

Valorization of the Blends Polystyrene/Light Cycle Oil and Polystyrene–Butadiene/Light Cycle Oil over HZSM-5 Zeolites

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

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

Danilo López-Valerio

Facultad de Ingeniería Química, Universidad Nacional de Ingeniería, Apartado 5595, Managua, Nicaragua

Gabriela de la Puente

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

The conversions and yields of the fractions of gases (C_1 , C_2), LPG (C_3 , C_4), gasoline (C_5 – C_{12}), and coke and their compositions have been studied in the catalytic cracking of blends made up of polystyrene and polystyrene–butadiene with a LCO (light cycle oil, which is a secondary refinery product) used as the solvent. The catalysts were prepared from HZSM-5 zeolites of different total acidities. The reaction was carried out in the 450–550 °C range and under the standard conditions of FCC units. The important effects both of the total acidity of the zeolite and of the temperature on the conversion and yield of styrene are demonstrated. Total recovery of the monomer styrene is attained at 550 °C. Likewise, the LCO is valorized, as high yields of both the C_5 – C_{12} aromatic fraction and LPG (olefinic) are obtained with low yields of gases (C_1 , C_2) and coke.

1. Introduction

The high amount of post-consumer plastics in developed countries (estimated at 50 million tons in 2001, with an annual increase of 4 wt %) is an environmental problem and, at the same time, a problem of raw material waste that requires an urgent solution once energy recovery by combustion has been discarded because of environmental regulations.

The goal in plastic waste recycling is the implementation of an economically viable technology to obtain useful chemicals. Pyrolysis is the tertiary recycling method that provides the most helpful results and that can treat all plastics together, thus avoiding separation costs. The studies in the literature are focused on partially solving some of the following problems: (1) the diverse composition of waste plastics resulting from their different origins (municipal, packaging, agricultural, automotive, and electrical); (2) the difficulty in handling the plastic materials, which are sticky at their melting points and have low thermal conductivities; and (3) the control of the pyrolysis products to lead the reaction toward the generation of monomers, feedstock, or fuels. The aforementioned difficulties partially explain the great divergence in the kinetic results of pyrolysis and the lack of kinetic results at the high temperatures required for useful products to be obtained.

The physical difficulties in the pyrolysis of waste plastics have been partially solved with the technology based on the fluidized bed reactors,^{1–4} although other reactors that attempt to eliminate the stickiness and agglomeration of particles coated with fused plastic have been proposed.^{5–10}

* To whom correspondence should be addressed. Telephone: +34-946012511. Fax: +34-944648500. E-mail: iqpaesj@lg.ehu.es.

Furthermore, thermal pyrolysis produces a wide distribution of products, and the selectivity to useful products can be increased by the use of acid catalysts. Catalytic transformations have been carried out following different strategies: on-line catalytic transformation of the gaseous products obtained in the thermal pyrolysis,^{11,12} catalytic transformation of the liquid obtained in the thermal pyrolysis,^{13,14} and degradation of the plastic mixed with the catalyst.^{15–17}

The economic viability of plastic waste valorization requires improvements in both the technology of pyrolysis reactors and knowledge of the kinetic behavior of the catalysts, which implies the solution of problems such as deactivation and regeneration. However, a very important point concerns the future integration of the pyrolysis process in the operations of the petrochemical industry, so that reaction and separation equipment can be used and capital costs saved.^{18,19} This objective follows the present trend in the petrochemical industry based on the improvement of its economy through the valorization of streams of secondary interest to the refineries themselves.

In this paper, the valorization by catalytic transformation of polystyrene (PS) and polystyrene–butadiene (PS–BD) dissolved in LCO (light cycle oil) has been studied on HZSM-5 zeolites. The LCO is a product stream of FCC (fluid catalytic cracking) units with a high aromatic content whose boiling point range is higher than that of the gasoline fraction. In a previous paper, an interesting synergistic effect was found in the catalytic cracking of LCO when either polyethylene or polypropylene was fed.²⁰ The catalytic cracking of polyolefins dissolved in vacuum gas-oil has already been studied.²¹

Here, the catalytic transformation is studied under the usual conditions (temperature, contact time, catalyst/

Table 1. Characterization Data for LCO

		composition	wt %
density, 15 °C (g/cm ³)	0.9132	saturates	20.7
sulfur (wt %)	0.60	paraffins C _n H _{2n+2}	7.9
viscosity, 100°C (cSt)	1.0	monocycloparaffins	5.6
flash point (°C)	93	C _n H _{2n}	
simulated distillation (wt %)	temp (°C)	dicycloparaffins	2.7
IP	125	C _n H _{2n-2}	
5	175	tricycloparaffins	4.5
10	187	C _n H _{2n-4}	
20	203	tetracycloparaffins	0.0
30	219	C _n H _{2n-6}	
40	231	aromatics	66.9
50	249	monocyclic	33.0
60	264	dicyclic	33.1
70	282	tricyclic	0.8
80	302		
90	329	sulfur compounds	12.4
95	350	thiophenes	0.4
EP	390	benzothiophenes	12.0

oil ratio) of industrial FCC units. These conditions are suitable for obtaining useful products by pyrolyzing plastics, because they minimize secondary reactions. Furthermore, from the results obtained under these conditions, the possibility of using the well-developed FCC technology for treating mixtures such as plastic/LCO or feeds made up of such mixtures with a suitable proportion of the usual FCC feed can be analyzed.

The interest in studying catalysts prepared from HZSM-5 zeolites lies in the need to achieve a balance between properties such as activity, selectivity, and resistance and deactivation. Acid catalysts lower the activation energy of the pyrolysis of PS by changing the mechanism. Thus, in the thermal process, pyrolysis occurs via free radicals, whereas in the catalytic process, pyrolysis occurs following several steps that start with the protonation of aromatic rings.^{12,16} The shape selectivity of the HZSM-5 zeolite limits the formation of indenenes and indanes. This restriction in the formation of polyaromatic structures, which are coke precursors, minimizes coke formation. In the pyrolysis of polyolefins, it has been shown that the deactivation of HZSM-5 zeolite is lower than that of HY zeolite.²² Deactivation by coke might be a conditioning factor in the selection of the catalyst for this process, because both the solute and the solvent in the PS/LCO and PS-BD/LCO blends have an aromatic nature that favors coke formation.

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 (polybutadiene) content, 8.8 wt %] supplied by Dow Chemical S.A. By means of thermogravimetric analysis (Setaram TAG 24), the degradation ranges were determined to be 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 LCO (light cycle oil), whose composition is shown in Table 1. As can be seen, 30.0 wt % of the LCO is made up of hydrocarbons with boiling points in the range of gasoline (C₅–C₁₂). This solvent was 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 separate identification of 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 (25 wt % plastic) was carried out in a stirred tank at 100 °C.

Catalysts. Three catalysts based on HZSM-5 zeolite were prepared with different Si/Al ratios (Si/Al = 24, 42, and 78). The method followed is that indicated in the Mobil patents.^{23,24} The zeolite is agglomerated with an inert matrix made up of silica gel, which is prepared by a conventional method of precipitation from sodium silicate.²⁵ The catalysts are calcined at 600 °C for 4 h in a N₂ 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.²⁶

The more relevant physical properties of the catalysts are reported in Table 2. The porous structures and surface areas (BET) of the catalysts were characterized from N₂ adsorption–desorption isotherms measured with a Micromeritics ASAP 2000 instrument. The micropores of the catalyst correspond to the pores of the HZSM-5 zeolite, which are formed as two different elliptical channels that cross perpendicularly, with some arranged in a straight line (5.3 × 5.6 Å) and others in zigzag formation (5.1 × 5.5 Å). The silica that makes up the matrix of the catalyst has an exclusively mesoporous structure containing pores with diameters of between 30 and 300 Å.

The acidity studies included the following measurements: (1) The Brønsted/Lewis acid site ratio (Table 2) was determined by analyzing FTIR spectra of the adsorption of pyridine at 250 °C and ascertaining the ratio between the intensity of the bands corresponding to B-pyridine (1550 cm⁻¹) and L-pyridine (1455 cm⁻¹). This study was 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).²⁷ (2) The acidity strength distribution (Figure 1) and total acidity (Table 2) were determined by the differential adsorption of NH₃, which was carried out in a differential scanning calorimeter (Setaram DSC 111) on-line with a Hewlett-Packard 6890 gas chromatograph. The calorimeter was used to evaluate the adsorption heat (heat associated with the neutralization of the acidic sites) of pulses of the base (at 150 °C), and the chromatograph was used to assess the amount of base adsorbed.²⁸

Table 2. Physical Properties of the Catalysts

catalyst	Si/Al ratio in HZSM-5 zeolite	acidity (mmol of NH ₃ g ⁻¹)	Brønsted/Lewis site ratio	BET surface area (m ² g ⁻¹)	micropore surface area (m ² g ⁻¹)	pore volume (cm ³ g ⁻¹)	micropore volume (cm ³ g ⁻¹)	micropore diameter (Å)	mesopore diameter (Å)
1	24	0.15	3.63	200	106	0.55	0.058	5.5	30–300
2	42	0.10	3.40	195	101	0.54	0.059	5.5	30–300
3	78	0.04	2.86	181	87	0.52	0.058	5.5	30–300

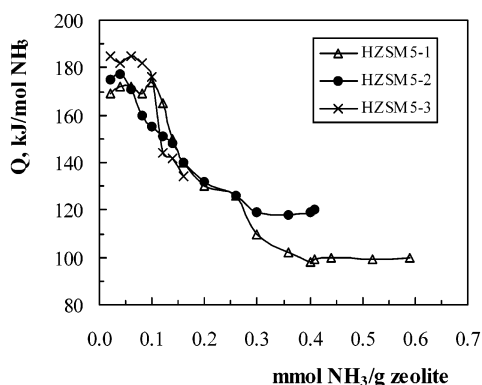


Figure 1. Distributions of the acid strength of the catalysts determined by calorimetric measurements of the differential adsorption heat of NH_3 .

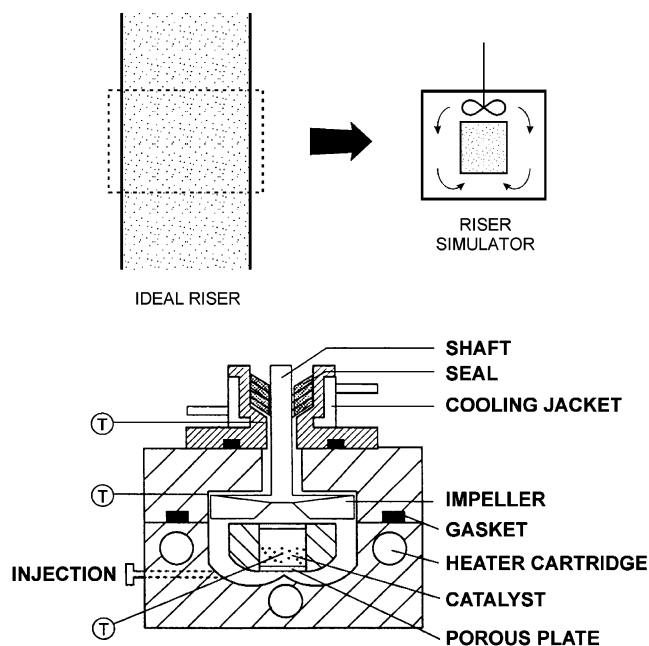


Figure 2. Scheme of the reactor riser simulator.

It has been shown that the acidities of catalysts prepared using the three HZSM-5 zeolites are almost identical to those of pure zeolites, which is evidence that the silica matrix has no significant acidity. By analyzing the acidity of a silica gel prepared independently by the aforementioned techniques, it was confirmed that the acidity of the silica is insignificant.

In Figure 1, one can see that the Si/Al ratio barely affects the acidity strength of the sites of the HZSM-5 zeolites, which is around $110 \text{ kJ} (\text{mol of } \text{NH}_3)^{-1}$ at the adsorption temperature used, 150°C . Nevertheless, when the Si/Al ratio is increased, the total acidity measured as the amount of NH_3 adsorbed at 150°C is noticeably affected.

Reaction Equipment and Conditions. In order for the results of catalytic cracking to be interesting as a test of the reaction in industrial FCC units, the experiments must be carried out under conditions similar to those of an industrial riser.²⁹ The equipment used in this work is a reactor riser simulator (Figure 2). It is an internal recycle reactor modified for catalytic cracking and has been previously described.^{30–32} The equipment is easy to run, and the operation bed voidage is high, as in the industrial riser. Its outstanding characteristics are (1) operation with low and precise values

of the contact time in the range 1–10 s and (2) a suitable feed-catalyst contact, as the reaction occurs in the dilute fluidized bed regime with perfect mixing 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 of the reactor. At time zero, 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 into 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. The reliable behavior of this reactor for the kinetic study of catalytic cracking has been demonstrated in previous papers.^{33,34}

The runs were carried out at 1 atm, in the $450\text{--}550^\circ\text{C}$ range, with a catalyst/feed ratio by weight of C/O = 6 (0.75 g of catalyst and 0.125 g of blend) and with a contact time of 3 s. These conditions correspond to those of industrial FCC units. The low value of the contact time used minimizes the contributions of both thermal cracking and secondary reactions between the primary products obtained in thermal and catalytic pyrolysis.

Silica was used instead of the catalyst in the experiments on thermal cracking. The silica used was Silicagel 60 from Merck (code 107733.1000) with a particle size between 0.2 and 0.5 mm. Prior to its use, the silica was calcined at 873 K for 2 h in a N_2 stream. The physical properties were determined on the basis of N_2 adsorption isotherms in a Micromeritics ASAP 2000 instrument. These properties are as follows: BET surface area, $314 \text{ m}^2 \text{ g}^{-1}$; micropore surface area, $14 \text{ m}^2 \text{ g}^{-1}$; mesopore volume, $1.0 \text{ cm}^3 \text{ g}^{-1}$; micropore volume, $0.01 \text{ cm}^3 \text{ g}^{-1}$.

Product Analysis. Product analysis was 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 the contact time.

Product identification was carried out on-line by GC-FTIR spectroscopy using the Nicolet/Aldrich library, by means of an 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). The product stream of the riser simulator was analyzed on-line with MS or FTIR spectroscopy.

To check and assign the retention times in the chromatographic analysis of compounds in the $\text{C}_5\text{--}\text{C}_{12}$ range, pure compounds and mixtures were used as standards. The assignment of the retention times of the components of the gasoline lump was carried out using Alphasgaz PIANO (Air Liquide) calibration standards, which consist of 19 paraffinic, 35 isoparaffinic, 39 aromatic, 30 naphthenic, and 25 olefinic components. The amount of the ($\text{C}_5\text{--}\text{C}_{12}$) lump was determined as that corresponding to the components with boiling points between those of *n*- C_5 paraffins (*n*-pentane) and *n*- C_{12} paraffins (*n*-dodecane). The relative error of the chromatographic results obtained in various series of five experiments under the same conditions is $\pm 1.0\%$.

The coke deposited on the catalyst was measured by thermogravimetric analysis in a Setaram TAG 24 thermoanalyzer. The deactivated catalyst from the reactor was dried at 110°C in a nitrogen stream and subsequently subjected to combustion with air at a programmed temperature ramp of 5°C min^{-1} to 700°C .

Table 3. Conversions and Yields (wt %) in the Thermal Cracking of LCO and of the Dissolved Plastics of the Total Feed

feedstock	<i>T</i> (°C)	conversion (wt %)	gases, C ₁ –C ₄ (wt %)	gasoline, C ₅ – (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

Prior to combustion in the thermogravimetric equipment, the catalyst was subjected to a sweeping step in a He stream for 30 min at 550 °C.

When the mass balance was performed with the experimental results of yields of the different lumps, the sum of the products was in all cases above 99.5 wt % of that in the feed. Consequently, the maximum experimental error is 0.5 wt %. To show the results on a basis of 100%, this small difference is assigned to the different lumps in proportion to their experimental yields.

3. Results

Conversion and Yields. The conversion is defined in weight percent and is calculated as the sum of the yields in weight of gases (C₁–C₄), gasoline (C₅–C₁₂), 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 (C₁, C₂), LPG (C₃, C₄), gasoline (C₅–C₁₂) and coke are reported 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 % hydrocarbons with boiling points in the range corresponding to gasoline.

The results in Table 3 are evidence of the high conversions and yields of the C₅–C₁₂ fraction obtained in the treatment of the blends. This operation was studied in detail in a previous paper.³⁵ Nevertheless, when the results of Tables 3 and 4 are compared, it can be seen that the conversion of LCO significantly increases when catalysts with HZSM-5 zeolite are used. Consequently, the main interest for a future process involving the catalytic cracking of dissolved plastics lies in the cracking of both the plastic and the solvent, which must be chosen according to the commercial interests 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. This

result shows that the conversion of PS and of PS–BD contained in these blends is much lower than that of the solvent at low temperatures and that it significantly increases with temperature. Thus, at the highest temperature studied, 550 °C, the conversions of the PS/LCO blend for the three catalysts are even higher than those corresponding to LCO at this temperature. Nevertheless, the maximum conversion of the PS–BD/LCO blend is lower than the maximum conversion of LCO.

The important effect of temperature in the cracking of PS/LCO is evidence of the need for a higher temperature to activate the protonation of PS aromatic rings.

The difference in the results between the catalytic cracking of PS/LCO and that of PS–BD/LCO cannot be attributed to the deactivation of the catalyst because the yields of coke for the PS–BD/LCO blend are very similar to those for the PS/LCO blend. Consequently, this difference must be attributed to a higher stability of PS–BD against electrophilic attack and to the protonation of the phenolic groups that generate the intermediate cationic complexes in the cracking mechanisms. In other words, the mechanism of cracking by the generation of free radicals, which is characteristic of thermal cracking, is more important with PS–BD/LCO than with PS/LCO. This mechanism explains the high formation of gases (C₁, C₂) in the cracking of the PS–BD/LCO blend.

The different effects of catalyst acidity (Table 2) on the cracking of the three feeds is noteworthy. The conversion of LCO is only slightly affected by catalyst acidity, which is explained by the high activity of the HZSM-5 zeolite in the cracking of hydrocarbons of high molecular weight. Although the access of the reactants to the porous structure of the HZSM-5 zeolite is largely restricted by the small size of the channels (5.1 × 5.6 Å), the high conversion is explained by the contribution to cracking of the external acid sites of the zeolite crystals. These sites can crack naphthenes, olefins, high-molecular-weight paraffins, and side chains and connecting chains in aromatic rings, but they cannot crack these rings. The high yield of the gasoline fraction C₅–C₁₂ in the cracking of LCO, even with catalyst 3 of lower total acidity, shows that a moderate acidity is sufficient for cracking LCO. It must be taken into account that the acidity of catalyst 3 is much higher than that of commercial cracking catalysts used in FCC units. Although this catalyst has been used in successive reaction–regeneration cycles, a residual acidity remains that is sufficient for gas-oil cracking under FCC conditions.³⁶

Nevertheless, the total acidity of the catalyst plays an important role in the cracking of PS/LCO, for which an important difference in conversion was obtained between the three catalysts, especially at low temperature (e.g., 450 °C, Table 4). This effect attenuates at 550 °C. In the whole range of temperature, the level of conversion is in agreement with the level of total acidity of the catalyst: 1 > 2 > 3. This need for a high level of acidity in the cracking of polystyrene supports the idea that the first step of the different cracking mechanisms is the protonation of the aromatic rings.^{12,16,37}

This effect of the total acidity of the catalyst is also observed when the conversion data of PS–BD/LCO cracking with the different catalysts are compared. Nevertheless, when temperature is increased, conversion increases, but to lower values than those obtained in the cracking of PS/LCO. Obviously, this difference is

Table 4. Conversions and Yields (wt %) 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

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	56.4	0.2	2.8	50.7	2.7
		500	57.0	0.5	4.2	49.5	2.8
		525	57.6	0.8	4.4	49.5	2.9
		550	59.7	1.7	5.4	49.5	3.1
LCO	2	450	55.9	0.2	2.6	50.7	2.4
		500	56.5	0.5	2.8	50.7	2.5
		525	56.7	0.7	2.8	50.6	2.6
		550	57.1	1.3	3.1	50.1	2.6
LCO	3	450	54.5	0.3	2.3	50.0	1.9
		500	55.0	0.5	2.7	49.9	1.9
		525	55.3	0.8	2.7	49.6	2.2
		550	55.5	1.2	3.1	48.6	2.6
PS/LCO	1	450	42.7	0.9	2.7	37.0	2.1
		500	49.8	1.5	3.1	43.0	2.2
		525	54.2	1.6	3.2	46.9	2.5
		550	63.4	1.9	3.2	55.3	3.0
PS/LCO	2	450	35.5	0.5	1.3	31.8	1.9
		500	45.1	0.7	1.4	40.9	2.1
		525	52.5	0.7	1.9	47.5	2.4
		550	62.2	1.0	2.3	56.3	2.6
PS/LCO	3	450	34.3	0.3	1.1	31.0	1.9
		500	42.4	0.6	1.4	38.4	2.0
		525	52.3	0.7	1.7	47.7	2.2
		550	61.2	0.8	2.2	55.8	2.4
PS–BD/LCO	1	450	42.6	1.2	3.3	35.1	3.0
		500	47.0	2.3	3.5	37.8	3.4
		525	49.5	2.8	3.9	39.1	3.7
		550	52.5	2.8	4.0	41.9	3.8
PS–BD/LCO	2	450	39.6	0.4	1.5	35.4	2.3
		500	42.1	0.4	1.7	37.1	2.9
		525	43.1	0.8	2.1	37.1	3.1
		550	49.5	1.8	2.7	41.8	3.2
PS–BD/LCO	3	450	36.4	0.3	1.4	32.9	1.8
		500	39.9	0.3	1.7	36.0	1.9
		525	40.1	0.5	2.0	35.6	2.0
		550	46.8	1.6	2.2	40.9	2.1

attributable to the greater resistance by the aromatic rings in the PS–BD to electrophilic attack.

In the cracking of the three feeds, as temperature or catalyst acidity is increased, in general, there is an increase in the yield of each of the fractions: dry gases (C₁, C₂), LPG (C₃, C₄), gasoline (C₅–C₁₂), and coke. Nevertheless, when the yields corresponding to the cracking of LCO and PS/LCO are compared, it is observed that the increase in the maximum conversion (at the higher temperature, 550 °C) when PS is fed is mainly due to the increase in the yield of gasoline (C₅–C₁₂) and is compensated by a decrease in the yield of LPG.

Although the effect of the total acidity of the catalyst is evident (Table 2), the difference in acid strength distribution (Figure 1) can be expected to have a small effect on the kinetic behavior. First, because this difference, which was obtained by changing the Si/Al ratio in the preparation of the HZSM-5 zeolites, is of low significance and, second, because the very strong acid sites generated in these zeolites are rapidly deactivated by coke, so that the acid strength of the remaining sites is rapidly homogenized.

When the results of PS–BD/LCO cracking are compared with those of LCO cracking, in general, it is observed that the decrease in the conversion when plastic is fed is mainly due to the decrease in the yield of gasoline, although a lower decrease in the yield of

LPG and significant increases in the yields of dry gases and coke also occur. The increase in the yield of coke for catalysts 1 and 2 is important because of the effect it might have on the deactivation of these catalysts.

Special attention should be paid to the coke content deposited on the catalyst. The maximum contents (for catalyst 1 at 550 °C) are 0.75 and 0.95 wt % for the transformations of the PS/LCO and PS–BD/LCO blends, respectively. These contents are lower than those for FCC units operating with commercial catalysts prepared from HY zeolites and with standard feeds, for which the maximum coke contents range between 1.5 and 2 wt %. The coke content is important because thermal equilibrium in FCC units is maintained by the heat generated in the combustion of the coke in the regenerator.

Concerning the deactivation of pure HZSM-5 zeolite in other processes, it has been found that deactivation in the MTG (methanol-to-gasoline) process is almost complete (with total pore blockage) for a coke content of approximately 5 wt %, which corresponds to 1.25 wt % for our catalyst (with 25 wt % zeolite).³⁸ From this point of view, our catalyst has undergone severe deactivation.

Figure 3 shows the effect of temperature on the selectivity of the lumps of gases (C₁, C₂), LPG (C₃, C₄), the C₅–C₁₂ fraction, and coke, for the three feeds LCO, PS/LCO, and PS–BD/LCO. The results correspond to

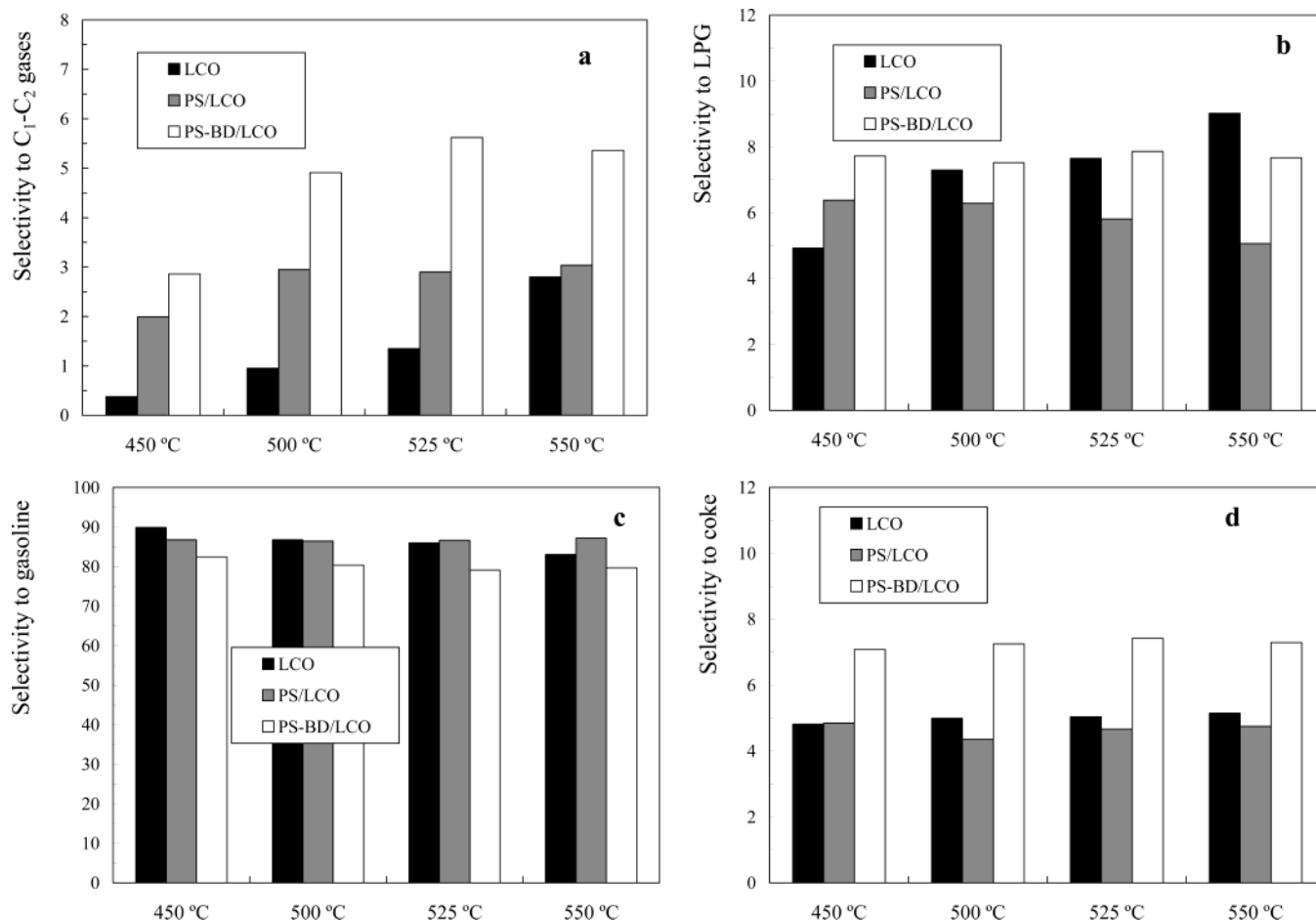


Figure 3. Effects of temperature on the selectivities to the products (in wt %) in the cracking of LCO, PS/LCO, and PS-BD/LCO: (a) gases (C₁, C₂), (b) LPG (C₃, C₄), (c) C₅-C₁₂ fraction, (d) coke.

catalyst 1, for which the conversion is the highest. The selectivity was calculated as

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

As can be observed in Figure 3, the selectivities to gases (C₁, C₂) (Figure 3a) and to coke (Figure 3d) increase as the temperature is increased for the three feeds. The increase in the selectivity to coke is very small, which is because cracking also affects the coke precursor intermediates. The effect of temperature on the selectivity to LPG is uneven (Figure 3b). Specifically, in the cracking of LCO, selectivity to LPG increases as temperature is increased; it is almost constant in the cracking of PS-BD/LCO, and it decreases in the cracking of PS/LCO.

The selectivity to the C₅-C₁₂ fraction is very high for the three feeds. This selectivity is slightly affected when PS is co-fed and is considerably affected when PS-BD is co-fed. The fact that the selectivity to the C₅-C₁₂ fraction is almost constant with temperature in the range studied is an interesting aspect for a hypothetical industrial process, which combines high production and high selectivity to obtain gasoline.

When the selectivities determined for the cracking of feeds containing dissolved plastic are compared with those determined for solvent cracking, the role of PS-BD in increasing the selectivity to dry gases (C₁, C₂) and especially to coke is significant. An interpretation

of this result is that the butadiene chains of the polymer mainly undergo two undesired processes from the point of view of product interest: (1) the formation of polyaromatic structures, from which those retained in the catalyst make up the coke and those that are volatilized are not considered in the calculation of conversion, because of their high boiling points (corresponding to C₁₂₊ alkanes), and (2) the cracking of polybutadiene chains and lateral chains of polyaromatics, which produce gases (C₁, C₂). The first step of the mechanisms of both processes is the formation of cations after the protonation of the carbons corresponding to the double bonds of polybutadiene. This protonation is energetically more favorable than that of the phenolic group of PS, which explains the low efficiency of this step and, consequently, the low conversion of PS chains in the cracking of PS-BD.

Apparent Conversion of the 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 each mixture, the apparent yield of each lump obtained from the plastic was calculated by using the results obtained for the yields from the transformation of LCO and assuming that these yields remain constant when the mixture is transformed, i.e.

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

Table 5. Compositions of the C₅–C₁₂ Fractions Obtained in the Cracking of LCO, PS/LCO, and PS–BD/LCO on Catalyst 1

feedstock	T (°C)	<i>n</i> -paraffins	<i>i</i> -paraffins	olefins	naphthenes	aromatics
LCO	450	4.9	3.7	8.4	2.9	80.1
	500	5.2	3.9	9.1	3.0	78.8
	525	5.2	3.6	8.4	2.7	80.1
	550	4.9	3.3	8.3	3.1	80.4
PS/LCO	450	3.3	2.0	3.1	0.6	91.0
	500	2.5	1.5	2.0	0.5	93.5
	525	1.9	1.1	1.8	0.5	94.7
	550	1.3	0.7	1.6	0.3	96.1
PS–BD/LCO	450	3.0	4.0	4.0	0.7	88.3
	500	2.2	4.0	3.3	0.6	89.9
	525	2.1	3.9	3.1	0.5	90.4
	550	1.8	3.3	3.0	0.4	91.5

When the results in Table 4 are substituted into eq 3, it becomes clear that the highest apparent yield from the dissolved PS and PS–BD is that corresponding to the lump of gasoline (C₅–C₁₂) and that this yield increases significantly as the reaction temperature is increased, up to 72.7 wt % for PS and 19.1 wt % for PS–BD at 550 °C for catalyst 1. The apparent conversions at this temperature are 74 and 30.9 wt %, respectively. The result for PS–BD means that a higher temperature is advisable, although the temperature will be limited by the apparent yield of coke, which significantly increases with temperature, being 2.7 wt % for PS and 5.9 wt % for PS–BD.

C₅–C₁₂ Composition. Table 5 shows the compositions of the C₅–C₁₂ fractions obtained in the cracking of LCO, PS/LCO, and PS–BD/LCO. The results were obtained with catalyst 1. 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 % at 450 °C, and independent of temperature, the presence of plastics in the feed notably increases this content. The contents of aromatics in the cracking of PS/LCO and PS–BD/LCO increase to 96.06 and to 91.49 wt %, respectively, as temperature is increased up to 550 °C. This result reveals the important contribution of dissolved plastics in 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 can be explained by the reactivity of these compounds with the cations of PS to form indanes and indenenes, which, because of their high boiling point, are not considered in the C₅–C₁₂ fraction.¹⁶

Because of the significant aromatic content of the C₅–C₁₂ fraction, potential interest in the valorization of the blends studied in this paper might lie in the separation of these aromatics, whose commercial interest is expected to increase over the next decade.³⁹ Figure 4 shows the effect of temperature on the compositions, in weight percent, of different components and lumps of the fractions of aromatics of the C₅–C₁₂ product stream obtained in the cracking of LCO, PS/LCO, and PS–BD/LCO. The results correspond to catalyst 1. The results corresponding to the other catalysts are qualitatively similar.

In these results, the important effects of the co-feeding of plastics and of the cracking temperature are noteworthy. For the cracking of PS/LCO and PS–BD/LCO, the concentration of the C₈ fraction, which is mainly made up of the monomer styrene, increases almost linearly as the temperature is increased (Figure 4c). The

concentrations of the fractions C₉ (Figure 4d) and C₁₀–C₁₂ (Figure 4e) decrease as the temperature is increased, and the concentrations of benzene (Figure 4a) and toluene (Figure 4b) pass through a maximum at 500 °C.

These results can be explained by a change in the cationic mechanisms of PS decomposition, which have alternative ways of obtaining stable products, such as 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 reported in the literature to be significant above 130 °C.¹⁶

Figure 5 shows the yields of the aromatic components in the cracking of PS/LCO (Figure 5a) and PS–BD/LCO (Figure 5b). The yield of styrene at 550 °C is 99.9 wt % for the PS fed in the PS/LCO blend and 99.8 wt % for that in the PS–BS/CO blend. It must be pointed out that almost all of the styrene comes from the cracking of PS because the content of styrene in the aromatic fraction of the products obtained in the cracking of LCO has been shown to be insignificant. Given that PS is totally converted into styrene at 550 °C, the remaining aromatic components in the product stream obtained in the cracking of the PS/LCO and PS–BD/LCO blends has its origin in the cracking of LCO.

This high yield of styrene is higher than that reported in the literature for the thermal pyrolysis of PS when the PS is fed as a pure component in solid state. Thus, in fixed-bed reactors, Zhang et al. obtained a yield of 56 wt % at 350 °C,¹² and Nishizaki et al. obtained a yield of 50 wt % at 450 °C.⁴⁰ In a fluidized-bed reactor, Kaminsky obtained a yield of 64.9 wt % at 580 °C,⁴¹ and Aguado et al. obtained a yield of 64.5 wt % in a conical spouted bed at 450 °C.⁴²

The total recovery of the monomer must be attributed to the process conditions and to the shape selectivity of the catalyst. Both factors minimize undesired secondary reactions. Thus, given that the polymer is diluted, the heating rate is high; this allows for the reaction to be completed in a short contact time, 3 s, which minimizes the secondary reactions between the primary products and the melted plastic (which are important in the pyrolysis of plastics when they are fed in the solid state). The shape selectivity of the catalyst plays an important role in the inhibition of the mechanisms of formation of indanes and indenenes, which are alternative to the formation of styrene through β -scission. These steps require the rearrangement and hydride abstraction of

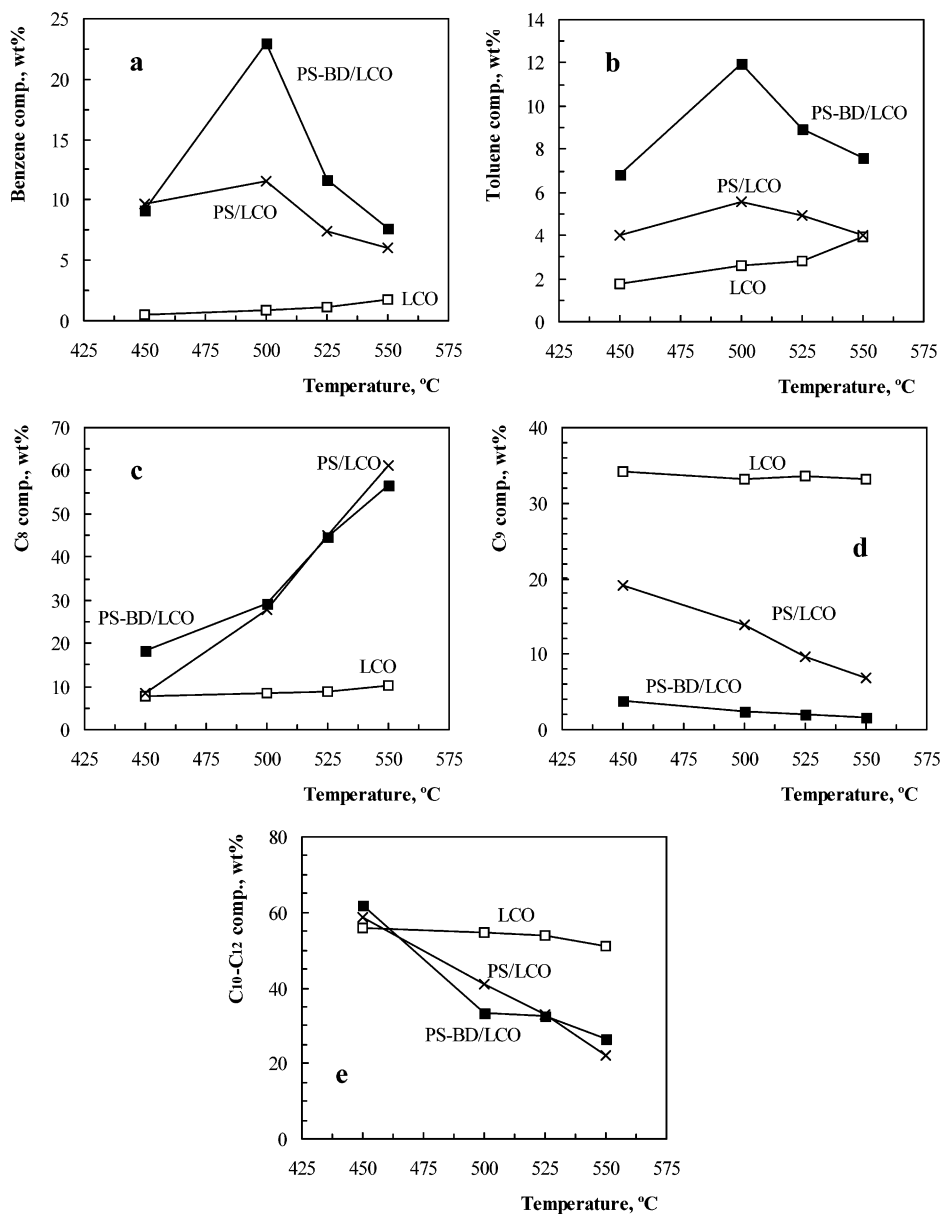


Figure 4. Effect of temperature on the compositions (in weight percent) of the aromatic components of the C₅–C₁₂ fraction in the cracking of LCO, PS/LCO, and PS–BD/LCO on catalyst 1: (a) benzene, (b) toluene, (c) C₈ fraction, (d) C₉ fraction, (e) C₁₀–C₁₂ fraction.

macroocations, which are limited by the small size of the channels of the HZSM-5 zeolite.

Furthermore, this result is evidence that, under the conditions used, the components of LCO are inert in the depolymerization of PS to styrene.

Gas Composition. Figures 6–8 show the effect of temperature on the composition of the total fraction of gases (C₁–C₃ and C₄ fractions) for each of the feeds. Figure 6, corresponding to the cracking of LCO, shows that, at 450 °C, the C₁–C₃ fraction (Figure 6a) is mainly made up of propylene and that, as temperature is increased, the concentration of ethylene increases, but the concentrations of gaseous paraffins are maintained at low values. This increase in the concentration of ethylene is attributed to the cracking of butenes, whose concentration decreases as temperature is increased, as is shown in Figure 6b. The formation of ethylene is attributed to the mechanism of oligomerization–cracking of propylene.⁴³

In the gaseous product obtained in the cracking of PS/LCO, the concentration of propylene (Figure 7a) is

slightly lower than that obtained in the cracking of LCO (Figure 6a). Nevertheless, ethylene is present at a concentration of 20 wt % for temperatures above 450 °C. The concentration of ethylene increases with temperature, which is partially due to the cracking of *iso*-butene, whose concentration decreases as temperature is increased (Figure 7b) and to the oligomerization–cracking of propylene.

The concentration of propylene in the cracking of PS–BD/LCO (Figure 8a) is slightly lower than that corresponding to the aforementioned feeds (Figures 6a and 7a), and it decreases in a less pronounced way as the temperature is increased. The concentration of ethylene is also slightly lower than that found for the cracking of PS/LCO.

The concentration of butenes in the cracking of PS–BD/LCO (Figure 8b) lies between the values obtained for the other two feeds, and a significant concentration of butadiene is observed at 550 °C. The yield in the recovery of the monomer butadiene is low, 10.4 wt %, compared to the content in the feed, which is explained

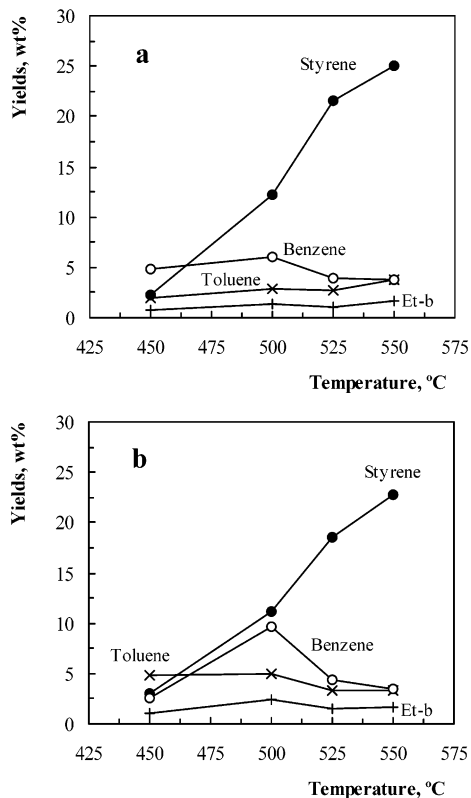


Figure 5. Yields of the aromatic components in the cracking of the blends on catalyst 1: (a) PS/LCO, (b) PS-BD/LCO.

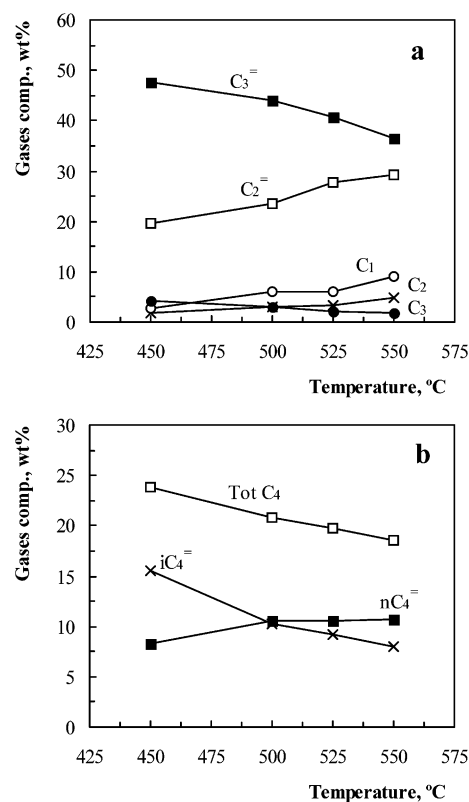


Figure 7. Effect of temperature on the compositions of the fractions of gases in the cracking of PS/LCO on catalyst 1: (a) C₁-C₃ fraction, (b) C₄ fraction.

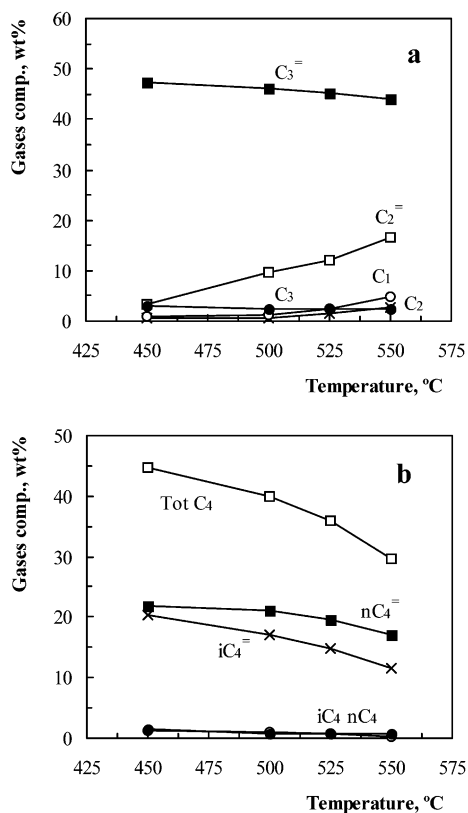


Figure 6. Effect of temperature on the compositions of the fractions of gases in the cracking of LCO on catalyst 1: (a) C₁-C₃ fraction, (b) C₄ fraction.

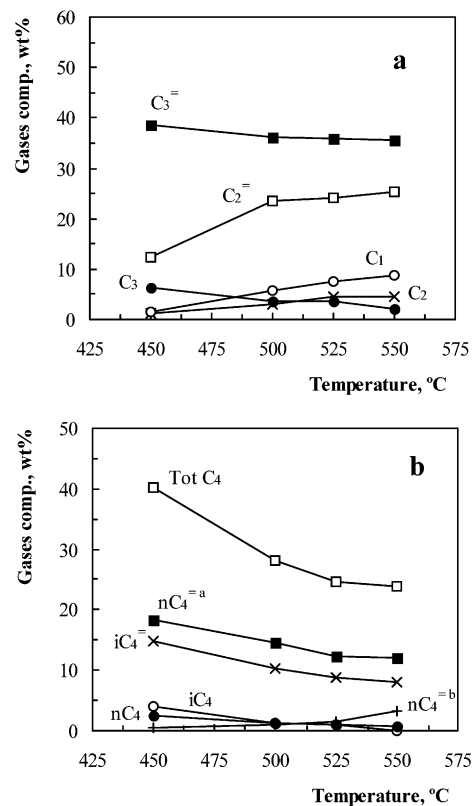


Figure 8. Effect of temperature on the compositions of the fractions of gases in the cracking of PS-BD/LCO on catalyst 1: (a) C₁-C₃ fraction, (b) C₄ fraction [*n*-C₄ = (a) 1-*cis*- and *trans*-butene, (b) butadiene].

by the fact that, although the chain-breaking mechanisms of the two copolymers favor the recovery of the monomer styrene, the unsaturated chains of polybuta-

diene are cracked with relative ease by the Brønsted acid sites of the catalyst.

For the three feeds, the resulting increase in the concentration of ethylene with temperature and decrease in the concentrations of propylene and butenes are evidence of the well-known mechanism of oligomerization–cracking of these light olefins on HZSM-5 zeolites with the formation of ethylene as the final product.⁴³ Other authors have demonstrated the high selectivity to ethylene in the cracking on HZSM-5 zeolites.^{33,44–46} den Hollander et al.⁴⁷ attribute the higher ethylene yield on HZSM-5 to the small pores of this zeolite and the associated high electrical fields and interaction with adsorbed carbenium ions.

Under the conditions of total recovery of the styrene contained in the plastics, as occurs at 550 °C, the composition of the remaining products is different from that obtained when LCO is fed. This is explained by the hypothesis that, under these conditions, overcracking of LCO products occurs. It must be taken into account that the content of LCO in the blends is 75 wt % that of the feed made up of pure LCO. This explains the aforementioned findings of the increase in the yields of gases and coke and of the evolution of gas composition with increasing concentration of ethylene.

4. Conclusions

The cracking on HZSM-5 zeolite catalysts of PS and PS–BD dissolved in an aromatic LCO obtained in a commercial refinery unit allows for the total recovery of styrene at 550 °C under the standard conditions of a FCC unit. The process is also interesting for the valorization of LCO, from which high yields of C₅–C₁₂ aromatics, olefinic LPG, and ethylene are obtained, together with low yields of dry gases (C₁, C₂) and coke. Co-feeding PS contributes to an increase in the conversion of LCO, whereas co-feeding PS–BD partially inhibits the conversion of LCO at 550 °C. Co-feeding both plastics contributes to a substantial increase in the aromatic content in the C₅–C₁₂ fraction and to a significant decrease in the concentrations of *n*-paraffins, olefins, and naphthenes.

It has been demonstrated that the acidity of the catalyst plays an important role in the conversion and that a high total acidity is required, as is the case for an HZSM-5 zeolite with a Si/Al ratio of 24 prepared under conventional conditions and moderately equilibrated (by calcination at 600 °C). Likewise, in the 450–550 °C range studied, the conversion increases with temperature in the cracking of the PS/LCO and PS–BD/LCO blends. Temperature has an important effect on the composition of the gaseous olefins, where the concentrations of butenes and propylene decrease as the temperature is increased whereas that of ethylene increases.

The aforementioned results are encouraging for the valorization of secondary-interest feeds in refineries, such as LCO, given that, by using LCO as a solvent for the plastics that make up post-consumer wastes, both materials can be valorized with a maximum exploitation of the refinery capacity.

Acknowledgment

This work was carried out with the financial support of the University of the Basque Country (Project 9/UPV 00069.310-13607/2001) and of the Ministry of Science and Technology of the Spanish Government (Project

PPQ2000-1286). We are indebted to Petronor S.A. and Dow Chemical S.A. for their generous provision of materials.

Literature Cited

- (1) Scott, D. S.; Czernik, S. R.; Piskorz, J.; Radlein, A. G. Fast Pyrolysis of Plastic Wastes. *Energy Fuels* **1990**, *4*, 407–411.
- (2) Kaminsky, W.; Schlesselmann, B.; Simon, C. J. Olefins from Polyolefins and Mixed Plastics by Pyrolysis. *J. Anal. Appl. Pyrol.* **1995**, *32*, 19–27.
- (3) Williams, P. T.; Williams, E. A. Fluidized Bed Pyrolysis of Low-Density Polyethylene to Produce Petrochemical Feedstock. *J. Anal. Appl. Pyrol.* **1999**, *51*, 107–126.
- (4) Mastral, F. J.; Esperanza, E.; García, P.; Juste, M. Pyrolysis of High-Density Polyethylene in a Fluidised Bed Reactor. Influence of the Temperature and Residence Time. *J. Anal. Appl. Pyrol.* **2002**, *63*, 1–15.
- (5) Lovett, S.; Berruti, F.; Behie, L. A. Ultraprolytic Upgrading of Plastics Wastes and Plastics/Heavy Oil Mixtures to Valuable Light Gas Products. *Ind. Eng. Chem. Res.* **1997**, *36*, 4436–4444.
- (6) Westerhout, R. W. J.; Waanders, J.; Kuipers, J. A. M.; van Swaaij, W. P. M. Development of a Continuous Rotating Cone Reactor Pilot Plant for the Pyrolysis of Polyethylene and Polypropene. *Ind. Eng. Chem. Res.* **1998**, *37*, 2316–2322.
- (7) Bockhorn, H.; Hentschel, J.; Hornung, A.; Hornung, U. Environmental Engineering Stepwise Pyrolysis of Plastic Waste. *Chem. Eng. Sci.* **1999**, *54*, 3043–3051.
- (8) Masuda, T.; Kushino, T.; Matsuda, T.; Mukai, S. R.; Hashimoto, K.; Yoshida, S. Chemical Recycling of Mixture of Waste Plastics Using a New Reactor System with Stirred Heat Medium Particles on Steam Atmosphere. *Chem. Eng. J.* **2001**, *82*, 173–181.
- (9) Serrano, D. P.; Aguado, J.; Escola, J. M.; Garagorri, E. Conversion of Low-Density Polyethylene into Petrochemical Feedstocks Using a Continuous Screw Kiln Reactor. *J. Anal. Appl. Pyrol.* **2001**, *58–59*, 789–801.
- (10) Gaisán, B. Technological Development of Plastic Pyrolysis in a Conical Spouted Bed. Ph.D. Dissertation, University of the Basque Country, Bilbao, Spain, 2002.
- (11) Ohkita, H.; Nishiyama, R.; Tochihara, Y.; Mizushima, T.; Kakuta, N.; Morioka, Y.; Ueno, A.; Namiki, Y.; Tanifuji, S.; Katoh, H.; Sunazuka, H.; Nakayama, R.; Kuroyanagi, T. Acid Properties of Silica–Alumina Catalysts and Catalytic Degradation of Polyethylene. *Ind. Eng. Chem. Res.* **1993**, *32*, 3112–3116.
- (12) Zhang, Z.; Hirose, T.; Nishio, S.; Morioka, Y.; Azuma, N.; Ueno, A.; Ohkita, H.; Okada, M. Chemical Recycling of Waste Polystyrene into Styrene over Solid Acids and Bases. *Ind. Eng. Chem. Res.* **1995**, *34*, 4514–4519.
- (13) Songip, A. R.; Masuda, T.; Kuwahara, H.; Hashimoto, K. Test to Screen Catalysis for Reforming Heavy Oil from Waste Plastics. *Appl. Catal. B: Environ.* **1993**, *2*, 153–164.
- (14) Songip, A. R.; Masuda, T.; Kuwahara, H.; Hashimoto, K. Kinetic Studies for Catalytic Cracking of Heavy Oil from Waste Plastics over REY Zeolite. *Energy Fuels* **1994**, *8*, 131–135.
- (15) Marcilla, A.; Beltran, M.; Conesa, J. A. Catalyst Addition in Polyethylene Pyrolysis. Thermogravimetric Study. *J. Anal. Appl. Pyrol.* **2001**, *58–59*, 117–126.
- (16) Lin, R.; White, R. L. Acid-Catalyzed Cracking of Polystyrene. *J. Appl. Polym. Sci.* **1997**, *63*, 1287–1298.
- (17) Ukei, H.; Hirose, T.; Horikawa, S.; Takai, Y.; Taka, M.; Azuma, N.; Ueno, A. Catalytic Degradation of Polystyrene into Styrene and a Design of Recyclable Polystyrene with Dispersed Catalysts. *Catal. Today* **2000**, *62*, 67–75.
- (18) Kastern, H.; Kaminsky, W. Recycle Plastics into Feedstocks. *Hydrocarbon Process.* **1995**, *May*, 109–112.
- (19) Kaminsky, W.; Hartmann, F. New Pathways in Plastics Recycling. *Angew. Chem., Int. Ed.* **2000**, *39*, 331–333.
- (20) Arandes, J. M.; Ereña, J.; Bilbao, J.; López-Valerio, D.; de la Puente, G. Valorization of Polyolefins Dissolved in Light Cycle Oil over HY Zeolites under Fluid Catalytic Cracking Unit Conditions. *Ind. Eng. Chem. Res.*, in press.
- (21) Ng, S. H. Conversion of Polyethylene Blended with VGO to Transportation Fuels by Catalytic Cracking. *Energy Fuels* **1995**, *9*, 216–224.
- (22) Hesse, N.; Lin, R.; Bonnet, E.; Cooper, J., III; White, R. L. In Situ Analysis of Volatiles Obtained from the Catalytic Cracking of Polyethylene. *J. Appl. Polym. Sci.* **2001**, *82*, 3118–3125.

- (23) Argauer, R. J.; Landolt, G. R. Crystalline Zeolite HZSM-5 and Method of Preparing the Same. U.S. Patent 3,702,886, 1972.
- (24) Chen, N. Y.; Miale, J. N.; Reagan, W. J. Preparation of Zeolite, Example 5. U.S. Patent 4,112,056, 1973.
- (25) Romero, A.; Bilbao, J.; Aguayo, A. T. The Vacuum Drying of Silica Gel for Utilization as a Support for Silica-Alumina Catalysts. *Int. Chem. Eng.* **1986**, *26*, 90–96.
- (26) Benito, P. L.; Aguayo, A. T.; Gayubo, A. G.; Bilbao, J. Catalyst Equilibration for Transformation of Methanol into Hydrocarbons by Reaction-Regeneration Cycles. *Ind. Eng. Chem. Res.* **1996**, *35*, 2177–2182.
- (27) Aguayo, A. T.; Gayubo, A. G.; Ereña, J.; Olazar, M.; Arandes, J. M.; Bilbao, J. Isotherms of Chemical Adsorption of Bases on Solid Catalysts for Acidity Measurement. *J. Chem. Technol. Biotechnol.* **1994**, *60*, 141–146.
- (28) Aguayo, A. T.; Benito, P. L.; Gayubo, A. G.; Olazar, M.; Bilbao, J. Acidity Deterioration and Coke Deposition in a H-ZSM-5 Zeolite in the MTG Process. *Stud. Surf. Sci. Catal.* **1994**, *88*, 567–572.
- (29) Sedran, U. Laboratory Testing of FCC Catalysts and Hydrogen Transfer Properties Evaluation. *Catal. Rev.-Sci. Eng.* **1994**, *36*, 405–431.
- (30) Kraemer, D. W. Modelling Catalytic Cracking in a Novel Riser Simulator. Ph.D. Dissertation, University of Western Ontario, London, Ontario, Canada, 1991.
- (31) Kraemer, D. W.; de Lasa, H. I. Catalytic Cracking of Hydrocarbons in a Riser Simulator. *Ind. Eng. Chem. Res.* **1988**, *27*, 2002–2008.
- (32) de Lasa, H. I. Riser Simulator for Catalytic Cracking Studies. U.S. Patent 5,102,628, 1992.
- (33) Arandes, J. M.; Abajo, I.; Fernández, I.; Azkoiti, M. J.; Bilbao, J. Effect of HZSM-5 Zeolite Addition to a FCC Catalyst. Study in a Laboratory Reactor Operating under Industrial Conditions. *Ind. Eng. Chem. Res.* **2000**, *39*, 1917–1924.
- (34) Arandes, J. M.; Abajo, I.; Bilbao, J.; Azkoiti, M. J.; de Lasa, H. I. Consistency of the Ten-Lump Kinetic Model for Cracking. Study in a Laboratory Reactor and Use for Simulation of a FCCU. *Chem. Eng. Commun.* **2003**, *190*, 254–284.
- (35) Arandes, J. M.; Ereña, J.; Azkoiti, M. J.; Olazar, M.; Bilbao, J. Thermal Recycling of Polystyrene and Polystyrene-Butadiene Dissolved in LCO. *J. Anal. Appl. Pyrol.*, in press.
- (36) Arandes, J. M.; Abajo, I.; López-Valerio, D.; Fernández, I.; Azkoiti, M. J.; Olazar, M.; Bilbao, J. Transformation into Fuels of Several Plastic Wastes by Catalytic Cracking. *Ind. Eng. Chem. Res.* **1997**, *36*, 4523–4529.
- (37) Audisio, G.; Bertini, F.; Beltrame, P. L.; Carniti, P. Catalytic Degradation of Polymers. Part III. Degradation of Polystyrene. *Polym. Degrad. Stabil.* **1990**, *29*, 191–200.
- (38) Benito, P. L.; Gayubo, A. G.; Aguayo, A. T.; Olazar, M.; Bilbao, J. Deposition and Characteristics of Coke over a HZSM5 Zeolite Based Catalyst in the MTG Process. *Ind. Eng. Chem. Res.* **1996**, *35*, 3991–3998.
- (39) Weitkamp, J.; Raichle, A.; Traa, I. Novel Zeolite Catalysts to Create Value from Surplus Aromatics: Preparation of C₂₊ n-alkanes, a High-Quality Synthetic Steamcracker Feedstock. *Appl. Catal.* **2001**, *222*, 277–297.
- (40) Nishizaki, H.; Sakakibara, M.; Yoshida, K.; Endoh, K. Oil Recovery from Atactic Polypropylene by Fluidized Reactor. *Nippon Kagaku Kaishi* **1977**, 1899–1904 (in Japanese).
- (41) Kaminsky, W. Recycling of Polymeric Materials by Pyrolysis. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 381–393.
- (42) Aguado, R.; Olazar, M.; Gaisán, B.; Prieto, R.; Bilbao, J. Polystyrene Pyrolysis in a Conical Spouted Bed Reactor. *Chem. Eng. J.* **2003**, *92*, 91–99.
- (43) Buchanan, J. S.; Santiesteban, J. G.; Haag, W. O. Mechanistic Considerations in Acid-Catalyzed Cracking of Olefins. *J. Catal.* **1996**, *158*, 279–287.
- (44) Buchanan, J. S.; Adewuyi, Y. G. Effects of High Temperature and High ZSM-5 Additive Level on FCC Yields and Gasoline Composition. *Appl. Catal.* **1996**, *134*, 247–262.
- (45) Corma, A.; Miguel, P. J.; Orchillés, A. V. Product Selectivity Effects During Cracking of Alanes at Very Short and Longer Times on Stream. *Appl. Catal.* **1996**, *138*, 57–73.
- (46) Biswas, J.; Maxwell, L. E. Octane Enhancement in Fluid Catalytic Cracking. I. Role of ZSM-5 Addition and Reactor Temperature. *Appl. Catal.* **1990**, *58*, 1–18.
- (47) den Hollander, M. A.; Wissink, M.; Makkee, M.; Moulijn, J. A. Gasoline Conversion: Reactivity towards Cracking with Equilibrated FCC and ZSM-5 Catalysts. *Appl. Catal.* **2002**, *223*, 85–102.

Received for review January 15, 2003

Revised manuscript received May 23, 2003

Accepted June 3, 2003

IE030045J