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ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · FEBRUARY 1997

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Influence of Gas-Phase Reactions on the Product Yields Obtained in the Pyrolysis of Polyethylene

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The characterization of the product fractions obtained from the pyrolysis of polyethylene (PE) in a laboratory-scale fixed bed reactor was performed. The experimental system allowed quantitative information to be obtained on the global tar, char, and gas yields. Pyrolysis runs were performed using reactor temperatures ranging between 500 and 800 °C. The influence of the residence times in the reactor of the primary volatiles generated by the pyrolysis process was also discussed. The secondary reactivity of the tar originated from PE pyrolysis was examined. A lumped-parameters approach was used in order to evaluate the global kinetic parameters for the gas-phase tar-cracking process. PE tars resulted to be more refractory to thermal decomposition than those obtained in the pyrolysis of biomass and lignocellulosic materials, but more reactive than tars obtained in the pyrolysis of coal.

Introduction

The amount of plastic wastes is growing year after year, and the fraction of plastics in municipal solid wastes (MSW) and in refuse-derived fuels (RDF) is progressively increasing. Pyrolysis and gasification processes appear to be promising routes for the upgrading of solid wastes to more usable and energy dense materials such as gas fuel and/or fuel oil or to high-value feedstocks for the chemical industry. Therefore the characterization of the pyrolysis behavior of plastic wastes is of interest in the optimization of pyrolysis processes for the recovery of energy rich or valuable product fractions. Furthermore, a pyrolysis step is always present in the initial stages of gasification and of combustion. Pyrolysis and gasification processes yield three different product fractions: a solid fraction (char), a condensable fraction (tar), and a gaseous fraction. The operating conditions (mainly heating rate and temperature) and the starting materials influence the composition and the relative amount of the three product fractions. Moreover the final product yields from pyrolysis and gasification processes are strongly influenced by secondary gas-phase reactions occurring to the primary products released during solid degradation.

Relevant work was done on the characterization and quantification of the product yields in the pyrolysis of biomass and lignocellulosic wastes. The influence of process severity on product yields and characteristics was ascertained in several studies, summarized in exhaustive reviews (Antal and Varhegyi, 1995; Di Blasi, 1993). The thermal and catalytic secondary tar-cracking reactions of lignocellulosic materials were also extensively examined (Antal, 1983; Boroson et al., 1989; Bridgewater, 1994; Evans and Milne, 1987; Stiles and Kandiyoti, 1989). On the other hand, there is still the need to study the product yields in the pyrolysis of plastic wastes and their dependency on the operating conditions. The studies present in the literature on the pyrolysis of polyethylene (PE), that is, the major com-

Table 1. Proximate and Ultimate Analysis of the LD-PE Used in Experimental Runs

	%		%	
humidity	—	N	—	
fixed carbon	0.1	H	15.4	
volatile matter	99.7	O ^a	traces	
ashes	0.2	S	—	
C	84.3	Cl	traces	

^a By difference.

ponent of plastic wastes, deal with the characterization of the weight loss rate during the primary thermal degradation (Darivakis et al., 1990; Jellinek, 1949; Madorsky, 1952; Oakes and Richards, 1949) and the primary product characterization (Hodgkin, 1982; Khal-turinskii, 1987; Madorsky, 1965; Sugimura and Tsuge, 1979). Other papers refer to full-scale and pilot-scale pyrolysis or gasification plants (Kaminsky, 1992). However, a fundamental analysis of the product yields dependency on the operating variables is still lacking. Furthermore, no quantitative studies on homogeneous gas-phase reaction kinetics of tars originated from the pyrolysis of plastic wastes are present in the literature, although it was found that plastic may generate more refractory tars than lignocellulosic materials (Alden et al., 1992).

The focus of this paper is the characterization of the product fractions during the pyrolysis of PE in a laboratory-scale fixed bed reactor. The influence of process conditions on the product yields and composition was also studied. The main pyrolysis products were characterized and quantified as a function of reactor temperature and residence time. Quantitative information was obtained on the secondary reactivity of tars generated in the pyrolysis of polyethylene. Global kinetic parameters were estimated for the overall tar-cracking process and were compared to literature data.

Experimental Section

Materials. Low-density polyethylene (LD-PE) pellets were used in experimental runs. Proximate and ultimate analysis of the material are reported in Table 1.

Experimental Techniques. Preliminary characterization of the LD-PE was carried out using thermogravimetric analysis (TGA) and differential scanning

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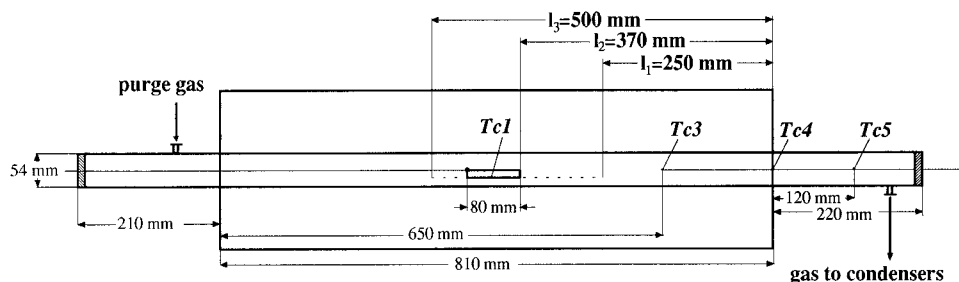


Figure 1. Fixed bed reactor.

calorimetry (DSC). Experimental information on high-temperature LD-PE pyrolysis and gas-phase reactions were achieved using a laboratory-scale tubular fixed bed reactor (FBR).

TGA and DSC. Thermogravimetric (TG) runs were performed using a Mettler TA-3000 system. TG and differential thermogravimetric (DTG) curves in pyrolysis conditions were recorded using pure N₂ as the purge gas (0.1 L/min) and constant heating rates of 5, 10, and 20 °C. "Isothermal" TG data were obtained inserting PE samples within the preheated TG furnace. Typical sample weights were 15 mg.

DSC experimental data were collected using a Mettler DSC 25 calorimeter, using a constant heating rate (10 °C/min), pure N₂ as a purge gas, and typical sample weights of 5 mg.

FBR. This experimental device is similar to that used in a previous study (Cozzani et al., 1995), so only the essential features and the main modifications introduced will be discussed. The reactor consisted of an Inconel inner tube mounted coannularly within the furnace refractory. PE samples were inserted in a semicylindrical sample holder (Figure 1). The reactor was fluxed by a 1 L/min helium stream. Typical sample weight was about 15–20 g. Residence times of 60 min were used in order to achieve complete sample conversion. Upon exiting the reactor, volatile products passed through a filter followed by a train of cold traps, where condensables were recovered. The uncondensed gases were sampled in a reservoir system and analyzed using a Perkin Elmer Sigma 2B gas chromatograph equipped with a TCD detector and a Chromosorb 102 silica gel column. Different product fractions were separated and recovered in experimental runs. These were operationally defined as: (a) char, the solid fraction collected at the end of the run in the sample holder, on the reactor walls, and in the filter; (b) tar, the condensable volatile material that was recovered from the cold traps and other piping system surfaces following the reactor; (c) gas, what was not condensed in the trap system. The procedures used for experimental runs and product characterization were fully described elsewhere (Cozzani et al., 1995). This device allows one to obtain data on global yields of gas, tar, and char, on the composition of gaseous pyrolysis products, and on the rates of gas evolution. Further characterization of the solid fraction (char) included ultimate analysis and structure analysis by scanning electron microscopy (SEM).

FBR Characterization. The FBR geometry allows for the presence of gas-phase reactions. Volatiles generated by the thermal degradation of PE in the sample holder pass through an extended hot tubular zone before leaving the reactor (see Figure 1), and gas-phase reactions may have an important influence on the final product yields and characteristics. Thus, the charac-

terization of the "homogeneous section" of FBR is important in order to fully understand the gas-phase phenomena.

Gas temperatures resulted slightly below the programmed furnace temperature (less than 20 °C, due to heat transfer limitations), but limited temperature variations along axial and radial coordinates were detected (less than 10 °C). In the following, the furnace temperature will be used to identify the run.

The estimated heating times of volatiles resulted negligible with respect to the residence time within the reactor (Cozzani et al., 1995). Thus, the homogeneous section of the FBR is an isothermal tubular section where gas-phase reactions may take place. Assuming a plug-flow behavior, the residence time of the volatiles in this tubular section can be evaluated with the following expression

$$\tau = \frac{Sl}{Q_p + Q_v} \quad (1)$$

where S is the reactor cross section, l is the length of the tubular section after the sample holder, Q_p is the volumetric flow rate of the purge gas, and Q_v is the estimated volumetric flow rate of volatiles. Three different positions of the sample holder were used in experimental runs: $l_1 = 250$, $l_2 = 370$, $l_3 = 500$ mm (see Figure 1). The different positions of the sample holder result in different residence times of the volatiles in the homogeneous section of the reactor. Thus the study of the effect of volatiles residence time on the final product yields and characteristics was possible. It must be pointed out that the heating rates of the sample are not affected by the use of different axial positions for the sample holder. This is confirmed by the experimental temperature profiles recorded by thermocouple Tc1 positioned inside the sample holder (Boschi, 1995). The residence times estimated by eq 1 are reported in Figure 2 and range between 1 and 20 s.

Results and Discussion

TGA and DSC Data. TG, DTG, and DSC experimental curves obtained at a heating rate of 10 °C/min (0.167 °C/s) in pure nitrogen are reported in Figure 3. In the TG runs, the weight loss process is completed at temperatures lower than 500 °C at a heating rate of 0.167 °C/s. The char yields obtained in constant heating rate runs are always less than 1%. Also in the "isothermal" runs at temperatures between 450 and 600 °C the char yields are never higher than 1%. The endothermic heat of reaction obtained from DSC data for the thermal degradation process was 650 J/g.

FBR Data. Figure 4 reports the global yields of tar, gas, and char as a function of the furnace temperature and of the residence time of the volatiles generated by

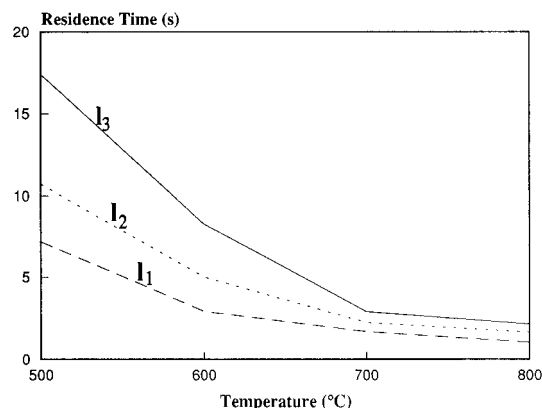


Figure 2. Residence time of volatiles in the FBR homogeneous section as a function of temperature and sample holder position.

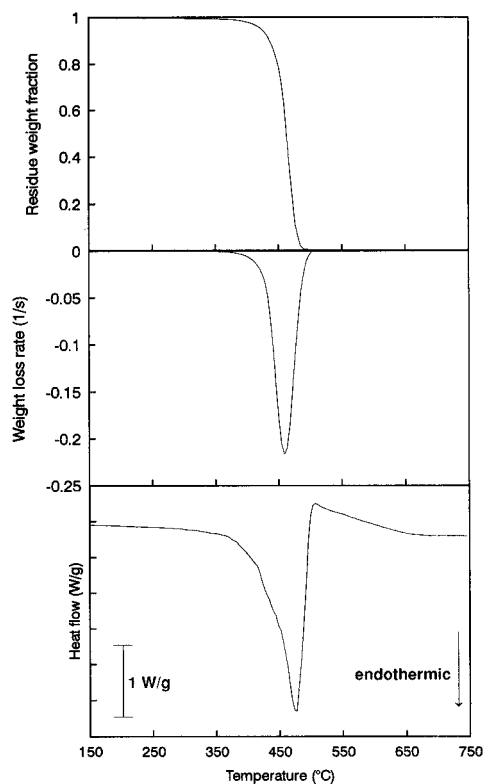


Figure 3. TG, DTG, and DSC data.

the pyrolysis process in the homogeneous section of the FBR. All data shown (points) represent the mean values obtained from at least five experimental runs. Repeatability of experimental yields resulted better than $\pm 3\%$. The gas mass fraction reported in Figure 4 is calculated by difference. However, experimental data were obtained evaluating the average molecular weight of uncondensables by gas analysis data and considering the gas production on mass basis from the volumetric gas flow rates. The estimated experimental gas mass fractions resulted in a mass balance better than 95%. Most of the discrepancy is maybe due to leakages in the gas recovery system and to errors in the estimate of mean gas molecular weight throughout the process.

Figure 4 shows that PE pyrolysis yields mainly tar at low temperatures (about 90% by weight of virgin PE). Increasing furnace temperatures results in the drastic depletion of tar yield (from 90% at 500 °C to about 5% at 800 °C of the virgin PE) and in higher yields of both gas and char fractions. The residence time influences significantly the global product yields only for reactor temperatures above 500 °C. The increase of residence

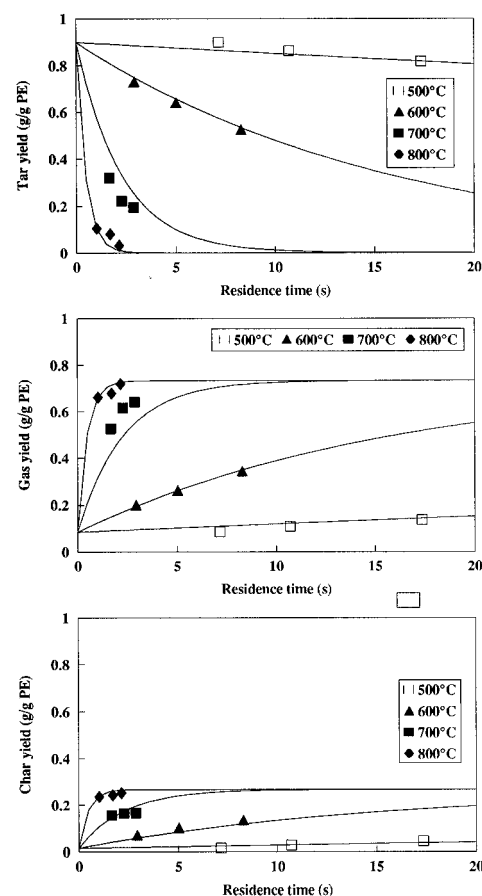


Figure 4. Global yields of tar, gas, and char in the FBR as a function of temperature and residence time. Symbols: experimental data. Lines: kinetic model predictions.

time also results in lower tar yields and in greater char and gas yields.

The literature on polymer thermal decomposition reports that the major products of the primary pyrolysis process are low or high molecular weight tars rather than gases (Sugimura and Tsuge, 1979; Hodgkin et al., 1982; Iida et al., 1975; Khalturinskii, 1987; Darivakis et al., 1990). The experimental data obtained in the FBR at low temperature (500 °C) confirm these results. However, the increase of char and gas yield at higher reactor temperatures suggests that the influence on product yields of secondary gas-phase processes becomes prevalent at temperatures higher than 600 °C in the present experimental configuration. These reactions are responsible for the conversion of the high molecular weight condensables to char and to gaseous compounds of lower molecular weight. The decrease of tar yield as the temperature is raised is generally observed in the pyrolysis of biomass, municipal solid wastes, and refuse-derived fuels (Hajaligol et al., 1982; Antal, 1983; Antal, 1985; Chan et al., 1988; Scott et al., 1988; Kojima et al., 1991; Evans and Milne, 1987). The presence of gas-phase reactions that lead to the formation of gas and char is confirmed by the deposition of char found in the homogeneous section of the FBR. At temperatures of 700–800 °C, most of the char is collected on the walls of the tubular reactor. Since primary pyrolysis reactions take place within the sample, positioned inside the sample holder, the presence of char on the reactor walls points out the role of the secondary reactions of the volatiles generated by the primary pyrolysis process on the final products. Furthermore, the char yields in the

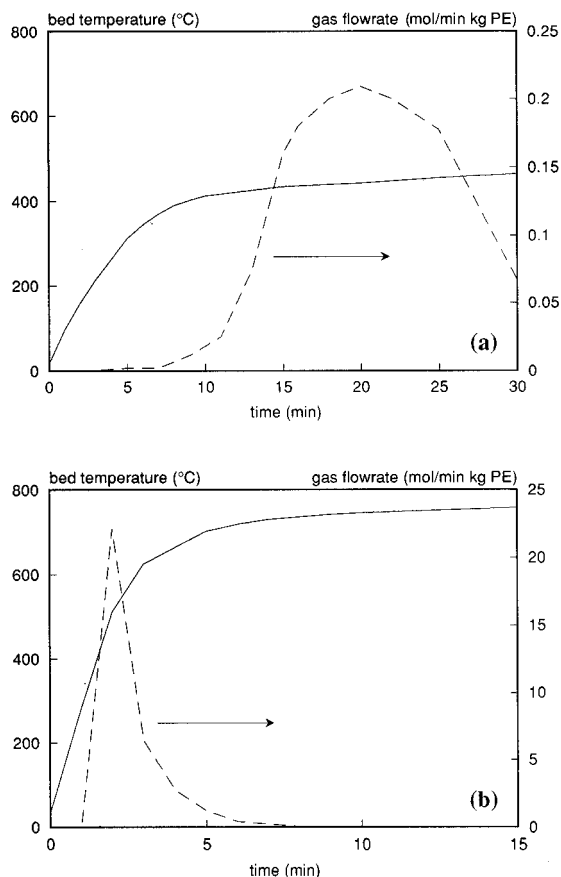


Figure 5. Experimental sample temperature and flow rate of pyrolysis gases as a function of time after sample insertion for two different reactor temperatures: (a) 500 °C; (b) 800 °C.

FBR at high temperature are far higher than those obtained in TGA runs.

The presence of both primary and secondary pyrolysis reactions in the FBR requires a careful analysis of the results presented in Figure 4 in order to identify the separate effects of the two processes on the final product yields. The primary pyrolysis process in the FBR takes place mainly during the heating transient, at sample temperatures always below 600 °C. In Figure 5 typical sample temperature profiles are reported as a function of time for two different furnace temperatures (500 and 800 °C, respectively). The temperature profiles are compared with the experimental overall evolution rates of the pyrolysis gas. The heating rate of the sample is only weakly influenced by the furnace temperature and ranges between about 1 °C/s at 500 °C and 2.5 °C/s at 800 °C. The comparison of parts a and b of Figure 5 points out that the evolution of volatile products takes place between 400 and 600 °C, independently of furnace temperature. Figure 5b shows that also at the higher furnace temperatures the evolution of pyrolysis products and thus the pyrolysis process are almost ended at temperatures lower than 600 °C. The temperatures and the heating rate present during the primary pyrolysis process are only slightly affected by the furnace temperature of the experimental run. Hence the primary yields can be supposed to present only minor variations depending on furnace temperature. Furthermore tar-cracking reactions are almost absent at 500 °C (Evans and Milne, 1987; Stiles and Kandiyoti, 1989; Bingyan et al., 1992). Therefore as a working hypothesis the products obtained in FBR from the 500 °C run with the minimum residence time were considered as the primary pyrolysis products.

Products Characterization

Gas. Figure 6 reports the molar gas composition (%) as a function of temperature for different residence times obtained from GC analysis. Table 2 reports the global mass yields of single gaseous species as a function of reactor temperature and of residence time, estimated from the GC and volumetric flow rate data. All data reported in Figure 6 and Table 2 are referred to the product gases considered free of carrier gas. The data are the mean values of at least three experimental runs. The repeatability was better than $\pm 5\%$. More details on the procedure and the evaluation of cumulative gas production data are given in a previous paper (Cozzani et al., 1995).

The composition and the yield of the gas obtained by the pyrolysis process are strongly influenced by reactor temperature. The uncondensable gaseous products obtained from the pyrolysis of PE are mainly hydrogen, methane, and ethylene. Unsaturated compounds (ethylene and propylene) molar fraction in the gas ranges between 10 and 50% (up to 45% by weight of the virgin PE) depending on operating temperature. A higher reactor temperature generally results in higher global mass yields of almost all the gaseous species detected. The overall LHV of the gas also slightly increases as FBR temperature is increased, mainly because of the increase in hydrogen content. Raising furnace temperature has a limited effect on the content of methane and of saturated hydrocarbons of the gas and results mainly in the increase of hydrogen content and in the decrease of ethylene and propylene molar fraction. The increase of hydrogen content of the gas at temperatures higher than 600 °C is probably caused by dehydrogenation reactions leading to char formation but may also suggest the presence of reactions leading to the formation of condensable aromatic or unsaturated compounds not present in the primary tar.

Longer residence times in the homogeneous section enhance the global gas yield, as shown by Figure 4, but have only a minor effect on gas composition. This may be evinced from Figure 6, where the molar fractions of the gas species are reported for different residence times. No marked effect of residence time can be observed, and the variations of the values of the percentile molar composition are within the experimental error. It must be recalled that the composition of the gas fraction obtained from pyrolysis runs in the FBR is mainly influenced by the gas-phase tar-cracking reactions. The absence of an evident effect of residence time on gas composition and on the other side the higher gas yields obtained with longer residence times suggest that the gaseous compounds are produced as a result of a global secondary reaction pathway where the rate-controlling step is the cracking of the high molecular weight compounds. Reactions among the light molecular weight uncondensable species, if present, are probably much faster than the cracking reactions and can be considered to be instantaneous at equilibrium.

Char. The char yield of the pyrolysis process becomes relevant (20–25% by weight) when high furnace temperatures (700–800 °C) are used. The char is collected mainly on the furnace walls at the end of the experimental runs. This confirms that gas-phase tar-cracking reactions are responsible for the large char yields at high temperatures. The ultimate analysis of the char is given in Table 3. As expected char is mainly composed of carbon, and the hydrogen content decreases with temperature. The ash content decreases with

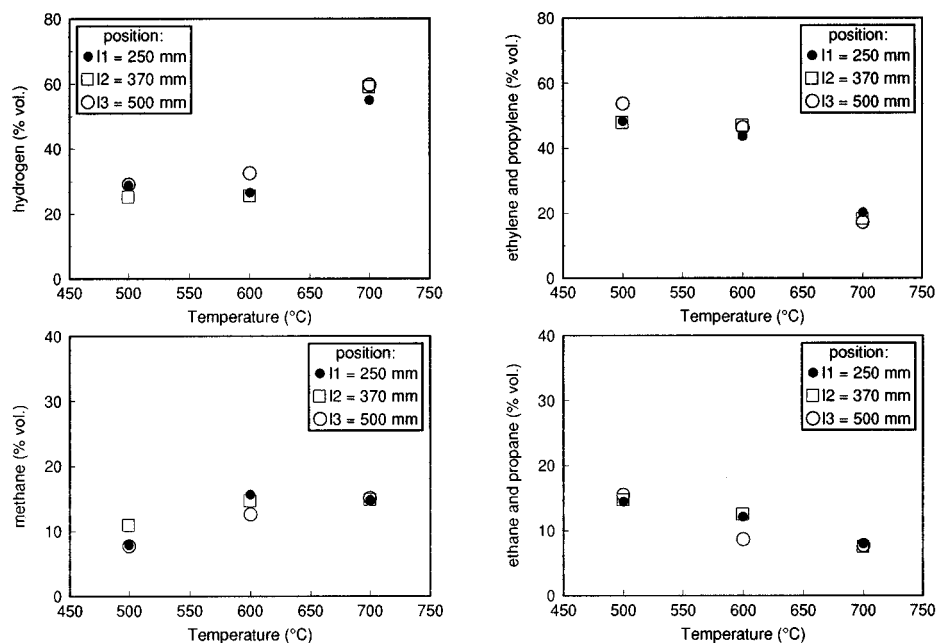


Figure 6. Volumetric composition of the gas produced from PE pyrolysis as a function of reactor temperature and residence time (the three different sample holder positions are related to the residence times reported in Figure 2).

Table 2. Cumulative Gas Production (g/100 g PE) and Lower Heating Value of the Gas at the Different Temperatures and Residence Times Used in Experimental Runs

temp (°C)	residence time (s)	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	total	LHV (kJ/g)
500	7.2	0.10	0.16	0.42	0.30	0.71	0.53	2.22	50.0
	10.7	0.13	0.42	1.20	0.60	1.76	0.61	4.73	48.7
	17.4	0.20	0.43	2.18	0.90	4.33	1.14	9.16	48.2
600	2.9	0.43	2.08	5.99	1.65	7.90	0.62	18.66	48.5
	5.0	0.47	2.70	6.66	2.49	8.74	1.06	22.12	48.5
	8.3	1.23	4.54	8.23	3.75	12.26	1.52	31.56	49.8
700	1.7	1.85	7.88	16.18	6.04	18.03	0.70	50.69	49.7
	2.3	2.43	8.75	17.56	6.12	22.32	1.14	58.32	50.1
	2.9	3.59	9.55	18.62	6.36	24.44	1.54	64.11	51.1

Table 3. Ultimate Analysis of the Char Obtained from PE Pyrolysis at Different Reactor Temperatures

%	500 °C	700 °C	800 °C
C	50.86	75.76	88.37
H	2.09	0.12	0.20
N	traces	traces	traces
ashes	47.05	24.12	11.43

temperature. The weight of the ash fraction present in the char is roughly equal to that of ashes in the virgin PE.

The structure of the char is evidenced in the SEM microphotography reported in Figure 7. The figure shows that the char seems to be comprised of clusters of submicronic particles. Both the composition and the morphology of char recall that of soot. Since the char must be separated from the gas stream before the use of the gas in a power generation system, the high char yields obtained when high temperatures are used may cause problems in energy recovery by gasification processes.

Tar. Less attention has been devoted in the present work to the characterization of the liquid phase obtained from the experimental runs, since exhaustive literature data can be found on the composition of the primary tar originated by PE pyrolysis (Sugimura and Tsuge, 1979; Hodgkin et al., 1982). The tar is mainly composed of high molecular weight linear aliphatic hydrocarbons (mainly C₈–C₂₃). The formation of light aromatics and



Figure 7. SEM microphotography of the char produced at 800 °C.

of PAH by gas-phase tar repolymerization reactions during the pyrolysis of PE at high temperatures has been reported in the literature (Blazso et al., 1993). The possible presence of these processes in the experimental conditions used in the present work seems to be confirmed by the global hydrogen mass balance. The marked increase of the hydrogen content of the pyrolysis gas at temperatures higher than 600 °C requires a pronounced decrease of hydrogen content of the tar fraction at 700–800 °C. This may suggest the activation of repolymerization reactions leading to the formation of secondary aromatic and unsaturated condensable products of high molecular weight at temperatures higher than 600 °C.

Overall Kinetics of Tar-Cracking Reactions

An indicative estimate of the global kinetic parameters of the tar-cracking process was obtained from the FBR data. Assuming as a working hypothesis that the volatiles obtained at 500 °C with the minimum residence time can be considered as the primary pyrolysis

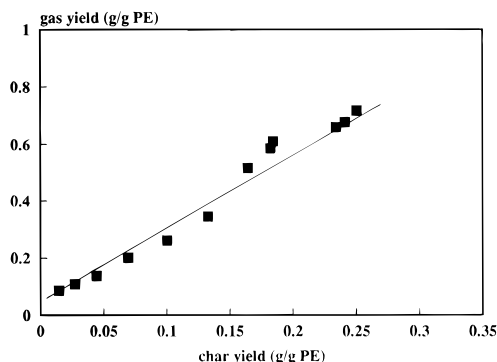


Figure 8. Correlation between gas and char yields. Symbols: experimental data.

products, the overall kinetics of the gas-phase process was evaluated. The complex reaction pathway that leads to the conversion of high molecular weight compounds (tar) to char and to low molecular weight gases was lumped to a single-step reaction mechanism



where also the reagents and the products of the global reaction pathway have been lumped in three categories: tars, gas, and char, defined in the experimental section of the paper. The global coefficients of the reaction, α and β , were obtained from the experimental gas to char mean mass ratio, plotted in Figure 8. The estimated values are $\alpha = 0.72$ and $\beta = 0.28$. The good correlation of the estimated coefficients to the experimental data obtained at different temperatures and residence times allows the use of constant global coefficients in the lumped reaction scheme.

A first-order Arrhenius kinetic rate equation was used to correlate experimental data

$$\frac{d\xi}{dt} = Ae^{-E_a/RT}(1 - \xi) = K(T)(1 - \xi) \quad (2)$$

where A is the frequency factor, E_a the apparent activation energy, R the universal gas constant, T the gas temperature, K the kinetic constant, and ξ the tar conversion, defined as

$$\xi = \frac{w_0 - w}{w_0} \quad (3)$$

where w is the weight fraction of tar and w_0 is the weight fraction of tar in the primary pyrolysis products ($w_0 = 0.9$, from the data at 500 °C). The initial condition used to integrate eq 2 was the following

$$\xi(t=0) = 0 \quad (4)$$

The relation between the conversion and the residence time of the volatiles in the homogenous section of the FBR is given by the following expression

$$\xi(\tau, T) = 1 - e^{-K(T)\tau} \quad (5)$$

where a plug-flow behavior has been assumed in the homogeneous section.

Frequency factor and apparent activation energy were obtained by a least-squares minimization technique. The logarithm of the estimated kinetic constant (K) is compared to the experimental data in Figure 9. The tar, char, and gas yields predicted by the kinetic model were calculated as a function of reactor temperature and

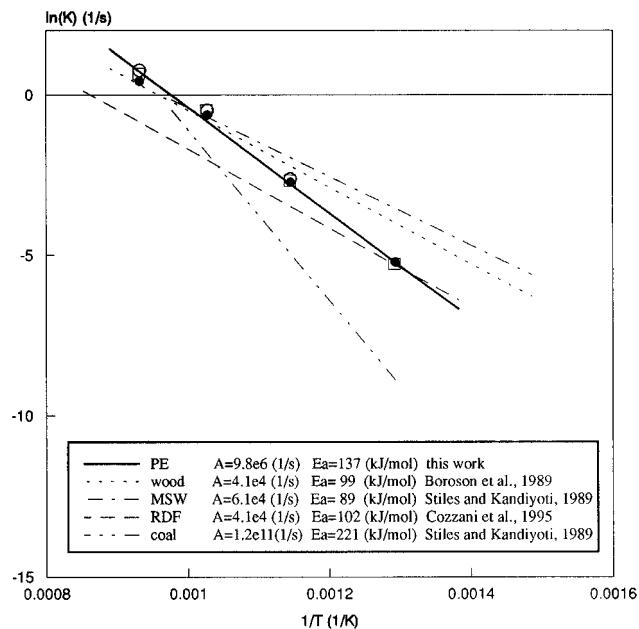


Figure 9. Comparison of kinetic data for the secondary reactivity of the tars produced in the pyrolysis of various starting materials. Symbols: experimental data obtained for the reactivity of PE tar (the three different sample holder positions are related to the residence times reported in Figure 2).

residence time. The calculation was performed considering the experimental yields obtained at 500 °C with the minimum residence time as the yields of the primary pyrolysis process. The results are compared to the experimental data in Figure 4. The good correlation of the experimental data to the model predictions and to the estimated kinetic parameters shown respectively by Figures 4 and 9 points out the effectiveness of this lumped-parameters approach in the overall description of the tar-cracking process.

Figure 9 reports also the data found in the literature for the secondary pyrolysis tar-cracking reactions of various starting materials: sweet gum hardwood, low-rank bituminous coal, municipal solid wastes, and refuse-derived fuel. The kinetic parameters obtained for the global tar-cracking process of PE tar are comparable to those obtained for the secondary reactivity of the tars obtained from other starting materials. Although some difficulties may arise in drawing general conclusions, the tar from the PE pyrolysis seems to be less reactive than the tars obtained from the pyrolysis of lignocellulosic materials and more reactive than the tars obtained from the pyrolysis of coal. The tar fraction obtained from the pyrolysis of MSW and RDF have a secondary reactivity that is comprised between that of lignocellulosic materials and that of PE. The variability in the reactivity of the MSW and RDF tars probably depends on the relative amount of cellulosic and plastic wastes present in the starting material.

With respect to other global models reported in the literature for the tar-cracking process, the kinetic model used in the present paper is able to fit the experimental data without the use of an ultimate value of the conversion in the kinetic rate expression given by eq 2. This means that in the experimental conditions used in the FBR runs, the ultimate value of the tar yield approaches zero, thus excluding the presence of a significant "nonreactive" tar fraction. The use of a nonzero value for the ultimate yield of tar is a working definition based on the process severity (Borison et al., 1989) that limits the validity of the kinetic parameters

obtained. Since no "minimum" tar yield was assumed to fit experimental data in the present study, the activation energy and frequency factor obtained seem to have a more general validity. Obviously the obtained kinetic parameters should be considered only as indicative estimates, as the assumptions made lead to an oversimplified kinetic model. However, this kinetic model has been extensively used for the description of the gas-phase conversion kinetics of volatiles generated by substrates as coal, wood, and MSW and RDF (Howard, 1981; Boroson et al., 1989; Stiles and Kandiyoti, 1989). The good performance of this simple model is possibly due to the important role of the first-order reactions in the gas-phase cracking of high molecular weight species, such as the cracking of tars to lower molecular weight species.

Conclusions

The product yields from the pyrolysis of PE at temperatures between 500 and 800 °C were characterized and quantified by different experimental techniques. Tar, char, and gas yields were independently determined with a mass balance to better than 95%.

In the experimental conditions used in the present work, the product yields were observed to be mainly influenced by the gas-phase tar-cracking process. Higher temperatures and residence times of the volatiles in the reactor resulted in the decrease of tar yield and in the increase of gas and char yields. The tar-cracking process was found to cause relevant char formation at temperatures of 700–800 °C. The formation of carbonaceous particles may cause fouling problems in pyrolysis and gasification processes.

The secondary reactivity of the tar originated from PE pyrolysis was also examined. PE tars were found to be more refractory to thermal decomposition than those obtained in the pyrolysis of biomass and lignocellulosic materials, but more reactive than tars obtained in the pyrolysis of coal. A lumped-parameters approach was used in order to evaluate the global kinetic parameters for the gas-phase tar-cracking process. This approach lead to an oversimplified kinetic model, so that the kinetic parameters obtained in the present study should be considered only as indicative estimates. However, a good accordance was found between the model results and the experimental data.

Nomenclature

A = frequency factor (s^{-1})
 E_a = activation energy (J/mol)
 K = kinetic constant (s^{-1})
 l = length of the tubular section of FBR after the sample holder (mm)
 Q_p = volumetric flow rate of the purge gas (mm^3/s)
 Q_v = volumetric flow rate of volatiles (mm^3/s)
 R = universal gas constant (8.31 J/mol)
 S = reactor section (mm^2)
 t = time (s)
 T = temperature (°C)
 w = weight fraction of tar
 w_0 = initial weight fraction of tar
 τ = residence time in the homogeneous section of FBR (s)
 ξ = conversion

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Received for review December 27, 1995

Revised manuscript received September 7, 1996

Accepted September 7, 1996*

IE950779Z

* Abstract published in *Advance ACS Abstracts*, November 15, 1996.