

# Conversion of waste plastics into fuels Recycling polyethylene in FCC

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## Abstract

Low density polyethylene was dissolved into toluene and converted at 500 °C over three different commercial FCC catalysts in a laboratory *Riser Simulator* reactor. Short reaction-times up to 12 s were used. All the catalysts had qualitatively similar behaviors. The specific contribution of the polymer to the product slate of FCC was centered in hydrocarbons in the range of gasoline, with high aromatic content and highly olefinic C<sub>3</sub>–C<sub>4</sub> gases. Saturated C<sub>4</sub>–C<sub>5</sub> products were mainly isoparaffins. The additional coke formed by the polymer would make coke yields to increase moderately in relation to the standard operation. These facts confirmed that this recycling option, which is based on a proven technology, represents an interesting alternative to solve a major environmental problem. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In view of their versatility and relatively low cost, the consumption of plastic materials has been growing steadily, although the disposal of waste plastics constitutes a severe environmental problem due mainly to their chemical inertness. While polymers recycling is a requirement to mitigate their impact on the environment [1], various tertiary recycling processes are attractive, since they produce valuable chemicals or fuels [2,3].

Considering polyolefins, polyethylene and polypropylene have a massive production and consumption in a large number of applications. The tertiary recycling of polyolefins (particularly polyethylene) has been attempted under different approaches. The most used

laboratory technique with some variations, is that of contacting the plastic with the catalyst in a closed environment, heating them together until reaction-temperature, and allowing for a certain reaction-time; products are then separated and analyzed (e.g. [4,5]). In this way, the reaction-products are indeed the result of continuously changing conditions and consequently, they represent a kind of average behavior of the system. In other case, melted polyethylene was fed continuously over a bed of catalysts [6]. Among others, USY, mordenite, ZSM-5, SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> and mesoporous MCM-41 were used as catalysts over which wide product distributions were obtained (e.g. [7,8]). On the contrary, the pyrolysis of plastics is a purely thermal process in which polymers are heated at high temperature, their macro-molecular structure being broken down to smaller molecules. A mixture of gaseous, liquid and even solid hydrocarbon products are obtained [9,10]. However, these products are not good as fuels and need to be upgraded [11].

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While it is certainly possible to develop commercial processes based on these approaches, it is to be noted that at present they are far from being implemented. A more interesting approach, however, is that of adding waste polymers into the usual feed-stocks of the process of fluid catalytic cracking of hydrocarbons (FCC) because, under standard process conditions, a large number of plastics, including polyolefins, can be dissolved into vacuum gas oils (VGO) and in this way, they can be converted into a mixture of hydrocarbon compounds. The idea has been tested with different plastics and laboratory conditions. Polystyrene and polybutadiene–polystyrene were converted in a *Riser Simulator* reactor under conditions similar to commercial ones, to observe positive contributions from the standpoint of the composition of the gasoline cuts [12,13]. Ng [14] used a MAT reactor to convert polyethylene–VGO mixtures and concluded that an increase in gasoline yield was observed only when more than 10% of plastic was dissolved into VGO. An interesting observation from the conversion of polystyrene over various acidic catalysts like ZSM-5, mordenite, FCC catalysts and sulfur promoted zirconia [15] is that equilibrium FCC catalysts exhibited the best performance to yield hydrocarbons in the range of gasoline. Considering that the FCC process follows a delicate heat-balanced operation based on the equilibrium between the heat released by coke combustion and its consumption by cracking reactions, the yield of coke from the plastics deserves special consideration, since it is significant and could govern the implementation of this option. Interestingly, this approach does not imply to develop new commercial technologies, but to take advantage of a fully proven and established process, since adding waste polymers to the feed-stocks of FCC would be straightforward.

It is the objective of this work to ascertain the specific contribution to the product slate of the FCC process made by polyethylene recycled into the usual feed-stocks, by means of its conversion dissolved into toluene over commercial equilibrium catalysts at standard conditions in a *Riser Simulator* laboratory reactor.

## 2. Experimental

Two equilibrium commercial FCC catalysts without pentasil additives sampled from running refineries (E-Cat A, BR1160, Engelhard, UK and E-Cat B, Vision 418, FCC S.A., Brazil), and an amorphous silica–alumina (Cat C, LA-LPV, Ketjen, The Netherlands) treated with 100% steam during 4 h at 770 °C in a fluidized bed reactor were used. The main properties of the catalysts are shown in Table 1. E-Cat A is a conventional, high unit cell size catalyst, while E-Cat B is an octane catalyst, with low unit cell size; silica–aluminas (case of Cat C) are older FCC catalysts.

The conversion of commercial low density polyethylene dissolved in toluene (approximately 2.0 wt.%) was conducted at 500 °C in a *Riser Simulator* reactor [16,17]. Its basic design concept (refer to Fig. 1) considers that a slice of the environment of an ideal riser reactor, involving certain mass of catalyst and gases and moving along it during a given residence-time, is located into this batch reactor; then, reaction-time evolved in the *Riser Simulator* is equivalent to contact-time and motion, along the ideal riser. An impeller rotating at very high speed on top of the chamber that keeps the catalyst between two metal porous plates, induces the internal circulation of the reacting mixture in an upwards direction through

Table 1  
Catalysts properties

Catalysts	Unit cell size (Å) <sup>a</sup>	BET specific surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>b</sup>	Zeolite content (%) <sup>c</sup>	Rare earth oxide content (%)	Ni (ppm)	V (ppm)	Fe (%)
E-Cat A	24.31	175	9.1	1.31	270	1200	0.350
E-Cat B	24.23	139	16.9	1.26	3995	2675	0.546
Cat C	–	147	–	–	–	–	–

<sup>a</sup> ASTM D-3942-85.

<sup>b</sup> BET method, with N<sub>2</sub> adsorption.

<sup>c</sup> Johnson's method [24] with N<sub>2</sub> adsorption.

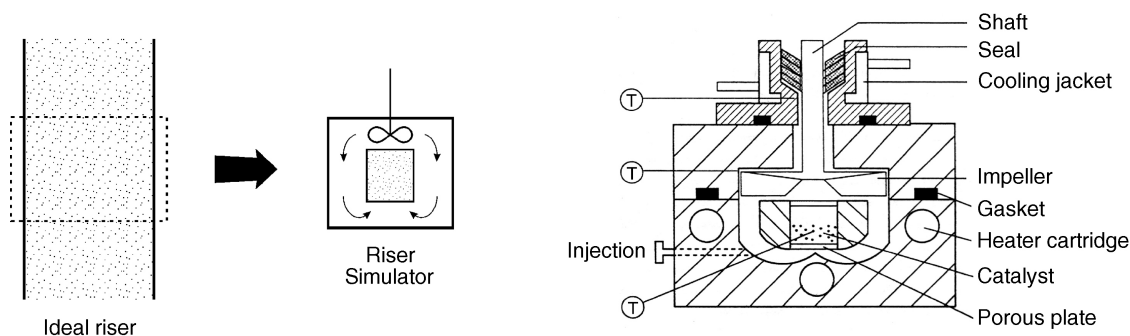


Fig. 1. Schematic representation of the *Riser Simulator* reactor.

the chamber, thus, fluidizing the catalyst. When the reactor is at the desired experimental condition the reactant is fed through an injection port and immediately after the reaction-time is attained, products are evacuated and analyzed by gas chromatography. The volume of solution injected into the reactor was 0.2 ml in all the cases and the masses of catalysts were 0.6 g (E-Cat A), 0.4 g (E-Cat B) and 0.8 g (Cat C), according to their activity in the conversion of toluene. Reaction-times were 3, 6, 9 and 12 s. Duplicate experiments were performed with pure toluene as the reactant, in order to elucidate products from its conversion to be deducted from products in the case of using solutions; experiments showed that under these conditions neither non-aromatic compounds nor products in the  $C_1$ – $C_5$  range were formed from toluene. The amount of coke on the catalysts was assessed by means of a temperature-programmed oxidation and further methanation procedure and coke loads due to the solvent were determined in the solvent-only experiments.

Additional experiments aimed at clarifying some issues about the product distributions observed in the conversion of polyethylene were performed over catalyst E-Cat A with 1-pentene diluted at 2% in toluene as the reactant. Conditions were the same as those enumerated above.

### 3. Results and discussion

Considering the very high catalyst to reactant polyethylene ratio and temperature used, product yields in this work were determined assuming that

the conversion of the polymer was complete (a fact observed in other works, see, e.g. [4,7]). The yields of gaseous and non-aromatic liquid products were assessed directly from the GC analysis, while aromatics yields, since they are also produced to some extent by the solvent, were determined following a mass balance (amount of plastic injected minus gases, non-aromatic liquid and coke yields). It was observed in our experiments with pure toluene as the reactant that the products in the  $C_6$ – $C_{12}$  range were only aromatic compounds, mainly benzene and xylenes, which are the products from toluene disproportionation reaction. However, toluene converts mildly under FCC conditions and conversion was always lower than 6.5% (E-Cat B, 12 s). Then, it can be stated that in the case of the conversion of polyethylene dissolved in toluene, all the effluents with less than six and more than 12 C atoms per molecule, and also the non-aromatic compounds in the  $C_6$ – $C_{12}$  range, are only due to the polymer itself. It is well-known that the conversion of polymers over acidic catalysts leads to the production of a complex mixture of hydrocarbons, the composition of which depends on the polymer, the experimental conditions and the catalyst properties (see e.g. [9]).

The yields of gases  $C_1$ – $C_4$ , gasoline  $C_5$ – $C_{12}$  and coke for the three catalysts are presented in Fig. 2, where it can be appreciated that the performances of all the catalysts were qualitatively similar. It can be seen that the productions of gasoline are very high, with yields as high as 80% at the shortest contact-times (case of E-Cat A), the amorphous  $SiO_2$ – $Al_2O_3$  yielding 70%. Gasoline yield profiles showed to be decreasing as a function of reaction-time. On the contrary, the yields of gases and coke showed values that

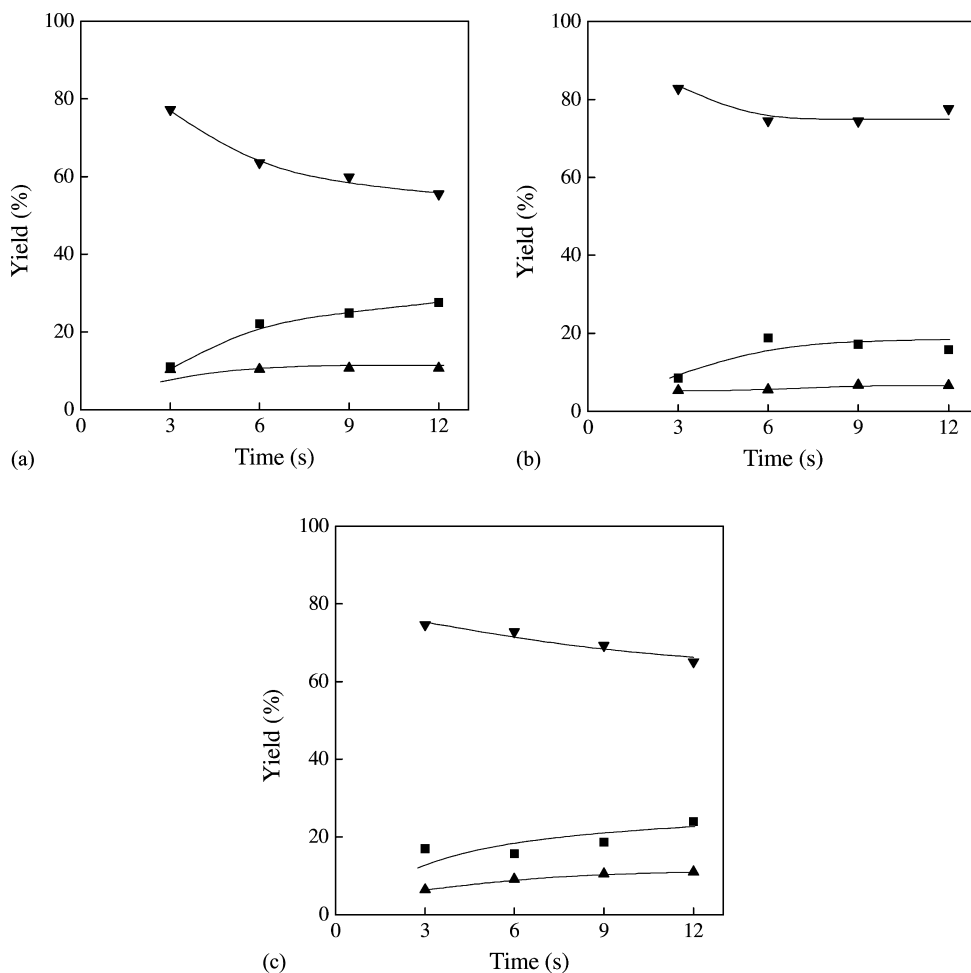


Fig. 2. Yields of gases (■), gasoline (▼) and coke (▲) in the conversion of polyethylene as a function of reaction-time: (a) E-Cat A; (b) E-Cat B and (c) Cat C.

increased as a function of reaction-time. The highest gas yield was observed on E-Cat A, with about 28% at the longest reaction-time, while catalysts E-Cat B and Cat C yielded around 20%. In all the cases coke yields were always lower than 10%, and it was particularly low on E-Cat B. Finally, the products also included  $C_{12+}$  hydrocarbons, their yields being always lower than 7% (data not shown).

The composition of the gaseous fraction of products for the case of E-Cat A, which is also representative of the other catalysts, and the changes as a function of reaction-time, are shown in Fig. 3. It can be observed that  $C_4$  olefins and propylene (it was by

far the most important compound in the  $C_3$  fraction, data not shown) were the most significant products among gases. Since isobutane was essentially the only saturated compound in the  $C_4$  group, it is easy to observe that the olefinicity (that is, the percentage of olefins in a given group) is very high in this  $C_4$  fraction, initially more than 80%. It is interesting to see that this ratio is much higher than that observed in the cracking of VGO feed-stocks, which is about 60–65% for the various operative modes [18]. The same trend was observed for isopentane and the  $C_5$  hydrocarbons. The important incidence of catalytic cracking along with the high proportion of branched

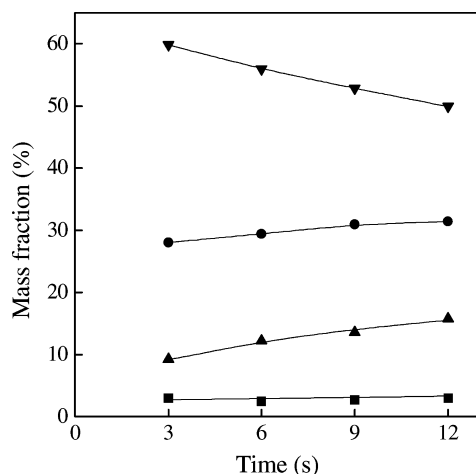


Fig. 3. Composition of the C<sub>1</sub>-C<sub>4</sub> fraction as a function of reaction-time (E-Cat A). Dry gas C<sub>1</sub>-C<sub>2</sub> (■), C<sub>3</sub> (●), isobutane (▲) and olefins C<sub>4</sub> (▼).

polymer chains in low density polyethylene [7] may explain these observations. The high proportion of branched C<sub>4</sub> and C<sub>5</sub> compounds is in part coincident with observations from other authors that used various zeolite catalysts [5,19], but differences exist mainly in the ratios between olefins and paraffins, which were observed to be higher in this work. However, it has to be considered that the catalysts used and particularly, the experimental techniques, were very different from those in this work. Olefins are initial products in catalytic cracking and, apparently in this system, they are not suffering important hydrogen transfer that saturates them into paraffins.

It is interesting to see that most of the initial products in the gasoline cuts were aromatic compounds. In effect, the average values of the aromatic selectivities (the ratio between C<sub>6</sub>-C<sub>12</sub> aromatics and total gasoline fractions) were about 43% (aromatic yield 26%) for E-Cat A, 64% (aromatic yield 48%) for E-Cat B, and 77% (aromatic yield 56%) for Cat C. The yields of aromatics decreased as a function of reaction-time in all the cases. This high aromaticity in the gasoline fraction assures a positive contribution to the standard products in the FCC process from the standpoint of fuel quality.

The possibility that aromatics are indeed formed by the interaction between products of the conversion of the polymer and the solvent (i.e. that toluene alkyla-

tion is important), was excluded based on experiments performed under the same conditions with 1-pentene dissolved into toluene in about the same proportion as the plastic. It was verified that the formation of alkylaromatic compounds was negligible (less than 1%) in every case. This could be extrapolated to the case in which plastics are dissolved in actual VGO feed-stocks, since common FCC product distributions (i.e. coming from VGO) include an important portion of aromatic compounds in the naphtha fraction, of about 24–30% [18,20]. Aromatics then would not be subjected to significant alkylation by products from the polymer. This low interaction between aromatics in FCC naphtha and products from the intrinsic conversion of the recycled polymers allows mass balance calculations to estimate the product distributions that result from using polymer-VGO solutions as the feed-stock (see below). Concerning the yields of aromatic hydrocarbons from the conversion of polyethylene, a wide dispersion in the experimental information is observed. Again depending on catalysts and experimental approach, some works report low aromaticity in gasoline range products (e.g. [9,19,21]), while others state the opposite (e.g. [8]).

The catalytic action of FCC catalysts on polyolefin addition polymers, leading to the wide distribution of products observed in this work, can be understood on the following basis: carbenium ions could be formed from the polymer chains or fractions that can be protonated at olefinic bonds, either at random or end positions [7,8]; also hydride abstraction from them would lead to carbenium ions. Once formed, they could be subjected to a large number of reactions, including  $\beta$ -cracking, hydride transfer, isomerization, cyclization, aromatization, etc. [22]. It is to be expected then, that light olefins, isoparaffins and aromatics be formed significantly.

These observations about product distributions suggest that the FCC process may reinforce its role as a raw materials supplier for the petrochemical industry in case waste polyethylene is recycled by incorporation into the standard feed-stocks, since both low molecular weight olefins and isobutane (the most important gas products in polyethylene conversion) are valuable chemicals. It is to be noted that in general, at 12 s reaction-time, about 30% of the recycled polyethylene was converted into light olefins C<sub>3</sub>-C<sub>5</sub>.

If the various yields are calculated for polymer-VGO mixtures at 10% dilution (e.g. using the experimental information from E-Cat A, 6 s reaction-time), the comparison against typical FCC yields (different catalysts, [20]), shows that C<sub>4</sub> olefin yields are increased in about 10–15%, while isobutane yields do not change significantly. Moreover, the very low yield of dry gas C<sub>1</sub>–C<sub>2</sub> is also a positive issue, since the capacity of compressors in the FCC units would not be compromised: calculations show dry gas yields about 8–10% lower in comparison with VGO feed-stocks. The same example calculations show that slight increases in gasoline yields are to be expected and, concerning its composition, the proportion of aromatics would increase only from 24 to 26% [20]. This proportion of aromatics would not interfere with gasoline blending operations. However, it should be noted that these figures are just an example and actually, each case in a given refinery (catalyst, standard feed-stock, operative conditions) should be evaluated separately.

Another issue that needs to be considered is the yield of coke, due to the delicate FCC heat-balance. Even though the maximum coke yields from polyethylene (10% in E-Cat A and cat C; 7% in E-Cat B) are somewhat higher than the one produced by standard feed-stocks (usually around 5%, [18]), they would not interfere, because the overall coke yield would increase to about 5.7% in case waste plastics are added at a rate of 10%. This figure is under the average coke yield observed in the processing of residue feed-stocks [23].

This recycling alternative does not need the development of a new process because it would represent merely an addition of the waste polymer to the usual feed-stocks of FCC, which is a mature and cost-effective process. Additional experimentation with VGO feed-stocks is needed in order to confirm that this course of action is advantageous.

#### 4. Conclusions

Under the approach of recycling waste polymers by their addition to FCC feed-stocks, the conversion of low density polyethylene dissolved in toluene over commercial FCC catalysts allowed to determine their specific contribution to products in the process.

Results were qualitatively similar in all the catalysts. The contribution is centered mainly in the gasoline fraction, with high aromatic content, although the production of gases is also important, with a high proportion of valuable light olefins C<sub>3</sub>–C<sub>4</sub>; isoparaffins C<sub>4</sub>–C<sub>5</sub> are significant as well. The additional coke load originated by the conversion of the plastic would not represent any problem for the operation of the FCC units. It was confirmed that, besides benefits in the products obtained and because it is based on a proven, cost-effective process, this recycling alternative does not need the development of new technologies, thus making it a very interesting option to solve a major environmental problem.

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