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# Valorization of Polyolefin/LCO Blend over HZSM-5 Zeolites

José M. Arandes, Javier Ereña, Martin Olazar, Javier Bilbao, and Gabriela de la Puente

## Abstract

The cracking of low density polyethylene (PE) and of polypropylene (PP) dissolved in LCO (light cycle oil, product of a commercial FCC unit) is studied in the 450–550 °C range, by using a reactor simulating a FCC riser. The reaction was carried out on catalysts prepared based on HZSM-5 zeolites with different Si/Al ratio. The results are explained by the shape selectivity of the HZSM-5 zeolite and by the total acidity, which decreases as the Si/Al ratio of the zeolite is increased. A feed with polyolefin content higher than 5 wt% limits the conversion of LCO. The cracking on HZSM-5 zeolite catalysts of PE/LCO and PP/LCO blends produces a yield of C5–C12 fraction, which is highly aromatic and with a high content of styrene, and a low yield of C1 and C2 gases and of coke. A feed made up of polyolefins and LCO contributes to increasing the yield of light olefins, of which the concentration of ethylene increases with temperature. When compared to the coke selectivity of LCO cracking, a feed with PP contributes to increasing it, whereas PE decreases it.

**KEYWORDS:** catalyst, zeolites, polyolefins, valorization

## 1. INTRODUCTION

The thermal degradation of post-consumer plastics is considered to be the method with higher possibility of large scale implementation for valorization of these materials in order to obtain fuel or petrochemical feedstock (from mixtures of plastics) or to recover monomers as styrene or methyl methacrylate (from polystyrene or polymethyl methacrylate, respectively). The fluidized bed reactor is the more developed technology because it has good gas solid contact and bed isothermality (Kaminsky, 1992, 1995; Williams and Williams, 1999).

The use of acid catalyst allows the pyrolysis temperature to be reduced and the product distribution to be modified. Numerous acid catalysts have been studied in experiments carried out in fixed bed reactors, either in one stage, with the catalyst and the plastic mixed (Audisio et al., 1984; Ishihara et al., 1990, 1993; Mordi et al., 1992; Lin et al., 1997; Aguado et al., 1997; Sakata et al., 1999), or in two stages, by passing the vapours of the thermal pyrolysis through a catalytic bed (Ohkita et al., 1993; Uemichi et al., 1998; Takuma et al., 2000). Uemichi et al. (1999) arranged two beds in series (silica-alumina and HZSM-5 zeolite) in a catalytic reactor. In a fluidized bed reactor, catalytic pyrolysis may be carried out in one stage because bed isothermicity is guaranteed, due to its high heat transfer rate (Sharratt et al., 1997; Lin et al., 1998; Mastrale et al., 2002; Ali et al., 2002). The fused plastic coats the catalyst particles, which in turn contributes to fluidization, as does in thermal pyrolysis.

The fact that the catalytic reforming of the liquid product obtained by pyrolysis is carried out in a second stage allows for separately establishing the optimum conditions in the reactor of thermal pyrolysis and of catalytic reforming. Songip et al. (1993, 1994a,b) studied the catalytic reforming on different silica-alumina and on HZSM-5 and HY zeolites of the liquid product (mainly paraffinic) obtained by thermal pyrolysis of polyethylene at low temperature (450 °C). Joo and Guin (1997) have studied the reforming of a heavy fraction of the pyrolysis liquid fraction (boiling point > 205 °C) obtained from mixed plastics (high density polyethylene, polypropylene and polystyrene) by its hydrocracking on NiMo/alumina catalysts.

Nevertheless, the handling of plastics wastes entails such disadvantages as are the transportation of a material with great volume to pyrolysis plants and those inherent to feeding this material into the reactor. The operation in a fluidized bed reactor also has problems due to the stickiness of the particles coated with fused plastic, which are prone to forming agglomerates which lead to bed defluidization.

The transformation of the dissolved plastic is a strategy that has the following interesting aspects: 1) The dissolution of the waste plastics may be carried out at the point where they are collected and classified, which facilitates their transportation to the refinery, 2) as the catalytic transformation is carried out in the refinery, dissolved plastics coming from different places may be treated together and at large scale; 3) the products will be treated in the existing separation units in order to tailor their composition to market requirements, 4) the products will be commercialized together with the usual ones; 5) The solvents for dissolving the plastic will be chosen according to market circumstances. This fact contributes to upgrading secondary streams of the refinery (Fernández et al., 2002).

Ng et al. (1995) have studied the catalytic cracking of dissolutions containing 5 wt% and 10 wt% of high density polyethylene in a vacuum gas oil (VGO). The experimentation in continuous operation in a fixed bed was evidence of the synergistic effect of the feed components.

In a previous paper (Arandes et al., 1997), the catalytic upgrading of polypropylene and polystyrene dissolved in LCO was studied on a commercial FCC catalyst consisting of a HY zeolite interchanged with rare earth. The solvent used is a product stream coming from the FCC unit (and, consequently, partially refractory to catalytic cracking), which allows for identifying the contribution of the cracking of the dissolved plastics to the product stream. Encouraging results are obtained concerning the possibility of producing a gasoline with a high octane number, although the yield of gases and of coke is high, which implies a decrease in the yield of hydrocarbons and aggravates catalyst deactivation.

In this paper, the kinetic behaviour of several HZSM-5 zeolites prepared with different acidity are studied in order to ascertain the effect of this property on conversion, on deactivation by coke and on the product distribution in the cracking of polyethylene and polypropylene dissolved in LCO.

The main interest of the HZSM-5 zeolites lies in their good resistance to deactivation by coke. The high yield of coke is a disadvantage in the catalytic valorization of plastics and, furthermore, coke deposition causes rapid deactivation of the catalyst. The low deposition of coke on HZSM-5 zeolites in the pyrolysis of polyolefins has been widely proven in the literature (Aguado et al., 1997; Sakata et al., 1999; Ohkita et al., 1993; Uemichi et al., 1998; Uemichi et al., 1999; Sharratt et al., 1997; Lin et al., 1998) and is due to the moderate and uniform acid strength of their sites and to the three-dimensional structure of their pores (connected by intersections and not by cages), which facilitates the diffusion of coke precursor products towards the outside (Benito et al., 1996; Guisnet and Magnoux, 2001).

## 2. MATERIALS AND METHODS

### Feed

The plastics studied, supplied by Dow Chemical S.A, are low density polyethylene (PE) (MW,  $9.22 \times 10^4$ ; polydispersity, 5.1) and polypropylene (PP) (MW,  $12 \times 10^4$ ; polydispersity, 5.0). By means of thermogravimetric analysis (Setaram TAG24) the degradation ranges have been determined; these are 430–500°C for PE and 410–480°C for PP. The temperature corresponding to the maximum degradation range of the two materials is 460°C. The plastic diluent agent was a LCO whose composition is shown in Table 1. 30.0 wt% of the LCO is made up of hydrocarbons with a boiling point within the range of gasoline ( $C_5-C_{12}$ ). This solvent has been chosen because it is a product stream of a commercial FCC unit and, consequently, its reactivity for cracking will be low, which will allow for separately identifying the reactivity of the dissolved plastic. The aromatic nature of the LCO is similar to that expected for the products of catalytic cracking of polyolefins and, consequently, the synergistic effects of the products coming from the constituents of LCO and of the plastics will be minimized. The dissolution of the plastics in LCO was carried out in a stirred tank at 100°C. The feeds were made up of PE at 5 and 10 wt%, and of PP at 5 wt% (higher concentrations of PP led to very high viscosity and, consequently, problems of solidification in the reactor injection system).

Table 1. Characterization data for LCO

	Composition		wt%
density (15°C), g/cm <sup>3</sup>	0.9132		
sulfur, wt%	0.60	saturates	20.7
viscosity, 100°C cSt	1.0	paraffins $C_nH_{2n+2}$	7.9
flashpoint, °C	93	monocycloparaffins $C_nH_{2n}$	5.6
Simulated distillation, wt%	°C	dicycloparaffins $C_nH_{2n-2}$	2.7
I.P.	125	tricycloparaffins $C_nH_{2n-4}$	4.5
5	175	tetracycloparaffins $C_nH_{2n-6}$	0.0
10	187		
20	203	aromatics	66.9
30	219	monocyclic	33.0
40	231	dicyclic	33.1
50	249	tricyclic	0.8
60	264		
70	282	sulfur compounds	12.4
80	302	thiophenes	0.4
90	329	benzothiophenes	12.0
95	350		
E.P.	390		

## Catalysts

Three catalysts based on HZSM-5 zeolite have been prepared with different Si/Al ratio (Si/Al=24, 42, and 78). The method followed is that indicated in the Mobil patents (Argauer and Landolt, 1972; Chen et al., 1973). The zeolite is agglomerated in an inert matrix made up of silica gel, which is prepared by a conventional method of precipitation from sodium silicate (Romero et al., 1986). The catalysts are calcined at 570°C for 4 h in a  $N_2$  stream. Under these conditions, the acid structure is equilibrated and the catalysts recover their acidity in successive reaction-regeneration cycles when the regeneration is carried out by coke combustion in an air stream at 550°C (Benito et al., 1996b).

The more relevant physical properties of the catalysts are set out in Table 2. The porous structure and the surface area (BET) of the catalysts have been characterized from the isotherms of adsorption-desorption of  $N_2$  obtained in an ASAP 2000 equipment from Micromeritics. The micropores of the catalyst correspond to the HZSM-5 zeolite, whose pores are elliptical channels of two types which cross perpendicularly to each other, some are arranged in a straight line (0.53 x 0.56 nm) and the others in zigzag formation (0.51 x 0.55 nm). The silica that makes up the matrix of the catalyst has an exclusively mesoporous structure with pores of diameter between 30 and 300 Å.

Table 2. Properties of the catalysts

<i>Chemical properties</i>						
catalyst number	Si/Al ratio in the HZSM-5 zeolite	acidity, mmol $NH_3$ g <sup>-1</sup>	Brönsted/Lewis ratio			
1	24	0.15	3.63			
2	42	0.10	3.40			
3	78	0.04	2.86			

<i>Physical properties</i>						
catalyst number	BET surface area, m <sup>2</sup> g <sup>-1</sup>	micropore surface, m <sup>2</sup> g <sup>-1</sup>	pore volume, cm <sup>3</sup> g <sup>-1</sup>	micropore volume, cm <sup>3</sup> g <sup>-1</sup>	micropore diameter, Å	mesopore diameter, Å
1	200	106	0.5459	0.0584	5.5	30-300
2	195	101	0.5387	0.0587	5.5	30-300
3	181	87	0.5228	0.0578	5.5	30-300

The studies on acidity have consisted of: 1) the determination of the Brönsted/Lewis sites ratio, Table 2, by analyzing the FTIR spectra of adsorption of pyridine at 250°C and so ascertaining the ratio between the intensity of the bands corresponding to 1550 cm<sup>-1</sup> (B-pyridine) and 1455 cm<sup>-1</sup> (L-pyridine). This study has been carried out by means of *in situ* FTIR spectroscopy in a catalytic chamber (Spectra Tech) connected in series with the FTIR spectrophotometer (Nicolet 740SX) (Aguayo et al., 1994a); 2) the analysis of acidic strength distribution, Figure 1, and total acidity, Table 2, has been determined by differential adsorption of  $NH_3$ , which has been carried out in a differential scanning calorimeter (Setaram DSC 111) connected to a Hewlett Packard 6890 gas chromatograph. The calorimeter is used to evaluate the adsorption heat (heat associated with the neutralization of acidic sites) of pulses of the base (at 150°C) and the chromatograph is used to assess the amount of base adsorbed (Aguayo et al., 1994b).

It has been proven that the acidity of the catalysts prepared using the three HZSM-5 zeolites is almost identical to that of the pure zeolites, which indicates that the silica matrix has no significant acidity. By analysing a silica gel prepared independently by the aforementioned techniques, it has been confirmed that its acidity is insignificant.

In Figure 1 it is proven that the Si/Al ratio hardly affects the acid strength of the sites of the HZSM-5 zeolites, which is between the range from 100 to 180 kJ (mol de  $NH_3$ )<sup>-1</sup> at the adsorption temperature used, 150°C. Nevertheless, when the Si/Al is increased the total acidity, measured as the amount of  $NH_3$  adsorbed at 150°C, is noticeably affected.

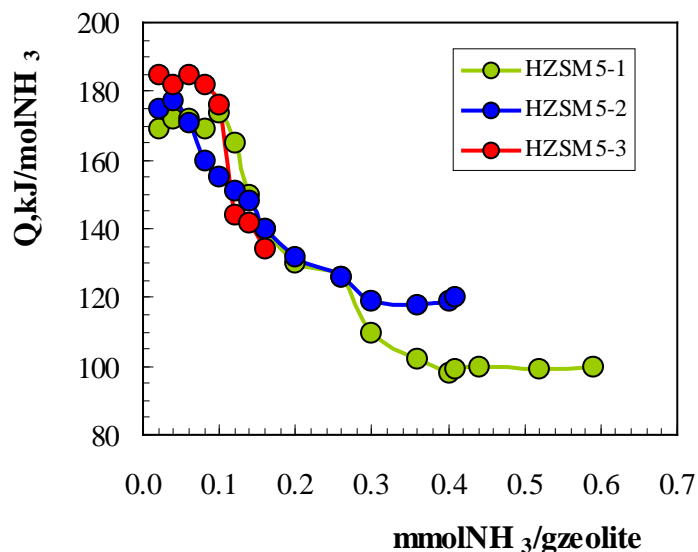


Figure 1. Distribution of the acid strength of the catalysts determined by calorimetric measurement of the differential adsorption heat of  $\text{NH}_3$

## Reaction Equipment

In order for the results of catalytic cracking to be interesting as an indication of the reaction in the industrial FCC unit, the experiments must be carried out under similar conditions to those of an industrial riser (Sedran, 1994). The equipment used in this work is a Riser Simulator Reactor, Figure 2. It is an internal recycle reactor specially designed for catalytic cracking and has been previously described (Kraemer, 1991; Kraemer and de Lasa, 1988; de Lasa, 1992). 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 range 1–10 s; 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 good behaviour of this reactor for the kinetic study of catalytic cracking has been proven in previous papers (Arandes et al., 2000, 2002).

The runs have been carried out at 1 atm, in the 450–550°C range, with a catalyst/feed ratio C/O = 6 by weight (0.75 g of catalyst and 0.125 g of blend) and with a value of contact time of 3 s. These conditions correspond to those of industrial FCC units, with a lower contact time established because the catalysts studied here are expected to have higher activity (due to the high acidity) than that of equilibrated FCC catalysts (Arandes et al., 1997). The low value of residence time minimizes the contribution of thermal cracking.

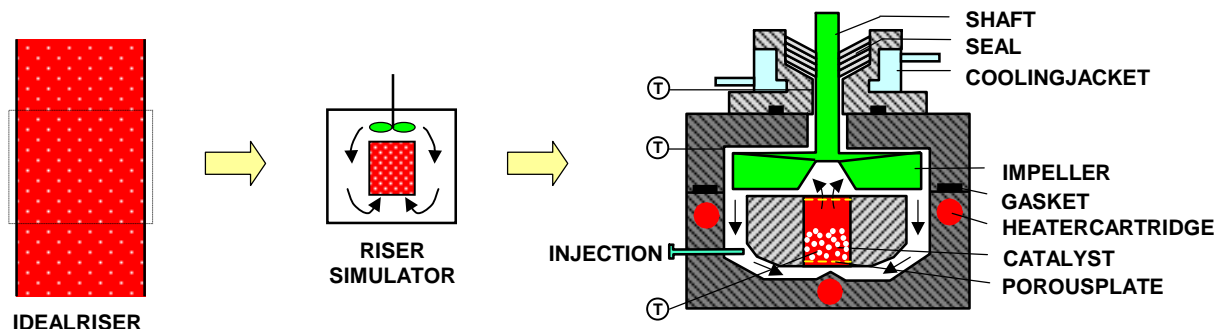


Figure 2. Diagram of the riser simulator reactor

## 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 740SX spectrophotometer connected to a Hewlett Packard 5890 II chromatograph. The results were verified by GC-MS (HP 6890 -MS Engine with electronic ionization). The product stream of the riser simulator was analyzed on-line with either MS or FTIR.

In order to check and assign the retention times in the chromatographic analysis of compounds in the C<sub>5</sub>-C<sub>12</sub> 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 Alphasgaz PIANO (Air Liquide) calibration standards, which consist of 39 aromatic components, 35 isoparaffinic, 30 naphthenic and 25 olefinic. The amount of the C<sub>5</sub>-C<sub>12</sub> lump has been determined as that corresponding to the components with boiling point between n-paraffins (n-pentane) and n-C<sub>12</sub> (n-dodecane).

The coke deposited on the catalyst was measured by thermogravimetric analysis in a Setaram TAG 24 thermoanalyser. 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<sup>-1</sup>) up to 700°C.

## 3. RESULTS AND DISCUSSION

### Conversion and Yields

The conversion is defined in weight percent and calculated as the sum of the yields in weight of gases (C<sub>1</sub>-C<sub>4</sub>), gasoline (C<sub>5</sub>-C<sub>12</sub>) and coke. Each yield is calculated as:

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

The results of conversion and yield of dry gases (C<sub>1</sub>, C<sub>2</sub>), LPG (C<sub>3</sub>, C<sub>4</sub>), gasoline (C<sub>5</sub>-C<sub>12</sub>) and coke are set out in Table 3 for the feeds LCO, PE(5)/LCO, PE(10)/LCO and PP/LCO, and for the three catalysts. When evaluating these results, it must be taken into account that the LCO is made up of 30.0 wt% of hydrocarbons with a boiling point within the range of gasoline. Consequently, this fact must be taken into account in the actual results of both conversion and yield of gasoline shown in Table 3. Given the fact that the mass balance has been closed at 98%, the difference has been added to all the yields proportionally to their measured value. The experiments have been replicated three times and the average relative error obtained is 2 wt%. The values indicated in Table 3 are average values.

As is shown in Table 3, the actual conversion of LCO follows an order for the three catalysts according to their total acidity, No. 1 > No. 2 > No. 3, although the difference in the conversions is small. Furthermore, conversion increases with temperature for the three catalysts. The increase in conversion from 450°C to 550°C is approximately 3 wt% for catalyst No. 1 and 1 wt% for catalysts Nos. 2 and 3.

The high yield of C<sub>5</sub>-C<sub>12</sub> fraction obtained from LCO with the three catalysts is evidence that even a catalyst with an HZSM-5 zeolite of small acidity, as is the case of No. 3, is very active for cracking a wider range of molecules, from those of high molecular weight of LCO to those corresponding to the lump of gasoline. Furthermore, the maximum yield of C<sub>5</sub>-C<sub>12</sub> is obtained for the three catalysts at the lowest temperature studied, 450°C. As the temperature is increased, the lump of gases (C<sub>1</sub>, C<sub>2</sub>), LPG and coke increase.

Table 3. Results (in wt%) of conversion and yield of dry gases ( $C_1, C_2$ ), LPG ( $C_3, C_4$ ), gasoline ( $C_5-C_{12}$ ) and coke in the cracking of LCO, PE(5)/LCO, PE(10)/LCO and PP(5)/LCO on the different catalysts synthesized

feedstock	catalyst	T, °C	conversion, wt%	$C_1-C_2$ gases, wt%	$C_3-C_4$ gases, wt%	gasoline $C_5-C_{12}$ , wt%	coke, wt%	
LCO	1	450	56.41	0.21	2.78	50.69	2.72	
		500	57.06	0.54	4.17	49.50	2.85	
		525	57.56	0.78	4.40	49.48	2.90	
		550	59.56	1.67	5.37	49.45	3.07	
	LCO	2	450	55.93	0.26	2.56	50.75	2.36
			500	56.52	0.52	2.75	50.69	2.56
			525	56.73	0.69	2.83	50.64	2.57
			550	57.05	1.28	3.05	50.08	2.64
	LCO	3	450	54.57	0.29	2.34	50.01	1.92
			500	55.03	0.50	2.73	49.86	1.94
			525	55.36	0.75	2.74	49.64	2.22
			550	55.54	1.21	3.14	48.63	2.56
PE(5)/LCO	1	450	56.28	0.63	4.60	48.89	2.16	
		500	56.71	1.58	5.16	47.67	2.30	
		525	57.04	1.92	5.85	46.89	2.38	
		550	59.15	2.76	7.76	45.79	2.84	
	PE(5)/LCO	2	450	55.82	0.50	4.11	48.72	2.49
			500	56.08	0.97	5.09	47.81	2.21
			525	56.16	1.28	5.58	46.65	2.65
			550	58.01	2.35	7.19	45.67	2.80
	PE(5)/LCO	3	450	52.89	0.47	3.89	46.44	2.09
			500	54.11	0.98	4.62	46.31	2.20
			525	55.27	1.16	5.47	46.56	2.08
			550	55.53	1.39	5.81	46.08	2.25
PE(10)/LCO	1	450	42.21	1.06	4.67	33.89	2.59	
		500	44.59	1.10	5.96	34.77	2.76	
		525	45.71	1.40	6.17	34.28	3.86	
		550	50.30	2.17	8.43	34.42	5.28	
	PE(10)/LCO	2	450	41.16	0.41	4.57	33.58	2.60
			500	43.29	0.83	6.03	33.72	2.71
			525	44.86	1.20	6.09	34.01	3.56
			550	48.46	2.07	7.53	34.03	4.83
	PE(10)/LCO	3	450	40.45	0.30	4.33	33.19	2.63
			500	43.49	0.77	6.51	33.57	2.64
			525	44.28	1.10	5.95	33.90	3.33
			550	48.11	1.97	7.24	34.27	4.63
PP(5)/LCO	1	450	56.85	0.81	3.65	49.07	3.32	
		500	57.20	1.44	4.86	47.18	3.72	
		525	57.53	2.18	5.38	46.22	3.75	
		550	59.39	3.18	5.50	46.48	4.23	
	PP(5)/LCO	2	450	55.52	0.51	3.52	48.56	2.93
			500	56.14	0.90	4.24	47.48	3.52
			525	56.21	1.73	4.63	46.32	3.53
			550	58.49	2.74	5.09	46.87	3.79
	PP(5)/LCO	3	450	53.62	0.43	2.92	48.04	2.23
			500	53.70	0.79	3.06	46.95	2.90
			525	54.38	1.06	3.59	46.84	2.89
			550	54.90	1.66	3.64	46.66	2.94



When the yields of transformation of LCO are compared for the three catalysts, it is observed that as the catalyst acidity is increased the yield of coke, of dry gases and, more significantly, that of LPG increase. As a consequence of the effect of acidity whereby there is an increase in the conversion and yield of the other fractions, the yield of C<sub>5</sub>-C<sub>12</sub> fraction has its maximum for catalyst No. 2, which has an intermediate acidity.

By analysing the results of conversion of the PE(5)/LCO and PP(5)/LCO blends shown in Table 3, it is observed that conversion is very similar to that obtained for LCO. This result is evidence that the conversion of PE and of PP contained in these blends is very similar to that of the solvent under all the operating conditions studied. Nevertheless, the results of conversion of the PE(10)/LCO blend are noticeably lower, which is evidence of the effect of the plastic content in the blend. It may be the existence of a maximum plastic/catalyst mass ratio above which the cracking is limited by blockage of HZSM-5 zeolite pores by macromolecular chains. This limitation will also affect the cracking of LCO components because the decrease in the conversion of the PE(10)/LCO blend over that of LCO is higher than 10 wt% (which is the content of plastic in the blend).

This hypothesis about the limitation to the access of the channels of the HZSM-5 zeolite in the cracking of the PE(10)/LCO blend is ratified by the effect of temperature on conversion and by the results of yields. As temperature is increased, conversion increases significantly as a consequence of the decrease in the capacity for adsorption of macromolecular chains and of the increase in the coefficients of diffusion of reactants and products. Furthermore, when the yields of cracking of the PE(10)/LCO blend are compared with those corresponding to the cracking of LCO, it is observed that the yield of C<sub>5</sub>-C<sub>12</sub> fraction is lower for the blend, whereas the yields of coke, gases (C<sub>1</sub>, C<sub>2</sub>) and LPG are higher. These results are a consequence of the retention of the plastic chains adsorbed on the catalyst surface. The partial blockage of the porous structure by the macromolecular chains causes the overcracking of LCO components retained within the pores.

In the cracking of the PE(5)/LCO and PP(5)/LCO blends the yields of C<sub>5</sub>-C<sub>12</sub> fraction are lower than those corresponding to the cracking of LCO, whereas the yields of gases (C<sub>1</sub>, C<sub>2</sub>), LPG and coke are generally higher. These results agree with the aforementioned effect of overcracking of the components trapped in the porous structure. When these results are compared with those corresponding to the cracking of PE(10)/LCO, it is concluded that this effect is noticeably reduced when the content of plastic in the blend is decreased.

Figure 3 shows the effect of temperature on the selectivity of the lumps of gases (C<sub>1</sub>, C<sub>2</sub>), LPG (C<sub>3</sub>, C<sub>4</sub>), C<sub>5</sub>-C<sub>12</sub> fraction and coke, for LCO, PE(5)/LCO and PP(5)/LCO. The results correspond to catalyst No. 1, for which the selectivity is the highest. These selectivities have been calculated as:

$$\text{Selectivity to lump } i = \frac{\text{mass of lump } i}{\text{total mass of the products}} \cdot 100 \quad (2)$$

The results of Figure 3 show that the selectivity to gases (C<sub>1</sub>, C<sub>2</sub>) (Figure 3a), from LPG (Figure 3b) and from coke (Figure 3d) increases as temperature is increased, whereas the selectivity to C<sub>5</sub>-C<sub>12</sub> fraction (Figure 3c) decreases. The results of Figure 3 are average values corresponding to three experiments and the relative error estimated is 2 wt%.

The presence of dissolved polyolefins has an important effect on the cracking of the solvent LCO in the blend. In Figure 3c it is observed that the decrease in the selectivity to lump C<sub>5</sub>-C<sub>12</sub> (as a consequence of feeding polyolefin) is important and is even more important than that corresponding to the non-contribution of dissolved polyolefin to the formation of this lump. Consequently, polyolefins inhibit the formation of this lump. Furthermore, polyolefins in the feed contribute to increasing the selectivity to LPG and gases (C<sub>1</sub>, C<sub>2</sub>) and to decreasing the selectivity to gasoline as compared to the results corresponding to the cracking of LCO.

When the selectivities corresponding to the feeds PE(5)/LCO and PP(5)/LCO are compared, it is observed that those corresponding to gases (C<sub>1</sub>, C<sub>2</sub>) and C<sub>5</sub>-C<sub>12</sub> are similar. Nevertheless, in the cracking of PE(5)/LCO the selectivity to LPG is higher and that to coke is lower. The higher yield of coke corresponding to PP(5)/LCO is a consequence of the greater degradability to coke of propylene (main primary product of polypropylene cracking) over that of ethylene (*idem* of polyethylene cracking), via oligomerization and Diels-Alder condensation (Dimonet al., 1993). This higher coke deposition agrees with the slight yield increase in dry gases, where the main product is

methane. The formation of methane increases simultaneously to the formation of coke because it is a product obtained in the cracking of side chains of the aromatic constituents of the coke (Gayubo et al., 2002).

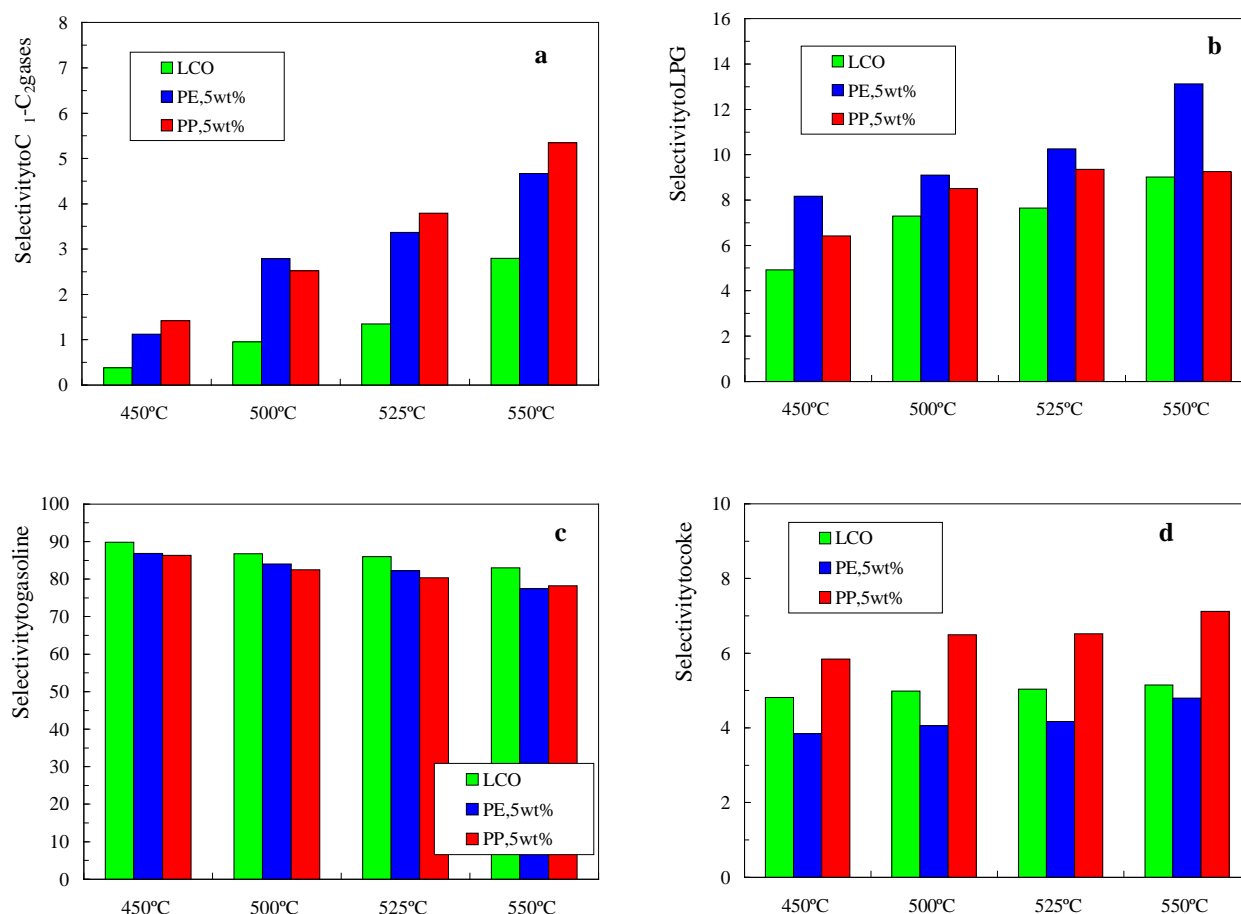


Figure 3. Effect of temperature on the selectivity to products (in wt%) in the cracking of LCO, PE(5)/LCO and PP(5)/LCO, for catalyst No. 1. Graph a, gases (C<sub>1</sub>, C<sub>2</sub>). Graph b, LPG (C<sub>3</sub>, C<sub>4</sub>). Graph c, C<sub>5</sub>-C<sub>12</sub> fraction. Graph d, coke

## C<sub>5</sub>-C<sub>12</sub> Composition

Table 4 shows the composition of C<sub>5</sub>-C<sub>12</sub> fraction obtained as a product of cracking LCO, PE(5)/LCO and PP(5)/LCO. The results correspond to catalyst No. 1. The results corresponding to the other catalysts are qualitatively similar.

Although the aromatic content of C<sub>5</sub>-C<sub>12</sub> fraction obtained in the cracking of LCO is high, approximately 80 wt% at 450°C and almost irrespective of temperature, the presence of plastics in the feed notably increases this content. The aromatic content is approximately 89 wt% for the cracking of PP(5)/LCO and 87 wt% for the cracking of PE(5)/LCO. The capacity of the HZSM-5 zeolite for synthesizing aromatic components has been emphasized in the literature in the pyrolysis of polyolefins above 400°C in fixed bed (Uemichi et al., 1998, 1999; Takuma et al., 2000) and in fluidized beds (Ali et al., 2002). Ohkita et al. (1993) attribute this capacity for aromatization to the Brønsted sites of the catalyst. Furthermore, a high reactivity is attributed to the radicals of polyethylene and polypropylene (the latter are more reactive) for taking part in the successive steps of oligomerization-cracking-Diels-Alder together with the olefins obtained as product in the cracking of LCO. Likewise, the results agree with the high reactivity of propylene over that of ethylene for the reactions of oligomerization and Diels-Alder condensation (vanden Berget al., 1983).

Table 4. Composition of the C<sub>5</sub>-C<sub>12</sub> fraction obtained by cracking of LCO, PE(5)/LCO and PP(5)/LCO on catalyst No. 1

feedstock	T, °C	n-paraffins	i-paraffins	olefins	naphthenes	aromatics
LCO	450	4.97	3.66	8.39	2.86	80.12
	500	5.22	3.78	9.14	3.05	78.81
	525	5.18	3.56	8.43	2.70	80.12
	550	4.94	3.25	8.28	3.08	80.44
PE(5)/LCO	450	5.09	1.83	4.96	0.43	87.69
	500	5.34	1.87	5.09	0.38	87.32
	525	5.45	1.73	5.46	0.31	87.04
	550	5.20	1.68	7.96	0.33	84.84
PP(5)/LCO	450	2.41	2.72	4.79	1.26	88.83
	500	3.26	2.56	4.47	1.15	88.55
	525	3.09	2.37	4.71	1.09	88.74
	550	3.05	2.25	4.52	1.09	89.09

Due to the strong aromatic content of C<sub>5</sub>-C<sub>12</sub> fraction, the potential interest for valorization of the blends studied in this paper lies in the separation of the aromatic components, whose commercial interest is expected to increase in the next decade, except for toluene (Zehnder, 1998). Figure 4 shows the effect of temperature on composition, in wt%, of the different components and lumps of the aromatic fraction within the C<sub>5</sub>-C<sub>12</sub> fraction obtained in the cracking of LCO, PE(5)/LCO and PP(5)/LCO. The results correspond to catalyst No. 1.

In graphs a and b of Figure 4 it is observed that the contents of benzene (graph a) and of toluene (graph b) increase with temperature for the three feeds. A feed with plastic contributes to increasing the concentration of these aromatics.

C<sub>8</sub> fraction (Figure 4c) also increases with temperature and its concentration is higher in the product stream obtained by cracking dissolved PP. In the cracking of LCO this fraction is mainly constituted (> 80 wt% of the whole C<sub>8</sub>) by xylenes and to a lesser extent by ethylbenzene and styrene, which are present in a similar proportion. In the products stream obtained by cracking dissolved plastics, styrene concentration has its maximum value at 550 °C and is approximately 50 wt % of C<sub>8</sub> fraction for the cracking of dissolved PE, and lower, 40 wt%, for the cracking of dissolved PP. This important formation of styrene is attributable to the reduced capacity for hydrogen transfer of the HZSM-5 zeolite and, consequently, the double bond is maintained in the side chains subsequent to the Diels-Alder condensation of the olefins obtained as products of the primary cracking.

The content of C<sub>9</sub> aromatic compounds is lower in the product stream obtained in the cracking of dissolved plastics than in the cracking of LCO (Figure 4d), which implies that a feed with polyolefins does not contribute to the generation of these aromatic compounds on the HZSM-5 zeolite.

The result corresponding to the composition of C<sub>10</sub>-C<sub>12</sub> aromatic fraction, Figure 4e, is evidence that the cracking of dissolved PE contributes to increasing this fraction. This result and those corresponding to the other graphs of Figure 4 must be interpreted on the basis of the ability of the radicals obtained in the cracking of polyolefins to react with the heavy components of the thermal cracking of LCO. Furthermore, it is expected that the aromatic compounds C<sub>9</sub> and C<sub>10</sub>-C<sub>12</sub> will mainly come from mechanisms of alkylation-hydrogenation-cracking of the aromatic molecules contained in the LCO feed.

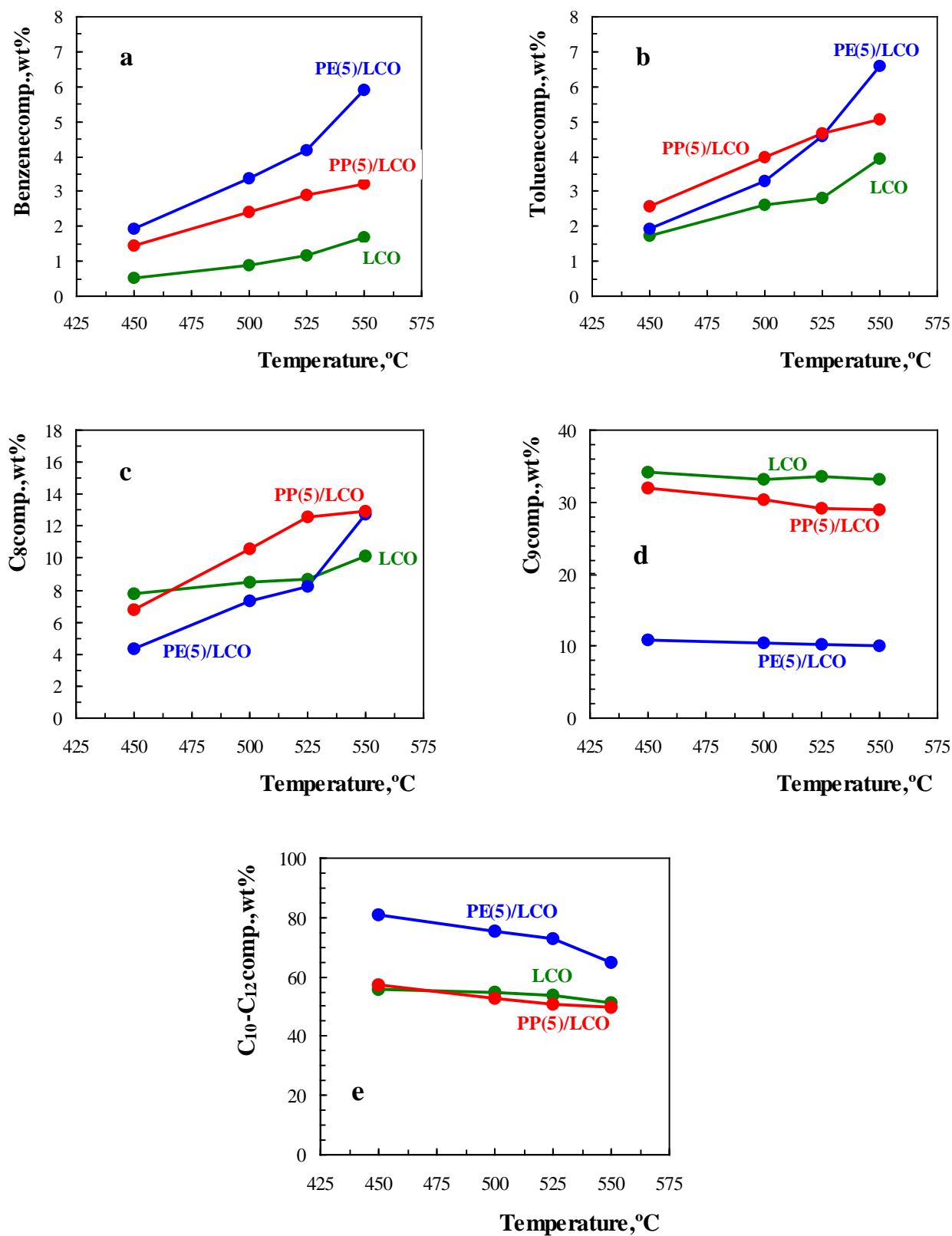


Figure 4. Effect of temperature on the composition (in wt%) of aromatic components in the C<sub>5</sub>-C<sub>12</sub> fraction of the cracking of LCO, PE(5)/LCO and PP(10)/LCO on catalyst No. 1. Graph a, benzene. Graph b, toluene. Graph c, C<sub>8</sub>. Graph d, C<sub>9</sub>. Graph e, C<sub>10</sub>-C<sub>12</sub>.

8.

### GasComposition

Figures 5, 6 and 7 show the effect of temperature on the composition of the gas fraction, for each one of the feeds. Figure 5, corresponding to the cracking of LCO, shows that at 450°C the C<sub>1</sub>-C<sub>3</sub> fraction (Figure 5a) is mainly made up of propylene and that as temperature is increased the concentration of ethylene increases and the concentrations of the gaseous paraffins are low. This increase in the concentration of ethylene is a consequence of the cracking of butenes, Figure 5b.

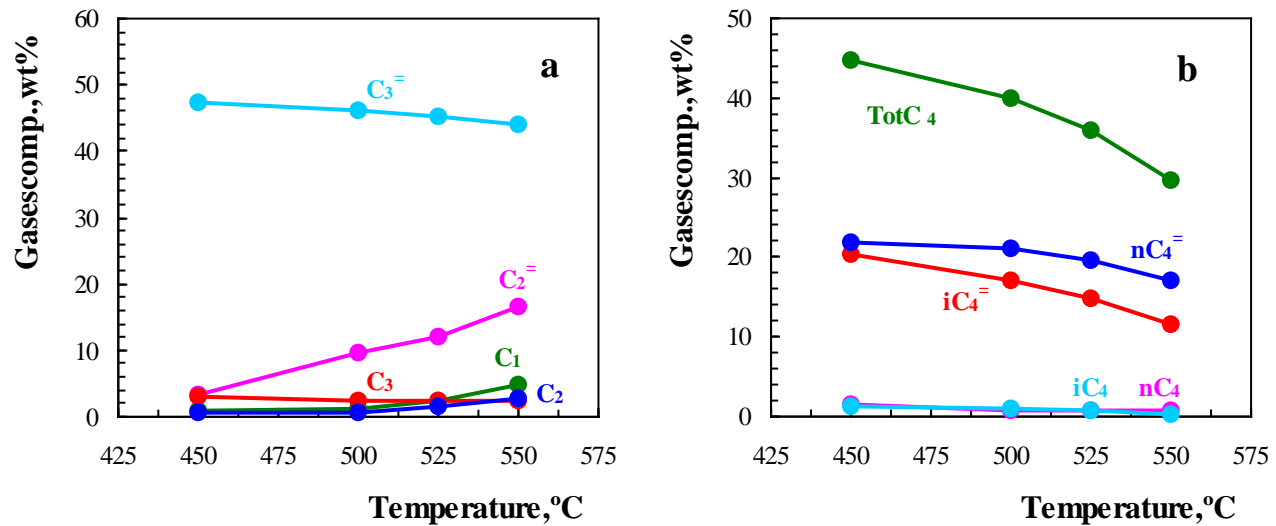


Figure 5. Effect of temperature on the composition of the gas fraction in the cracking of LCO on catalyst No. 1. Graph a, C<sub>3</sub>. Graph b, C<sub>4</sub>

In the C<sub>1</sub>-C<sub>3</sub> fraction obtained as product of the cracking of PE(5)/LCO, Figure 6a, the concentration of propylene is almost equal to that corresponding to the cracking of LCO, Figure 5a. Nevertheless, ethylene is present in a concentration of 10 wt% above 450°C. The concentration of ethylene increases with temperature, which is partially due to cracking of butenes, whose concentration decreases as temperature is increased, as is shown in Figure 6b.

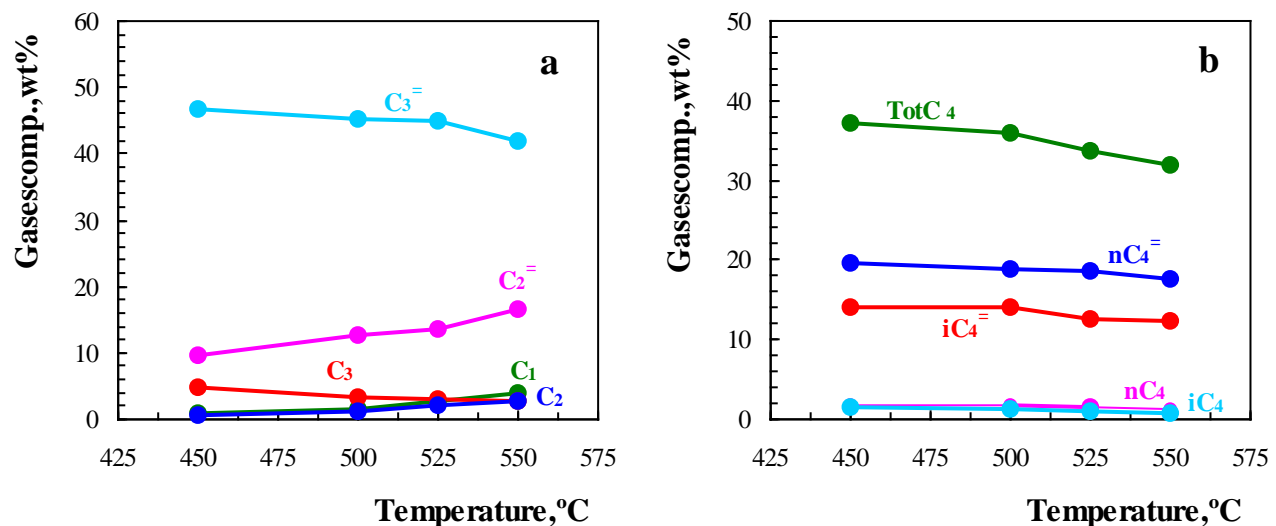


Figure 6. Effect of temperature on the composition of the gas fraction in the cracking of PE(5)/LCO on catalyst No. 1. Graph a, C<sub>3</sub>. Graph b, C<sub>4</sub>

In the cracking of PP(5)/LCO the concentration of propylene, Figure 7a, is similar to that corresponding to the previous feeds, Figures 5a and 6a, and the concentration of ethylene is similar to that obtained in the cracking of PE(5)/LCO. Likewise, the concentration of butenes decreases as temperature is increased as a consequence of the increasing the level of cracking, Figure 7b.

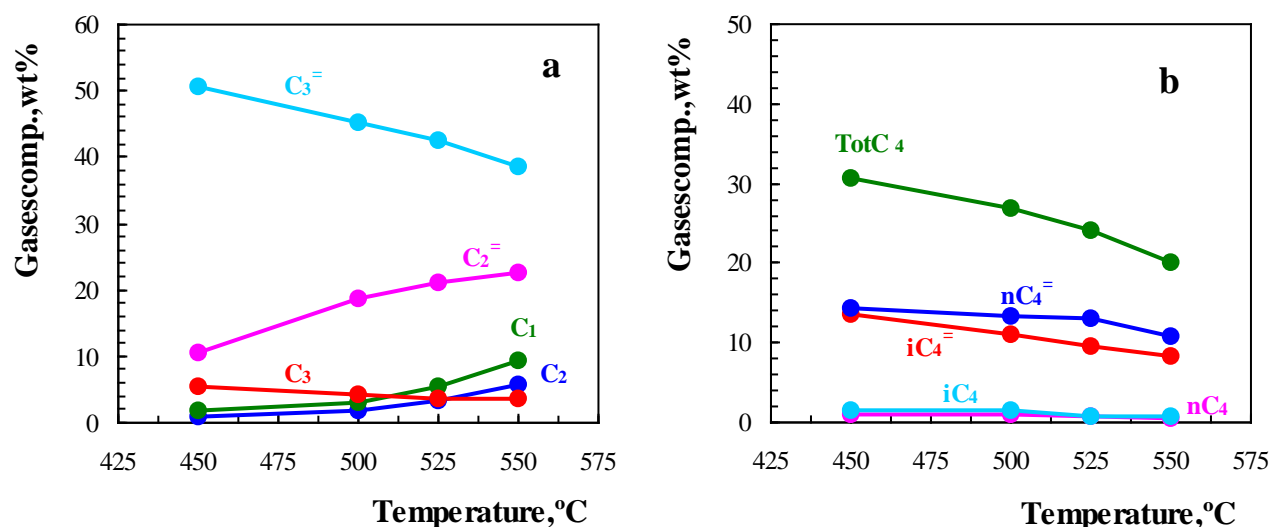


Figure 7. Effect of temperature on the composition of the gas fraction in the cracking of PP(5)/LCO on catalyst No.

1. Graph a, C<sub>3</sub>. Graph b, C<sub>4</sub>

The result obtained for the three feeds whereby the concentration of ethylene increases and that of propylene and butenes decrease as temperature is increased agrees with the well-known mechanism of oligomerization-cracking of these light olefins on HZSM-5 zeolites in order to form ethylene as the final product (Buchanan et al., 1996). Other authors have proven the high selectivity of ethylene in the cracking on HZSM-5 zeolites (Biswas and Maxwell, 1990; Buchanan and Adewuyi, 1996; Corma et al., 1996; Arandes et al., 2000). Den Hollander et al. (2002) attribute the higher ethylene yield on HZSM-5 zeolites to the small pores of this zeolite and to the associated high electrical fields and interaction with adsorbed carbenium ions.

#### 4. CONCLUSIONS

In the 450-550°C range and under conditions similar to those of commercial units of catalytic cracking, HZSM-5 zeolites only require a moderate total acidity level for being active in the transformation of polyolefins dissolved in LCO. The diffusional restriction to access into the porous structure explains that a feed made up of a mixture with a polyolefin content higher than 5 wt% reduces the cracking of the solvent. This is explained by the blockage of the access of macromolecular chains of the dissolved polyolefin to the channels of the zeolite.

The cracking on HZSM-5 zeolites of PE and PP dissolved in an aromatic LCO stream of a commercial refining unit produces a high yield of C<sub>5</sub>-C<sub>12</sub> fraction (highly aromatic) with a low yield of C<sub>1</sub> and C<sub>2</sub> gases and coke. The joint feeding of polyolefins contributes to increasing the yield of LPG, which is mainly made up of light olefins and in which the concentration of ethylene increases with temperature according to a mechanism of oligomerization-cracking. These results agree with those obtained in the literature in the cracking of heavy feeds of different compositions on HZSM-5 zeolites and in the pyrolysis of polyolefins fed in solid state into fixed and fluidized bed reactors.

A feed of dissolved polyolefins increases the yield of aromatic compounds and, to a great extent, affects the composition of this fraction, which has a higher styrene concentration and a lower C<sub>9</sub> aromatic concentration than those corresponding to the cracking of LCO.

The aforementioned results are encouraging for considering that the valorization of secondary interest feeds in the refinery, as is the case of LCO, for its use as a solvent of polyolefins in post-consumer plastic wastes is a way of upgrading both material through an optimum use of the refinery capacity.

## ACKNOWLEDGEMENTS

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