

Valorization of the Blends Polystyrene/Light Cycle Oil and Polystyrene–Butadiene/Light Cycle Oil over Different HY Zeolites under FCC Unit Conditions

José M. Arandes,* Javier Ereña, Martin Olazar, and Javier Bilbao

Departamento de Ingeniería Química, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

Gabriela de la Puente

Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (FIQ, UNL-CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

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The catalytic cracking of blends made up of polystyrene and polystyrene–butadiene with a light cycle oil (refinery stream) has been studied under the standard conditions of a FCC process. The catalysts used have been prepared based on HY zeolites of different acidity and porous structure. The results reveal the interest of the FCC process for recovering styrene and obtaining a C₅–C₁₂ pool of high aromatic content, together with a stream of olefinic gases. The presence of dissolved plastics improves conversion and yields of interesting products over that corresponding to the cracking of the solvent. The acidity of the catalyst is a limiting factor in both the catalytic activity and the formation of coke. Coke formation is largely attenuated by a steaming treatment of the zeolite, which decreases acidity and generates micropores of greater size.

1. Introduction

Thermal transformation is the method with best perspectives for the valorization of waste plastics in order to obtain fuel and feedstocks. The technology developed at the largest scale is the pyrolysis in fluidized bed of plastics fed in the solid state.^{1–4} Unfortunately, this technology presents serious problems of heat transfer and defluidization, due to the stickiness of the sand particles coated with fused plastic.⁵ The use of catalysts seeks a reduction in temperature and an improvement in product distribution, which has now provided a new stimulus⁶ for carrying out numerous studies of catalytic cracking by using mainly acid zeolites.^{7–18} When the PVC contained in the waste

plastics is not separated beforehand, a previous dechlorination step¹⁹ or a subsequent treatment of the liquid fuel obtained in the pyrolysis is required.²⁰

The FCC (fluid catalytic cracking) unit, which was originally designed for obtaining gasoline and olefins from vacuum gas-oil (VGO), has undergone numerous design modifications in order to pursue versatility for the treatment of feeds than are heavier than standard ones.²¹ Consequently, the feed of plastic blends together with standard ones is coherent with this philosophy. The short residence time of the product stream in the riser reactor of the FCC and its efficient heat transfer are suitable conditions for minimizing the secondary reactions in the cracking of plastics, which lead to undesired polyaromatic components, gaseous paraffins, and coke.²²

* Author to whom all correspondence should be addressed. Telephone: 34-94-6012511. Fax: 34-94-4648500. E-mail: iqparejs@lg.ehu.es.

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The catalytic transformation of blends of polyethylene with VGO has already been approached in the literature.²³ The transformation of blends of plastics with different low value refinery streams has important advantages over the cracking of solid plastics when continuous operation is carried out. Thus, first, the dissolved plastic is easy to feed into the reactor and the feed stream has a high heat transfer capacity. Furthermore, the fact that the reaction is carried out in a refinery allows for using the refinery equipment and the treatment of the products together with standard ones. Additionally, this strategy has the advantage of plastic transportation (of low density) if the dissolving operation is carried out at the point where municipal solid wastes (MSW) are collected and classified. Thus, the plastic material will be transported to the refinery as a liquid product. Finally, the solvent, which is transformed into products of added value, is also valorized in the same process.

In previous papers,^{24,25} the catalytic cracking of the blends polystyrene/benzene and polystyrene/light cycle oil has been studied on commercial FCC catalysts (fresh and equilibrated) and encouraging results that indicate the importance of the catalyst properties have been obtained. The aim of this paper is to study the role of the physical properties and surface acidity of the HY zeolites in the cracking of the blends polystyrene/light cycle oil and polystyrene–butadiene/light cycle oil. The two plastics fed are important in municipal solid wastes (polystyrene accounts for approximately 20 wt %) and in the rubber industry (in which polystyrene–butadiene is one of the raw materials). The main interest in the valorization of both materials is the recovery of the monomer styrene by minimizing the yield of coke, which in addition to being an undesired product (although its combustion in the regeneration section closes the energy balance in the FCC unit) is the cause of the catalyst deactivation.²⁶

2. Experimental Section

Feed. The plastics studied are polystyrene (PS) (MW, 3.116×10^5 ; polydispersity, 2.39) and polystyrene–butadiene (PS–BD) (MW, 1.843×10^5 ; polydispersity, 2.77; PBD content, 8.8 wt %) supplied by Dow Chemical S. A. By means of thermogravimetric analysis (Setaram TAG 24), the degradation ranges have been determined: 385–440 °C for PS and 405–475 °C for PS–BD. The temperature corresponding to the maximum degradation rate is 415 °C for PS and 440 °C for PS–BD, for a heating ramp of 10 °C min⁻¹. The plastic diluent agent was a light cycle oil (LCO) whose composition is detailed in Table 1. An amount of 30 wt % of the LCO corresponds to hydrocarbons with a boiling point within the range of gasoline (C₅–C₁₂). 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

Table 1. Characterization Data for LCO

		composition	wt %
density (15 °C), g/cm ³	0.9132		
sulfur, wt %	0.60	saturation	20.7
viscosity, 100 °C cSt	1.0	paraffins C _n H _{2n+2}	7.9
flash point, °C	93	monocycloparaffins C _n H _{2n}	5.6
simulated distillation, wt %	°C	dicycloparaffins C _n H _{2n-2}	2.7
I.P.	125	tricycloparaffins C _n H _{2n-4}	4.5
5	175	tetracycloparaffins C _n H _{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		

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 (25% weight of plastic) was carried out in a stirred tank at 100 °C.

Catalysts. Three catalysts have been prepared based on a commercial HY zeolite from Engelhard. This zeolite has been subjected to three different treatments with the aim of obtaining different porous structures and surface acidity levels. The zeolite named A has been obtained by ion exchange with ammonium ions in order to reduce the content of Na. The zeolite is stirred in a solution of 2.5 N NH₄NO₃ at 80 °C where the solution/zeolite mass ratio is 10. Subsequently, the steps of filtration and rinsing with distilled water are carried out and the product is calcined following a sequence of programmed temperature up to 520 °C and maintaining this temperature for 4 h. The previous steps of ion exchange and subsequent calcination are repeated three times in order to obtain a reproducible final structure.

The zeolite named B is obtained by dealumination of the commercial zeolite. The metathesis reactions involving removal of Al³⁺ in T sites followed by Si⁴⁺ substitution using aqueous ammonium hexafluorosilicate, (NH₄)₂SiF₆, are well-known.²⁷

The zeolite named C is obtained by steaming the commercial zeolite in a fluidized bed reactor of 2.7 cm internal diameter made of refractory steel. The treatment consists of successive steps of steaming at 200 °C, 540 °C, and 820 °C, for 3 h each step. Between the second and the third steps a treatment of ion exchange is carried out in a solution of NH₄NO₃ (as that aforementioned for zeolite A, but without the final calcination step).

The final catalysts, as they are to be used in the cracking reaction, are obtained by incorporating each one of these zeolites into a silica matrix. The zeolite content is 25 wt %. The silica source is Na₂SiO₃·12H₂O, where the zeolite is dispersed. The gel is formed by ammonia addition, extrusion, two-step drying (at room temperature and in an oven at 110 °C), and finally calcination in a nitrogen stream at 650 °C for 2 h. The catalysts have been named A, B, and C and correspond to the zeolites with the same denominations and whose preparation has been explained above.

The more relevant physical properties of the zeolites are set out in Table 2. The porous structure and the BET surface area have been characterized from the isotherms of adsorption–desorption of N₂ carried out in a Micromeritics ASAP 2000.

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Table 2. Properties of the HY-Zeolites

catalyst	Si/Al ratio	acidity, mmol NH ₃ g ⁻¹	Brönsted/Lewis ratio	BET surface area, m ² g ⁻¹	micropore surface, m ² g ⁻¹	mesopore volume, cm ³ g ⁻¹	micropore volume, cm ³ g ⁻¹	average micropore diameter, Å	average mesopore diameter, Å
untreated	6.4	0.15	3.55	934	802	0.03	0.31	8.8	-
A	7.8	0.72	3.68	1017	844	0.03	0.33	9.3	-
B	8.6	0.88	3.83	928	788	0.03	0.30	9.2	-
C	18.6	0.20	2.57	432	332	0.21	0.13	9.9	40

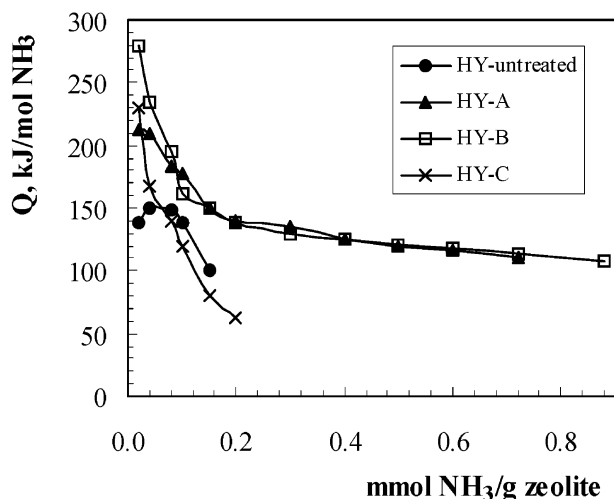


Figure 1. Distribution of acid strength of the catalysts determined by calorimetric measurement of NH₃ differential adsorption.

The micropores of the catalyst are those corresponding to the HY zeolite. The silica that makes up the matrix of the catalyst has an exclusively mesoporous structure with pores of diameter between 30 and 300 Å.

The studies of 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 by ascertaining the ratio between the intensity of the bands corresponding to 1550 cm⁻¹ (B-pyridine) and 1455 cm⁻¹ (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 740 SX);²⁸ (2) the analysis of acidic strength distribution, Figure 1, and total acidity, Table 2, by differential adsorption of NH₃, which has been carried out in a differential scanning calorimeter (Setaram DSC 111) on-line with 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 to assess the amount of base adsorbed.²⁹

Figure 1 shows the important effect of the treatment performed on the surface acidity of the zeolite. The ion exchange (zeolite A) produces a higher number of sites than the original zeolite. Furthermore, the sites formed are more acid, with an adsorption heat between 120 and 200 kJ (mol of NH₃)⁻¹. Chemical dealumination (zeolite B) produces, on one hand, strongly acid sites with an adsorption heat higher than 200 kJ (mol of NH₃)⁻¹, and on the other, moderately acid sites with an adsorption heat around 120 kJ (mol of NH₃)⁻¹. The generation of strongly acid sites involves an increase in the Brönsted/Lewis ratio over that of zeolite A, Table 2.

Dealumination by steaming (zeolite C) causes a severe deterioration of the acid structure and only a small fraction of sites maintains an acceptable NH₃ adsorption capacity. This acidity deterioration involves a significant decrease in the Brönsted/Lewis ratio, Table 2.

It has been proven that the acidity of the catalysts prepared based on the three zeolites is almost equal to that of the pure zeolites, which is evidence that the silica matrix has no significant acidity. In addition, a silica gel has been prepared independently and absence of acidity has been verified by means of the aforementioned techniques.

Reaction Equipment and Conditions. In order for the catalytic cracking results to be interesting as a test reaction of what happens in the industrial FCC unit, the experiments must be carried out under similar conditions to those of the industrial riser.³⁰ The equipment used in this work is a Reactor Riser Simulator, Figure 2. It is a Berty internal recycle reactor modified for catalytic cracking and has been previously described.³¹ The equipment is easy to operate and high bed voidages, like those of the industrial riser, are obtained. Its outstanding characteristics are (1) capacity 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 dilute fluidized bed regime with perfect mix for the catalyst and for the reaction mixture. In other words, the equipment is a discontinuous reactor of perfect mix, Figure 2. 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 thermostated at 300 °C. These products are sent through a thermostated line to a gas chromatograph by means of a six-port-valve. In previous papers, the excellent behavior of this reactor for kinetic studies of catalytic cracking has been proven.^{32,33}

The runs have been carried out at 1 atm, in the 450–550 °C range, with a catalyst/feed ratio of 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. The contact time is lower due to the expected higher activity (given its greater acidity) of the catalysts studied here than that corresponding to an equilibrated FCC catalyst, which has a very low acidity.²⁵ The low value of residence time used minimizes the contribution of thermal cracking and the reactivity of the catalytic cracking products.

Silica was used instead of the catalyst in the thermal cracking experiments. The silica used was Silicagel 60 of Merck (code 107733.1000) with a particle size between 0.2 and 0.5 mm. Prior to use, it was calcined at 873 K for 2 h in a N₂ stream. The physical properties have been determined on the basis of N₂ adsorption isotherms in a Micromeritics ASAP 2000. These properties are: BET surface area, 314 m² g⁻¹; micropore surface area, 14 m² g⁻¹; mesopore volume, 1.0 cm³ g⁻¹; and micropore volume, 0.01 cm³ g⁻¹.

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.

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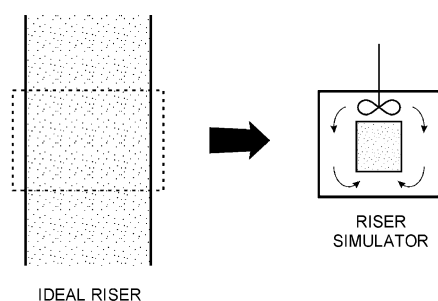


Figure 2. Diagram of the riser simulator reactor.

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 on-line 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.

To check and assign the retention times in the chromatographic analysis of compounds in the C_5 – C_{12} range, pure compounds and mixtures were used as reference standards. The assignation 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 19 paraffinic components, 35 isoparaffinic, 39 aromatic, 30 naphthenic, and 25 olefinic. The amount of (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 TAG 24 thermoanalyzer. The deactivated catalyst from the reactor is dried at 110 °C in a nitrogen stream and is subsequently subjected to combustion with air over a programmed temperature ramp (5 °C min⁻¹) up to 700 °C.

3. Results

Conversion and Yields. The conversion is defined in weight percent and calculated as the sum of the yields in weight of gases (C_1 – C_4), gasoline (C_5 – C_{12}) and coke. Each yield is calculated as:

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

The results of conversion and yields of dry gases (C_1 , C_2), LPG (C_3 , C_4), gasoline (C_5 – C_{12}), and coke are set out in Tables 3 and 4 for the feeds LCO, PS/LCO, and PS-BD/LCO. Table 3 corresponds to thermal cracking and Table 4 to results for the three catalysts. These results are average values of three experiments carried out under the same conditions, for which a maximum relative error of 0.5% is determined.

When evaluating these results, it must be taken into account that the LCO is made up of 30.0 wt % of hydrocarbons with boiling point within that of gasoline.

The results of Table 3 are evidence of high conversion and yields of the C_5 – C_{12} fraction obtained in the treatment of the blends. This operation has been studied in detail in a previous paper.³⁴ Nevertheless, when the results of Tables 3 and 4 are compared, it is observed that the conversion of LCO significantly increases when

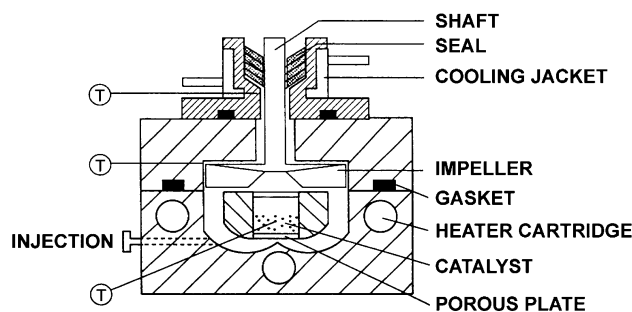


Table 3. Conversion and Yields in the Thermal Cracking of LCO and of the Dissolved Plastics, in wt % of the Total Feed

feedstock	T, K	conversion, wt %	gases, C_1 – C_4 wt %	gasoline, C_5 – C_{12} , wt %	coke, wt %
LCO	450	36.8	0.1	35.8	0.9
	500	38.0	0.5	36.6	0.9
	525	38.7	0.7	37.0	1.0
	550	39.3	1.1	37.2	1.0
PS/LCO	450	50.1	0.6	47.9	1.6
	500	55.1	1.7	51.8	1.6
	525	58.4	2.0	54.7	1.7
	550	60.6	2.5	56.4	1.7
PS-BD/LCO	450	44.2	0.5	42.3	1.4
	500	51.1	1.3	48.4	1.4
	525	56.1	2.3	52.3	1.5
	550	60.3	4.2	54.6	1.5

the catalysts with HY zeolite are used. Consequently, the main interest of a future process of the catalytic cracking of dissolved plastics lies in the cracking of both the plastic and the solvent, which must be selected according to the commercial interest of the refinery.

When the results of conversion shown in Table 4 are analyzed, an important effect of temperature on the conversion of the PS/LCO and PS-BD/LCO blends is observed, whereas this effect is lower for LCO. The conversion of PS and PS-BD contained in the blends increases significantly with temperature. Thus, at the highest temperature studied, 550 °C, the conversion of the blends with the three catalysts is significantly higher than that corresponding to LCO at this temperature. This important effect of temperature in the cracking of PS/LCO and of PS-BD/LCO shows that a high temperature is required to activate the protonation of the aromatic rings of PS.

The results of conversion corresponding to the three catalysts must be interpreted on the basis of their different properties. The conversion level of the PS/LCO and PS-BD/LCO blends corresponds to the order of total acidity of the catalysts: catalyst B > catalyst A > catalyst C. This requirement of a high level of acidity confirms that the initial step of the different mechanisms of the catalytic cracking of PS is the protonation of the aromatic rings.^{7,35–37}

Nevertheless, in the cracking of LCO, as generally in the cracking of hydrocarbons of high molecular weight, the accessibility to the active sites is the conditioning

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Table 4. Results (in wt %) of Conversion, Yields, and Selectivities of Dry Gases (C₁,C₂), LPG (C₃,C₄), Gasoline (C₅–C₁₂), and Coke Obtained in the Cracking of LCO, PS/LCO, and PS–BD/LCO on the Different Catalysts Synthesized^a

feedstock	catalyst	T, °C	conversion, wt %	C ₁ –C ₂ gases		C ₃ –C ₄ gases		gasoline (C ₅ –C ₁₂)		coke	
				Y (wt %)	S (wt %)	Y (wt %)	S (wt %)	Y (wt %)	S (wt %)	Y (wt %)	S (wt %)
LCO	A	450	56.7	0.2	0.4	1.2	2.1	48.6	85.7	6.7	11.8
		500	56.8	0.5	0.9	2.1	3.7	47.3	83.3	6.9	12.1
		525	57.0	0.7	1.2	3.3	5.8	45.9	80.5	7.1	12.5
		550	57.3	1.4	2.4	3.9	6.8	44.9	78.4	7.1	12.4
LCO	B	450	58.6	0.3	0.5	2.6	4.4	46.5	79.4	9.2	15.7
		500	61.2	1.0	1.6	4.2	6.9	45.8	74.8	10.2	16.7
		525	61.7	1.0	1.6	4.5	7.3	45.0	72.9	11.2	18.2
		550	61.9	1.4	2.3	4.7	7.6	42.8	69.1	13.0	21.0
LCO	C	450	55.4	0.5	0.9	3.6	6.5	45.6	82.3	5.7	10.3
		500	55.8	0.6	1.0	3.9	7.0	45.3	81.2	6.0	10.8
		525	57.3	1.0	1.7	4.5	7.9	45.1	78.7	6.7	11.7
		550	58.4	1.8	3.1	5.3	9.1	44.0	75.3	7.3	12.5
PS/LCO	A	450	57.5	0.3	0.4	1.7	3.0	50.4	87.7	5.1	8.9
		500	62.0	0.6	1.0	1.8	2.9	53.6	86.5	6.0	9.6
		525	65.0	0.7	1.1	2.2	3.4	55.1	84.8	7.0	10.7
		550	68.7	1.5	2.2	2.9	4.2	56.0	81.5	8.3	12.1
PS/LCO	B	450	58.0	0.6	1.0	3.1	5.3	44.3	76.4	10.0	17.3
		500	63.9	0.6	1.0	3.2	5.0	49.8	77.9	10.3	16.1
		525	66.6	1.1	1.7	3.6	5.4	50.3	75.5	11.6	17.4
		550	70.8	1.6	2.3	3.7	5.2	53.4	75.4	12.1	17.1
PS/LCO	C	450	52.7	0.3	0.6	2.7	5.1	46.3	87.9	3.4	6.4
		500	57.7	0.7	1.1	2.8	4.9	49.6	86.0	4.6	8.0
		525	60.6	1.1	1.8	3.0	5.0	51.2	84.5	5.3	8.7
		550	64.0	1.5	2.3	3.3	5.2	53.3	83.3	5.9	9.2
PS–BD/LCO	A	450	59.4	0.5	0.8	4.6	7.7	47.2	79.5	7.1	12.0
		500	65.3	0.7	1.0	4.7	7.2	52.6	80.6	7.3	11.2
		525	66.5	0.8	1.2	4.9	7.4	53.4	80.3	7.4	11.1
		550	70.1	1.3	1.9	5.1	7.3	56.1	80.0	7.6	10.8
PS–BD/LCO	B	450	63.8	0.4	0.6	4.8	7.5	47.7	74.8	10.9	17.1
		500	65.6	0.9	1.4	5.3	8.1	48.2	73.5	11.2	17.0
		525	69.1	1.5	2.2	5.7	8.2	50.7	73.4	11.2	16.2
		550	72.6	1.7	2.3	6.1	8.4	53.3	73.5	11.5	15.8
PS–BD/LCO	C	450	53.6	0.3	0.6	2.8	5.2	46.1	86.0	4.4	8.2
		500	56.8	0.6	1.1	3.1	5.4	47.1	82.9	6.0	10.6
		525	59.4	0.8	1.3	3.2	5.4	48.5	81.7	6.9	11.6
		550	66.3	1.3	2.0	3.5	5.3	53.8	81.1	7.7	11.6

^a Y = yield of lump *i*; S = selectivity of lump *i*.

factor of activity, which explains the high conversion at 550 °C reached with catalyst C (the one that is less acid and whose microporous structure is more accessible).

The fact that acidity is the factor conditioning the activity of the catalysts in the cracking of PS/LCO and PS–BD/LCO means that the cracking occurs in two steps. In the first one, the dissolved plastics undergo thermal cracking on the silica that makes up the matrix and catalytic cracking on the external surface of the zeolite crystals. In the second step, the resulting chains undergo catalytic cracking within the microporous structure of the zeolite.

In addition to this effect on conversion, the acidity of the catalyst is the determining factor on the yields of dry gases (C₁,C₂), LPG (C₃,C₄), and coke, which generally increase with acidity, whereas the yield of the gasoline fraction (C₅–C₁₂) decreases.

Furthermore, the effect of temperature is similar for the three catalysts and as temperature is increased the yield of the gasoline pool (C₅–C₁₂) decreases and that of the gases C₁–C₂, of LPG and of coke increase.

When the results shown in Table 4 for the three feeds are compared, it is observed that, when co-feeding PS and PS–BD, conversion increases over that corresponding to the cracking of LCO. This result is a consequence of the increase in the pool of gasoline. It is noteworthy

that the yield of coke in the cracking of the blends is very similar to that corresponding to the cracking of LCO. It is also observed that the composition of the feed has a great incidence on the yields.

Special attention should be paid to the coke content deposited on the catalyst. The maximum contents (for catalyst B at 550 °C) are 2.0 and 1.9 wt % for the transformation of the PS/LCO and PS–BD/LCO blends, respectively. These contents are similar to those of the FCC units operating with commercial catalysts prepared based on HY zeolites and with standard feeds. This coke content is important because thermal equilibrium in an FCC unit is maintained due to the heat generated in the combustion of the coke in the regenerator.

The aforementioned results show the great importance of catalyst properties on the selectivity to the different products in the cracking. Table 4 show the effect of temperature on the selectivity to C₅–C₁₂ fraction and to coke, for the three catalysts and for the three feeds. The selectivity has been calculated as

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

In Table 4, it is observed that the selectivity to gasoline decreases as temperature is increased for the

Table 5. Composition of the C₅–C₁₂ Fraction Obtained in the Cracking of LCO, PS/LCO, and PS–BD/LCO on Catalyst A

feedstock	T, °C	n-paraffins	i-paraffins	olefins	naphthenes	aromatics
LCO	450	4.6	6.3	6.7	2.4	80.0
	500	4.5	6.0	6.9	2.3	80.3
	525	4.5	5.9	7.2	2.2	80.2
	550	4.2	5.9	7.7	1.7	80.5
PS/LCO	450	3.7	3.7	4.2	0.9	87.5
	500	3.3	2.3	3.2	0.8	90.4
	525	2.6	2.1	3.2	0.7	91.4
	550	2.5	1.8	2.5	0.5	92.7
PS–BD/LCO	450	3.0	9.6	3.0	1.1	83.3
	500	2.7	7.7	4.8	1.0	83.8
	525	2.5	5.3	5.1	0.9	86.2
	550	2.2	3.9	5.1	0.7	88.1

three catalysts. This decrease is more important for the cracking of LCO than for the blends. Whereas the higher selectivity to gasoline in the cracking of LCO is obtained with catalyst A (the one of higher surface area), in the cracking of PS/LCO the selectivities to gasoline are similar with catalysts A and C, and in the cracking of PS–BD/LCO the higher selectivity to gasoline corresponds to catalyst C.

The good behavior of catalyst C must be attributed to the fact that its properties largely attenuate coke formation. The selectivity to coke is significantly lower for this catalyst, particularly for the cracking of PS/LCO and for the cracking at low temperature of LCO and PS–BD/LCO. This result obtained with catalyst C must be attributed, on one hand, to its lower activity (as a consequence of its lower acidity) for the mechanisms of formation of coke precursors and, on the other hand, to its porous structure having micropores that are bigger than in the other catalysts and mesopores which favors the circulation of coke precursors toward the outside of the zeolite crystals.

Additionally, the high selectivity to coke of catalyst B is attributable to its properties (high acidity, with a high site density), because its surface area is notably lower than that of catalyst A, which contributes to attenuating coke deposition on it. Furthermore, catalyst B has an important fraction of strongly acid sites, which are very active in the mechanisms of formation of coke precursors by oligomerization, Diels–Alder condensation and polycondensation.²⁶ The yield of coke is of vital importance in the economy of a future process of catalytic cracking of plastics. The increase in the yield of coke is important because it means a decrease in the selectivity to commercial products and because of the effect that it may have on the deactivation of the catalyst. Nevertheless, in the FCC process, the combustion of coke in the regeneration section provides the heat required for the heat balance of the unit, which means that the coke content should not vary significantly from the standard amount in industrial units.^{38,39}

Conversion and Apparent Yields of the Dissolved Plastics. For the purpose of determining the yields of the different lumps of products and the conversion (sum of the yields) of the plastic contained in the mixture, the apparent yield of each lump obtained from the plastic has been calculated. This has been achieved by using results obtained for the yields of transforma-

tion of LCO and by assuming that these yields remain constant when the mixture is transformed:

$$\begin{aligned} \text{yield of lump } i \text{ for the blend} = \\ (\text{yield of lump } i \text{ from LCO}) 0.75 + \\ (\text{apparent yield of lump } i \text{ from the plastic}) 0.25 \quad (3) \end{aligned}$$

By substituting the results of Table 4 in eq 3, it is clear that the higher apparent yield of the dissolved PS and PS–BD is that corresponding to the lump of gasoline (C₅–C₁₂), and it significantly increases as the reaction temperature is increased, up to 89.3 wt % for PS and 89.7 for PS–BD, at 550 °C and for catalyst A. The apparent conversions of the plastics (calculated by summation of the apparent yields of the lumps of products) at this temperature are 102.9 wt % for PS and 108.5 wt % for PS–BD and for catalyst A. The result of apparent yields higher than 100 means that the presence of plastic in the blend has a synergistic effect on the transformation of LCO.

It is also noteworthy that a higher apparent yield of lump C₅–C₁₂ is obtained for both dissolved plastics when the catalyst of higher surface area (catalyst A) is used. Nevertheless, the lower apparent yield of coke is obtained with catalyst C (1.7 wt % by feeding PS and 8.9 wt % by feeding PS–BD), which is explained by the greater mobility of coke precursor intermediates within the internal channels of the catalyst.

C₅–C₁₂ Composition. Table 5 shows the composition of the C₅–C₁₂ fraction obtained in the cracking of LCO, PS/LCO, and PS–BD/LCO. The results correspond to catalyst A. The results corresponding to the other catalysts are qualitatively similar.

Although the content of aromatics in the C₅–C₁₂ fraction obtained in the cracking of LCO is high, around 80 wt %, and independent of temperature, the presence of plastics in the feed notably increases this content. The content of aromatics in the cracking of PS/LCO and PS–BD/LCO increases as temperature is increased, up to 92.66 wt % and 88.12 wt %, respectively, at 550 °C. This result shows the important contribution of the dissolved plastics to the generation of aromatics and the low yield of the remaining components of the C₅–C₁₂ fraction. The inhibition in the formation of olefins and naphthenes is noteworthy and is explained by the reactivity of these compounds with the cations of PS to form indanes and indenenes, which due to their high boiling point are not considered in the C₅–C₁₂ fraction.³⁵

Given the important aromatic content of the C₅–C₁₂ fraction, the potential interest for the valorization of the blends studied in this paper may lie in the separation

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(39) Arandes, J. M.; Abajo, I.; Fernández, I.; López, D.; Bilbao, J. *Ind. Eng. Chem. Res.* **1999**, *38*, 3255–3260.

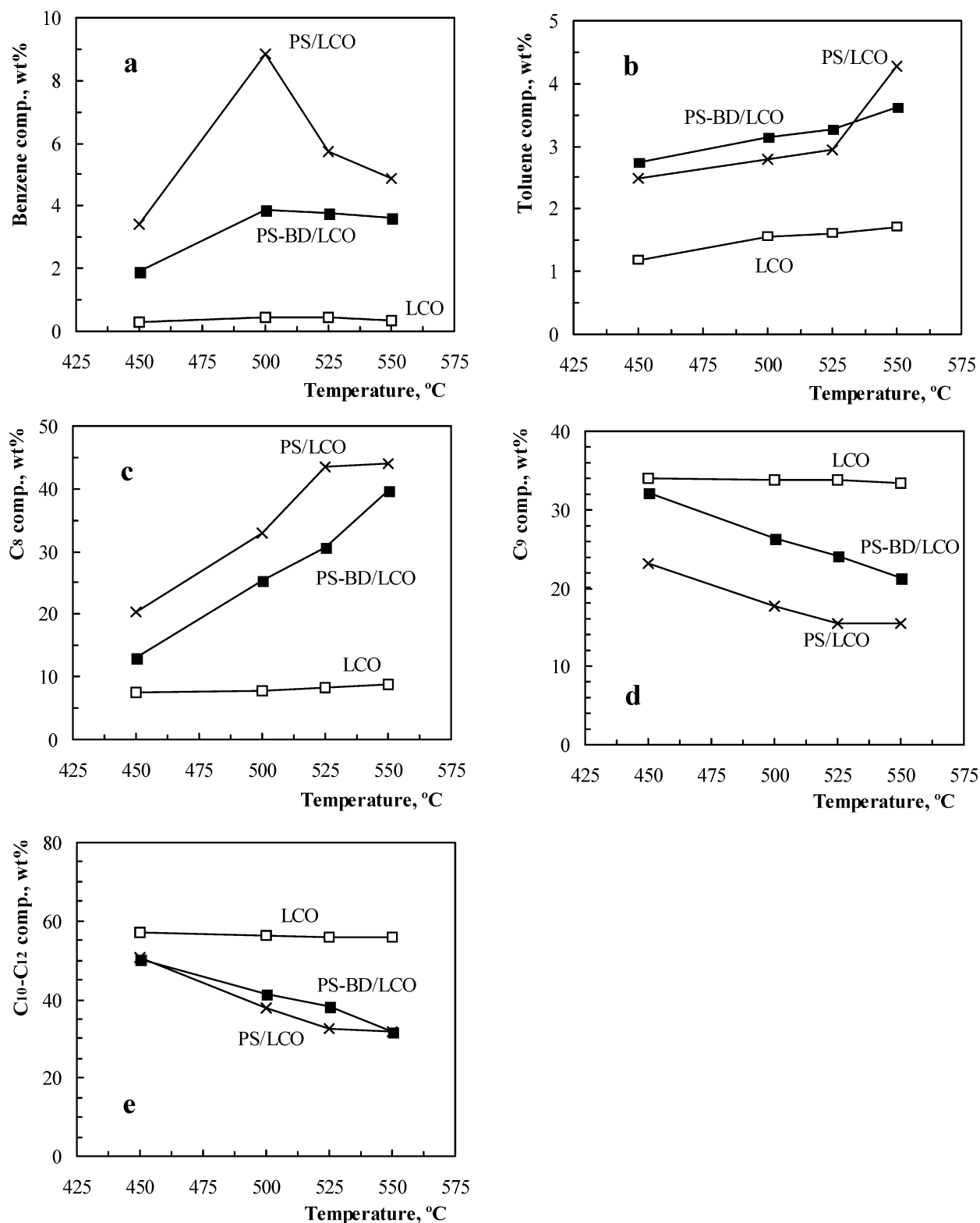


Figure 3. Effect of temperature on the composition (in wt %) of the aromatic components of the C₅–C₁₂ fraction obtained in the cracking of LCO, PS/LCO, and PS–BD/LCO on catalyst A. (a) Benzene, (b) toluene, (c) C₈, (d) C₉, (e) C₁₀–C₁₂.

of these aromatics, whose commercial interest is expected to increase over the next decade.⁴⁰ Figure 3 shows the effect of temperature on the composition, in wt %, of different components and lumps of the fraction of aromatics of the C₅–C₁₂ product stream obtained in the cracking of LCO, PS/LCO, and PS–BD/LCO.

In these results, the importance of the effect of co-feeding plastics and of the cracking temperature is

noteworthy. For the cracking of PS/LCO and PS–BD/LCO, the concentration of toluene (Figure 3b) and the concentration of C₈ fraction (Figure 3c), which is mainly made up of the monomer styrene, increase almost linearly as temperature is raised. The concentra-

(40) Weitkamp, J.; Raichle, A.; Traa, I. *Appl. Catal.* **2001**, 222, 277–297.

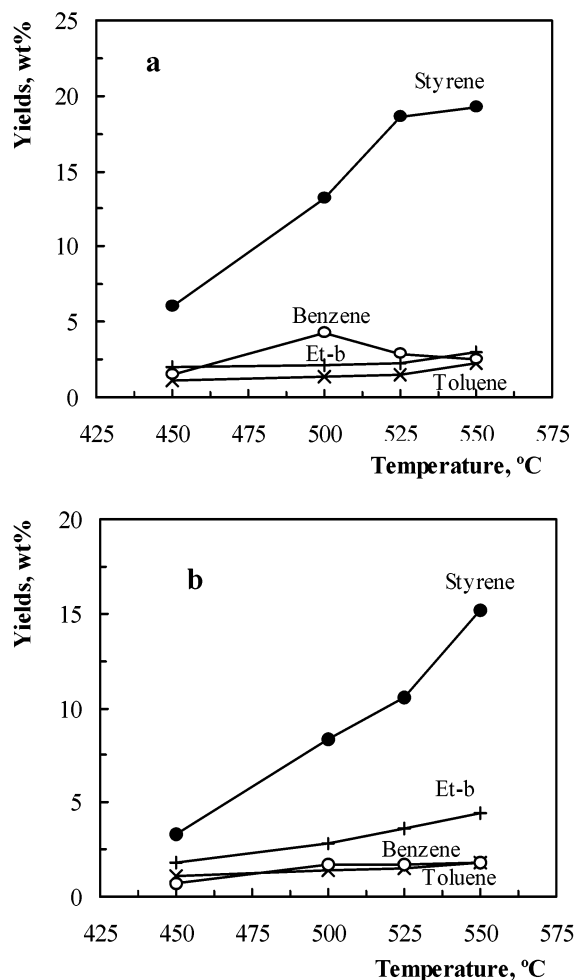


Figure 4. Effect of temperature on the yields of the aromatic components of the gasoline fraction on catalyst A. (a) PS/LCO, (b) PS-BD/LCO.

tion of the fractions C_9 (Figure 3d) and C_{10} – C_{12} (Figure 3e) decreases as temperature is increased and the concentration of benzene (Figure 3a) peaks at 500 °C.

The increase in the yield of styrene with temperature and the attenuation in the formation of benzene are explained by a change in the cationic mechanisms of PS decomposition, which have alternative paths for obtaining stable products, among which there is benzene and styrene. The results show that as temperature is increased, the formation of styrene is favored by β -scission of intermediate macrocations, which are formed by successive protonations. This mechanism has a higher activation energy than the direct formation of benzene by decomposition of ortho-protonated aromatic rings in the polymer chain, which has been proven in the literature to be significant above 130 °C.³⁵

Figure 4 shows the yield of the aromatic components obtained in the cracking of PS/LCO (Figure 4a) and of PS-BD/LCO (Figure 4b). The yield of styrene at 550 °C is 76.92 wt % of the PS fed in the PS/LCO blend and 66.49 wt % of that contained in the PS-BD/LCO blend. It must be pointed out that almost all the styrene comes from the cracking of PS, because it has been proven that the content of styrene in the aromatic fraction of the products obtained in the cracking of LCO is insignificant.

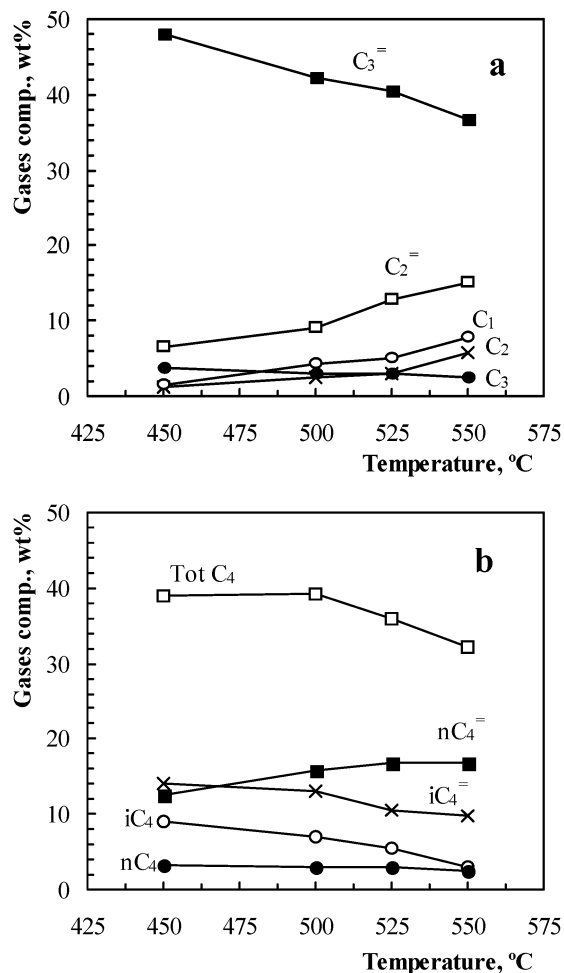


Figure 5. Effect of temperature on the composition of the fraction of gases obtained in the cracking of LCO on catalyst A. (a) C_3 , (b) C_4 .

This high yield of styrene is greater than that obtained in the literature in the thermal pyrolysis of PS, when this is fed as a pure component in solid state. Thus, in fixed bed, Zhang et al.⁷ obtained a yield of 56 wt % at 350 °C. In fluidized bed, Kaminsky¹ obtained 64.9 wt % at 580 °C, and Aguado et al.⁴¹ obtained 64.5 wt % in a conical spouted bed in the 450–500 °C range.

The high level of monomer recovery must be attributed to the process conditions and to the shape selectivity of the catalyst. Both factors minimize the undesired secondary reactions. Thus, given the short contact time, secondary reactions between the primary products of thermal and catalytic cracking are minimized. The secondary reactions between the primary products and the fused plastic, which are important in the pyrolysis of plastics when they fed in the solid state, are also avoided.

Gas Composition. Figures 5, 6, and 7 show the effect of cracking temperature on the composition of the total gas fraction (C_1 – C_2 and LPG fractions), for each one of the feeds. In Figure 5 corresponding to the cracking of LCO, it is observed that at 450 °C the C_1 – C_3 fraction (Figure 5a) is mainly made up of propylene and that, as temperature is increased, the concentration of propylene decreases, that of ethylene increases and the

(41) Aguado, R.; Olazar, M.; Gaisán, B.; Prieto, R.; Bilbao, J. *Chem. Eng. J.* **2003**, *92*, 91–99.

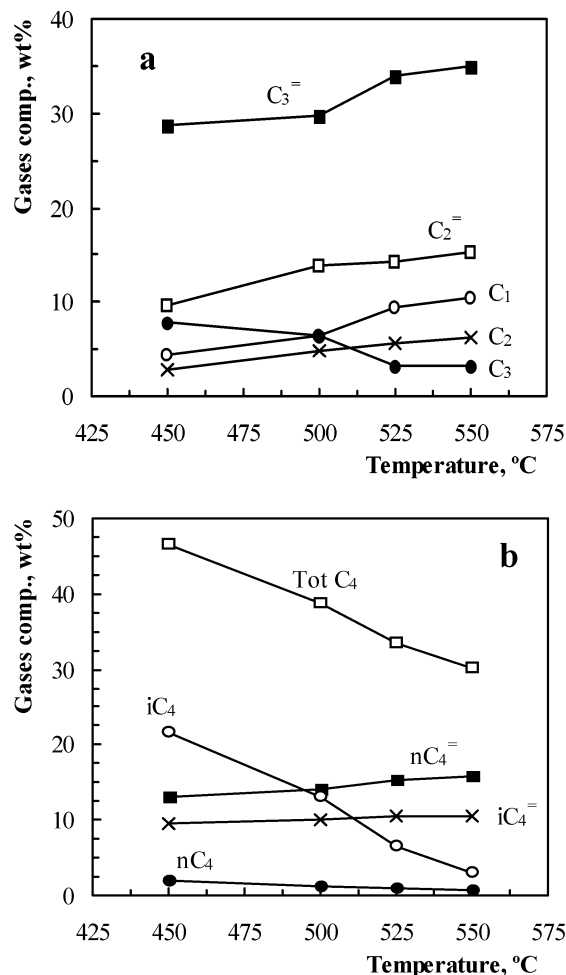


Figure 6. Effect of temperature on the composition of the fraction of gases obtained in the cracking of PS/LCO on catalyst A. (a) C₃, (b) C₄.

concentrations of gaseous paraffins are maintained at low values. This increase in the concentration of ethylene is attributed to the cracking of butenes (especially *i*-butene, because it is more crackable than the linear butenes), whose concentration decreases as temperature is increased, as is shown in Figure 5b. The mechanism of oligomerization-cracking of propylene may also contribute to the formation of ethylene.⁴²

In the gas obtained in the cracking of PS/LCO the concentration of propylene (Figure 6a) is slightly lower than that corresponding to the cracking of LCO (Figure 5a). Nevertheless, the concentration of ethylene is higher and that of *i*-butane is especially important (22 wt %) at 450 °C (Figure 6b). The concentrations of propylene and of ethylene increase as temperature is raised (Figure 6a) as a consequence of cracking of *i*-butane, whose concentration decreases as temperature is increased (Figure 6b). The hydrogen transfer capacity on the HY zeolites contributes to transformation of gaseous paraffins into olefins in the cracking of *i*-butane.

In the cracking of PS-BD/LCO, the absence of butadiene in the product stream is noteworthy. The concentration of propylene (Figure 7a) is higher than that corresponding to the previous feeds (Figures 5a and 6a) and decreases as temperature is increased. The concen-

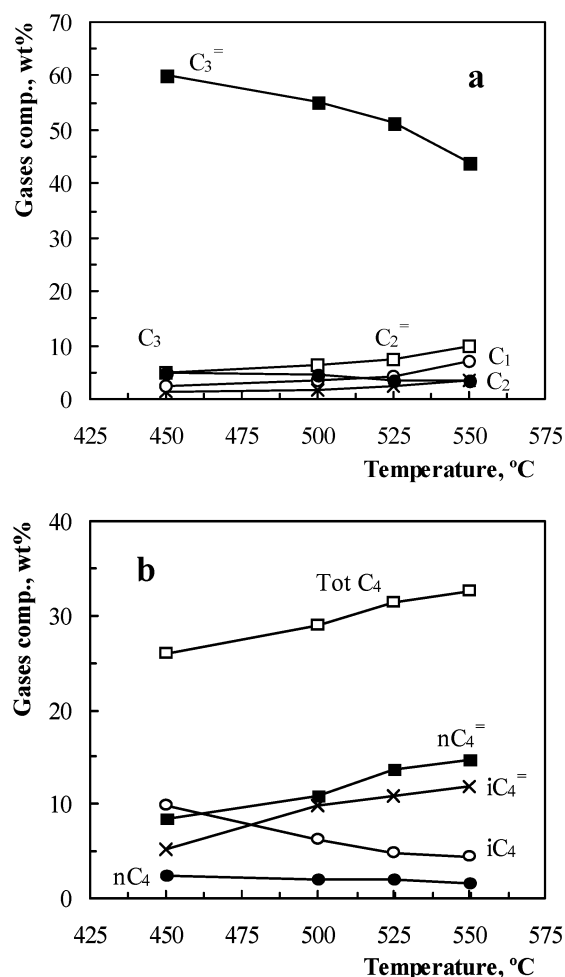


Figure 7. Effect of temperature on the composition of the fraction of gases obtained in the cracking of PS-BD/LCO on catalyst A. (a) C₃, (b) C₄.

tration of ethylene is lower than that in the cracking of PS/LCO and increases as temperature is increased. This concentration and the one corresponding to butenes (*n*- and *i*-, Figure 7b) increase as temperature is increased.

This result obtained for the cracking of PS-BD/LCO shows the reactivity of butadiene under the process conditions. The capacity for both cracking and hydrogen transfer of the HY zeolite favors the formation of butenes, propylene and ethylene.

4. Conclusions

The cracking of the blends made up of PS and PS-BD with LCO under standard conditions of FCC units is an interesting method for valorization of both residual feeds to obtain a high yield in the recovery of the monomer styrene.

The yield of the C₅-C₁₂ pool obtained in the product stream is high, with a high aromatic content, and this yield is increased over that corresponding to the cracking of LCO by co-feeding PS and PS-BD. Furthermore, by co-feeding PS, the yield of coke is lower than that corresponding to LCO, whereas by co-feeding PS-BD it is similar.

The physical properties and surface acidity of the HY zeolite play an important role in the selectivity of the

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cracking of plastic/LCO blends. The reactivity order of the catalyst follows that of total acidity. Nevertheless, a high acidity provokes a higher level of coke deposition and a higher selectivity to dry gases and LPG.

Coke deposition is attenuated by a severe steaming treatment and, although it provokes an important deterioration of catalyst acidity, the residual acidity is sufficient for attaining a high level of conversion of the blends under the operating conditions of FCC units.

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