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Effect of catalyst properties on the cracking of polypropylene pyrolysis waxes under FCC conditions

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Abstract

The catalytic cracking of polyolefin pyrolysis waxes has been studied under conditions that mimic the operation of a catalytic cracking unit (FCC). Two commercial catalysts of different properties were used. Yields and compositions of the lumps (dry gases, LPG, gasoline and coke) were compared with those corresponding to the actual feed in the refinery (vacuum gas-oil). The effect of process operating conditions (temperature and contact time) is significant. Catalyst acidity has a significant effect on conversion (at a temperature around 525 °C) and on yields and compositions of lumps (in the 500–550 °C range). The main effect of increasing catalyst acidity is an increase in coke content on the catalyst by decreasing the yield to dry gases. Due to the higher hydrogen transfer capacity, the gasoline obtained using the catalyst with higher acidity has a higher aromatic (especially C_6–C_8) and paraffinic content, and lower olefin content, being these two latter fractions less branched. An increase in catalyst acidity leads to a lower yield of light olefins and to an increase in the yield of paraffins.
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Keywords: Waxes; Waste polyolefins; Catalytic cracking; FCC; HY zeolite

1. Introduction

Viability of waste plastic valorization may involve process incorporation to refinery operation [1]. In the strategy studied in this paper, valorization of polyolefinic plastics (more than 2/3 of the whole amount of waste plastics) is raised in two steps: (1) pyrolysis at the location where the plastics are collected and classified; (2) incorporation of the liquid product obtained in their pyrolysis to a standard FCC feed. This strategy allows refineries to have a feed (waxes) that is easily transported and stored, with a uniformed composition and that may be controlled and adapted to the requirements of a FCC unit feed. Moreover, given that the processes of pyrolysis and cracking are separated, they may be individually optimized. Given that pyrolysis process is highly endothermic, maximization of wax (primary products) yield implies minimization of energy requirement [2]. The performance of cracking in a large-scale and versatile unit, such as in a FCC unit, allows for using refinery equipment for both cracking and the subsequent operations of separation and adequation of the product stream for its marketing as fuel of petrochemical raw material.

Catalytic cracking of waxes has been studied in the literature under different conditions [3–5], but in this paper it is studied under similar conditions to those of a FCC unit and, consequently, the results will be useful for refineries.

The direct cracking of waxes is an alternative to the cracking of dissolved polyolefins. This latter strategy performs well by using solvents like vacuum gas-oil (the standard VGO feed of FCC units) [6], pure aromatics (due to its refractory nature in the cracking and in order to determine polyolefin transformation) [7] and LCO (light cycle oil) [8,9]. The use of LCO as feed has the additional advantage that the solvent is also valorised, given that LCO is a stream of secondary interest in the refinery.

The results obtained in the cracking of waxes dissolved in VGO [1,10] have shown that wax cracking produces more gasoline than the cracking of FCC unit standard feeds (VGO) and that the gasoline is more olefinic (with a high proportion of C_5–C_6 fraction) and less aromatic than that obtained by

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Table 1
Simulated distillation of waxes

wt%	T (°C)
I.P.	182
5	241
10	275
30	362
50	440
70	512
90	591
95	618
E.P.	–

cracking VGO. Nevertheless, the results are sensitive to the operating conditions (catalyst/feed ratio, temperature and contact time). In this paper, a study has been carried out on effect of catalyst properties (physical and chemical) on the yields and composition of the different product fractions obtained in the cracking of waxes.

2. Experimental

2.1. Waxes

The waxes have been obtained by flash pyrolysis of polypropylene (PP) at 500 °C. The reaction equipment has been described elsewhere [11]. The simulated distillation of the waxes (Table 1) has been carried out in a GC PerkinElmer 8500, provided with a semicapillary column, WCOT Unimetal of 5 m × 0.53 mm × 0.17 μm and FID detector. A number average molecular weight of 363 and a weight average molecular weight of 2405 have been determined by gel permeability chromatography. The density is 0.89 g/cm^3. A clearly olefinic nature has been determined by FTIR spectrophotometry. The properties of the waxes obtained by pyrolysis of polyethylene (from both low and high density) are almost identical to those obtained from polypropylene and similar to the commercial waxes [2,11].

2.2. Catalysts

CAT-1 and CAT-2 are commercial prepared based on HY zeolite, supplied by Repsol S.A. (Spain) and Petrobras S.A. (Brazil), where they have been used in FCC units. Consequently, they are catalysts equilibrated in the industrial process. The properties of the catalysts are set out in Table 2. The physical properties have been determined by means of N_2 adsorption isotherms in a Micromeritics ASAP 2010. Total acidity and acid strength distribution (Fig. 1) have been measured by combining calorimetry and thermogravimetry (SDT 2960 Simultaneous DTA-TGA, TA Instruments) in the differential adsorption of NH_3 at 150 °C [12]. The Bronsted/Lewis site ratio has been determined from the intensity ratio of the bands at 1545 and 1455 cm^{-1} monitored by pyridine adsorption and FTIR spectrophotometry (Nicolet 740 SX).

The results in Fig. 1 show a significant difference in the total acidity and acid strength distribution of the catalysts. CAT-1 is the one that has less sites (total acidity = 0.018 mmol of NH_3 (g catalyst)$^{-1}$), but it has a fraction of very strong sites (in the 125–140 kJ (mol NH_3)$^{-1}$ range). CAT-2 has a more homogeneous acid strength (around 120–125 kJ (mol NH_3)$^{-1}$) and higher total acidity (0.058 mmol of NH_3 (g catalyst)$^{-1}$).

Table 2
Catalysts properties

	CAT-1	CAT-2
Zeolite percentage (wt%)	14	21
Particle size (μm)		
0–20 (wt%)	0	
0–40 (wt%)	7	
0–80 (wt%)	58	
Acidity (mmol NH_3 ($g_{catalyst}^{-1}$)	0.018	0.058
Acid strength (kJ (mol NH_3)$^{-1}$)	125–140	120–125
Bronsted/Lewis ratio	6.3	1.6
BET surface area (m^2 g^{-1})	123	179
Zeolite area (m^2 g^{-1})	89	140
Average micropore diameter (Å)	7.8	7.7
Average mesopore diameter (matrix) (Å)	146	125

2.3. Reaction equipment

The equipment used in this work is a Riser Simulator Reactor (Fig. 2). It is an internal recycle reactor specially designed for catalytic cracking and has been previously described [13]. The equipment is easy to operate and its main characteristics are: (1) capability for operating with low and precise values of contact time in the 1–10 s range; (2) a suitable feed-catalyst contact, as the reaction occurs in a dilute fluidized bed regime with perfect mix for the catalyst and for the reaction mixture. The catalyst is in a basket and the gases circulate through the basket, impelled by a turbine located in the upper part. At zero time the established amount of feed is injected and a timer is activated. Once the programmed time has elapsed, a valve is opened and the reaction products pass to a vacuum chamber, maintained at 300 °C. These products are sent through a thermostated line to a gas chromatograph by means of a six-port-valve.

The runs have been carried out at 1 atm, in the 500–550 °C range, with a catalyst/feed ratio C/O = 5.5 by weight and with a

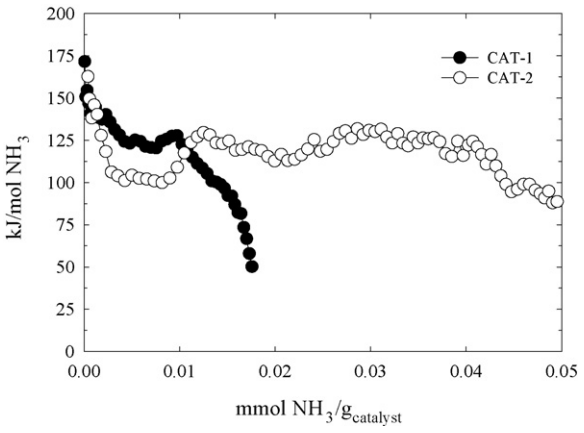

Fig. 1. Acid strength distribution of the catalysts.

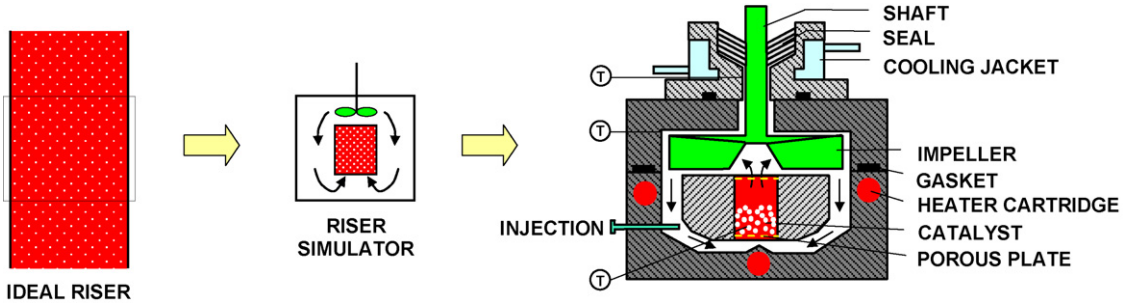

Fig. 2. Diagram of the riser simulator reactor.

value of contact time of 3–12 s. These conditions correspond to those of industrial FCC units. The low value of residence time minimizes the contribution of thermal cracking.

2.4. Product analysis

Product analysis has been carried out by means of a device for reaction product sampling connected to a Hewlett Packard 6890 chromatograph. The sampling is activated by a timer that controls the desired value of contact time. Product identification was carried out on-line by GC-FTIR using a Nicolet/Aldrich library, by means of a FTIR Nicolet 740 SX spectrophotometer connected to a Hewlett Packard 5890 II chromatograph. The results were verified by GC–MS (HP 6890-MS Engine with electronic ionization).

In order to check and assign the retention times in the chromatographic analysis of the compounds in the C_5–C_{12} range, pure compounds and mixtures were used as standards. The assignment of the retention times of the components of the gasoline lump has been carried out by using Alphagaz PIANO (Air Liquide) calibration standards, which consist of 39 aromatic components, 35 isoparaffinic, 30 naphthenic and 25 olefinic. The amount of the C_5–C_{12} lump has been determined as that corresponding to the components with boiling point between *n*-C_5 paraffins (*n*-pentane) and *n*-C_{12} (*n*-dodecane).

The coke deposited on the catalyst was measured by thermogravimetric analysis in a Setaram TG-DSC 111 calorimeter-thermobalance. The deactivated catalyst from the reactor is dried at 110 °C in a nitrogen stream and is subsequently subjected to combustion with air at a programmed temperature ramp (5 °C min^{-1}) up to 700 °C.

3. Results

Conversion has been determined as the sum of yields to dry gases (C_1–C_2), LPG (C_3–C_4), gasoline (C_5–C_{12}) and coke. Each yield is calculated as

$$\text{yield of lump } i = \frac{\text{mass of lump } i}{\text{total mass in the feed}} \times 100 \quad (1)$$

3.1. Yield and composition of products

The conversion of waxes and VGO is compared in Fig. 3 for different temperatures and contact times. It is observed that wax conversion is higher than that of VGO in the whole range of temperatures and contact times, except for the higher temperature (550 °C) and shorter contact time (3 s). Under these conditions conversion is similar for both feeds. This result is explained by the favourable composition of the waxes, which are more olefinic and, consequently, more favourable for cracking under FCC conditions than the vacuum gas-oil, whose aromatic content is 41.1% in weight.

Fig. 4 shows a comparison of the yields of the different product fractions obtained at 500 °C (graph a) and at 550 °C (graph b). It is observed that cracking of waxes produces a higher yield of gasoline than the cracking of VGO. This high yield of gasoline has already been proven by Songip et al. [3] in the cracking of a similar feed, although they used non-equilibrated HY zeolites (and consequently more active than under FCC conditions), at a considerably lower temperature than in this study. At 500 °C (graph a in Fig. 4) the main fraction in the product stream is LCO for both feeds. This result is explained because the composition of waxes calculated by simulated distillation corresponds to LCO (a 20% fraction). Furthermore, part of HCO fraction of waxes may be cracked to LCO.

Under more severe cracking conditions (550 °C and contact times longer than 6 s), the main fraction in the product stream is gasoline, with yields of 42 wt% in the cracking of waxes (Fig. 4b).

At 500 °C (Fig. 4a) the yield of LPG is much lower in the cracking of waxes than in the cracking of VGO. Nevertheless,

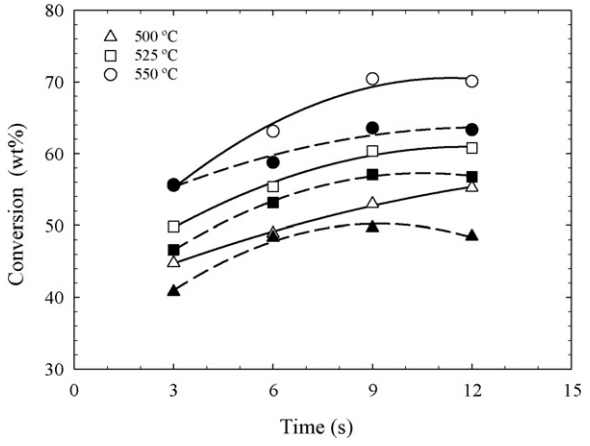

Fig. 3. Comparison of the conversions obtained in the cracking of waxes (white points and solid lines) and of VGO (black points and dashed lines). CAT-1. C/O = 5.5.

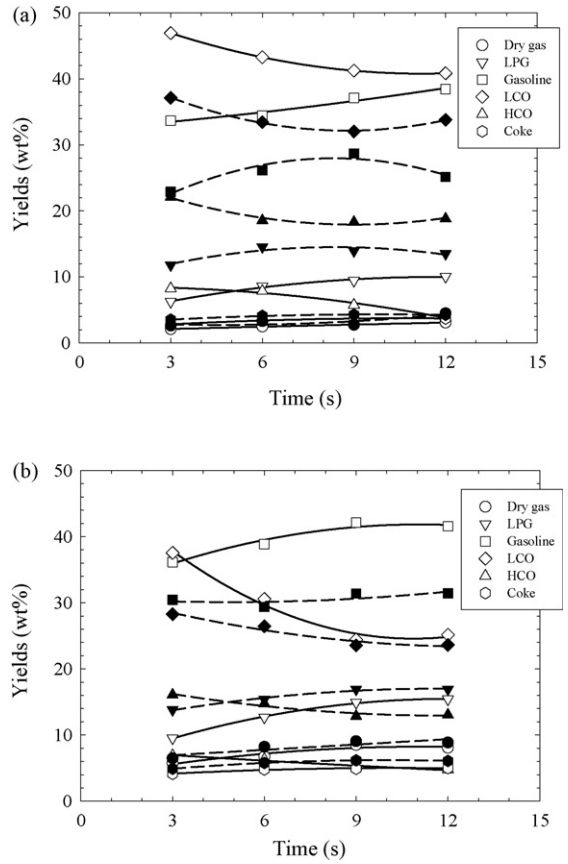

Fig. 4. Comparison of the yields of the different product fractions obtained in the cracking of waxes (black points and solid lines) and of VGO (white points and dashed lines), for different contact times. CAT-1. C/O = 5.5. Graph a: 500 °C. Graph b: 550 °C.

under more severe cracking conditions (550 °C, Fig. 4b), the yields of LPG are closer for both feeds. These results are consistent with those of Ng [14], who also obtained a lower yield of LPG and a higher yield of gasoline in the cracking of polyethylene dissolved in VGO than in the cracking of VGO, for high contents of polyethylene in the mixture. The result will be reverse for low concentrations of HDPE and will be explained by the overcracking of the gasoline obtained under these conditions [15]. The explanation of the results for individual cracking of waxes and VGO may be due to two causes: (i) overcracking of the gasoline obtained from VGO is more favoured; (ii) cracking of VGO gives more LPG as a consequence of the fact that simultaneous cracking of both feeds follows different mechanisms.

The cracking of waxes produces lower yields (approximately 1% less) of dry gases and coke than the cracking of gas-oil. In the case of dry gases, the reason is the low reactivity of the waxes for thermal cracking and, in the case of coke, the composition of the waxes (without aromatics) is less appropriate for generating coke precursor components. The yield of coke in the cracking of waxes is within the 2.8–5.0% range and is acceptable in order to satisfy the energy balance in the interconnected reaction-regeneration sections in a FCC unit.

The higher olefinicity of C_3 components, and especially of C_4 ones, obtained by cracking waxes is noteworthy [1]. The increase in the olefinicity as temperature is increased is a consequence of the fact that cracking to olefins by β scission is favoured [16]. This effect is less relevant in the cracking of waxes than in the cracking of VGO. Contact time has small effect in the olefinicity of C_3, although its increase tends to decrease the olefinicity of C_4 components.

The gasoline obtained by cracking waxes has a significantly different composition than that obtained by cracking the standard FCC feed (VGO), which is due to the different nature of these feeds. A comparison of these gasolines is shown in Fig. 5. Graph a corresponds to mild cracking conditions (500 °C and t = 3 s) and graph b to severe cracking (550 °C and t = 12 s). These graphs show that cracking severity does not affect to the concentration of aromatic, naphthenic and *n*-paraffinic compounds. Nevertheless, severity favours an increase in the concentration of olefins, whereas isoparaffins concentration decreases.

As is observed, the cracking of waxes produces a gasoline with a higher content of olefins, naphthenes, paraffins and isoparaffins and with lower content of aromatics (at 550 °C) than the cracking of VGO. This is a consequence of wax composition, which have linear olefinic chains, and of VGO composition, which is conditioned by its aromatic nature.

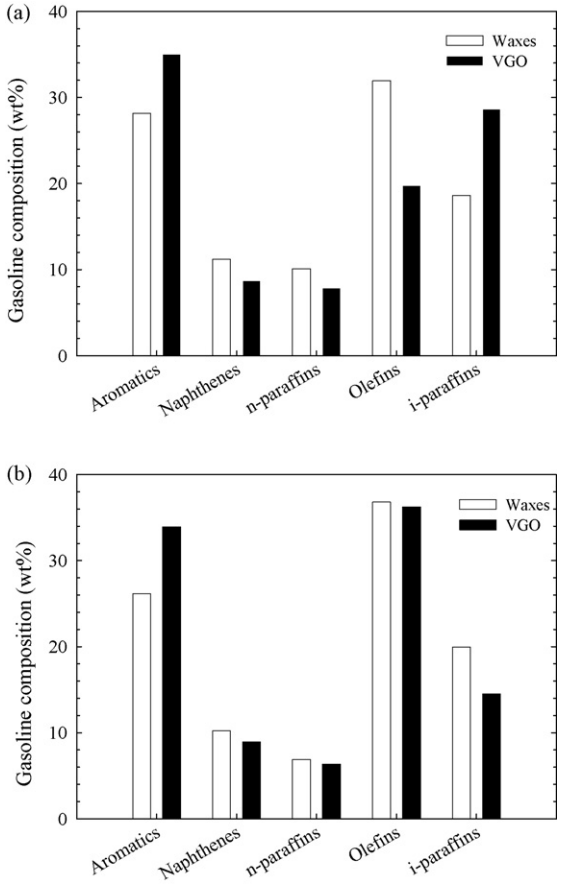

Fig. 5. Comparison of the composition of the gasolines obtained by cracking waxes and VGO, under two levels of severity. Graph a: mild cracking conditions (500 °C, t = 3 s). Graph b: severe cracking conditions (550 °C, t = 12 s). C/O = 5.5.

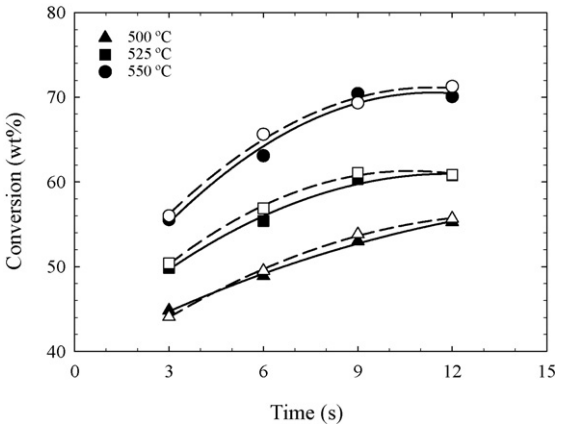

Fig. 6. Comparison of the conversions obtained in the cracking of waxes with the two HY zeolite catalysts, for different temperatures and contact times. Black points and solid lines, CAT-1. White points and dashed lines, CAT-2.

3.2. Catalyst effect

The results of conversion with both catalysts are compared in Fig. 6 for different temperatures and contact times. It is observed that the conversions obtained using CAT-2 at 500 and at 550 °C are slightly higher than those obtained using CAT-1. The difference is more pronounced at 525 °C. Comparison of physical properties and acidity (Table 2 and Fig. 1) clearly shows that CAT-2 has a higher surface area (179 $m^2\ g^{-1}$ compared to 123 $m^2\ g^{-1}$ of CAT-1) and higher total acidity (three times that of CAT-1). Nevertheless, this difference is not reflected proportionally in the result of conversion, which is evidence that the conversion attained is almost the maximum expected under FCC conditions.

In Fig. 7, the yields of the different fractions of products are compared for different conversions. As is observed, CAT-2 gives higher yields of coke and lower of dry gases, whereas the yields of commercially interesting fractions (gasoline and LPG) are not affected by catalyst acidity. The higher acidity of CAT-2 is effective for activation of coke evolution from the polyaromatic components in the product stream, whereas the lower acidity of the catalyst favours thermal cracking.

Although catalyst acidity does not affect significantly on the yield of LPG, it does considerably affect on the composition of this lump and, in general, on that of gases, which is a consequence of the fact that the higher acidity of CAT-2 favours hydrogen transfer reactions and these contribute to decreasing gas olefinicity.

This effect of catalyst acidity is shown in Fig. 8, in which the results of olefin fraction contained in C_3 (graph a) and C_4 components (graph b) of LPG are shown against conversion. The effect of acidity diminishes as temperature is increased, given that this variable attenuates hydrogen transfer reactions.

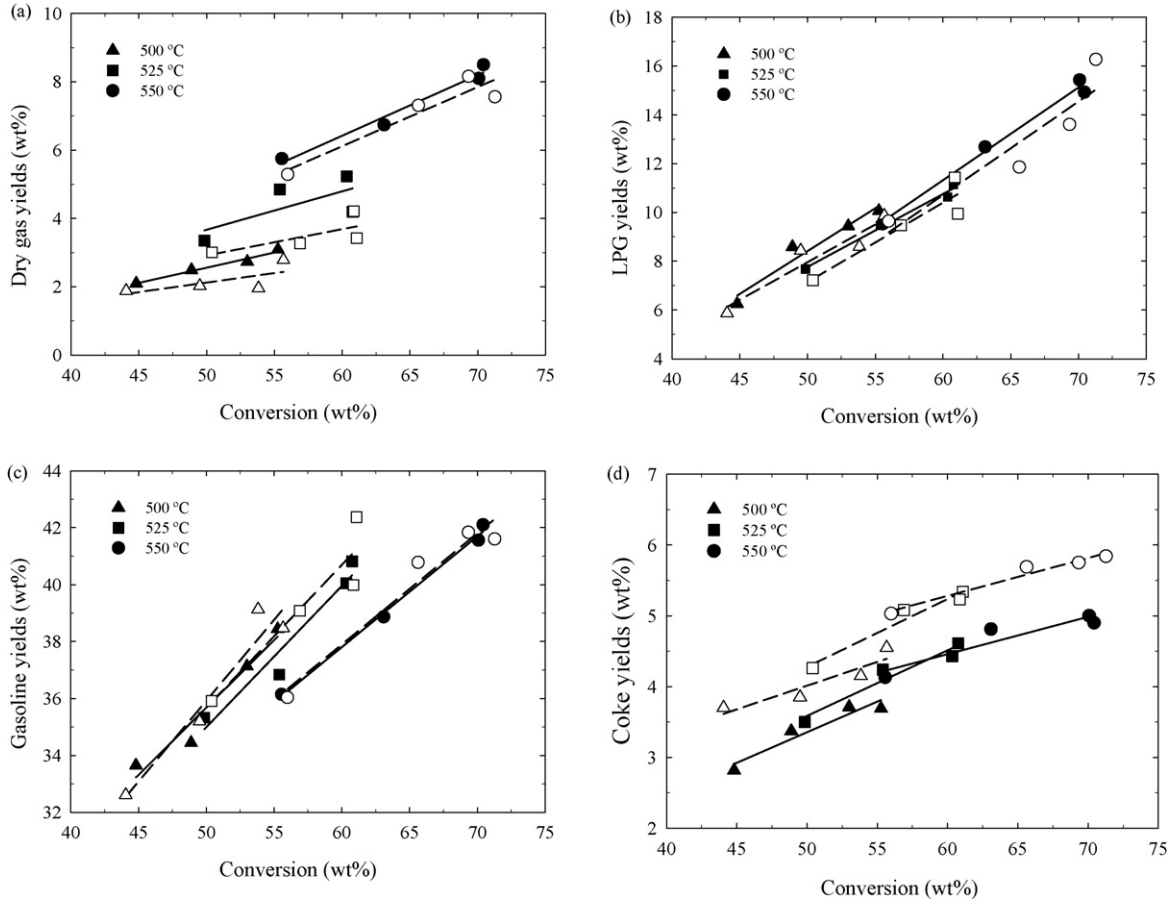

Fig. 7. Comparison of product fraction yields obtained in the cracking of waxes with the two HY zeolite catalysts. Black points and solid lines, CAT-1. White points and dashed lines, CAT-2.

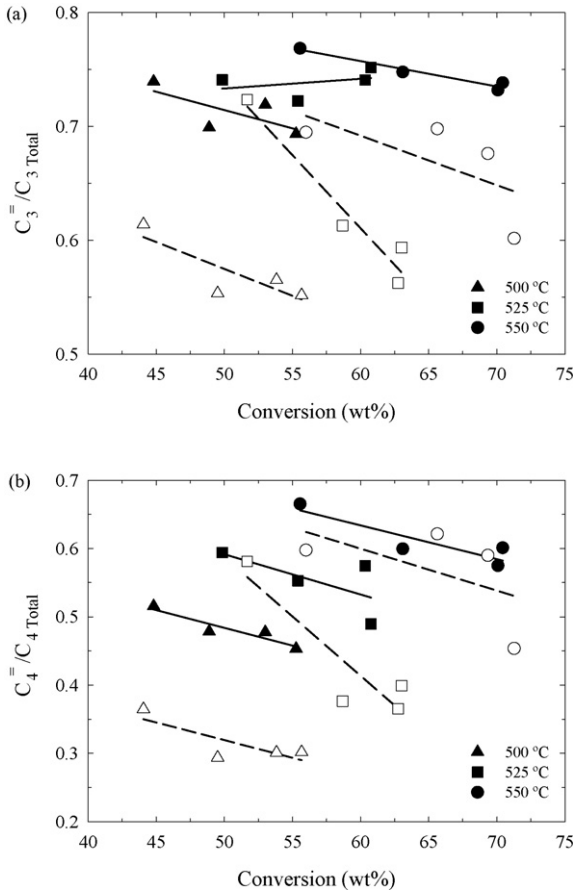

Fig. 8. Comparison of the olefinicity of C_3 components (graph a) and of C_4 components (graph b) of LPG for different conversions and temperatures. Black points and solid lines, CAT-1. White points and dashed lines, CAT-2.

In fact, at 550 °C the difference between the results corresponding to the two catalysts is smaller.

The different composition of gasoline (Fig. 9, corresponding to 525 °C and $t = 6$ s) is also explained by the different hydrogen transfer capacity of the two catalysts. CAT-2 has a higher acid site density and is more active for hydrogen transfer reactions. Consequently, it gives way to a higher concentration of aromatics and paraffins, both linear and branched, but a smaller concentration of olefins, which are cracked (preferably those of higher molecular weight) to components of LPG fraction.

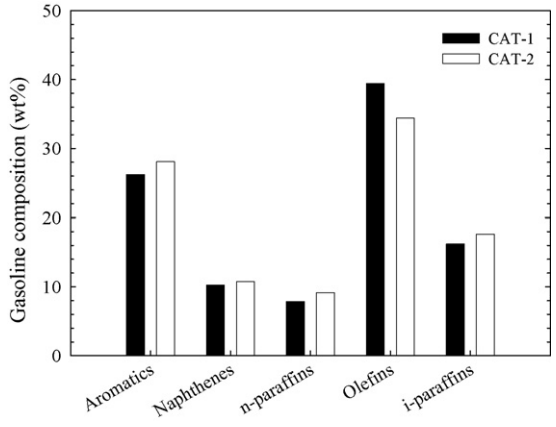

Fig. 9. Comparison of gasoline compositions obtained using the two HY zeolite catalysts (525 °C, $t = 9$ s).

Table 3
Octane number (RON) of the gasoline obtained using both HY zeolite catalysts, at different temperatures and contact times

t (s)	500 °C	525 °C	550 °C
CAT-1			
3	95.1	96.8	97.9
6	95.5	96.4	97.9
9	95.4	97.8	98.5
12	95.2	95.6	98.5
CAT-2			
3	95.3	94.6	98.4
6	94.9	95.6	99.6
9	94.8	96.7	99.7
12	94.9	97.9	99.0

A comparison of the gasoline components with different carbon atom numbers shows that CAT-2 gives way to a higher concentration of the whole range of aromatics, especially of C_6–C_8, which are formed by hydrogen transfer and dealkylation reactions. Likewise, CAT-2 gives way to higher concentration of linear paraffins in the whole range of gasoline.

Concerning the branching degree of C_5 and C_6 olefins, the less acid catalyst, CAT-1, provides higher values of $iC_5^=/nC_5^=$ and $iC_6^=/nC_6^=$ ratios, being the difference greater for the first ratio. CAT-1 also gives way to higher branching indices for C_5 and C_6 paraffins, which is important for gasoline quality.

The octane numbers (RON) of the gasolines obtained with both catalysts are shown in Table 3, for different temperatures and contact times. On the whole, CAT-2 gives way to lower values of RON at low temperatures, due to the lower concentration of olefins and to the higher concentration of linear paraffins, which are not balance by the higher concentration of aromatics and isoparaffins. As temperature is increased, the importance of hydrogen transfer reactions decreases, whereas those of cracking by β scission increases. Consequently, the RON of the gasoline obtained using catalyst CAT-2 increases considerably.

4. Conclusions

The cracking of the waxes obtained by polyolefin pyrolysis under FCC unit conditions is viable from the point of view of technology and gives way to yields and quality that are acceptable for refineries. The conversion of the waxes and the yields of the different product fractions (dry gases, coke, LPG, gasoline) are very sensitive to the values of contact time and temperature within the usual range in FCC catalytic cracking. A noteworthy fact is the high yield of gasoline, 42% for a contact time of 12 s at 500 °C and for contact times longer than 9 s at 550 °C. The yield of coke is within acceptable values, given that it changes from 2.8% for 3 s and 500 °C to 5.0% for 12 s at 550 °C. This yield is slightly lower than that corresponding to the cracking of VGO.

The LPG obtained by cracking waxes has propene as the main component and the olefinicity (particularly of $C_4^=$ ones) increases as temperature is increased. Likewise, cracking temperature has a significant effect on the composition of the gasoline obtained by cracking waxes. This gasoline has a higher content of olefins, naphthenes and paraffins, with less aromatics and more isoparaffins (at 550 °C) than that obtained by cracking the standard VGO.

The total acidity of the catalyst (measured by NH_3 adsorption at 150 °C) has a significant effect on conversion and gasoline yield at a temperature around 525 °C and this effect attenuates below and above this temperature. The increase in acidity has opposite effects, given that it increases the yield of coke but decreases the yield of dry gases (which is formed by thermal cracking).

The greater density of acid sites in the catalyst and the resulting greater hydrogen transfer capacity has a significant effect on gas composition, which is evident at low temperature (500 °C), given that paraffin concentration increases. The difference between the two catalysts attenuates at 550 °C.

Likewise, given the higher hydrogen transfer capacity, the catalyst with higher acid site density gives way to a gasoline with a higher concentration of aromatics and paraffins, both linear and branched, but it gives way to a lower concentration of olefins, which are cracked (preferably those of higher molecular weight) to LPG fraction components. At 550 °C the cracking capacity of the more acid zeolite prevails, which gives way to a higher concentration of C_6 olefins, due to the higher cracking capacity of heavy LCO fraction.

The opposite effect of acidity and cracking temperature on the gasoline range gives way to the fact that at 500 °C the RON of the gasoline obtained with the less acid catalyst is higher but at 550 °C that corresponding to the more acid catalyst is higher.

Acknowledgements

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