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# Pyrolysis of Polyethylene in a Fluidized Bed Reactor

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A fluidized sand bed reactor was used to study the production of gases from polyethylene (HDPE) at five nominal temperatures (ranging from 500 to 900 °C). Both HDPE primary decomposition and wax cracking reactions take place inside the reactor. Yields of 13 pyrolysis products (methane, ethane, ethylene, propane, propylene, acetylene, butane, butylene, pentane, benzene, toluene, xylenes, and styrene) were analyzed as a function of the operating conditions. The results are compared with the data obtained by pyrolysis of HDPE in a Pyroprobe 1000, where secondary wax and tar cracking is small. Correlations between the products analyzed with those of methane are discussed.

## Introduction

The yields of the products obtained from a pyrolysis process are due to the raw material decomposition (primary reactions) and to the reactions suffered by the primary volatiles (secondary reactions). The extension of the secondary reactions depends on the experimental equipment as well as the operating conditions. It is well-known that high residence times and high temperatures favor the secondary reactions.

Various experimental devices can be used to carry out primary and secondary processes of wastes. Hydrocarbons are formed from both primary and secondary reactions and normally in equipment with high heating rates of the samples. A fluidized bed reactor has been widely used for obtaining high yields of gases: Igarashi et al.<sup>1</sup> used a dual fluidized bed reactor to pyrolyze municipal solid waste; Kuester<sup>2</sup> used a fluidized sand bed reactor to obtain olefins from pyrolysis of different biomass; Scott and Piskorz<sup>3,4</sup> used a similar reactor to pyrolyze wheat straw, aspen-poplar wood and Scott and Czernik<sup>5</sup> to pyrolyze plastics; Font et al.<sup>6–9</sup> studied the pyrolysis of almond shells in a fluidized sand bed reactor at low and high temperatures; García<sup>10</sup> studied the pyrolysis of municipal solid waste in the fluidized bed; Beaumont and Shwob<sup>11</sup> used a reactor to pyrolyze beech wood; Kaminsky<sup>12–15</sup> and Kaminsky et al.<sup>16–21</sup> used the

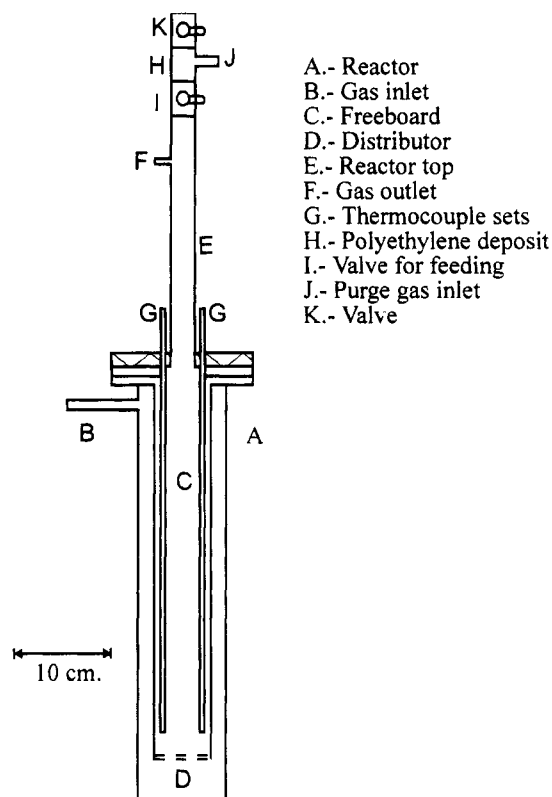


Figure 1. Reactor scheme.

fluidized sand bed reactor to pyrolyze various types of plastics, sewage sludge, etc. On the other hand, other

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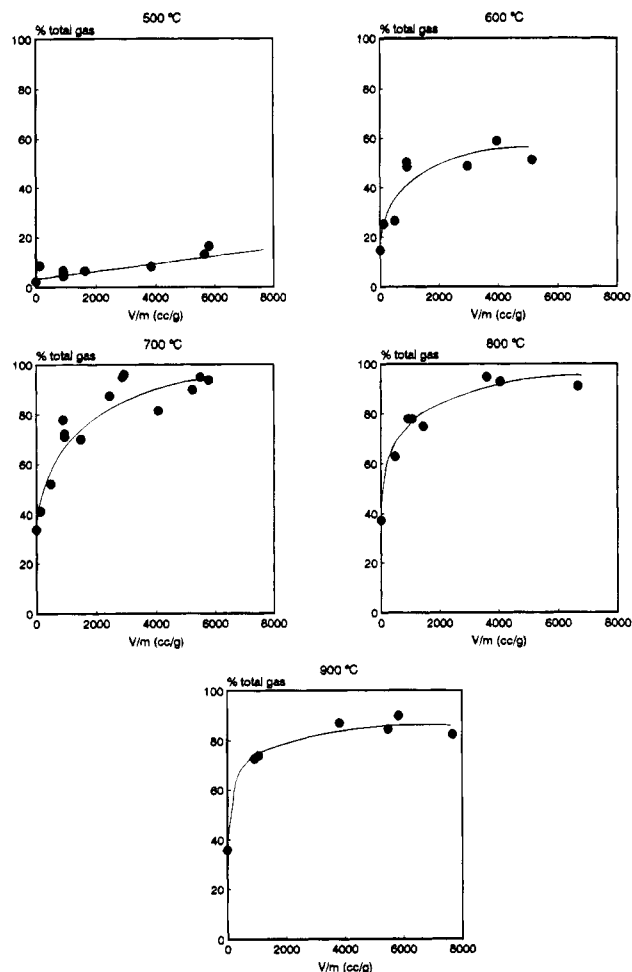
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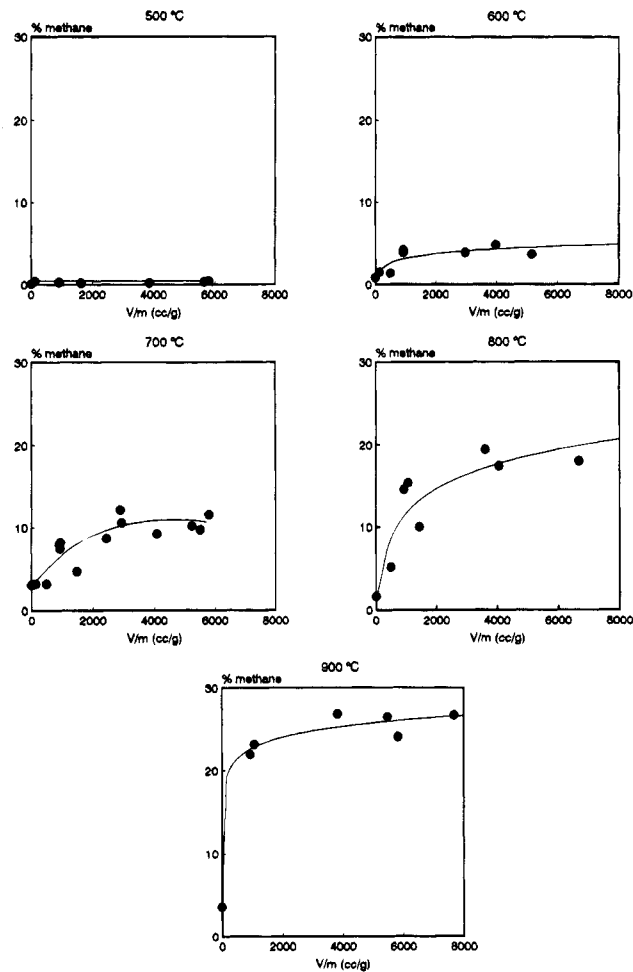
**Figure 2.** Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : total gas.

type of reactors were used, where the gas yield are also high: Antal<sup>22</sup> used a semibatch, laminar flow reactor to pyrolyze tars from cellulose and lignin, Sanner et al.<sup>23</sup> used an electrically heated retort to study municipal solid waste pyrolysis, Boroson et al.<sup>24</sup> studied the pyrolysis of wood tars in a two-stage reactor system, and Diebold<sup>25</sup> used a vortex reactor to pyrolyze biomass to vapors, followed by a tubular reactor to study the thermal cracking of those vapors.

In this work, the gas production by pyrolysis of HDPE was studied in a fluidized sand bed reactor, where primary and secondary reactions take place. The results are compared with those obtained in a Pyroprobe 1000, where the residence time of the volatiles in the hot zone of the probe is very short, and consequently, the secondary reactions do not take place (García et al.<sup>26</sup>).

The following aspects are considered in this paper:

(1) influence of pyrolysis temperature on yields of



**Figure 3.** Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : methane.

compounds obtained from pyrolysis of HDPE; (2) influence of residence time of volatiles in the hot zone of the reactor on yields of compounds obtained from HDPE pyrolysis; (3) analysis and discussion of the correlation of the different product yields; (4) comparison of the results presented with those obtained using a Pyroprobe 1000 (analytical apparatus).

## Experimental Section

The pyrolysis equipment used was a fluidized sand bed reactor, as shown in Figure 1. It is similar to the reactor described by Font et al.<sup>6</sup> to pyrolyze almond shells, although some aspects in the reaction zone as well as in the gas and liquid collection systems were modified.

Pyrolysis was carried out in a cylindrical 18/8 stainless steel reactor. The diameter of the reactor was 6.9 cm. and the length was 43.2 cm. The inert fluidized bed was sand of 0.105–0.210 mm particle size, calcined at 900 °C and washed by an acid solution of HCl. The inert gas used was helium of 99.999% purity.

Heating was achieved by means of a refractory oven. The bed surface temperature was controlled automatically at five different temperatures: 500, 600, 700, 800, and 900 °C. The reactor was not isothermal, showing a temperature gradient from the sand bed to the top of the reactor. Two chromel–alumel thermocouples were used to control and measure the temperature profile.

The experimental procedure was as follows: a 0.2–3 g sample of HDPE was placed in the feeder (see Figure 1); the flow of the inert gas was fixed and the oven was switched on.

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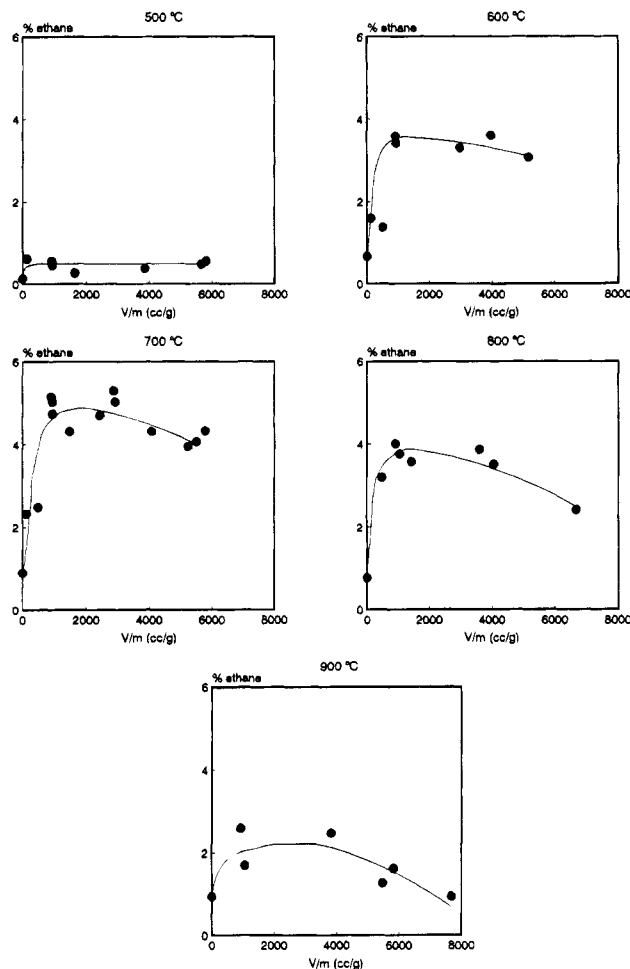
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**Figure 4.** Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : ethane.

When the reactor reached the selected temperature, the exit flow was shifted to the feeder in order to eliminate the air. After a few minutes, the feed valve was opened and the sample poured onto the hot sand bed (between 100 and 1500 g of sand). After the addition, gases evolved from the reactor were collected, to a volume of 40 L, in a Teflon bag provided with an in-out valve and a septum for sampling and analysis.

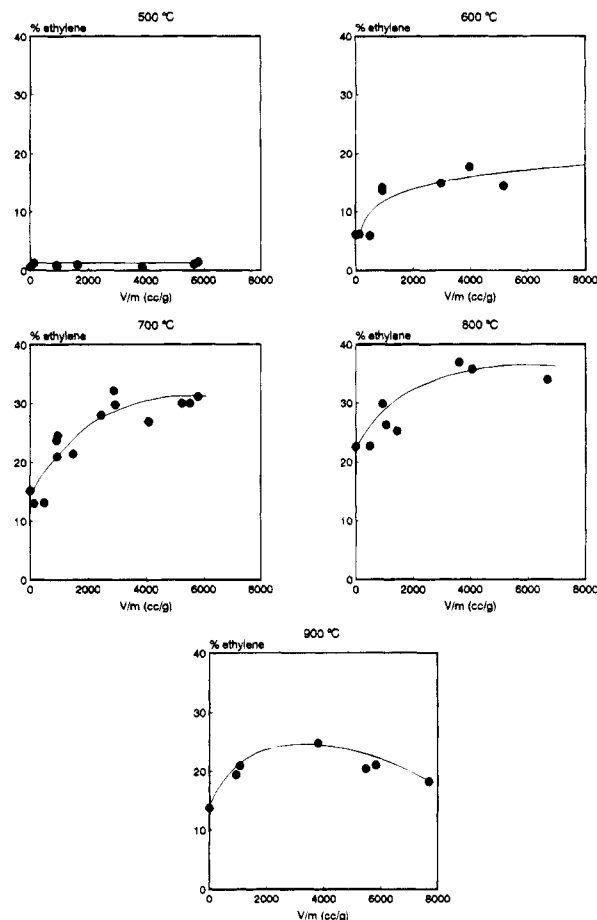
After each experiment, the temperature profile in the upper part of the reactor was measured.

The compounds obtained were identified and quantified by a Shimadzu GC-14A gas chromatograph using FID detector and two different columns: (a) alumina column for analyzing methane, ethane, ethylene, propane, propylene, acetylene, butane, butylene, pentane, and benzene; (b) Petrocol A column for toluene, xylenes and styrene.

## Experimental Results and Discussion

**Fluidization Conditions.** Several fluidization runs were performed at room temperature in a glass tube, in order to select the appropriate sample size and the inert gas flow to be used in the fluidized bed reactor, taking into account the following aspects:

**Particle Size.** Small sizes favor the internal heat transfer within the particle, while on the other hand, in fluidized bed reactors, the particles must be greater than a minimum, in order to avoid entrainment of fines. This aspect is not very important when the material has a large density, as in the case of HDPE. In addition, the HDPE melts at 120 °C, and consequently in the



**Figure 5.** Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : ethylene.

fluidized bed reactor working at 500–900 °C the samples will melt very rapidly.

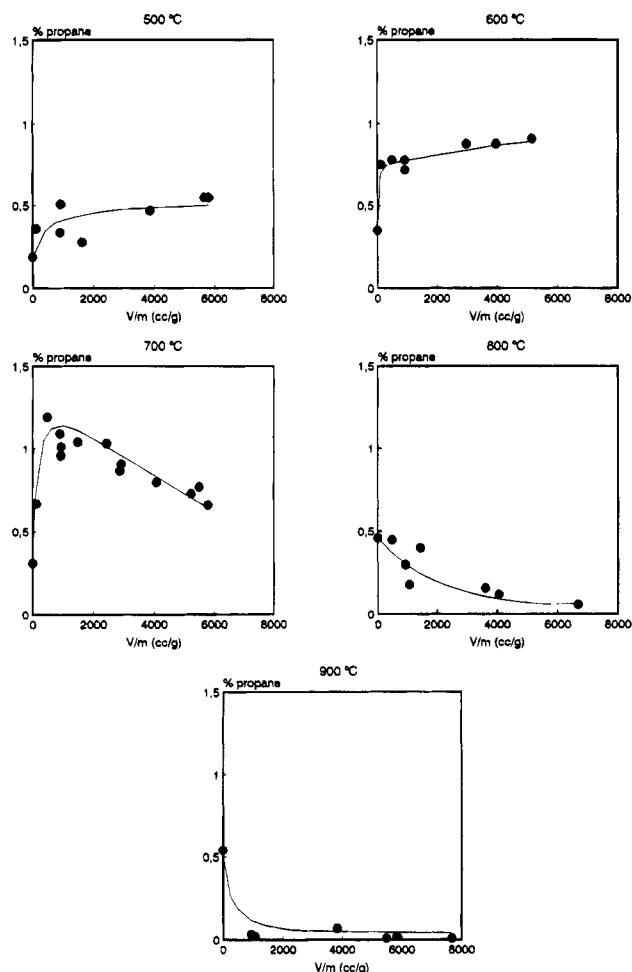
Nonprocessed HDPE with MW 22 000 and with an average diameter of 5 mm was pyrolyzed. Various runs were carried out with processed HDPE of the same size as nonprocessed HDPE, after its transformation in a toy factory.

It was observed in the glass tube that the HDPE particles and the sand particles mixed rapidly in the upper part of the sand bed. Within 10 s, the HDPE particles were covered by the sand particles. This shows a good contact between both materials. In the preliminary tests, high yields, however, were obtained when working with this HDPE particle size in the fluidized bed reactor at 500–900 °C. Due to this, all the runs were carried out with this HDPE particle size.

**Inert Gas Flow.** High flow rates improve the sand–solid mixing and the external heat transfer between the hot bed and the cold solid, while on the other hand, an excessive flow rate may cause a considerable entrainment of fines. Furthermore, the gas flow must be limited in order to allow the volatiles to be cracked in the upper part of the reactor.

The minimum fluidization velocity of sand ( $U_{mf}$ ), at the different operating temperatures was theoretically calculated using the Ergun equation (Kunii and Levenspiel<sup>27</sup>). The value  $U_{mf}$  slightly depends on temperature in the selected range, indicated as follows: 1.43

(27) Kunii, D.; Levenspiel, O. *Fluidization Engineering*; John Wiley and Sons: New York, 1969.



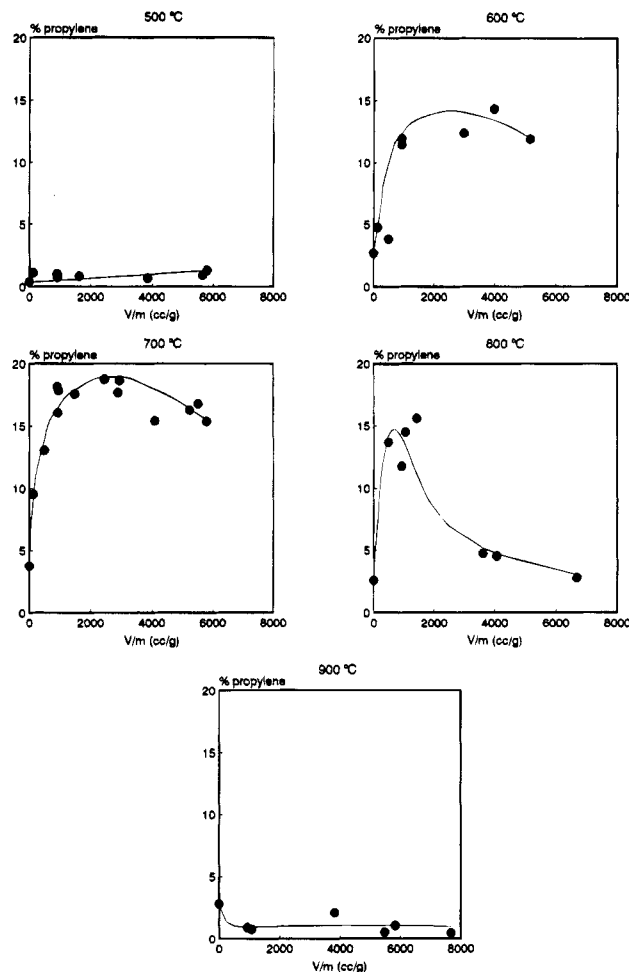
**Figure 6.** Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : propane.

cm/s at 500 °C, 1.35 cm/s at 600 °C, 1.29 cm/s at 700 °C, 1.23 cm/s at 800 °C, and 1.19 at 900 °C. Consequently, if the helium flow is kept constant in the range 500–900 °C, the fluidization state of the sand bed as well as the heat transfer between the hot bed and the cold solids will be similar. The selected value for the gas velocity was 3.6 cm/s calculated at the nominal operating temperature of the sand bed, which is 3 times the  $U_{mf}$  at 900 °C (the highest operating temperature) and 2.5 times the  $U_{mf}$  at 500 °C (the lowest one). The experimental value for  $U_{mf}$  working at 700 °C was 1.26 cm/s, which is in good agreement with that predicted by the Ergun equation.

**Influence of Temperature and Residence Time on Yields of Products in the HDPE Pyrolysis.** In order to study the maximum yields of gases that can be obtained from HDPE pyrolysis, 41 experiments were carried out at five sand bed temperatures: from 500 to 900 °C at 100 °C intervals. Yields of methane, ethane, ethylene, propane, propylene, acetylene, butane, butylene, pentane, benzene, toluene, xylenes, and styrene were determined in each experiment.

Both the height of the bed (or the mass of sand) and the weight of HDPE discharged onto the hot bed were modified in each experiment.

Four series of runs were carried out at five different temperatures. In each series, values of volume  $V$  or the sand bed mass and the polyethylene mass  $m$  were changed, in order to obtain different yields. The mass



**Figure 7.** Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : propylene.

of sand was varied from 100 to 1500 g and the HDPE discharged from 0.2 to 3 g. Thus, the mean residence time of volatiles is different in each run, depending on the mass of volatiles produced and the volume of the upper part of the reactor, from the top of the fluidized bed to the reactor head.

Since the reactor is not isothermal (temperature ranging from that of the sand bed to approximately 300 °C at the top of the reactor), it is difficult to find a parameter that is representative of the tar cracking extension. A magnitude that could be roughly proportional to the residence time is the ratio between the volume of the upper part of the reactor, above the sand bed ( $V$ ), and the mass of the HDPE discharged onto the bed ( $m$ ). When  $V$  is constant, the greater the value  $m$ , the lesser the residence time. When  $m$  is constant, then the greater the value  $V$ , the greater the residence time.

In order to test the reproducibility of the experiments, three runs with the same conditions were carried out. Table 1 shows the corresponding results. As can be seen, the variation coefficient is much greater for the minor compounds than for the major ones. Nevertheless, it is possible that the variation coefficient could be greater at other operating conditions.

Figures 2–12 show the variation of the yields vs the ratio  $V/m$  for the compounds analyzed at the five nominal temperatures. The plots for styrene, acetylene, and xylenes have not been considered due to the dispersion of experimental data. In these graphs, the

Table 1. Reproducibility of the Experiments<sup>a</sup>

	exp 1	exp 2	exp 3	std dev	av value	variation coeff (%)
methane	16.32	15.21	16.76	0.65	16.10	4.05
ethane	4.22	4.01	4.00	0.10	4.08	2.53
ethylene	30.66	31.15	30.19	0.39	30.66	1.29
propane	0.25	0.32	0.23	0.04	0.27	14.76
propylene	6.75	7.76	5.62	0.87	6.71	12.99
acetylene	0.03	0.03	0.02	0.00	0.03	15.74
butylene	0.56	0.79	0.49	0.13	0.61	21.33
butane	0.28	0.28	0.31	0.01	0.29	4.69
pentane	2.10	2.46	2.02	0.19	2.20	8.70
benzene	12.12	12.36	13.76	0.72	12.75	5.67
toluene	2.33	2.53	2.13	0.16	2.33	6.93
xylenes	0.05	0.07	0.04	0.01	0.05	24.75
styrene	0.01	0.00	0.01	0.00	0.00	70.91
total gas	75.68	76.98	75.59	0.64	76.08	0.84

<sup>a</sup> Sand mass = 200 g. HDPE mass = 1.015 g. Bed temperature = 800 °C.  $V/m = 1436 \text{ cm}^3/\text{g}$ .

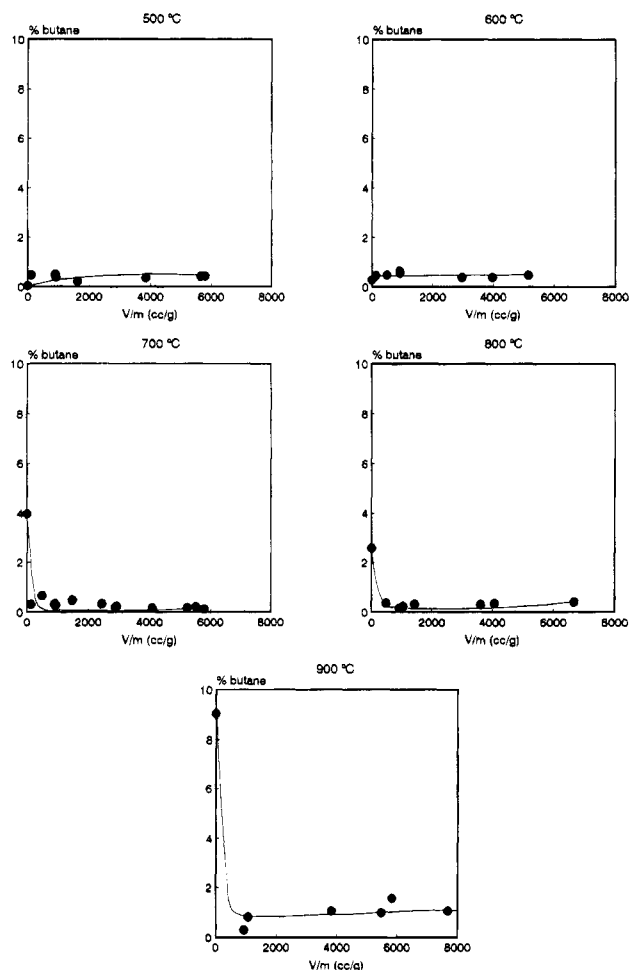


Figure 8. Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : butane.

primary reactions are represented by  $V/m = 0$  obtained in a Pyroprobe 1000 equipment with the following operating conditions: nominal heating rate, 20 000 °C/s; pyrolysis time, 20 s; pyrolysis temperature, 500, 600, 700, 800, and 900 °C; interphase temperature, 200 °C; sample mass, from 0.1 to 1.0 mg. Table 2 shows the results obtained.

In the Pyroprobe 1000, it can be assumed that the secondary cracking of the tars and waxes is small, due to the small volume of the probe that is at the nominal temperature. For nominal heating rates of 20,000 °C/s

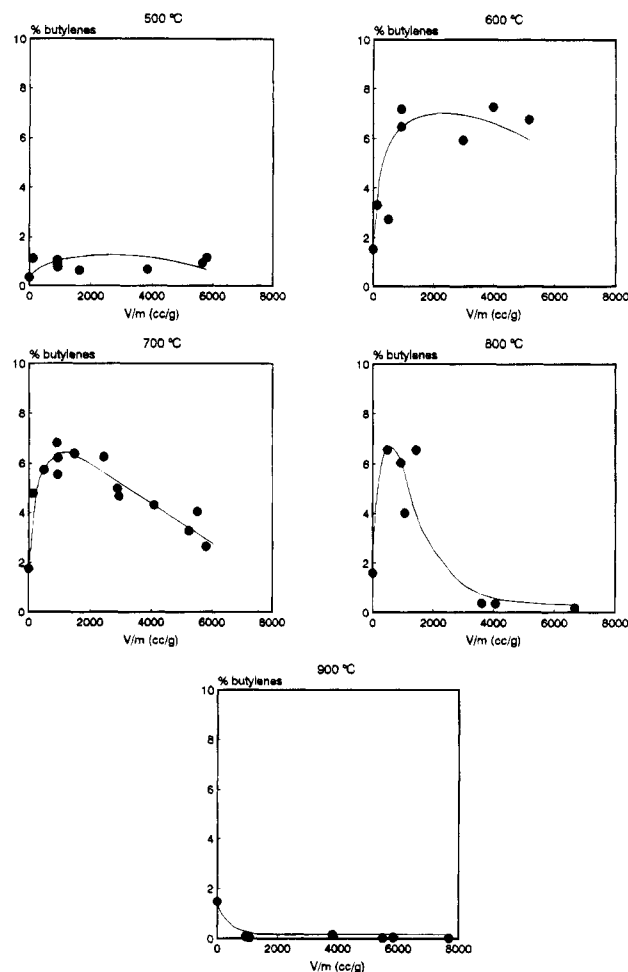


Figure 9. Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : butylene.

and nominal temperatures of 900, 800 and 600 °C, heating rates of 3375, 2700 and 2025 °C/s, were estimated, respectively (Caballero et al.<sup>28</sup>). More detail of the Pyroprobe and its performance can be found elsewhere (Font et al.,<sup>8</sup> Garcia et al.,<sup>10</sup> and Caballero et al.<sup>28</sup>).

The extrapolation of the results obtained in the fluidized bed reactor when  $V/m$  equals zero shows a good agreement with the results in the Pyroprobe 1000.

In the experiments carried out at 500 °C, the principal product is a degraded HDPE, obtained as a solid at room temperature. The molecular weight of those HDPE waxes (analyzed by GPC) is around 300, or about a  $C_{20}$  material.

Table 3 shows the maximum yields of all the compounds analyzed, as well as the operating conditions at which they were obtained.

In spite of the dispersion of the results, the following behaviors for gases as a function of the residence time could be deduced:

(a) Compounds whose yields increase clearly with the residence time of the volatiles in the reactor: methane, benzene and toluene.

(b) Compounds whose yield has a maximum at a determined  $V/m$ : ethane, propane, butane, butylene, ethylene, propane, propylene, and pentane. This be-

(28) Caballero, J. A.; Font, R.; Marcilla, A.; Garcia, A. N. *J. Anal. Appl. Pyrol.* **1993**, 27, 221–244.

Table 2. Yields of Products (wt %) Obtained from HDPE Pyrolysis in a Pyroprobe 1000

temp (°C)	methane	ethane	ethylene	propane	propylene	acetylene	butylene	butane	C5	benzene	toluene	xylenes	styrene	total gas	total waxes and tars
500	0.09	0.13	0.64	0.19	0.37	0.00	0.35	0.04	0.21	0.09	0.30	0.00	0.00	2.42	97.58
600	0.87	0.66	6.08	0.35	2.65	0.00	1.53	0.28	1.68	0.29	0.19	0.04	0.00	14.62	85.38
700	3.10	0.89	15.11	0.31	3.75	0.03	1.77	3.98	2.49	1.88	0.33	0.21	0.00	33.84	66.16
800	1.67	0.76	22.65	0.46	2.59	0.04	1.58	2.57	1.68	2.34	0.51	0.39	0.00	37.23	62.77
900	3.57	0.93	13.76	0.54	2.80	0.25	1.50	9.04	1.77	1.18	0.39	0.10	0.00	35.82	64.18

Table 3. Maximum Yields of Each Compound and Operating Conditions

compound	V/m (cm <sup>3</sup> /g)	temp (°C)	sand mass (g)	HDPE mass (g)	yield (wt %)
total gas	2874	700	300	0.4809	96.45
methane	5835	900	100	0.2650	24.06
ethane	2874	700	300	0.4809	5.30
ethylene	3608	800	300	0.3831	37.02
propane	484	700	1500	0.7969	1.19
propylene	2436	700	300	0.5674	18.77
acetylene	5835	900	100	0.2650	0.24
butylene	3972	600	300	0.3840	7.27
butane	5835	900	100	0.2650	1.57
pentane	920	800	300	1.5020	6.00
benzene	5835	900	100	0.2650	30.56
toluene	5505	700	300	0.2511	6.41
xylenes	5485	900	300	0.2520	6.67
styrene	5835	900	100	0.2650	2.56

havior is also the tendency shown by the total gases: within the 500–800 °C temperature range, when the bed nominal temperature is increased, a lower residence time to achieve the maximum yield is required; nevertheless, at 900 °C the total gas yield is lower than that for 800 °C at any residence time, showing the presence of craking to soot.

**Correlation of Results.** In order to correlate the results obtained by HDPE pyrolysis in a fluidized bed reactor, logarithms of yields corresponding to each product obtained vs. logarithm of methane yields have been plotted for each run (Figure 13–17). This method is widely used in literature: Funazukuri et al.,<sup>29–31</sup> Scott et al.,<sup>32</sup> Font et al.,<sup>9</sup> García et al.,<sup>10</sup> and Caballero et al.<sup>28</sup> In the pyrolysis of lignocellulosic tars, methane is related because its formation takes place through a mechanism which is very sensitive to temperature. In this work, methane has also been related in these plots.

If methane yield is considered as an indicator of the extension of pyrolytic reactions, different behaviors can be deduced from Figure 3:

1. Yields of ethane, ethylene, propane, propylene, butylene, and pentane show maximums at temperatures near 700 °C, as a consequence of the secondary cracking undergone by these hydrocarbons.

In the figures for ethane, ethylene, propylene, butylene, and pentane a straight line of slope 1 is shown. As can be seen, there is a good correlation until temperatures near 700 °C. If the temperature is higher than 700 °C, the cracking of these compounds, with the increase in methane production, is observed from these curves.

2. Yields of benzene increase as the methane yield increases, but yields of toluene are not a function of methane yield (within the experimental errors).

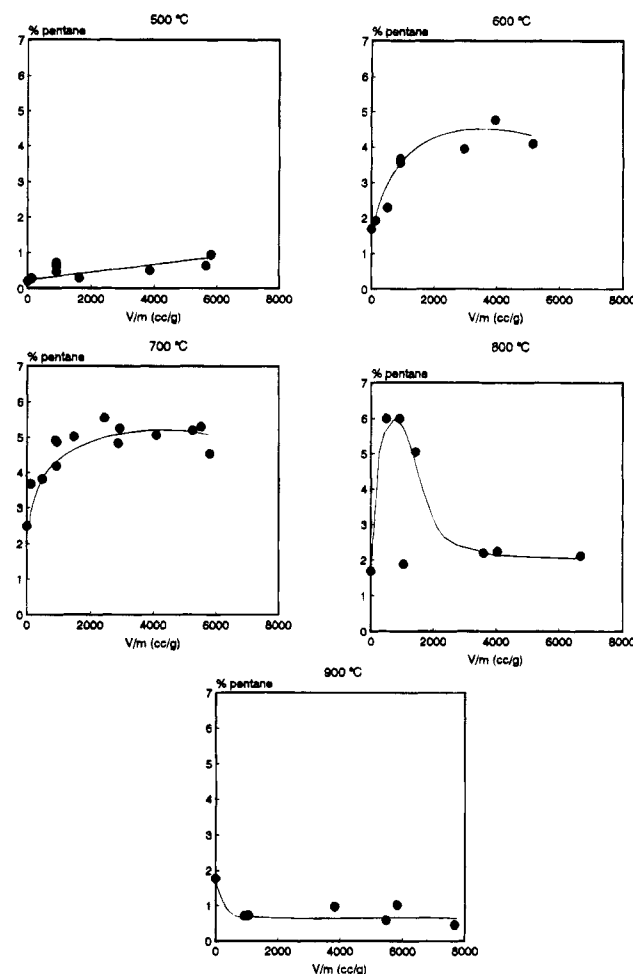


Figure 10. Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : pentane.

3. The butane is cracked very quickly in comparison with the other hydrocarbons.

Although the aim of this paper is not to study the mechanisms through which the pyrolysis of polyethylene takes place, some comments have, however, been introduced based on literature.

For polyethylene pyrolysis, Rice and Rice<sup>33</sup> suggested a mechanism which involves steps of formation and free radicals and abstraction of hydrogen by radicals. Simha et al.<sup>34</sup> proposed a similar mechanism to explain the process of thermal degradation of olefins and other polymers. This mechanism involves several steps: initiation, propagation or free-radical transfer, and termination. With regard to a free radical formed in the initiation or in any other steps, one of two competing reactions may follow: (1) propagation (unzipping) to yield monomers, and (2) free-radical transfer involving

(29) Funazukuri, T.; Hudgins, R. R.; Silveston, P. L. *Ind. Eng. Chem., Prod. Des. Dev.* **1986**, *25*, 172.

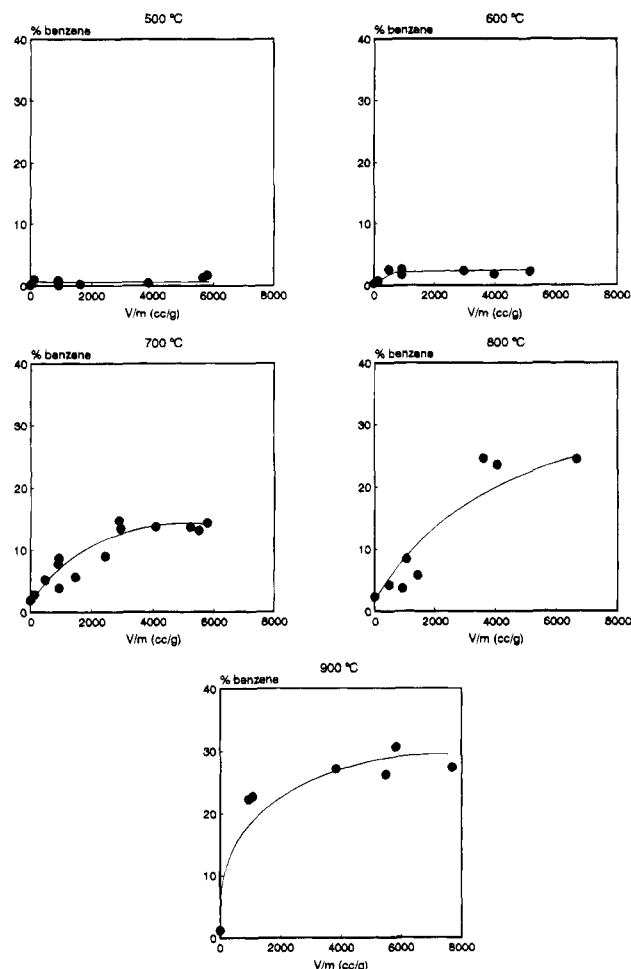
(30) Funazukuri, T.; Hudgins, R. R.; Silveston, P. L. *J. Anal. Appl. Pyrol.* **1986**, *9*, 139.

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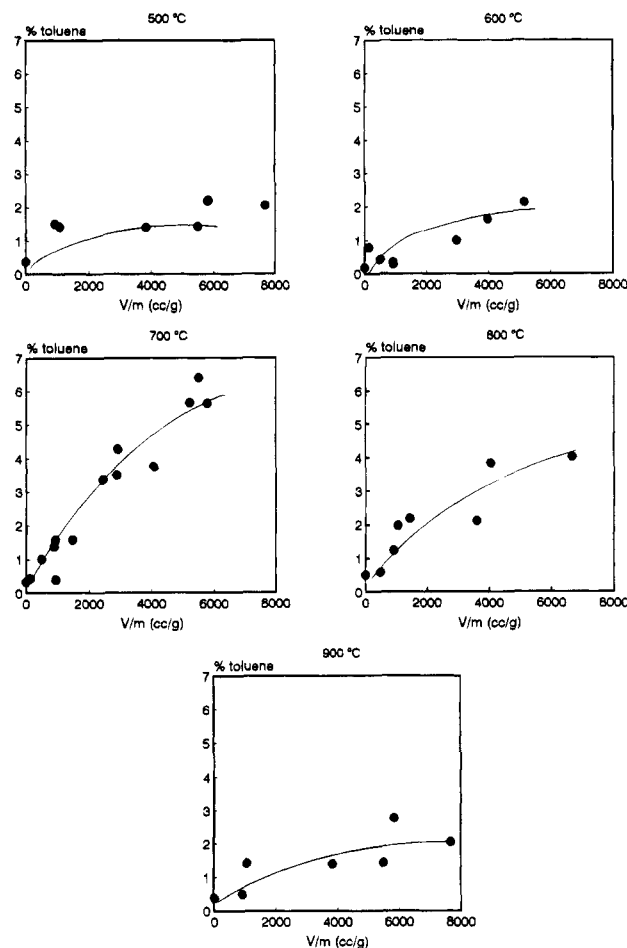


**Figure 11.** Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : benzene.

an abstraction of hydrogen from a polymer chain and resulting in the formation of one saturated end, one unsaturated end, and a new free radical. Which of these alternatives will prevail will depend on the amount of hydrogen in the chain.

Oakes and Richards<sup>35</sup> found that polyethylene is stable at temperatures up to 290 °C, but at higher temperatures the molecular weight decreases, and the products of mild degradation are plastics similar to the original polyethylene or hard waxes. More extensive degradation yields semisolid pastes or liquids, but gaseous products are not formed in any appreciable quantity below 370 °C, and even then ethylene is only a minor constituent of the volatile primary product. The authors also state that the degree of unsaturation increases as the extent of the reaction increases. The production of vinyl double bonds in the initial phase of degradation is less than in the latter stages. Wall et al.<sup>36</sup> found similar results on pyrolyzing polymethylene. Thus, for polyethylene or polymethylene, the transfer reaction is the predominant one. As a result, the degradation products in primary pyrolysis consist of chain fractions of various sizes with very few monomers.

On considering these previous studies and in accordance with the experimental results of this paper, it



**Figure 12.** Variation of the hydrocarbon yields vs the ratio between the volume  $V$  of the upper part of the reactor and the discharged mass  $m$ : toluene.

can be deduced that the primary pyrolysis of the HDPE in the condensed phase takes place through a free-radical transfer that leads to low yields of gases, including ethylene, and high yields of waxes. Nevertheless, the high yields of ethylene obtained from the secondary pyrolysis of waxes at the gas phase can be interpreted as a consequence of the propagation reaction.

The high yields of propylene from the pyrolysis of waxes could be explained in two ways: (a) in the propagation reaction, the last radical formed has three carbons, and (b) there are ramifications that favor a hydrogen transfer before the propagation step (in order to make a more stable radical), and the propagation yields propylene.

The high yield of methane is due to cracking reactions at the end of the chain, as occurs in many pyrolytic processes of hydrocarbons. The formation of methane in the pyrolysis is the most probable, but it cannot yield the most stable species.

On the other hand, Irwin<sup>37</sup> shows that for vinyl polymers (as PVC, polyethylene, polypropylene, etc.) the elimination of small neutral molecules is common: in the PVC the loss of HCl is dominant, and this is followed by "kick-back" fission through a six-membered transition state to yield benzene as the major product.

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Table 4. Processed and Virgin HDPE Pyrolysis in a Fluidized Bed Reactor

$T$ (°C)	700		700		800		800		800	
sand (g)	100		300		200		300		300	
PE (g)	0.267	0.261	0.384	0.3840	1.015	1.0180	0.486	0.4860	1.502	1.502
$V/m$ (cm <sup>3</sup> /g)	5791	5924	3600	3600	1436	1432	2844	2844	920	920
sample	virgin	processed	virgin	processed	virgin	processed	virgin	processed	virgin	processed
methane	11.57	7.76	9.90	7.80	16.10	14.51	14.74	14.45	14.63	15.32
ethane	4.33	3.68	4.68	3.54	4.08	3.72	3.71	2.68	4	4.03
ethylene	31.14	35.09	28.34	23.46	30.66	31.55	31.16	29.73	29.89	27.25
propane	0.66	0.58	0.86	0.62	0.27	0.26	0.28	0.12	0.3	0.27
propylene	15.35	17.16	17.05	14.66	6.71	6.21	10.17	9.94	11.75	10.13
acetylene	0.08	0.00	0.01	0.03	0.03	0.02	0.04	0.03	0	0.02
butylene	2.65	3.52	4.51	2.97	0.61	0.81	3.46	3.24	6.04	4.32
butane	0.13	0.21	0.20	0.09	0.29	0.34	0.31	0.30	0.15	0.27
pentane	4.53	5.65	5.16	4.19	2.20	2.41	3.63	1.89	6	5.28
benzene	14.30	12.20	13.58	11.90	12.75	18.87	15.21	18.80	3.72	9.31
toluene	5.64	3.30	4.02	5.40	2.33	4.17	2.19	4.45	1.25	4.47
xylene	2.15	1.54	1.17	2.06	0.05	1.22	0.02	1.54	0.25	1.64
styrene	1.31	0.82	0.54	1.72	0.00	1.74	0.02	2.76	0.01	2.11
total analyzed	93.84	91.51	89.98	78.42	76.08	85.62	84.91	89.94	77.99	84.42

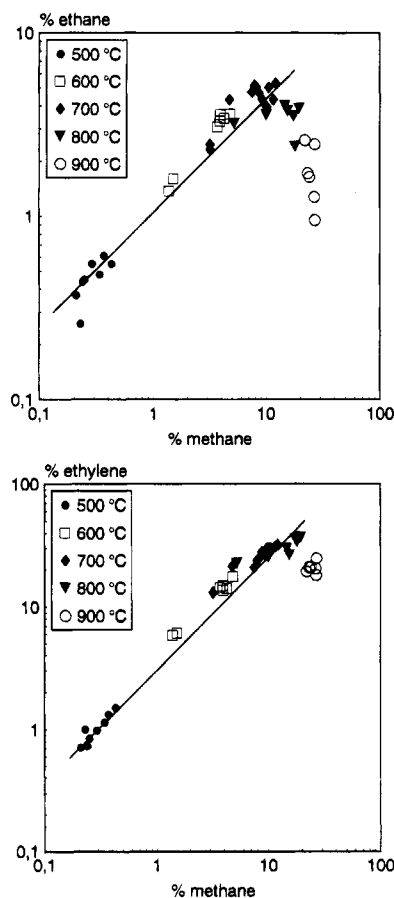


Figure 13. Logarithm of the hydrocarbon yield vs logarithm of methane yield: ethane and ethylene.

**Processed HDPE Pyrolysis.** Five runs were also carried out with the HDPE of the same type, after its transformation in a toy factory, and with the same size as the nonprocessed HDPE.

The processed polyethylene samples are wastes of a toy factory of the area. This processed polyethylene is formed by a mixture of high-density polyethylene (around 90–95 wt %) and rubber (5–10 wt %). More details about its composition are not available.

Table 4 shows the results, in comparison with those obtained with virgin HDPE. Comparing the results between virgin and processed polyethylene, it can be concluded that the differences are not great. Only yields of aromatic compounds at 800 °C are higher with the processed HDPE than those with virgin HDPE.

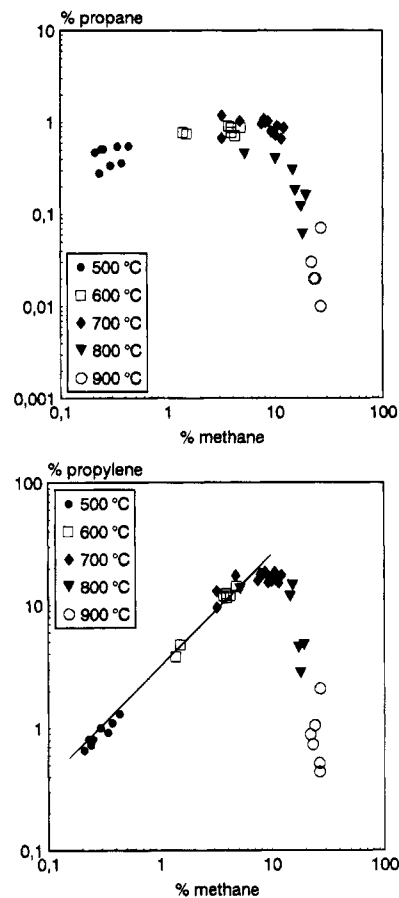
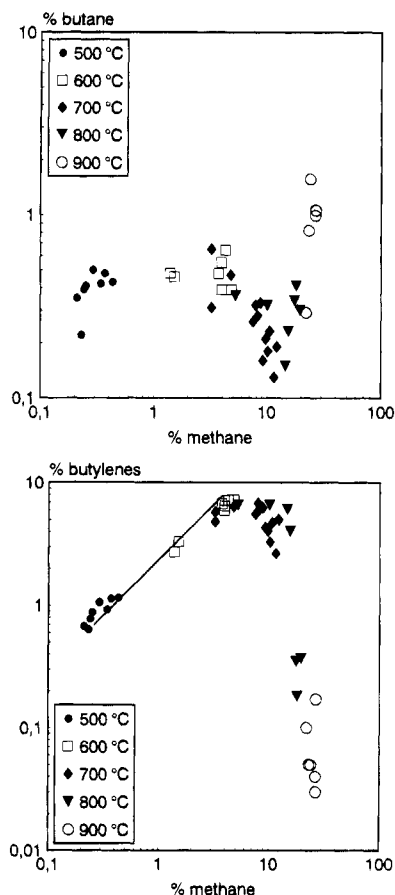


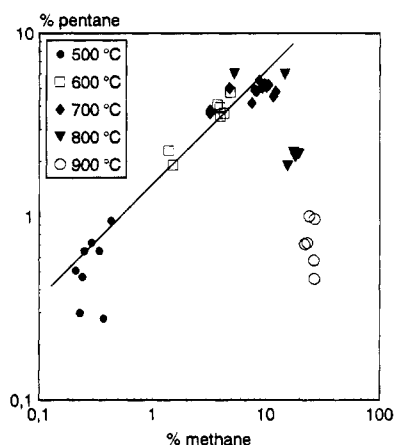
Figure 14. Logarithm of the hydrocarbon yield vs logarithm of methane yield: propane and propylene.

In all runs, as in the case of nonprocessed HDPE, the weight of the solid pyrolysis product was negligible and was determined by calcination at 900 °C of sand and the product.

**Comparison with Other Literature Results.** In the literature there is not much information about polyethylene pyrolysis and the formation of the products. Kaminsky studied the pyrolysis of polyethylene and other polymers. With respect to the polyethylene pyrolysis, Kaminsky<sup>12</sup> obtained total yields of gases similar to those obtained in the present work: at 810 °C at pilot plant scale, the major products were methane (18.8%), ethane (6.2%), ethylene (17.9%), propylene (7.2%), butadiene (1.5%), benzene (21.6%), and toluene (3.8%). The total of gas was around 96%. Some

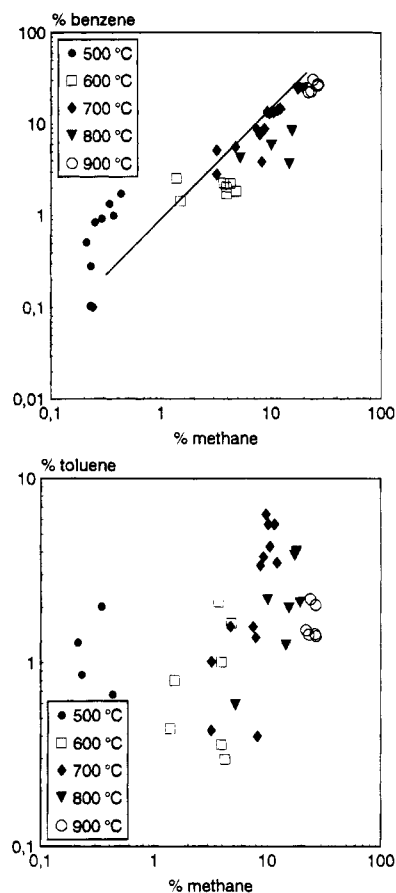


**Figure 15.** Logarithm of the hydrocarbon yield vs logarithm of methane yield: butane and butylene.



**Figure 16.** Logarithm of the hydrocarbon yield vs logarithm of methane yield: pentane.

important differences can be observed with respect to the experimental data presented in this work: Kaminsky<sup>13</sup> found that methane has a maximum ( $\approx 20\%$ ) at  $770\text{ }^{\circ}\text{C}$  approximately, and ethylene production at  $720\text{ }^{\circ}\text{C}$  ( $\approx 18\%$ ). In the present work, methane increases continuously (to  $24.0\%$ ) and the maximum for ethylene production was at  $800\text{ }^{\circ}\text{C}$  ( $37.0\%$ ). With regard to the influence of the residence time of volatiles, Kaminsky et al.<sup>17</sup> obtained similar results to those obtained in the present work for methane, propylene, and aromatic compounds, but they observed a minimum in the ethylene production. These differences may be due to the different reactor used (continuous fluidized sand bed reactor with pyrolysis gas recycling and feeding at the bottom of the bed) and to the polymer used.



**Figure 17.** Logarithm of the hydrocarbon yield vs logarithm of methane yield: benzene and toluene.

On the other hand, Scott et al.<sup>5</sup> found that methane, ethylene, ethane, and propylene increase their yield at temperatures between  $515$  and  $790\text{ }^{\circ}\text{C}$ , when pyrolyzing low density polyethylene in a sand fluidized bed reactor (maximum yields  $6.4$ ,  $31.1$ ,  $2.7$ , and  $12.8\%$ , respectively).

Stammbach et al.<sup>33</sup> found that the solid residue increases as temperature increases in the range  $720$ – $840\text{ }^{\circ}\text{C}$  (between  $0.5$  and  $4.2\%$ ), whereas the amount of gas decreases, which is in good agreement with that shown above.

## Conclusions

From the study of HDPE pyrolysis in a fluidized sand bed reactor, the following conclusions can be deduced:

1. Yield of total gas obtained increases in the range  $500$ – $800\text{ }^{\circ}\text{C}$  from  $5.7$  to  $96.5\%$ . At higher temperatures, the yield of total gas decreases slightly.
2. The formation of methane, benzene, and toluene is favored by high residence times, but ethane, ethylene, propane, propylene, butane, butylene, and pentane undergo cracking to different extents at increasing residence times and/or temperature.
3. The maximum yield of total gas obtained at  $800\text{ }^{\circ}\text{C}$  from HDPE pyrolysis is  $94.5\%$  with the following composition:  $20\%$  methane,  $3.8\%$  ethane,  $37\%$  ethylene,  $0.2\%$  propane,  $4.7\%$  propylene,  $0.3\%$  butane,  $0.4\%$  butylene,  $2.2\%$  pentane,  $24\%$  benzene,  $2.1\%$  toluene,  $0.01\%$  acetylene, and  $0.02\%$  xylenes and styrene.

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