 900°C, $\Delta H_{\text{cleavage}}$ = 67 kcal/mol for these bonds but $\Delta H_{\text{cleavage}}$ = 85 kcal/mol for the other C-C bonds), and the cleavage of the molecule at this point occurs more easily and selectively. The resulting products are linear 1-olefins and unsaturated esters of the CH_2=CH-$(CH_2)n$-$COOCH_3$ type. Concerning CO_2 formation, several authors (12,21,23) explain it by a radical decarboxylation reaction (loss of CO_2 by cleavage in α of the ester group). CO formation may be explained by a decarbonylation of methyl-colzate molecules. This reaction, used by Stern *et al.* (19) to manufacture linear olefins, occurs in two stages:

$$C_{17}H_{35}COOCH_3 \rightarrow CO + CH_3OH + C_{17}H_{34} \qquad [4]$$

$$CH_3OH \rightarrow CO + 2H_2 \qquad [5]$$

The decomposition of methanol into CO and H_2 is total at the temperatures at which we were working (29).

Concerning the yields of C_{10}–C_{14} olefins ($Rj = Sj\ (C) \times X_t/100$), Figure 5 shows a maximum at around 750°C. However, the yield is no more than 1.1%. It then decreases at higher temperature. The evolution of unsaturated ester yields (Fig. 6) is the same as for olefins. There is a maximum around 750°C (5% heavy unsaturated esters and 1% light unsaturated esters), then a decrease in yields at higher temperature.

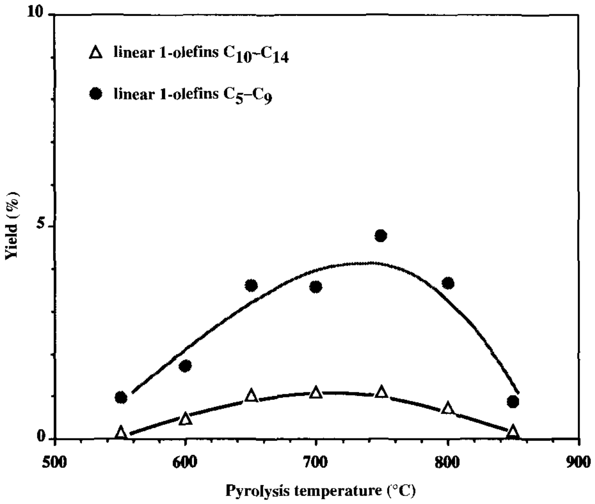

FIG. 5. Yields of linear 1-olefins as a function of pyrolysis temperature.

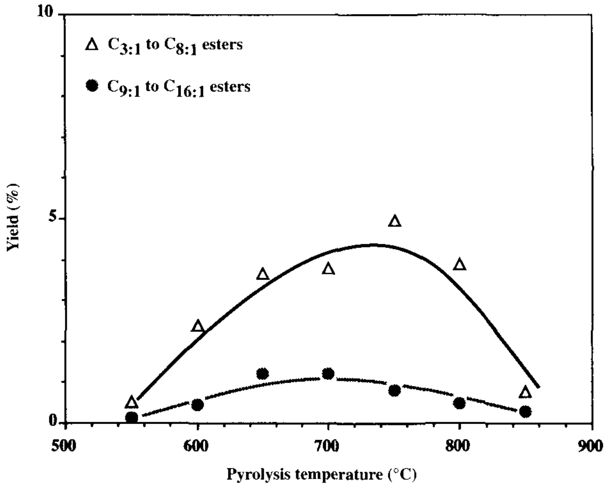

FIG. 6. Yields of unsaturated esters as a function of pyrolysis temperature.

The equipment and analysis methods used have led to satisfactory and reproducible results, no matter what the operating conditions of cracking were. We have shown that the pyrolysis of methyl colzate between 550 and 850°C leads mainly to the formation of hydrocarbons of the olefinic type and unsaturated esters. Heavy products are favored by low temperature. They are degraded into lighter secondary products as temperature and conversion increase. Light hydrocarbons, CO, CO_2, and H_2 tend to be favored by high temperatures. The best yields of C_{10}–C_{14} olefins and $C_{6:1}$–$C_{12:1}$ unsaturated esters, while minimizing the formation of light products, are obtained in a temperature range around 700°C. However, under such conditions, the yields of such high-added-value products are low.

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