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Semivolatile and volatile compounds in combustion of polyethylene

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Abstract

The evolution of semivolatile and volatile compounds in the combustion of polyethylene (PE) was studied at different operating conditions in a horizontal quartz reactor. Four combustion runs at 500 and 850 °C with two different sample mass/air flow ratios and two pyrolytic runs at the same temperatures were carried out. Thermal behavior of different compounds was analyzed and the data obtained were compared with those of literature.

It was observed that α,ω-olefins, α-olefins and *n*-paraffins were formed from the pyrolytic decomposition at low temperatures. On the other hand, oxygenated compounds such as aldehydes were also formed in the presence of oxygen. High yields were obtained of carbon oxides and light hydrocarbons, too. At high temperatures, the formation of polycyclic aromatic hydrocarbons (PAHs) took place. These compounds are harmful and their presence in the combustion processes is related with the evolution of pyrolytic puffs inside the combustion chamber with a poor mixture of semivolatile compounds evolved with oxygen. Altogether, the yields of more than 200 compounds were determined.

The collection of the semivolatile compounds was carried out with XAD-2 adsorbent and were analyzed by GC–MS, whereas volatile compounds and gases were collected in a Tedlar bag and analyzed by GC with thermal conductivity and flame ionization detectors.

Keywords: PAHs; PE; Combustion; Furnace; Emissions

1. Introduction

There is a steady increase in the consumption of plastics worldwide due to some of their properties such as flexibility, affordability, endurance, durability, etc., which allow them to be suitable in almost every field. According to a report published by the Association of Plastic Manufacturers in Europe (2003), in the year 2002 the consumption of polymers for plastic applications in Western Europe was 38 123 000 tonnes, an increase of 6% from 2000. Each individual in this region consumed on average 94.8 kg of virgin plastics. The plastics with the greatest demand were polyethylene, both low (LDPE) and high density (HDPE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). The total production of plastic waste in Europe in 2002 was 20 391 000 tonnes, and 38% of the total collectable plastic waste was recovered, up from 36% in 2000. In tonnage terms, this represented an increase of 11%. Energy was recovered from 4 688 000 tonnes of plastic waste in 2002, an increase of 6.3% on 1999 figures and

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representing 23% of the total collectable plastic waste. Thermal treatments, both pyrolysis and combustion, are important alternatives to the disposal of plastic wastes in landfills. However, thermal processes in general have been shown to release toxic compounds. For this reason, it is important to know more about the behavior of plastics when they are burnt.

Some recent papers concerning the analysis of organic by-products in great or small concentrations in combustion and pyrolysis of different kind of wastes such as plastics or wood can be found in literature (Esperanza et al., 2000; Fullana et al., 2000; Launhardt and Thoma, 2000; Ciccioli et al., 2001; Friedli et al., 2001). There is an increasing interest in the determination, analysis and proposal of solutions for the semivolatile compounds evolved in many thermal processes of coal, industrial oils, biofuels and wastes, since toxic by-products must be processed or destroyed correctly. On the other hand, pyrolytic puffs can be evolved in a furnace, so many of the toxic by-products generated in a pyrolysis process can also be present in the combustion of the waste.

Pyrolysis of polyethylene has been widely studied in several papers (Wampler, 1989; Conesa et al., 1997; Williams and Williams, 1999; Predel and Kaminsky, 2000; Mastral et al., 2002). However, there are fewer works concerning combustion of polyethylene.

Hodgkin et al. (1982) determined some low molecular weight products from burning polyethylene, including some oxidative degradation compounds such as acetone, acetaldehyde, acetic acid or acrolein. Mitera and Michal (1985) characterized some compounds detected in the combustion of polyethylene, comparing them with those produced using polypropylene, polystyrene and polyamide (PA).

Hawley-Fedder et al. (1984, 1987) studied the products evolved in the combustion of polyethylene in a polymer mixture (PE, PS and PVC) at 800–950 °C, observing alkyl benzenes, hydrocarbons, alkenes, biphenyls and PAHs. Wheatley et al. (1993) made an exploratory study on the combustion and PAH emissions of selected municipal waste plastics. The gas temperature and residence time were varied and the effects of both the flame and the postflame conditions on the PAH emission levels were investigated. Minimization of toxic hydrocarbons species was found only at the highest postflame gas temperature and longest residence time explored in this study, 1150 °C and 2 s. Panagiotou et al. (1996a,b) determined the aromatic hydrocarbon emissions from combustion of PS, PE and PVC, concluding that, unless the resulting particles of PE were very small and burnt in extremely dilute clouds, low PAH emissions were not ensured. Piao et al. (1999) characterized combustion products of PE, observing the presence of olefins and *n*-hydrocarbons at low temperature and PAHs at higher temperatures, their major contribution consisting of identifying more than 100 PAH compounds with 2–7 fused rings with a high-performance GC–MS. Li et al. (2001) studied the presence of PAHs in the raw waste, stack flue gas and bottom ashes in controlled-air incineration of PVC, HDPE and PP plastic waste, and found that PAHs present in the raw waste were almost entirely destroyed and proposed CO as a surrogate indicator for total PAH emissions, since both could be correlated.

PAHs are always present in any thermal process of an organic compound. Both their formation and destruction have been considered by different researchers. Mastral and Callén (2000) and Richter and Howard (2000) have reviewed the emission and generation of PAHs from energy generation processes. In literature, there are some references concerning the mechanisms of formation and destruction of organic compounds in different types of flames, and the catalytic combustion, but this does not form part of the aims of this paper.

The main objective of this work has been the qualitative and quantitative determination of the toxic by-products that can be evolved in the combustion of polyethylene considering both the effect of the temperature and sample mass/air flow ratio in their formation and thermal destruction. Combustion experiments were carried out in substoichiometric conditions. The estimation of the yields corresponding to the different compounds at these conditions can be useful, since the formation of puffs of the semivolatile ones is likely to occur in combustors, where they can circulate maintaining their identity.

2. Experimental

2.1. Raw material

High-density polyethylene (HDPE 10062E) from Dow Plastics was used in this work. Table 1 shows some characteristics of the material studied in this paper. In a previous work by Font et al. (2003), an elementary analysis of the major components was carried out in a

Table 1
Elementary analysis and net calorific value of polyethylene

Element	% weight
C	85.3
H	14.7
N	0.0
S	0.0
O (by difference)	0.0
Net calorific value:	10273 kcal kg^{-1}

Perkin–Elmer 2400. The calorific value was determined in a Leco AC-350 calorimetric bomb. From a TG run carried out in a Setaram TG-DSC at 15 °C min^{-1} both in He and He:O$_2$ 4:1, it was tested that decomposition takes place in the range 440–500 °C, and the amount of solid residue is negligible.

2.2. Laboratory scale furnace

The equipment used was a horizontal quartz reactor (Fig. 1), where the sample was introduced inside a crucible or holder. A small engine allowed the sample holder to be moved through the reactor at different velocities between 0.05 and 20 mm s^{-1}. An electric furnace with two separate parts was placed around the tube. The volatile compounds evolved underwent cracking reactions mainly in the second part of the reactor, which was filled with quartz rings.

The procedure to carry out an experiment was as follows: first, the furnace was switched on and the gas flow adjusted; then, when the temperature was stabilized at its nominal value, the sample was introduced inside the holder; afterwards, the motor pushing the holder was connected and the sample was introduced into the hot part of the reactor, where it remained for a short time. Finally, the holder came back out of the furnace. After the runs, no solid residue was observed inside the holder.

Altogether six runs were performed, since two different nominal temperatures (500 and 850 °C) and three sample mass/air flow ratios (one of them in pyrolytic conditions with nitrogen) were employed. Gas flow (air or nitrogen) was 280 ml min^{-1} (measured at 1 atm and 20 °C). The flow inside the hollow reactor was laminar with Reynolds numbers around 10–20, but it was tested that the packing of quartz rings produces a local good mixing of the gas, avoiding bypass of the gas. The residence time of the gas inside the central part of the reactor was calculated at about 4 s.

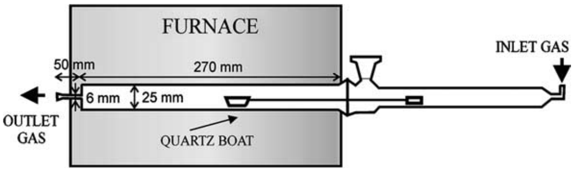

Fig. 1. Scheme of the reactor.

Table 2 presents the operating conditions of the six runs performed in this work. The mass flow of the sample was calculated assuming that the sample is uniformly distributed in the holder and burnt in a fixed front (as previously done by Fullana et al. (2000)), so the rate of advance of the boat can be related with the burning rate of the sample.

A parameter named bulk air ratio (λ) was defined as the ratio between the actual air flow and the stoichiometric air flow necessary for complete combustion, assuming that the combustion of the solid occurs at the same rate as that is being introduced. Therefore, it can be calculated as

$$\lambda = \frac{(m_{\text{air}})_{\text{actual}}}{(m_{\text{air}})_{\text{stoichiometric}}} = \frac{m_{\text{air}} \cdot 23}{\frac{m_{\text{sample}} \cdot v}{L}\left(\frac{\%\text{C}}{12} + \frac{\%\text{H}}{4} + \frac{\%\text{S}}{32} - \frac{\%\text{O}}{32}\right) \cdot 32}$$

In the previous expression, m_{air} is the air flow introduced, m_{sample} is the total sample mass, v is the rate of sample inlet, L is the length of the crucible and %C, %H, %O and %S are, respectively, the weight percentages of carbon, hydrogen, oxygen and sulfur in the sample. It is clear that $\lambda = 0$ in pyrolytic conditions, $\lambda = 1$ in stoichiometric conditions and $\lambda > 1$ in excess of oxygen.

In all the runs, the velocity of the holder with the sample going into the furnace was 1 mm s^{-1} for 120 s. Then, the sample was maintained for 100 s in the hot part of the reactor to ensure total decomposition.

The volatile compounds were collected for 220 s (100 + 120 s) in a Tedlar bag to perform the analysis of light hydrocarbons and gases, and a small tube containing the resin XAD-2 was used to collect the semivolatile compounds.

2.3. Analytical method

The compounds collected in the Tedlar bag were analyzed by gas chromatography in a Shimadzu GC-14A.

Table 2
Experimental conditions

Run	Nominal temperature (°C)	Sample mass (mg)	Sample mass flow (mg s^{-1})	Bulk air ratio (λ)
P1	500	51	2.04	0
C2	500	49	1.96	0.187
C3	500	20	0.80	0.458
P4	850	53	2.12	0
C5	850	49	1.96	0.187
C6	850	20	0.80	0.458

A capillary alumina-KCl plot column from Supelco with a flame ionization detector was used to analyze the light hydrocarbons, such as methane, ethane, ethylene, propylene, butane, acetylene, benzene, toluene, etc. For the analysis of O_2, N_2, CO_2 and CO, a packed CTR I column from Alltech with a thermal conductivity detector was used. This column consists of a column within a column. This permits two different packings to be used for the analysis of the sample. Identification and quantification was performed using standards of each compound.

The semivolatile compounds adsorbed in the resin were extracted with dichloromethane in accordance with the EPA 3540C method. Before the extraction, 10 μl of an internal deuterated standard (1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}), in a concentration of 2000 $\mathrm{mg\,l^{-1}}$, were spiked to the resin.

A DB-5 30 m column in a chromatograph gas (Fisons GC 8000) coupled to a mass spectrometer (Fisons MD 8000) was used to analyze semivolatile compounds. A qualitative identification of compounds was performed comparing their mass spectrums with those of the NIST database. However, other indicators such as Lee and Kovats retention indices (Lee et al., 1979; Rostad and Pereira, 1986), boiling points and logical correlation in chromatograms of different runs were used. The semivolatile compounds were quantified using the deuterated standards. The response factors of the different compounds were calculated by interpolation between the two nearest standards. For an exact identification and quantification of the compounds, a standard for each compound would have been required, but this was considered out of the scope of this work.

3. Results and discussion

The variation of the emission factors or yields (mg compound/kg sample) with both temperature and sample mass/air flow ratio was studied in the six runs carried out. Table 3 shows the results for the different compounds detected. Each compound has a code related to the confidence of its determination:

(a) an authentic quantitative standard was used,
(b) the confidence parameter of the NIST database was greater than 90%, referred to the coincidence between the experimental mass spectrum and the proposed compound mass spectrum,
(c) the confidence parameter was between 80% and 90%,
(d) the differences in Kovats and Lee retention indices were less than 1%,
(e) the boiling point of the proposed substance was logical in relation to the other substances.

The results were discussed from two viewpoints, since both the temperature and the bulk air ratio are two variables that influenced the yields of the compounds. Therefore, the compounds obtained were also classified according to their behavior related to these parameters. Some symbols were used to characterize the behavior:

(a) When bulk air ratio increases, IO, iO, DO, dO, SO, MO, mO and ?O mean that yields increase with oxygen, slightly increase, decrease, slightly decrease, are similar, have an intermediate maximum, a minimum or do not follow a similar behavior at the two temperatures, respectively.
(b) When temperature increases, IT, iT, DT, dT, ST and ?T mean, in this case, that yields increase with temperature, slightly increase, decrease, slightly decrease, are similar or do not follow a similar behavior at the three bulk air ratios, respectively. Due to the fact that the experiments were only carried out at two temperatures, it was not possible to consider intermediate maximum or minimum values.

Some different kinds of compounds were identified, including gases, volatile and semivolatile compounds. In this last group compounds such as substituted benzenes, aliphatic hydrocarbons, polycyclic aromatic hydrocarbons, alcohols, aldehydes or ketones could be distinguished.

3.1. Effect of temperature

When increasing temperature, carbon oxides decreased their yields. In the same way, volatile compounds such as light hydrocarbons from C_3 to C_6, also behaved like this. They were classified as DT or dT compounds. Nevertheless, methane, ethane, ethylene, benzene or toluene increased their yields in a considerable amount at high temperatures (IT and iT). One possible explanation for this last fact could be as follows: methane, ethane and ethylene are final products in cracking reactions, which take place extensively at high temperatures. On the other hand, toluene and benzene are both products in pyrosynthesis reactions with a high thermal stability (Taylor et al., 1990). Consequently, their yields are expected to increase and therefore, these results seem to be logical according to this explanation.

Heavy aliphatic hydrocarbons were found at low temperatures, whereas they practically disappeared at 850 °C (DT compounds). It was tested that the characteristic triplets of peaks corresponding to α,ω-olefins, α-olefins and *n*-paraffins were formed from the primary decomposition, as indicated in previous works (Hodgkin et al., 1982; Hawley-Fedder et al., 1984; Wampler, 1989; Piao et al., 1999; Williams and Williams, 1999; Font et al., 2003). These compounds showed a behavior

Table 3
Emission factors or yields in ppm (mg compound/kg sample)

Compound	Pyrolysis (P)/combustion (C)						Authors(1)	Type(2)
	P1	C2	C3	P4	C5	C6		
	Temperature (°C)							
	500	500	500	850	850	850		
	Bulk air ratio (λ)							
	0	0.187	0.458	0	0.187	0.458		
Carbon dioxide[a]	nm	947 297	1 229 416	nm	695 567	977 852	Mi, Li	IO-DT
Carbon monoxide[a]	nm	198 402	317 775	nm	84 082	98 127	Mi, Li	IO-DT
Methane[a]	nm	16 043	12 045	nm	71 564	34 298	Wi, Co, Ma	DO-IT
Ethane[a]	nm	4612	2669	nm	8066	2290	Ho, Wi, Co, Ma	DO-iT
Ethylene[a]	nm	80 823	59 879	nm	144 817	63 522	Ho, Wi, Co, Ma	DO-IT
Propane[a]	nm	2252	1554	nm	279	155	Ho, Wi, Co	DO-DT
Propylene[a]	nm	33 383	25 744	nm	9154	4527	Ho, Mi, Wi, Co	DO-DT
Isobutane[a]	nm	9910	6852	nm	8534	9445		SO-ST
Acetylene[a]	nm	964	633	nm	615	427	Co	dO-dT
n-Butane[a]	nm	16 889	11 995	nm	369		Mi, Co	DO-DT
trans-2-Butene[a]	nm	482	348	nm	143		Co	dO-dT
1-Butene[a]	nm	511	357	nm	111		Ho, Mi, Co	dO-DT
1,3-Butadiene[a]	nm	21 884	12 835	nm	8811	5121		DO-DT
n-Pentane[a]	nm	1321	956	nm	87		Co	dO-DT
Propyne[a]	nm	6152	3660	nm		7361		?O-?T
1-Pentene[a]	nm	1359	816	nm	536	422	Mi	dO-DT
2-Butyne[a]	nm	3665	2339	nm	4888	2246		DO-iT
1-Butyne[a]	nm	15 823	9855	nm	8995	8519		dO-dT
n-Hexane[a]	nm	2295	1456	nm	284			DO-DT
1-Hexene[a]	nm	9509	5350	nm	68		Ho, Mi	DO-DT
Benzene[a]	nm	12 160	7875	nm	63 910	26 108	Ho, Mi, Wi, Co	DO-IT
Toluene[a]	nm	3039	946	nm	4210	3013	Ho, Mi, Wi, Co	dO-iT
1-Octene[b,c]	398						Ho, Mi	DO-DT
n-Hexanal[b]		125	567					iO-DT
n-Octane[b,d,c]	249						Mi	DO-DT
2-Cyclopenten-1-one[b]		207	1075					IO-DT
2-Methylcyclopentanone[e]		107	694					IO-DT
2-Butanone[b]		144	654					IO-DT
Ethylbenzene[b,c]				76	32	32	Mi	SO-iT
p-Xylene[b,c]		40	125	139	100	110	Mi, Co	SO-ST
3-Hepten-2-ol		51	180					iO-DT
m-Xylene[b,c]				100	47	65	Mi, Co	SO-iT
Ethylidenecyclohexane	13							dO-dT
Phenylethyne[c,e]		95		174	317	564		iO-IT

Table 3 (*continued*)

Compound	Pyrolysis (P)/combustion (C)						Authors(1)	Type(2)
	P1	C2	C3	P4	C5	C6		
	Temperature (°C)							
	500	500	500	850	850	850		
	Bulk air ratio (λ)							
	0	0.187	0.458	0	0.187	0.458		
5-Hepten-2-one[b]		55						MO-dT
7-Octen-2-one[e]			432					IO-DT
2-Propenylcyclohexane[b]	36							dO-dT
1,8-Nonadiene[b,c]	135	108	410					iO-DT
Styrene[b,c]		505	172	5994	4491	5088	Mi, Pi, Co	?O-IT
1-Nonene[b,c]	1450	474	1549				Ho, Mi	mO-DT
Oxygenated		86	926					IO-DT
n-Nonane[b,d,c]	676	57					Mi	DO-DT
3-Hepten-2-ol[e] + others		170	1164					IO-DT
Oxygenated		90	389					IO-DT
2,5-Hexanedione[e]		38	251					iO-DT
2-Cyclohexen-1-one[b]		157	687					IO-DT
2,4-Hexadien-1-ol		58	293					iO-DT
Allylbenzene[b,c]				32	37			SO-iT
Benzaldehyde[b]		177	737					IO-DT
1,3,5-Trimethylbenzene[b,c]				43		149	Wi	mO-iT
4-Octanone[e]			368					IO-DT
Oxygenated			279					iO-dT
Oxygenated		815	2402					IO-DT
1,9-Decadiene[b,c]	745						Ha, Wi	DO-DT
m-Methylstyrene[b,c]				100	10	15	Ha	dO-iT
1-Decene[b,c]	5914	1010	1257				Ho, Ha, Mi, Wi	DO-DT
p-Methylstyrene[b,c]				631	526	309	Ha	dO-IT
o-Methylstyrene[b,c]				255	194	173	Ha	dO-iT
Oxygenated			335					IO-DT
n-Decane[b,d,c]	1638	155	313				Ha, Mi, Wi	mO-DT
n-Octanal[b]		113	725					IO-DT
trans-1-Propenylbenzene[b,c]				235	153	103		dO-iT
Indane[e]				124	98	67	Wi	dO-iT
Indene[b,d,c]		467	413	2873	3146	4330	Ha, Pi, Wi	iO-IT
Benzylic alcohol[e]		73	305					IO-DT
2-Propylheptanol			311					IO-DT
trans-Decahydronaphthalene[b,d]				276	17			dO-iT
4-Nonanone			328					IO-DT
Oxygenated			420					IO-DT

1,10-Undecadiene[b]	2748	833	749				Ha, Wi	DO-DT
o-Allyltoluene[b,c]		510		1716	19	5338		?O-IT
1-Undecene[b,c]	5022	1136	1422				Ho, Ha, Mi, Wi	DO-DT
p-Ethylstyrene[b,c]		490		588		1970		?O-IT
n-Undecane[b,d,c]	1619	214	358				Ha, Mi, Wi	DO-DT
cis-Decahydronaphthalene[b,c]				314	49			DO-IT
n-Nonanal[b]		149	664					IO-DT
m-Divinylbenzene[b]		92		334	204	252		SO-IT
Divinylbenzene[b]				353	80			DO-IT
1-Methyl-1H-indene[b]		118		352	223	252	Pi	?O-iT
1-Methylene-1H-indene[b]				612	417	301	Pi	dO-IT
1,2-Dihydronaphthalene[b,d]				229	131	78	Pi	dO-iT
Oxygenated			198					iO-dT
1,11-Dodecadiene[b]	659	429	682				Ha, Wi	mO-DT
1-Dodecene[b,c]	3054	1149	1105				Ho, Ha, Mi, Wi	DO-DT
Naphthalene[b,d,c]		287	195	9011	7911	7995	Ha, Wh, Pa, Li, Pi, Wi	SO-IT
n-Dodecane[b,d,c]	1733	263	428				Ha, Mi, Wi	mO-DT
n-Decanal		112	395					IO-DT
5-Decanone			157					iO-dT
5-Undecanone			218					iO-dT
Oxygenated			243					iO-dT
Oxygenated			292					iO-dT
1,12-Tridecadiene[b]	605	539	679				Ha, Wi	SO-DT
1-Tridecene[b,c]	3443	1029	969				Ho, Ha, Mi, Wi	DO-DT
10-Undecenal			430					IO-DT
n-Tridecane[b,d,c]	1390	232					Ha, Mi, Wi	DO-dT
2-Methylnaphthalene[b,d,c]		106		1892	1098	622	Ha, Wh, Pa, Pi, Wi	DO-IT
n-Undecanal		59	305					IO-DT
1-Methylnaphthalene[b,d,c]		61		1548	875	457	Ha, Wh, Pi, Wi	DO-IT
1-Ethylidene-1H-indene[b]				109	71	33	Pi	dO-iT
Byphenyl[b,d,c]				2289	1227	853	Ha, Wh, Pi	DO-IT
Oxygenated			224					iO-dT
1,13-Tetradecadiene[b]	731	518	632				Ha, Wi	SO-DT
1-Tetradecene[b]	4169	932	665				Ho, Ha, Mi, Wi	DO-DT
n-Tetradecane[e,d,c]	1442	197	92				Ha, Mi, Wi	DO-DT
11-Dodecenal			365					IO-DT
n-Dodecanal		40	293					iO-dT
1-Allylnaphthalene[b,c]				176	69	47		dO-dT
Biphenylene				23	50	73	Ha, Wh, Pa, Li, Pi	SO-iT
1-Vinylnaphthalene[b]				822	345	179	Ha, Pi	DO-IT
2,3-Dimethylnaphthalene[b,c]				151	60	36	Pi, Wi	dO-iT
2,6-Dimethylnaphthalene[b,d]				54	20		Wi	dO-iT
2-Vinylnaphthalene		64		2939	1441	823	Ha, Pi	DO-IT
Acenaphthylene[b,d,c]		182		4491	2367	2796	Ha, Wh, Pa, Li, Pi, Wi	?O-IT

Table 3 (*continued*)

Compound	Pyrolysis (P)/combustion (C)						Authors[(1)]	Type[(2)]
	P1	C2	C3	P4	C5	C6		
	Temperature (°C)							
	500	500	500	850	850	850		
	Bulk air ratio (λ)							
	0	0.187	0.458	0	0.187	0.458		
1,14-Pentadecadiene[b]	933	427	333				Ha, Wi	DO-DT
1-Pentadecene[b,c]	2412	1070	495				Ho, Ha, Mi, Wi	DO-DT
Acenaphthene[b,c]				937	380	243	Pa, Li, Pi, Wi	DO-IT
n-Pentadecane[b,d,c]	1563	209	148				Ha, Mi, Wi	DO-DT
4-Methyl-1,1-biphenyl[b,d,c]				242	109	90	Ha, Pi	dO-iT
12-Tridecenal		86	316					IO-DT
n-Tridecanal		30	195					iO-dT
2,3′-Dimethyl-1,1-biphenyl[e]				154	79	58		dO-iT
3-Methyl-1,1-biphenyl[b,c]				296	96	55	Ha, Pi	dO-iT
1H-Phenalene/fluorene or similar[b]				416	150	81	Ha, Wh, Pa, Li, Pi, Wi	dO-IT
1H-Phenalene/fluorene or similar[b]				368	136	94	Ha, Wh, Pa, Li, Pi, Wi	dO-IT
1,15-Hexadecadiene[b]	867	401	286				Ha, Wi	DO-DT
1H-Phenalene/fluorene or similar[b,d]				2094	976	920	Ha, Wh, Pa, Li, Pi, Wi	DO-IT
Methylbiphenyl or similar[e]				129	39	17		dO-iT
1-Hexadecene[b,c]	3518	793	458				Ho, Ha, Mi, Wi	DO-DT
n-Hexadecane[b,d,c]	1602	291	116				Ha, Wi	DO-DT
Methylfluorene or similar[e]				830	329	178		DO-IT
13-Tetradecenal[b]			167					iO-dT
7-Tetradecen-1-ol		41						MO-dT
1H-Phenalene/fluorene or similar[b,c]				364	176		Ha, Wh, Pa, Li, Pi, Wi	DO-IT
n-Tetradecanal		23	132					iO-dT
1H-Phenalene/fluorene or similar[e]				650	282	82	Ha, Wh, Pa, Li, Pi, Wi	DO-IT
1H-Phenalene/fluorene or similar[e]				24	56	157	Ha, Wh, Pa, Li, Pi, Wi	iO-iT
1,16-Heptadecadiene[b]	1046	478	276				Ha, Wi	DO-DT
4-Vinylbiphenyl[e]				66	28		Pi	dO-iT
1-Heptadecene[b,c]	2735	825	344				Ho, Ha, Wi	DO-DT
n-Heptadecane[b,d,c]	1261	240	99				Ha, Mi, Wi	DO-DT
14-Pentadecenal[b]			82					iO-dT
9-Pentadecen-1-ol		36						SO-dT
n-Pentadecanal		42	75					iO-dT
9,10-Dihydrophenanthrene[b]				108	41	19	Ha, Pi	dO-iT
2-Methyl-9H-fluorene[b,d]				497	252	135	Ha, Wh, Pi	dO-IT
Diphenylethyne				467	145	76	Ha, Pi	dO-IT
1-Methyl-9H-fluorene				190	78	38	Ha, Wh, Pi	dO-iT
9-Methylene-9H-fluorene[e]				88	48	27		dO-iT
1-Phenyl-1H-indene[c,e]				119	47	26	Pi	dO-iT

1,17-Octadecadiene[b]	990	512	145				Ha, Wi	DO-DT
1-Octadecene[b]	2590	768	272				Ho, Ha, Mi, Wi	DO-DT
n-Octadecane[b,d,c]	1234	479					Ha, Wi	DO-DT
Phenanthrene[b,d,c]		111	58	3956	1567	1714	Ha, Wh, Pa, Li, Pi, Wi	DO-IT
15-Hexadecenal[b]			71					iO-dT
Anthracene[b,d,c]		21		1605	663	504	Ha, Wh, Pa, Li, Pi	DO-IT
11-Hexadecen-1-ol		31						SO-dT
n-Hexadecanal		64	81					iO-dT
1-Phenylnaphthalene[b,d,c]				375	139	67	Ha, Pi	dO-iT
Methylanthracene/phenanthrene[b]				110	48	19	Ha, Wh, Pi	dO-iT
1,18-Nonadecadiene[b]	1208	496	95				Ha, Wi	DO-DT
1-Nonadecene[b]	2877	938	138				Ho, Ha, Mi, Wi	DO-DT
n-Nonadecane[b,d]	1379	304	28				Ha, Mi, Wi	DO-DT
16-Heptadecenal[b]			47					iO-dT
n-Heptadecanal		22	52					iO-dT
Methylanthr./phenant.[b]				236	72	36	Ha, Wh, Pi	dO-iT
Methylanthr./phenant.[b]				189	67	35	Ha, Wh, Pi	dO-iT
Methylanthr./phenant.[b,d]				150	50		Ha, Wh, Pi	dO-iT
Benzo(*def*)fluorene[b]				750	320	233	Pi	DO-IT
Methylanthr./phenant.[b,d]				200	72	56	Ha, Wh, Pi	dO-iT
1,19-Eicosadiene[b,d]	1164	620	79				Ha, Wi	DO-DT
2-Phenylnaphthalene[b,d,c]				661	324	156	Ha, Pi	DO-IT
1-Eicosene[b]	2949	1036	117				Ho, Ha, Mi, Wi	DO-DT
n-Eicosane[b,d]	1578	288	38				Ha, Wi	DO-DT
17-Octadecenal[b]		31	25					iO-dT
n-Octadecanal[e]		24	26					iO-dT
Phenylnaphthalene[e]				159	85	22		dO-iT
Vinylanthracene[e]				102	67	20	Pi	dO-iT
Fluoranthene[b,d,c]				726	609	370	Ha, Wh, Pa, Li, Pi	dO-IT
1,20-Heneicosadiene[e]	1305	675	44				Ha, Wi	DO-DT
1-Heneicosene[b]	3216	1056	71				Ho, Ha, Mi, Wi	DO-DT
n-Heneicosane[b,d]	1795	464	36				Ha, Wi	DO-DT
Acephenantrylene/aceanthrylene[b]		48		367	307	143	Wh, Pi	dO-IT
18-Nonedecenal[b]			20					iO-dT
Nonadecanol		35						SO-dT
n-Nonadecanal[b]		27	17					SO-dT
Acephenant./aceanthr.[b]				72	47	26	Wh, Pi	dO-iT
Pyrene[b,d,c]		64		1164	1045	513	Ha, Pa, Li, Pi	DO-IT
C22 (diene+ene+ane)[b,d]	6868	2462	145			109	Ho, Ha, Mi, Wi	DO-DT
Eicosanol		62						MO-dT
n-Eicosanal		23						SO-dT
7H-Benzo(*c*)fluorene[b]				238	233	95	Ha, Wh, Pi	dO-iT
11H-Benzo(*b*)fluorene[b]				136	140	88	Ha, Wh, Pi	dO-iT
Methylpyrene[b,d]				55	60	14	Ha, Wh, Pi	dO-iT

Table 3 (*continued*)

Compound	Pyrolysis (P)/combustion (C)						Authors[(1)]	Type[(2)]
	P1	C2	C3	P4	C5	C6		
	Temperature (°C)							
	500	500	500	850	850	850		
	Bulk air ratio (λ)							
	0	0.187	0.458	0	0.187	0.458		
Methylpyrene[b,d]				211	137	52	Ha, Wh, Pi	dO-iT
Methylpyrene[b,d]				111	86	66	Ha, Wh, Pi	dO-iT
C23 (diene+ene+ane)[b,d]	7161	2782	122			104	Ho, Mi, Wi	DO-DT
Heneicosenol		87						MO-dT
n-Heneicosanal		32						MO-dT
C24 (diene+ene+ane)[b,d]	8060	3330	135			70	Ho, Mi, Wi	DO-DT
21-Docosenal		67						MO-dT
n-Docosanal		96						MO-dT
Benzo(*c*)phenanthrene[b]				75	124	78	Ha, Wh, Pi	SO-iT
Benzo(*a*)anthracene + Cyclopenta(*cd*)pyrene[b,d]				182	242	152	Ha, Wh, Pa, Li, Pi	MO-iT
Triphenylene/chrysene[b,d,c]				108	298	232	Ha, Wh, Pi	MO-iT
1,2′-Binaphthalene[e]				26	58	32	Pi	SO-iT
C25 (diene+ene+ane)[b,d]	8298	4462	156				Ho, Mi, Wi	DO-DT
Tricosenol		77						MO-dT
n-Tricosanal		70	29					MO-dT
Bis(2-ethylhexyl)phthalate[b]		100	60		50	176		?O-?T
C26 (diene+ene+ane)[b,d]	9592	4238	183		61	56	Mi, Wi	DO-DT
23-Tetracosenal		128						MO-dT
n-Tetracosanal		58						MO-dT
C27 (diene+ene+ane)[b,d]	11 502	4209	257		133	71	Mi, Wi	DO-DT
Pentacosenol		61						MO-dT
Pentacosanal		42						MO-dT
C28 (diene+ene+ane)[b,d]	13 452	4081	453		287	195	Mi, Wi	DO-DT
Benzo(*j*)fluoranthene[b]				43	120		Ha, Wh	MO-iT
Benzo(*b*)fluoranthene[b,d]				12	80		Ha, Wh, Pa, Li, Pi	MO-iT
Benzo(*k*)fluoranthene[b,d]				13	84		Ha, Wh, Pa, Li, Pi	MO-iT
Benzo(*e*)pyrene[b]				26	118	93	Li, Pi	MO-iT
C29 (diene+ene+ane)[b,d]	17 520	4372	778		623	290	Wi	DO-DT
Benzo(*a*)pyrene[b]				51	260	212	Li, Pi	MO-iT
Perylene[e]				10			Li, Pi	dO-iT
C30 (diene+ene+ane)[b,d]	16 628	3602	753		600	183	Wi	DO-DT
C31 (diene+ene+ane)[b,d]	14 591	2713	571		393	257	Wi	DO-DT
1,12-Benzperylene[e]				10			Pi	dO-iT
C32 (diene+ene+ane)[b,d]	11 799	2073	348		239	89	Wi	DO-DT
Indeno(1,2,3-*cd*)pyrene[e]				15	45		Li, Pi	SO-iT
C33 (diene+ene+ane)[b,d]	10 439	1531	214		50		Wi	DO-DT

C34 (diene+ene+ane)[b,d]	12 655	1172	98	Wi	DO-DT
C35 (diene+ene+ane)[b,d]	10 445	865	57	Wi	DO-DT
C36 (diene+ene+ane)[b,d]	7029	644	137	Wi	DO-DT
C37 (diene+ene+ane)[b]	4421	471	141	Wi	DO-DT
C38 (diene+ene+ane)	2782	277	81	Wi	DO-DT
C39 (diene+ene+ane)	1611	193		Wi	DO-DT

nm: not measured.

Authors(1)—Co: Conesa et al. (1997), Ha: Hawley-Fedder et al. (1984, 1987), Ho; Hodgkin et al. (1982), Li: Li et al. (2001), Ma: Mastral et al. (2002), Mi: Mitera and Michal (1985), Pa: Panagiotou et al. (1996a,b), Pi: Piao et al. (1999), Wh: Wheatley et al. (1993), Wi: Williams and Williams (1999).

Type(2): See main text.

[a] Authentic quantitative standard.

[b] Confidence parameter greater than 90% referred to the coincidence between the experimental mass spectrum and the proposed compound mass spectrum.

[c] The boiling point of the proposed substance is logical in relation to the other substances.

[d] Difference in Kovats and Lee retention indices less than 1%.

[e] Confidence parameter between 80% and 90%.

similar to the light aliphatic hydrocarbons previously commented. They are primary products in polyethylene decomposition evolved in cracking reactions, so at high temperatures they turn into gases and polycyclic aromatic hydrocarbons. This last group of compounds is produced as a result of pyrosynthesis reactions. Therefore, their yields rise when increasing temperature (IT and iT). Compounds such as naphthalene, styrene, acenaphthylene, phenanthrene, 2-vinylnaphthalene, indene, biphenyl, fluorene, 2-methylnaphthalene or anthracene were obtained with the highest yields.

Some oxygenated compounds appeared in combustion experiments at low temperatures. They are intermediate products that are not very stable, so high temperatures allow their destruction. Saturated and unsaturated aldehydes were the main compounds of this group. Two peaks of the α-enal and *n*-anal with *n*-2 carbon atoms were mainly observed to appear after the corresponding peaks of the three hydrocarbons with *n* carbon atoms previously commented. On the other hand, some linear alcohols, linear and cyclic ketones were also identified. These oxygenated compounds were included in the DT and dT groups.

3.2. Effect of oxygen (λ)

Regardless of temperature, both carbon dioxide and carbon monoxide yields rose when bulk air ratio did (IO compounds). This is logical, since there is more oxygen available to react. However, the ratio between the former and the latter would be expected to follow the same trend, but they did not comply with this at 500 °C, as can be observed in Fig. 2. Anyway, the great yield of these two compounds is remarkable, compared with the rest. Therefore, as carbon oxides cannot be evolved in pyrolysis experiments, it can be concluded that the yields of light hydrocarbons must have been much greater in pyrolysis, since carbon total balance must be attained.

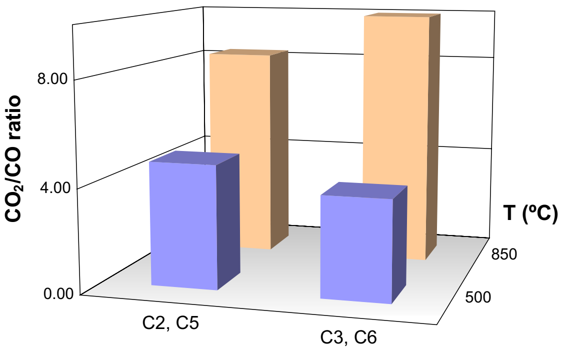

Fig. 2. CO_2/CO ratios.

The volatile compounds, benzene and toluene identified decreased their yields when bulk air ratio increased (DO and dO). There was a marked drop in compounds such as methane or ethylene at 850 °C. It is important to emphasize the great yields obtained for ethylene and propylene, which are expected taking into account the chemical structure of polyethylene. Moreover, it must be pointed out that there is a carcinogenic compound such as benzene that appeared in a remarkable quantity. On the other hand, propyne had a different behavior, since it did not appear at intermediate bulk air ratios but it suddenly raised at higher values at 850 °C.

With respect to semivolatile compounds, the results showed that, in general, both the aliphatic and the aromatic hydrocarbons decreased their yields when there was an increase in the bulk air ratio (DO and dO). However, the decrease was not observed in some cases: aliphatic compounds such as 1-nonene, *n*-decane, *n*-dodecane, 1,13-tetradecadiene showed a minimum at intermediate air bulk ratios (mO), while aromatic compounds such as benzofluoranthenes or benzo(*a*)pyrene had a maximum (MO), and even 1,3,5-trimethylbenzene, indene or *p*-ethylstyrene rose in a significant way at the highest bulk air ratio. This behavior is likely to indicate that either the amount of oxygen available was not enough to attack every compound evolved in pyrolysis or mixing with oxygen was inadequate and, thus, pyrolysis 'puffs' appeared. Having used higher bulk air ratios, a great decrease in the yields of these compounds should have been observed.

It was observed that the yields of partially oxygenated compounds rose with bulk air ratio (IO and iO), except the heaviest ones, which showed an intermediate maximum (MO). The rise for the lighter oxygenated compounds is explained because of the higher availability of oxygen. These are, however, only intermediate products in the total oxidation of hydrocarbons, so a decrease should be expected at higher bulk air ratios. On the other hand, it is reasonable that the yields of the heaviest compounds decreased at lower air bulk ratios more than the lightest ones, because the former can be considered as precursors of the latter.

It can be noted that the presence of oxygen very probably enhances the formation of radicals, which contributes to a more reactive situation. This could explain why some aromatics at 500 °C (*p*-xylene, styrene, benzaldehyde, indene, *o*-allytoluene, *p*-ethylstyrene, *m*-divinylbenzene, 1-methyl-1H-indene, naphthalene, methylnaphthalene, 2-vinylnaphthalene, phenanthrene, acenaphthylene, pyrene, …) and some aliphatic hydrocarbons at 850 °C (alkanes, alkenes and/or alkadienes from C22 to C32) appeared in combustion experiments whereas they were not identified in those of pyrolysis.

Figs. 3 and 4 show the total yields obtained for volatile and semivolatile compounds, respectively, in the experiments. It appears that the combination of high temperatures and air bulk ratios leads to a global decrease in yields for those compounds, which involves an increase in carbon oxides yields, as been pointed out previously.

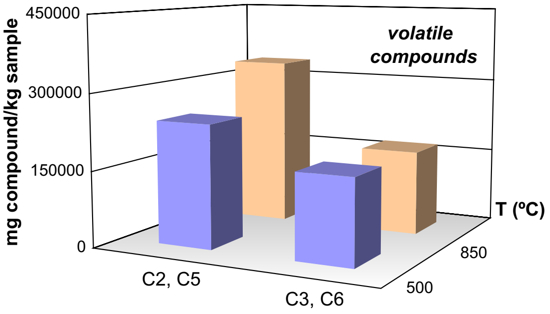

Fig. 3. Variation of total yields of volatile compounds vs. temperature and air bulk ratio (λ).

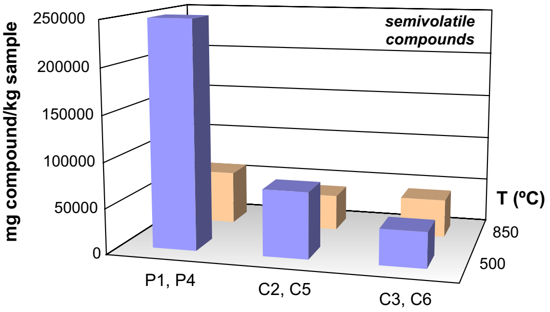

Fig. 4. Variation of total yields of semivolatile compounds vs. temperature and air bulk ratio (λ).

Table 3 also presents a review of the authors who also detected the different compounds present in the combustion or pyrolysis of polyethylene, observing many coincidences. For example, the results presented by Piao et al. (1999) in the combustion of polyethylene show yields of PAHs that fall within the same range of order as in this paper. On the other hand, it must be noted that there are some compounds that appear in the paper of these authors that have not been detected in this work.

4. Conclusions

It was tested that there is a wide range of products evolved in the combustion of polyethylene that can be obtained in a horizontal laboratory furnace, where both the influence of bulk air ratio and temperature were analyzed.

More than 230 products were detected, observing that higher values of the available oxygen led to a decrease in the yields of hydrocarbons, whereas oxygenated semivolatile compounds and carbon oxides increased. On the other hand, when increasing temperature both cracking and pyrosynthesis reactions were enhanced, so the results showing a rise in the yields of methane, ethane, ethylene, benzene or PAHs were logical, whereas the production of other linear hydrocarbons, oxygenated compounds and carbon oxides fell.

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