EXPERIMENTAL STUDY OF CO-PYROLYSIS OF POLYETHYLENE/SAWDUST MIXTURES

by

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A study of the behavior of the thermal decomposition of mixtures of biomass and thermoplastics, such as polyethylene, is of interest for processes for the thermal recovery of industrial and urban wastes such as pyrolysis or gasification. No solid residue is formed during the thermal degradation of pure polyethylene. However, the addition of biomass,which generates char, can vary the product distribution and increase the heating value of the gas obtained. A study of the thermal degradation of pine sawdust, polyethylene and mixtures of polyethylene and pine sawdust has been carried out in a fluidised bed reactor. Experiments were carried out at five different temperatures: 640, 685, 730, 780, and 850 ºC. The yields and composition of the derived oil, wax, and gas were determined.

The addition of polyethylene increases the gas production and decreases theproduction of waxes and liquids for the different temperatures tested. The main gases produced from the co-pyrolysis process were, at low temperatures, carbon monoxide, ethylene, carbon dioxide, propylene, butadiene, methane and pentadiene, while at high temperatures the gas composition changed drastically, the main components being carbon monoxide (more than 33 wt.%), ethylene, methane, benzene and hydrogen. The analysis of the liquid fraction shows a decrease of the concentration of oxygenated and aliphatic compounds.

Key words: *biomass, high density polyethylene, pyrolysis, fluidised bed reactor*

Introduction

Biomass and thermoplastic materials constitute an important fraction of municipal solid waste. In twelve European countries the municipal solid wastes show an average composition of 65% lignocellulosic materials and 15% polymeric materials. The residues produced by intensive agriculture in greenhouses are also a mixture of vegetable and plastic materials, basically polyethylene and polypropylene [1].

Important amounts of agricultural and forestal residues are generated which industrial activities do not take advantage of and which could constitute an important source of energy. Plastic residues are not biodegradable and only a small fraction is recycled by the industry in question. Most of these products are buried in garbage dumps and in some cases incinerated [2], although the recycling of these materials is now an important alternative to landfill.

Moreover, polyolefines show very convenient characteristics for use in the production of composite materials such as polymers reinforced with natural fibers. The increasing use of these materials poses some important challenges for the thermal treatment of biomass-plastic mixtures.

Thermochemical recovery processes allow the obtainment of combustible gases and/or energy. Gasification and pyrolysis do not crease the environmental problems caused by incineration, although the low energetic content of the gas obtained is a significant disadvantage [3].

The thermal decomposition of pine sawdust and other lignocellulosic residues has been studied in previous works, whim indicate that the thermal decomposition ranges from approximately 200 ºC to 400 ºC in an inert atmosphere [4, 5] . Numerous studies on the thermal decomposition of polyolefines and, in particular, polyethylene have been carried out, especially in vacuum or inert atmosphere [6-22]. Polyolefinic materials such as high density polyethylene (HDPE) show a different behavior to lignocellulosic materials. Under pyrolysis conditions, the material decomposition starts at approximately 400 ºC and progresses very rapidly up to 450-470 ºC without producing solid residue that could be used as combustible for supplying energy to the global process. The use of mixtures of biomass with other fuels of greater energetic content (coal or petroleum derived) in these processes (co-pyrolysis or cogasification) substantially increases the value of the gas produced and the thermal efficiency of the process [23]. In addition, the use of a mixture of renewable fuel with fossil or fossilderived fuels reduces the total CO_2 emissions and the environmental impact.

Little is known about interactions of plastic with biomass [24]. In principle, the possibility of a simultaneous degradation of biomass and HDPE is apparently difficult given the different temperature ranges of decomposition of each material. Different thermogravimetric studies suggest that, in general, lignocellulosic materials decompose at a lower temperature than plastic materials [3, 24-26]. The thermal degradation of the latter starts once the lignocellulosic material has been completely converted, implying that no apparent interaction exists between the materials.

Some authors however, using different types of experimental systems have indicated slight interactions, not yet well defined, but related with the presence of char generated during the biomass decomposition and to the interaction of the complex radical mechanisms of the degradation of both materials [26]. The main differences observed are that the maximum rate of decomposition of polyethylene decreased and the corresponding temperature was slightly higher. The product distribution was also affected by the presence of biomass char, the importance of this influence depending on the amount of char formed in the degradation of the lignocellulosic material [26].

In this work, co-pyrolysis of high density polyethylene (HDPE) and sawdust mixtures have been performed in a fluidised bed reactor, and the influences of the temperature on the product distribution and on the gas composition have been studied, together with any synergetic effect between the materials.

Experimental section

Materials

The results of the proximate and ultimate analysis of the pine sawdust used are shown in tab. 1. The particle size was 0.25 mm.

The polyethylene used in this work was HDPE (HOSTALEN GH 4765 by HOECHST) and the mean particle size was 0.225 mm.

Table 1. Proximate and ultimate analysis of pine sawdust

Characteristic	Value
Moisture [wt.%]	5.47
Proximate analysis (wt.% on dry basis)	
Volatile matter	82.94
Fixed carbon	15.88
Ash	1.08
Ultimate analysis (wt.% on dry basis)	
Carbon	51.87
Hydrogen	6.49
Oxygen	40.48
Nitrogen	0.07
Sulfur	0
Ash	1.08
Higher heating value [MJ/kg)]	18.20

Experimental techniques

Figure 1 shows a scheme of the laboratory plant. A stainless steel fluidised bed reactor of 4.8 cm in diameter and 23 cm in height was used. The material bed was 0.25-0.27 mm silica sand with static bed depth of 8 cm. The average minimum fluidisation velocity of this sand was obtained experimentally, being equal to 2.2 cm/s. Polyethylene and sawdust were fed continuously into the bed using two pneumatic feeders at a rate of 1 to 2.2 g/min., and at a ratio of approximately 1:1. The reactor was externally heated using an electrical ring furnace. The bed temperature was measured by a thermocouple inside the bed. The HDPE pyrolysis and gasification was carried out at bed temperatures of 640, 685, 730, 780, and 850 ºC. Nitrogen was used as carrier gas and fluidising agent. The residence time of the gas in the reactor was between 1 and 2.2 seconds at the bed temperature, taking into account the total gas flow produced.

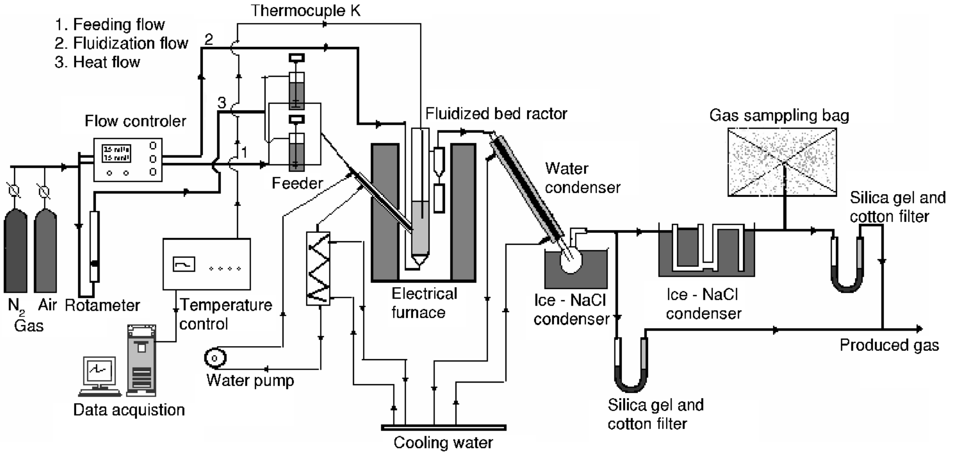

Figure 1. Experimental system diagram

The product stream was passed through a cyclone to remove any particulate matter. The resulting stream of vapours was passed through a cool water heat exchanger at 20 °C, where some heavy hydrocarbons were condensed (oil or waxes). The remaining lighter components were condensed using an ice-NaCl bath at –10 °C. The exit flow was divided into two fractions. The smaller fraction was passed through two ice-NaCl condensers at –10 ºC. Part of the flow from the condensers was collected on line in a nylon bag for analysis during the experiment. The duration of the experiments ranged from 14 to 31 minutes.

The gas fraction was analysed by gas chromatography using an HP 5890 series II, with a semi capillary column HPPLOT/Al_2O_3, 50 m × 0.53 mm × 15 μm, and a molecular sieve 0.9 m×3 mm packed with 45/60 mesh, using two detectors connected in series: a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID). The concentrations of H_2, N_2, CO, and CO_2 were analysed by the TCD detector whilst the rest of hydrocarbon components from C_1 to C_6 were detected by the FID.

Waxes and oils were collected, weighed and analysed by GC/MS. For purposes of analysis, the oil and waxes were first dissolved in tetrahydrofurane (THF). The gas chromatography mass spectrometry consisted of an HT-5 aluminum clad column, 25m × × 0.32 mm × 0.1 μm (non polar), with a $T_{\max}$ of 450 ºC. Helium was used as carrier gas with a flow rate of 1 ml/min. Samples of 1 μl were injected, with a split mode (20:1). The high temperature column enabled oven temperatures of 400 ºC to be reached, ensuring that hydrocarbons up to C_{60} could be analysed. In order to check the possible influence of the temperature during the analysis of the results obtained, an optimization of the analysis system was carried out. A temperature of 380 ºC was used for waxes, and 280 ºC for oils. No differences were observed. Moreover, no formation of aromatic compounds was observed, which occurs at high temperatures and it is a symptom of the degradation of the oil. A method of injection sandwich was used, with higher reproducibility. The ion trap detector had a mass range from 32 to 800 amu and was linked to a computer with a WILEY library.

Experimental results and discussion

In order to study the influence of the mixture, a series of previous experiments with the pure components were performed. The results obtained for pure HDPE, pine sawdust, and the mixtures are shown in tab. 2.

The analysis of the possible synergetic effects has been carried out calculating each product or fraction by average weigh from the results obtained in the experiments with pure sawdust and polyethylene. The following formula has been used:

$$g_{\mathrm{i,\,calc}} \quad \frac{(g_{i,\,\mathrm{sawdust}}\, g_{\mathrm{sawdust}} \quad g_{i,\,\mathrm{HDPE}}\, g_{\mathrm{HDPE}}}{\text{total weight}}$$

where $g_{\mathrm{i,calc}}$ is the calculated production of the compound i (g/100 g of feed) and $g_{i,\mathrm{sawdust}}$ and $g_{i,\mathrm{HDPE}}$ are the productions of the compound i in the experiments with sawdust and polyethylene respectively. The terms g_{sawdust} and g_{HDPE} refer to the amount (in grams) fed in the experiments with mixtures, the total weight being the sum of g_{sawdust} and g_{HDPE}.

The calculated production of each compound or fraction is compared with the values obtained experimentally. These results are shown in tab. 3. The products generated in the pyrolysis of mixtures of pine sawdust and polyethylene are similar to those obtained in the pyrolysis of these materials separately, although different amounts are observed.

The pyrolysis of polyethylene generates different hydrocarbons, basically a distribution of olefines and parafines of different molecular weight and, depending on the operating conditions, different aromatic compounds. No oxygenated compounds are observed. As the operation temperature increases, the relative importance of the wax fraction decreases, while there is a simultaneous increase of the gas production and the generation of aromatic substances in the liquid fraction. At high temperatures the gas yield decreases slightly probably due to the increase of the generation rate of aromatic compounds. The analysis of the gas obtained shows the presence of significant amounts of ethylene, propylene and butadiene that do not appear in the pyrolysis of pine sawdust.

The pyrolysis of pine sawdust generates chemical compounds different to those obtained in the pyrolysis of polyethylene. The composition of the liquid fraction includes oxygenated compounds: acetic acid, ketones, phenol and cresols. No hydrocarbons of high molecular weight appear. The composition of the gas fraction includes carbon monoxide and dioxide, which are not observed in the polyethylene pyrolysis.

Table 2. Product yields (wt.% of feed) for HDPE, sawdust, and mixture pyrolysis

Biomass	HDPE	Mixture	Sawdust	HDPE	Mixture	Sawdust	HDPE	Mixture	Sawdust	HDPE	Mixture	Sawdust	HDPE	Mixture	Sawdust
Tempe-rature / **Product yields**	640 °C			685 °C			730 °C			780 °C			850 °C		
Yield															
% Gas	31.5	55.4	39.1	60.4	58.5	55.9	82.0	84.0	67.3	90.4	87.0	69.9	83.8	90.5	78.3
% Oil	68.5	39.3	46.5	39.6	27.1	25.2	18.0	9.0	22.0	9.6	5.0	16.9	16.2	6.0	12.5
% Water	0.0	2.8	6.6	0.0	5.0	5.9	0.0	4.2	5.6	0.0	4.0	4.3	0.0	1.7	2.7
Gas															
H_2	0.1	0.6	0.3	0.6	0.4	0.7	0.6	0.5	0.9	0.6	1.7	1.5	1.5	3.0	1.9
CO	0.0	14.0	20.8	0.0	10.8	35.5	0.0	23.1	37.0	0.0	24.6	43.7	0.0	33.3	53.5
CO_2	0.0	7.3	8.1	0.0	3.8	10.8	0.0	5.1	10.5	0.0	4.1	9.1	0.0	2.7	7.9
CH_4	2.2	3.2	2.4	4.8	3.7	4.2	7.8	5.4	4.6	9.7	7.2	4.9	15.3	10.1	6.6
C_2H_4	7.6	7.1	1.1	17.0	9.3	2.3	25.3	13.1	2.8	37.0	16.1	3.4	40.5	20.0	4.7
C_2H_6	2.1	1.5	0.4	3.4	1.4	0.6	4.8	2.3	0.6	3.8	2.0	0.6	2.5	1.4	0.3
C_2H_2	0.0	0.0	0.1	0.0	0.1	0.3	0.0	0.1	0.3	0.0	0.1	0.2	0.0	0.3	0.5
C_3	8.0	6.4	1.0	17.4	7.2	1.6	23.7	11.7	3.9	20.0	8.8	1.9	5.4	2.9	1.1
C_4	9.5	4.5	1.3	17.0	4.9	2.7	17.0	8.2	2.8	13.0	5.0	1.8	4.8	1.7	0.7
Oils															
Olefines	**71.0**	**36.4**	**1.6**	**43.9**	**20.0**	**2.2**	**17.8**	**11.4**	**3.2**	**6.0**	**0.9**	**1.6**	**5.6**	**0.7**	**1.2**
C_5–C_8	14.9	2.7	1.6	31.1	3.3	2.2	13.1	4.7	3.2	5.3	0.7	1.6	5.6	0.7	1.2
C_9–C_{12}	7.7	2.4	0.0	4.1	6.2	0.0	1.9	2.5	0.0	0.7	0.1	0.0	0.0	0.0	0.0
C_{13}–C_{19}	14.4	5.7	0.0	5.9	4.3	0.0	1.7	3.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_{19}–C_{32}	23.0	14.2	0.0	2.8	5.3	0.0	1.1	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_{33}-C_{60}	11.0	11.4	0.0	0.0	0.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Oxygenated	**0.0**	**5.4**	**18.6**	**0.0**	**5.6**	**7.5**	**0.0**	**1.0**	**3.4**	**0.0**	**1.2**	**1.7**	**0.0**	**0.1**	**0.3**
Furans	0.0	0.7	1.8	0.0	1.2	0.5	0.0	0.2	0.1	0.0	0.2	0.1	0.0	0.0	0.0
Acids	0.0	2.5	12.1	0.0	2.5	4.5	0.0	0.9	2.0	0.0	0.6	1.0	0.0	0.1	0.3
Alcohols	0.0	0.4	0.0	0.0	0.3	0.4	0.0	0.0	0.1	0.0	0.2	0.0	0.0	0.0	0.0
Cetons	0.0	1.1	4.4	0.0	1.1	2.0	0.0	0.0	1.0	0.0	0.1	0.4	0.0	0.0	0.0
Aldehydes	0.0	0.5	0.1	0.0	0.4	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Esters	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Aromatics	**1.5**	**3.4**	**23.4**	**4.9**	**5.7**	**15.3**	**12.6**	**6.6**	**16.2**	**21.7**	**15.7**	**14.0**	**29.7**	**15.7**	**10.2**
Non oxygenated	*1.5*	*2.6*	*5.6*	*4.9*	*3.7*	*5.4*	*12.6*	*5.1*	*6.7*	*21.7*	*10.3*	*8.8*	*29.7*	*15.4*	*7.8*
1 ring	1.5	2.1	2.5	4.8	3.3	1.0	11.8	4.3	2.4	19.2	8.7	1.5	22.7	9.1	1.6
Indene	0.0	0.0	0.8	0.0	0.1	1.1	0.3	0.4	2.1	0.1	0.7	1.1	0.1	0.6	0.9
Naphthalene	0.0	0.1	0.5	0.0	0.2	1.1	0.4	0.3	1.4	1.5	2.6	5.0	5.0	3.2	3.8
UpNaphthalene	0.0	0.4	1.8	0.0	0.0	2.2	0.1	0.1	0.7	0.9	2.3	1.2	1.9	2.5	1.4

Table 2. Continuation

Biomass	HDPE	Mixture	Sawdust	HDPE	Mixture	Sawdust	HDPE	Mixture	Sawdust	HDPE	Mixture	Sawdust	HDPE	Mixture	Sawdust
Product yields / **Temperature**	640 °C			685 °C			730 °C			780 °C			850 °C		
Oils															
Oxygenated	*0.0*	*0.7*	*17.8*	*0.0*	*2.4*	*9.9*	*0.0*	*2.0*	*9.5*	*0.0*	*3.1*	*5.2*	*0.0*	*3.3*	*2.4*
Phenols	0.0	0.3	3.2	0.0	0.7	3.3	0.0	1.0	2.5	0.0	0.6	3.3	0.0	0.2	1.5
Cresols	0.0	0.4	4.0	0.0	1.1	2.1	0.0	0.6	3.1	0.0	0.4	1.0	0.0	0.0	0.1
Other alcohols	0.0	0.1	6.4	0.0	0.2	4.1	0.0	0.0	1.5	0.0	0.0	0.2	0.0	0.0	0.0
Biphenyls	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.2	0.1	0.0	0.1	0.2
Dibenzofurans	0.0	0.0	0.4	0.0	0.0	0.3	0.0	0.0	0.6	0.0	0.1	0.3	0.0	0.0	0.2
Other	0.0	0.0	3.8	0.0	0.4	0.1	0.0	0.5	1.3	0.0	1.7	0.3	0.0	3.0	0.4

Table 3. Product yields (wt.% of feed): calculated and experimental

Temperature / **Product yields**	640 °C		685 °C		730 °C		780 °C		850 °CCal	
	Cal.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.	Calc.	Exper.
Yield										
Gas yield	34.4	55.4	58.4	58.5	75.4	84.0	80.4	87.0	79.6	90.5
Wax yield	60.0	39.3	33.1	27.1	19.8	9.0	13.2	5.0	14.2	6.0
Aqueous yield	2.5	2.8	2.7	5.0	2.5	4.2	2.1	4.0	1.2	1.7
Gas										
H_2	0.2	0.6	0.6	0.4	0.7	0.5	1.0	1.7	1.6	3.0
CO	8.0	14.0	16.1	10.8	16.5	23.1	21.3	24.6	24.4	33.3
CO_2	3.1	7.3	4.9	3.8	4.7	5.1	4.4	4.1	3.6	2.7
CH_4	2.3	3.2	4.5	3.7	6.4	5.4	7.4	4.2	11.0	10.1
C_2H_4	5.1	7.1	10.3	9.3	15.2	13.1	20.6	16.1	23.3	20.0
C_2H_6	1.4	1.5	2.1	1.4	2.9	2.3	2.2	2.0	1.4	1.4
C_2H_2	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.3
C_3	5.3	6.4	10.2	7.2	14.8	11.7	11.2	8.8	3.3	2.9
C_4	6.3	4.5	10.5	4.9	10.6	8.2	7.5	5.0	2.8	1.7
Oils										
Olefins	44.3	36.4	25.0	20.0	11.3	11.4	3.9	0.9	3.5	0.7
Oxygenated	7.1	5.4	3.4	1.2	1.5	1.0	0.8	1.2	0.1	0.1
Aromatics	*9.9*	*3.4*	*9.6*	*5.7*	*14.2*	*6.6*	*17.9*	*15.7*	*20.2*	*15.7*
Non oxygenated	3.1	2.7	5.1	3.7	10.0	5.1	15.4	14.4	19.1	15.4
Oxygenated	6.8	0.7	4.5	2.0	4.3	1.5	2.5	1.4	1.1	0.3

The total production of gas is calculated by posing a balance to nitrogen. In the case of the experiments of co-pyrolysis of pine sawdust and polyethylene, the gas yield increases as the operation temperature increases. This behaviour is especially significant between 685 and 730 ºC. For higher temperatures, the gas is the main fraction obtained from the thermal degradation. It is observed that as the gas yield increases, the liquid and the water yields decrease. In addition, the composition of the wax and oil fractions becomes less complex as the temperature increases, with fewer compounds appearing in the mixture.The variation of the gas heating value for the different operation temperatures is shown in fig. 2. The most important increase is obtained between 685 and 780 ºC, due to the generation of combustible gases, and observing no significant variation over 780 ºC. At higher temperatures the yield to light gases still increases. However the cracking of C_2 and C_4 compounds is more intense, diminishing its concentration and explaining the observed trends.

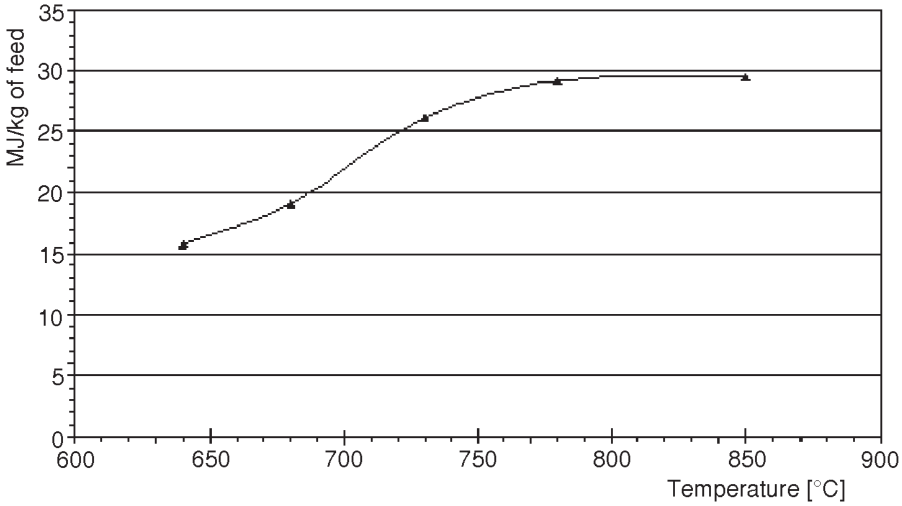

Figure 2. Heating value of gas products

Regarding the synergetic effects of the co-pyrolysis of the mixtures on the global yields, the actual gas production is greater than the calculated amount. The difference increases with the operation temperature, the maximum difference occurring at 850 ºC, indicating that the depolymerization occurs to a greater extent. This observation is coherent with the results obtained in thermogravimetric studies [24] and could be related to the greater importance of the reactions occuring in the freeboard.

Comparing the experimental and calculated gas compositions, the only significant differences are observed in the percentage of hydrogen and carbon monoxide.

Experimental production of hydrogen is higher than the calculated production at 640, 780, and 850 ºC, whilst this value is lower than the calculated figure for the other temperatures tested. The variation of hydrogen production (vol.%) *vs.* temperature is shown in fig. 3. It can be observed that despite the low values obtained when expressed in weight, hydrogen is one of the main components of the pyrolysis gas. The generation of hydrogen increases as the temperature increases, with a sharp increase for temperatures higher than 730 ºC.

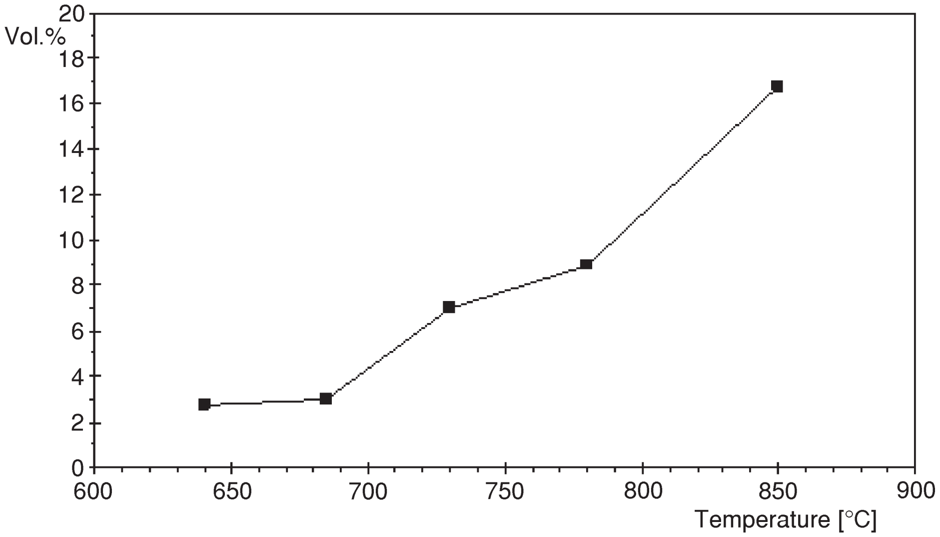

Figure 3. Evolution of hydrogen composition with pyrolysis temperature

The carbon monoxide obtained is originated by the biomass degradation, basically from the reaction of the formation of levoglucosan and its further degradation to form carbon monoxide and water, although CO is also formed in the decarboxylation reactions. The yield to CO at different temperatures follows a similar trend to that observed for hydrogen, and has been noted by various authors [27]. Since CO is originated by the sawdust decomposition, the increase in production in the case of mixtures indicates an acceleration of this process in the presence of polyethylene.

The experimentally obtained productions of methane and ethylene, basically formed during the pyrolysis of polyethylene, do not differ significantly from the calculated values. On the other hand, the C_3, C_4, and C_5 experimental yields are lower than the calculated ones (fig. 4). Although the variation is small its influence is important due to the contribution to the gas heating value.

Some differences between the experimental and calculated results are also observed in the composition of oils and waxes.

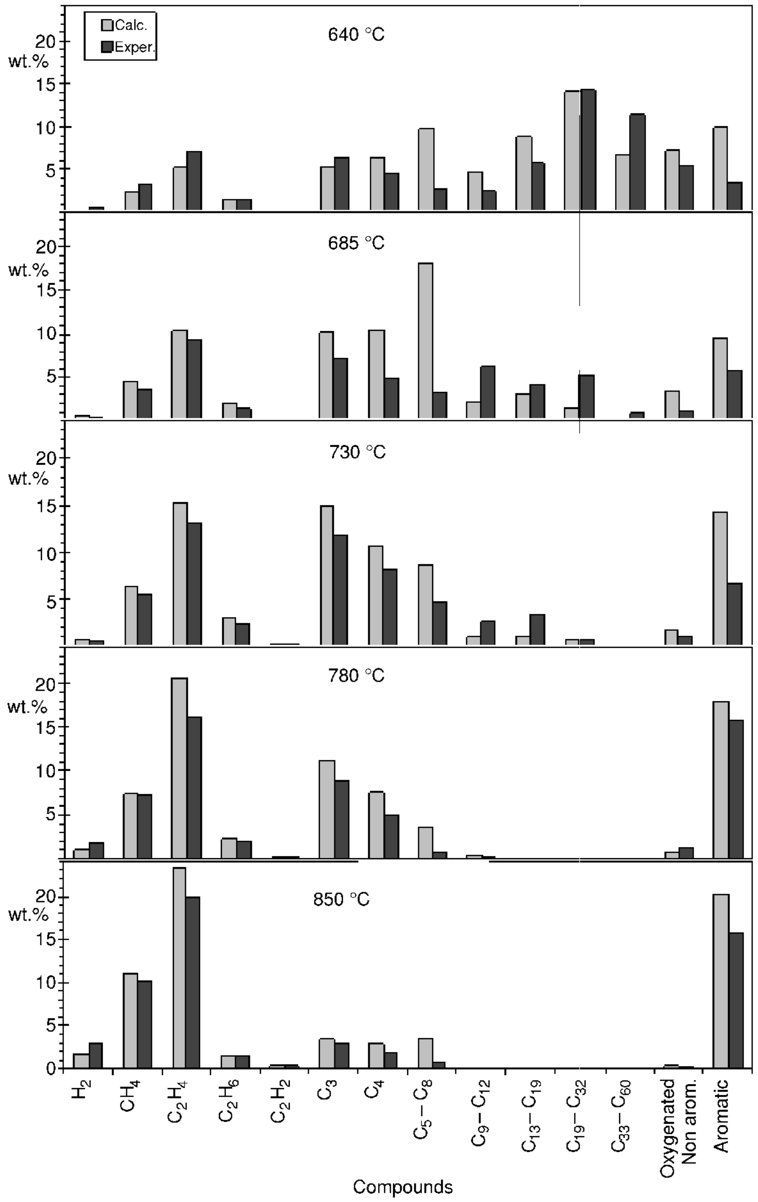

Figure 4. Pyrolysis of mixtures: product distribution at different temperatures

The production of oils decreases as the temperature increases. The experimental yields are always lower than the calculated average for the pyrolysis of pure sawdust and HDPE. The maximum difference is observed at 850 ºC, at which the yield in the co-pyrolysis experiments is 50% of that obtained in the pyrolysis of pine sawdust, and 30% of that obtained in the pyrolysis of HDPE. The generation of water in the co-pyrolysis experiments is higher than expected (twice the value calculated at 685, 730, and 780 ºC). The smallest difference is observed at 640 ºC.

The total amount of olefines experimentally obtained is lower than the calculated value. It is observed that the yield to heavier waxes (between C_{19} and C_{60}) is higher at lower temperatures, whilst the yields to C_5, C_9, and C_{19} are lower than the calculated values. A lower amount of intermediate fractions indicates an increasing importance of gas phase reactions, explaining the increasing yield to gas. As the operating temperature increases, the trend changes, the yield being lower than the calculated values. Apparently, at the low temperatures tested, the presence of the sawdust induces a delay in cracking of the heavier olefinic fraction. This effect is less significant at high temperatures.

The relative importance of the production of diolefines, olefines and parafines (fig. 5) has also been studied. In general, slight differences are observed. The relative importance of olefines and parafines decrease when compared to the production of diolefines. This behaviour becomes less evident as the temperature increases. These results differ from those presented by Jakab and Blazsó [28], who obtain a decrease of alcadienes and an increase of alkenes. However, it should be noted that the results correspond to mixtures of polyethylene and charcoal or carbon black, with acid groups that can act as H donors, leading to an hydrogenation of the primary radicals from polyehtylene. This would indicate, at least, a slight interaction between the processes of thermal degradation of sawdust and

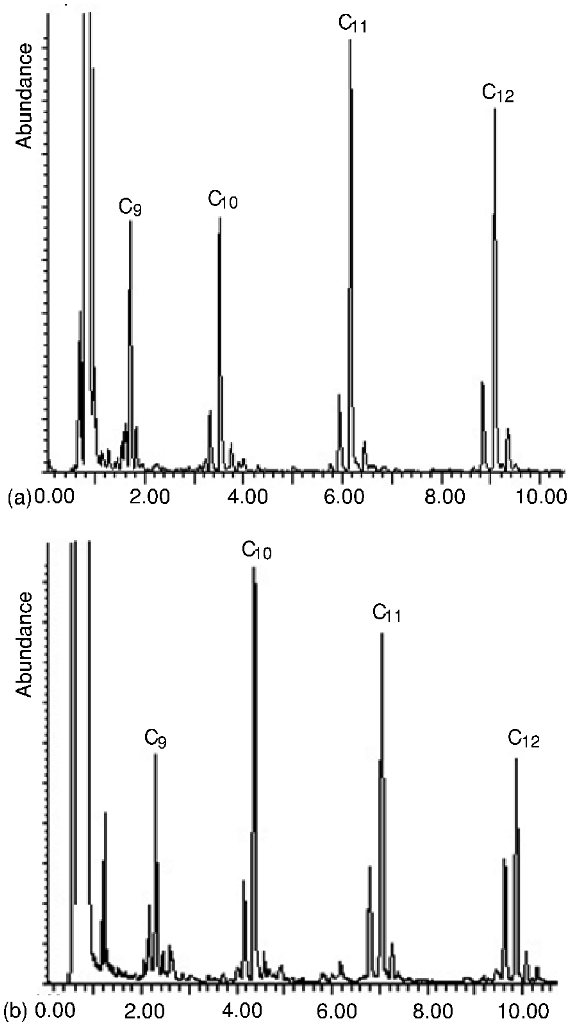

Figure 5. Pyrolysis total ion chromatograms of (a) HDPE and (b) mixture HDPE + sawdust

HDPE, which resulting in a faster decomposition of the sawdust. The interaction also affects the mechanism of HDPE decomposition, increasing the insaturation of the obtained products. In principle, the β-scission of primary radicals is favoured (generating alkenes and alkadienes) instead of the intermolecular hydrogen transfer (generating alkanes).

The experimental production of aromatic hydrocarbons is generally lower than the calculated values, with the maximum difference observed at 730 ºC. An analysis of the individual, non-oxygenated aromatic compounds (benzene, toluene, indene, naphtalene and heavier) shows that the experimental values are lower than the calculated values for the different temperatures tested. The generation of these compounds increases with the temperature. Regarding the possible synergetic effect, the maximum difference between experimental and calculated results is obtained at 730 ºC:10 $g/g_{mixture}$ *vs.* 5.1 $g/g_{mixture}$. It should be noted that the experimental yields to compounds heavier than naphtalene are higher than the calculated values for temperatures higher than 780 ºC, as can be observed in fig. 6.

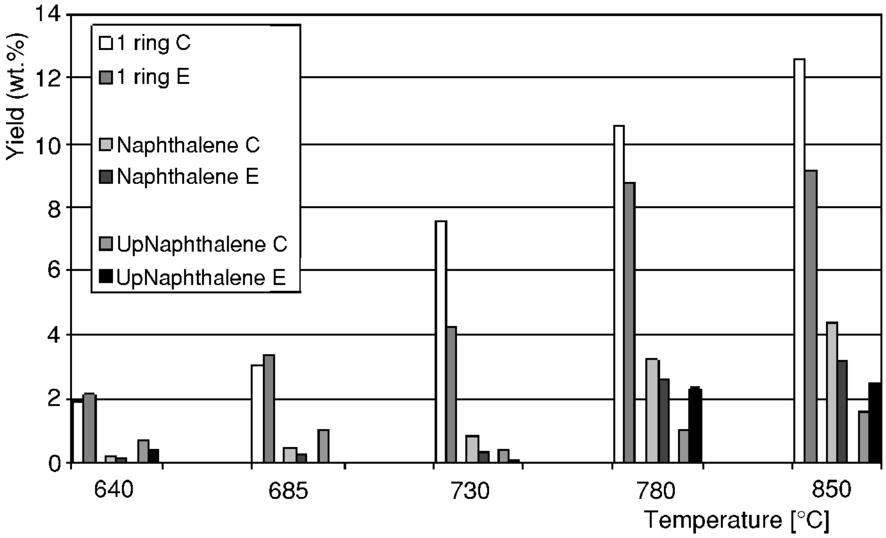

Figure 6. Experimental and calculated results of pyrolysis of mixtures: variation of yields of oxygenated aromatic compounds with temperature

Regarding the oxygenated aromatic compounds, the experimental production is lower than the calculated value for the different temperatures tested, as it can be observed in fig. 7. These compounds are formed in the thermal decomposition of pine sawdust. It appears that the co-pyrolysis of both materials favours the reactions of elimination of water from the oxygenated compounds, explaining the lower generation of this type of product and the higher production of water and H_2.

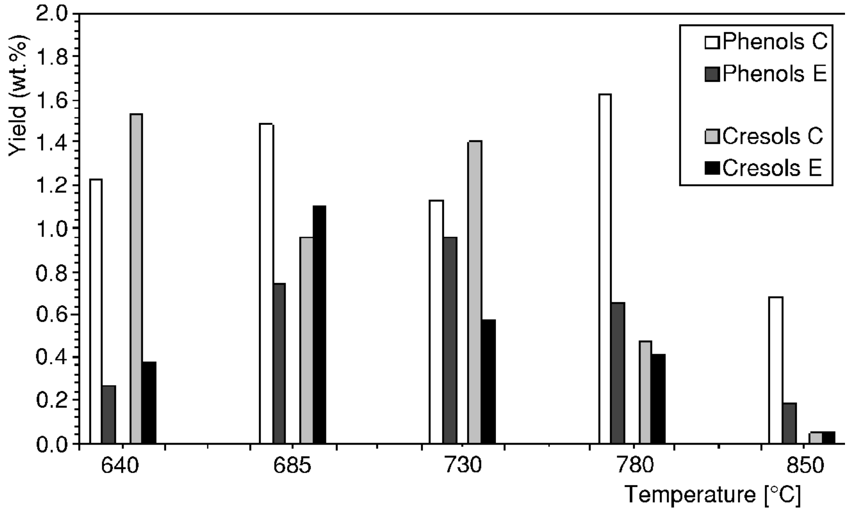

Figure 7. Experimental and calculated results of pyrolysis of mixtures: variation of yields of oxygenated aromatic compounds with temperature

From the above observations, it can be stated that during the co-pyrolysis of mixtures of pine sawdust and polyethylene, an increase of the gaseous fraction is observed, especially of hydrogen and carbon monoxide. The increase of the yield to H_2 is due to the fact that the reactions of water elimination from the oxygenated compounds are favoured. This would also explain the observed increase of the water production and a lower concentration of the oxygenated compounds found in the liquid fraction. Regarding the generation of CO, and given that it is formed only from the biomass, the increase observed could be due to an acceleration of the sawdust decomposition process. In principle, it is assumed that this acceleration is due to interaction with the radicals generated during the HDPE degradation [29]. This interaction would also explain the observed variations in the production of compounds C_3, C_4, and C_5 in the gas fraction and also the olefinic compounds in the liquid fraction, directly formed during the thermal decomposition of polyethylene [30, 31]. This behaviour seems to indicate a slower HDPE decomposition, possibly due to a higher consumption of radicals in the decomposition of the lignocellulosic material, and a lower rate of hydrocarbon cracking. The evolution of the different compounds is complex since they are products of the decomposition of the heavier fractions whim, in turn, decompose towards lighter fractions.

Conclusions

An experimental study of co-pyrolysis of mixtures of polyethylene and pine sawdust in a fluidised bed reactor carried out at different temperatures in pyrolytic conditions shows that the gas yield increases with the increase in the temperature for the pure components and for the mixture. The main gases produced from the co-pyrolysis process were, at low temperatures, carbon monoxide, ethylene, carbon dioxide, propylene, butadiene, methane and pentadiene, while at high temperatures the gas composition changed drastically, the main gas being carbon monoxide (more than 33 wt.%), and others being ethylene, methane, benzene and hydrogen. The co-pyrolysis of biomass and HDPE produces a gas of greater average heating value than the obtained with biomas alone, with a lower production of tars.

The higher yield of CO obtained in the co-pyrolysis for the different temperatures tested corresponds to a higher sawdust conversion. The emission of CO at low temperatures indicates an earlier degradation compared to the pyrolysis of pure sawdust, which coincides with a delay of the cracking of the waxes of high molecular weight and a lower production of light compounds in the liquid fraction from polyethylene pyrolysis.

The increase of the production of gas and the lower generation of fraction C_5–C_{19} could be due to a greater importance of the gas phase reactions, due to the particles of char formed.

In the co-pyrolysis, a lower amount of oxygen compounds is formed, basically aromatic alcohols, and there is an increase in the production of water. The production of liquids, apart from water, was lower than expected.

These results indicate the existence of a synergetic effect in the decomposition of these two materials, possibly due to the existence of particles of char originated in the pyrolysis of sawdust.

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References

[1] Sharypov, V. I. , Marin, N., Beregovtsova, N. G., Baryshnikov, S. V., Kuznetsov, B. N., Cebolla, V. L., WeberPinto, J. V., Co-Pyrolysis of Wood Biomass and Synthetic Polymer Mixtures, Part I: Influence of Experimental Conditions on the Evolution of Solids, Liquids and Gases, *J. Anal. Appl. Pyrolysis, 64* (2002), pp. 15-28

[2] Neto, R., Pinto, F., Technical Viability Study of Gasification Technology to Process Coal Mixed with Wastes, *Proceedings*, 1th World Conference on Biomass for Energy and Industry, Sevilla, Spain, June 5-9, 2000, James & James, Science Publishers Ltd., 2001, pp. 1537-1540

[3] L. Sørum, L., Grønli, M. G., Hustad, J. E., Pyrolysis Characteristics and Kinetics of Municipal Solid Wastes, *Fuel, 80* (2001), pp. 1217-1227

[4] Bilbao, R., Millera, A., Arauzo, J., Kinetics of Weight Loss by Thermal Decomposition of Xylan and Lignin. Influence of Experimental Conditions, *Thermochim. Acta, 143* (1989), pp. 137-148

[5] Bilbao, R., Millera, A., Arauzo, J., Kinetics of Weight Loss by Thermal Decomposition of Different Lignocellulosic Materials. Relation between the Results Obtained from Isothermal and Dynamic Experiments, *Thermochim. Acta, 165* (1990), pp. 103-112

[6] Conesa, J. A., Marcilla, A., Font, R., Caballero, J. A., Thermogravimetric Studies on the Thermal Decomposition of Polyethylene, *J. Anal. Appl. Pyrolysis, 36* (1996), pp. 1-15

[7] Westerhout, R. W. J., Waanders, J., Kuipers, J. A. M., van Swaaij, W. P. M., Kinetics of the Low-Temperature Pyrolysis of Polyethene, Polypropene, and Polystyrene Modeling, 20 Experimental-Determination and Comparison with Literature Models and Data, *Ind. Eng. Chem. Res., 36* (1997), pp. 1955-1964

[8] Bockhorn, H., Hornung, A., Hornung, U., Schawaller, D., Kinetic Study on the Thermal Degradation of Polypropylene and Polyethylene, *J. Anal. Appl. Pyrolysis, 48* (1999), pp. 93-109

[9] Oakes, W. G., Richards, W. G., The Thermal Degradation of Ethylene Polymers, *J. Chem. Soc., 4* (1949), pp. 2929-2935

[10] Wall, L. A., Madorsky, S. L., Brown, D. W., Straus, S., Simha, R., The Depolymerization of Polymethylene and Polyethylene, *J. Am. Chem. Soc., 76* (1954), pp. 3430-3437

[11] Ranzi, E., Dente, M., Faravelli, T., Bozzano, G., Fabini, S., Nava, R., Cozzani, V., Tognotti, L., Kinetic Modeling of Polyethylene and Polypropylene Thermal Degradation, *J. Anal. Appl. Pyrolysis, 40-41* (1997), pp. 305-319

[12] McCaffrey, W. C., Cooper, D. G., Kamal, M. R., Tertiary Recycling of Polyethylene-Mechanism of Liquid Production from Polyethylene by Termolysis Reactive, *Polym. Degrad. Stab., 62* (1998), pp. 513-521

[13] Poutsma, M. L., Fundamental Reaction of Free Radicals Relevant to Pyrolysis Reactions, *J. Anal. Appl. Pyrolysis, 54* (2000), pp. 5-35

[14] Lehrle, R. S., Pattenden, C. S., Intramolecular Hydrogen Transfer in Thermal Degradation: Comments on the Size Distribution of the Backbite Rings, *Polym. Degrad. Stab., 63* (1999), pp. 153-158

[15] Bockhorn, H., Hornung, A., Hornung, U., Mechanisms and Kinetics of Thermal Decomposition of Plastics from Isothermal and Dynamic Measurements, *J. Anal. Appl. Pyrolysis, 50* (1999), pp. 77-101

[16] Urzendowski, S. R., Guenther, A. H., Kinetics Constants of Polymeric Materials from Thermogravimetric Data, *J. Therm. Anal. 3* (1971), pp. 379-395

[17] Wu, C-H., Chang, C-Y., Hor, J-L., Shih, S-M., Chen, L-W., Chang, F-W., On the Thermal Treatment of Plastic Mixtures of MSW: Pyrolysis Kinetics, *Waste Manage., 13* (1993), pp. 221-235

[18] Font, R., Marcilla, A., García, A. N., Caballero, J. A., Conesa, J. A., Kinetic Models for the Thermal Degradation of Heterogeneous Materials, *J. Anal. Appl. Pyrolysis, 32* (1995), pp. 29-39

[19] Madorsky, S. L., Rates of Thermal Degradation of Polystyrene and Polyethylene in a Vacuum, *J. Polym. Sci., 9* (1952), 2, pp. 133-156

[20] Sawaguchi, T., Inami, T., Kuroki, T., Ikemura, T., Studies on Thermal Degradation of Synthetic Polymers. 12. Kinetic Approach to Intensity Function Concerning Pyrolysis Condition for Polyethylene Low Polymer, *Ind. Eng. Chem. Process Des. Dev., 19* (1990), 1, pp. 174-179

[21] Jellinek, H. H. G., Thermal Degradation of Polystyrene and Polyethylene. Part III, *J. Polym Sci., 4* (1949), 1, pp. 13-36

[22] Ranzi, E., Dente, M., Goldaniga, A., Bozzano, G., Favarelli, T., Lumping Procedures in Detailed Kinetic Modeling of Gasification, Pyrolysis, Partial Oxidation and Combustion of Hydrocarbon Mixtures, *Prog. Energy Combust. Sci., 27* (2001), pp. 99-139

[23] García-Pérez, M., Chaala, A., Yang, J., Roy, C., Co-Pyrolysis of Sugarcane Bagasse with Petroleum Residue. Part I: Thermogravimetric Analysis, *Fuel, 80* (2001), pp. 1245-1258

[24] Matsuzawa, Y., Ayabe, M., Nishino, J., Acceleration of Cellulose Co-Pyrolysis with Polymer, *Polym. Degrad. Stab., 71* (2001), pp. 435-444

[25] Di Blasi, C., Linear Pyrolysis of Cellulosic and Plastic Waste, *J. Anal. Appl. Pyrolysis, 40-41* (1997), pp. 463-479
[26] Jakab, E., Blazsó, M., Faix, O., Thermal Decomposition of Mixtures of Vinyl Polymers and Lignocellulosic Materials, *J. Anal. Appl. Pyrolysis, 58-59* (2001), pp. 49-62
[27] Aguado, R., Combustion and Pyrolysis of Wood Wastes in Conical Spouted Bed (in Spanish), Ph. D. thesis, Universidad del País Vasco, Bilbao, Spain, 1999
[28] Jakab, E., Blazsó, M., The Effect of Carbon Black on the Thermal Decomposition of Vinyl Polymers, *J. Anal. Appl. Pirolisis, 64* (2002), pp. 263-277
[29] Li, B., He, J., Investigation of Mechanical Property, Flame Retardancy and Thermal Degradation of LLDPE–Wood-Fibre Composites, *Polym. Degrad. Stab.*, *83* (2004), 2, pp. 241-246
[30] Lattimer, R. P., Pyrolysis Field Ionization Mass Spectrometry of Polyolefins, *J. Anal. Appl. Pyrolysis, 31* (1995), pp. 203-225
[31] Blazsó, M., Polyaromatization in Common Synthetic Polymers at Elevated Temperatures, *J. Anal. Appl. Pyrolysis, 25* (1993), pp. 25-35

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