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Devolatilization and Gasification of Plastic Wastes in a Fluidized Bed Reactor

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Pyrolysis and gasification processes of plastic wastes in a fluidized bed reactor can be schematically decomposed into three major steps: devolatilization; gas phase reactions in the bed; gas phase reactions in the freeboard. The devolatilization phase defines the true feed composition to the reactor and is the first step in the whole process.

The reactor model takes into account the specific behaviour of a bubbling fluidized bed by separately modelling the different reaction zones of the reactor. In particular, cracking of plastic waste occurs in the dense-emulsion phase while the product gases mainly react in the homogeneous phase in splashing and freeboard zones. Preliminary comparisons between experimental measurements, obtained under pyrolysis and gasification conditions, and model predictions provided useful information for a proper understanding of the complex behaviour of the fluidized bed and, mainly under pyrolysis conditions, clearly indicate the catalytic effect of the metallic reactor wall.

1. Introduction & background

Compared to other gas-solid reactors, fluidized beds have some rather peculiar properties that are desirable for thermal treatments of plastic waste pyrolysis and gasification. In a bubbling fluidized bed (BFB) the upper surface of the bed is clearly separated by the freeboard region. In the bed, gas bubbles coalesce and grow as they rise up to the top of the bed by promoting a perfect mixing of this reaction volume; the eruption of gas bubbles promotes a fairly good gas-solid mixing just above the bed surface (splashing zone) and a plug-flow hydrodynamic regime establishes in the freeboard region. The yields and quality of the products obtained from a pyrolysis process in a fluidized bed reactor are due to two contributions: the first, called primary cracking, is that of raw material degradation, i.e. the cracking of molten polymer, which occurs in the dense bed; the second contribution is that of secondary and ternary reactions involving the primary volatiles and occurring partially inside the bed and mainly along the freeboard (Arena and Mastellone, 2006).

Pyrolysis (or devolatilization) phase is also the first step of the gasification process and then affects the successive reactions in the bed and in the freeboard. The resulting product distribution is strongly dependent on the operating conditions and on presence of catalytic materials.

2. The phenomenological models

The high rates of mass and energy transfer inside the BFB make very fast the heating and layering process between bed materials of dense bed and fed polymers. As a consequence the primary cracking is related to a thin layer of polymer instead of to a whole pellet. This feature must be taken into account in the modelling of process since the internal resistance is obviously negligible and intrinsic kinetics is the controlling stage of the primary cracking process. The primary products are involved in a series of successive gas-phase reactions in the different regions of the reactor (two-phases dense bed, splashing zone and freeboard). Due to high mixing degree in the dense bed, this zone is considered as a perfect stirred reaction volume characterized by a limited mass transfer rate between emulsion phase and bubble phase. The freeboard zone is instead considered and is modelled as an ideal plug flow reactor. All these features have been taken into account in the reactor modelling as schematically illustrated in Figure 1.

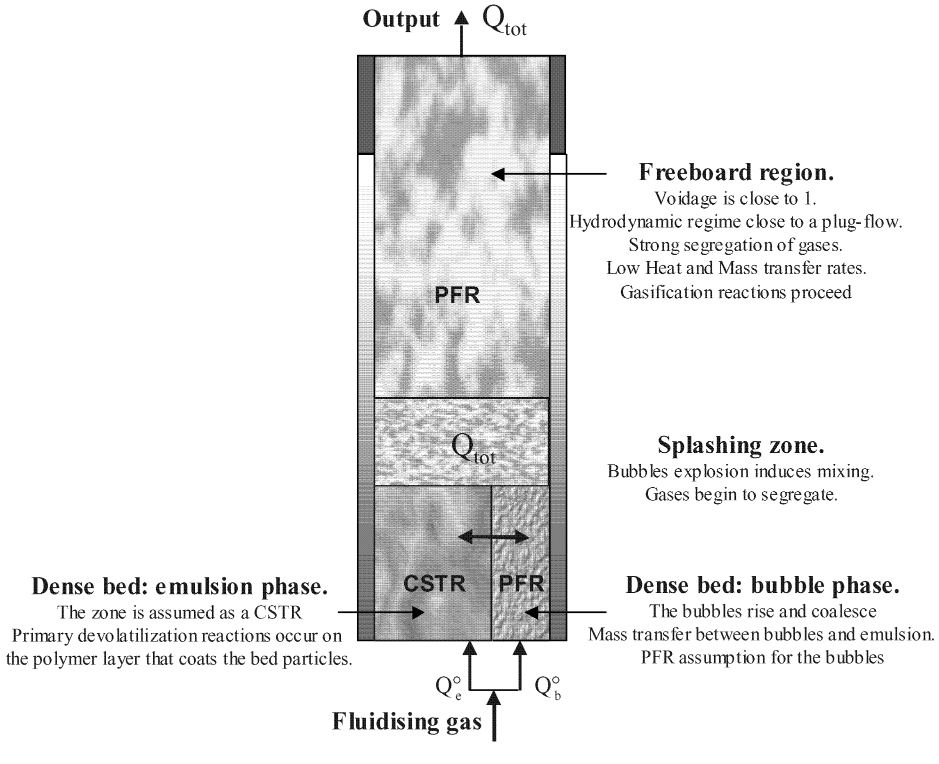

Figure 1 Simple scheme of the BFB reactor.

3. Experimental apparatus, materials and operating conditions

The experiments were carried out in a bubbling fluidized bed reactor, having an internal diameter of 102mm and a height of 1.05m. The reactor (schematically described in Figure 2) was equipped with pressure and temperature transducers located at the bed bottom and along the reactor and with a conditioning line that addresses the produced gas to the on-line analyzers. Nitrogen was used to fluidize the bed, made of 1440g of quartz sand. The whole reactor was warmed by means of three couples of electric heaters and the temperature was monitored in the pre-heater, in the bed and in the freeboard. The experiments were carried out by over-bed feeding of polyethylene (PE) by means of a screw-feeder located at the top of the freeboard.

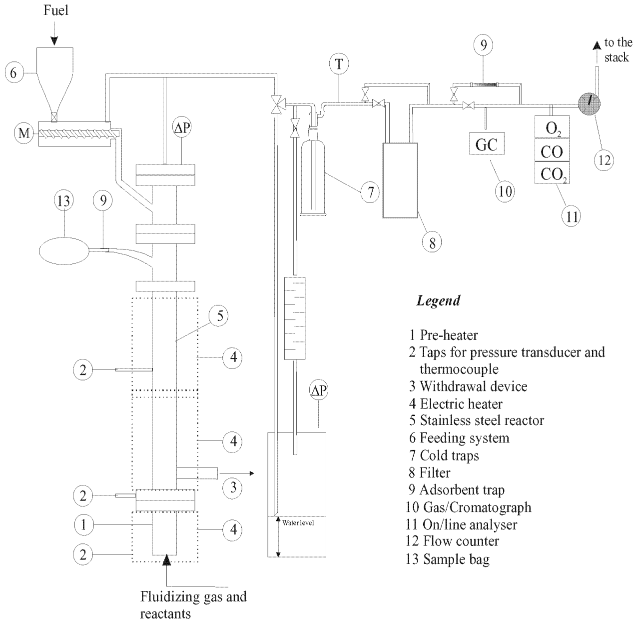

Figure 2 BFB reactor utilized for pyrolysis and gasification experiments

The plastic material melts during its passage along the freeboard, so that it reaches the bubbling bed in a liquid phase, enveloping sand particles. The operating conditions used in the pyrolysis tests are listed in Table 1. The produced gas was sent to the conditioning line connected to the on-line gas cromatograph Agilent MicroGC 3000 that measures the gas concentrations of hydrogen, oxygen, nitrogen, methane, carbon monoxide and light hydrocarbons (ethane, ethene, propane, propylene, acetylene, isobutene, 1-3 butadiene) each 300 seconds.

The gasification experiments were carried out in the same reactor with the same configuration. Fluidizing stream was composed by air and nitrogen in the mixing ratio able to reach different oxygen concentrations. Experiments were carried out by feeding a mass feed rate of 3g/min of PE and different equivalent ratios by varying the air/N_2 ratio. During gasification experiments an on-line CO_2 analyser was added to completely characterize the produced syngas stream.

Table 1. Operating conditions of the pyrolysis experiments.

Test	**Fuel**	**Gas velocity, m/s**	**Bed temperature, °C**
A	PE	0.16	800
B	PE	0.16	900

Table 2. Operating conditions of the gasification experiments (T=850°C).

Test	**Fuel**	**Gas velocity, m/s**	**Equivalence ratio, λ**
G	PE	0.26	0.2
H	PE	0.26	0.25
I	PE	0.26	0.3

4. Experimental results

4.1 Pyrolysis tests

Figure 3 reports the composition of the gas stream obtained by pyrolysing PE at three different reactor temperatures. Measurements have been taken during the steady-state regime that was approximately 1 hour. After each test the reactor head was removed in order to retrieve the bed and to take a sample of material adhered on the reactor wall. As expected [Dente and Ranzi, 1983], the wall was covered by a thickness of few millimetres of carbonaceous material that was characterized by means of TG-DTA, SEM and TEM microscopy and X-ray [Arena et al, 2005]. In the dense zone the movement of the bed continuously removed this carbon phase avoiding that fouling increased so much to reduce the catalytic activity of the bed zone. During these experiments a strong catalytic effect of iron, contained in the ferritic steel of reactor wall, was recognized. The iron was activated by the presence of hydrogen at high temperature so becoming reactive with a series of radicals produced by cracking of the polymer. The effect of iron, whose presence was detected by SEM-EDAx measurements on samples retrieved from the reactor after the tests, was the enhancing of dehydrogenation and carbonization of polymer. This feature is in accordance with a previous study [Dente et al., 2007] that described the fouling process as consisting in two mechanisms: a catalytic reaction between Fe and unsaturated radicals (produced by cracking of the polymer) and a following series of radicalic reactions. The deposit is mainly composed by carbon structures having nano- to micrometers sizes whose morphology changes with temperature. For experiments with PE the structures of solid phase, partly covering the bed particles, partly adhering to the reactor wall and partly elutriated out of the reactor, changes from nanofibres (from 500 to 650°C) to quasi-spherical particles (from 700 to 900°C). Under specific conditions MWCNTs were obtained during pyrolysis of PE at lower temperatures [Arena et al., 2005].

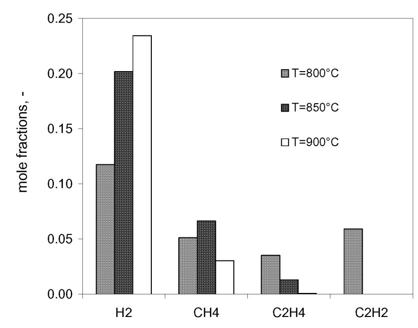

Figure 3 Pyrolysis of PE. Product distribution at three reactor temperatures.

4.2 Gasification tests

Two series of gasification experiments were carried out by adding from 5 to 11% of oxygen to the fluidization gas stream in order to obtain three different value of λ. Reactor temperature was kept at 850°C. Under these conditions partial oxidation of gases produced by the pyrolysis step occurred and CO, H_2, CO_2 and H_2O were obtained. During the first series of experiments, a considerable amount of carbon structures (with less than 1% of hydrogen) and corresponding high yields of molecular hydrogen in the gas phase were produced. After some hours of operation under gasification conditions the carbonaceous solid yield progressively decreased (from $0.65 g/g_{PE}$ to $0.066 g/g_{PE}$) and PAH (polycyclic aromatic hydrocarbons) and tars raised in importance. In the meantime, the hydrogen decreased in the gas phase and increases in the liquid (tar) phase and the ethylene, as well as BTX, increased. The reactor wall appeared covered not more by solid carbon phase, as in the first series of tests, but by a thin oil film.

	λ=0.2	λ=0.25	λ=0.3
N_2	0.828	0.828	0.840
H_2	0.084	0.070	0.066
CO_2	0.013	0.012	0.016
CO	0.044	0.054	0.054
CH_4	0.026	0.027	0.020
C_2-C_4	0.005	0.009	0.005

Table 3. Gasification of PE. Product distribution at three equivalent ratios. (molar fractions)

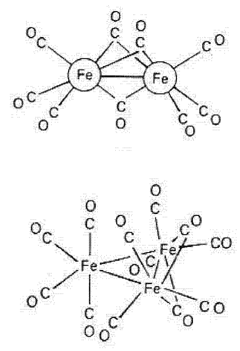

Figure 4 Two possible iron-carbonyls [$Fe_2(CO)_5$ and $Fe_3(CO)_{12}$].

This fact is explained by considering the reduced catalytic activity of iron during gasification related to the CO and H_2 presence. Carbon monoxide is in fact an important π acceptor and it is particularly reactive with transition metals (group d) with which it forms metal-carbonyls (Fig. 4). Iron carbonyls do not allow catalytic dehydrogenation since Fe is totally blocked inside the "sandwich" structures.

Table 3 reports the gas composition at different equivalence ratio, λ, as obtained in the second series of experiments. It is noteworthy that the catalytic activity of iron mentioned above, even though strongly reduced, was probably yet present.

5. Modelling results

The freeboard region is assumed as an isothermal PFR. The kinetic model TOT0512 was used to model pyrolysis and gasification process [Ranzi et al., 2001].

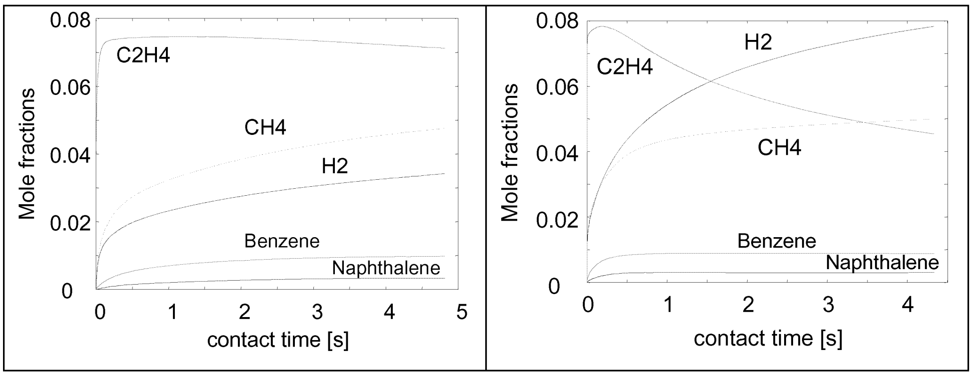

Figure 5 Modelling results for pyrolysis of PE at 800 °C (left) and 900 °C (right).

This model is able to analyse oxidation and pyrolysis of hydrocarbon mixtures from methane up to diesel fuels and it involves about 300 species and more than 8000 reactions. Comparisons between model predictions in pyrolysis conditions (Figure 5) clearly indicate that higher temperatures favour dehydrogenation reactions and contribute to H_2 formation. C_2H_4 consumption becomes important at 900°C, but still significant amounts of ethylene, benzene and higher PAH are predicted. The complete dehydrogenation and the formation of carbon structures, as observed during the experimental tests (Figure 3), can be then justified only on catalytic basis. Temperatures higher than 1150°C would be required to reach similar H_2 production.

Similar simulations, always assuming isothermal plug flow conditions at 850 °C, were performed also in presence of O_2, with equivalence ratios of 0.2, 0.25 and 0.3. N_2 mole fraction at the reactor outlet is always about 80%. Table 4 shows that an increase of λ leads to larger CO and CO_2 formation, with reduction of ethylene, methane and heavier hydrocarbons. Model predictions of H_2 formation are not significantly affected by oxygen injections. This result agrees with the experimental values reported in Table 3.

Table 4 Modelling results for gasification of PE at different equivalence ratios.

	λ = 0.2		**λ = 0.25**		**λ = 0.3**	
	xmol	**xmass**	**xmol**	**xmass**	**xmol**	**xmass**
N_2	0.8101	0.8397	0.7911	0.8239	0.7730	0.8081
H_2	0.0314	0.0023	0.0321	0.0024	0.0327	0.0025
H_2O	0.0346	0.0230	0.0436	0.0292	0.0529	0.0356
CO_2	0.0075	0.0122	0.0110	0.0181	0.0151	0.0248
CO	0.0596	0.0618	0.0698	0.0727	0.0786	0.0821
CH_4	0.0240	0.0142	0.0233	0.0139	0.0225	0.0135
C_2-C_4	0.0282	0.0296	0.0252	0.0266	0.0223	0.0235
C_6+ (Benzene)	0.0045	0.0167	0.0036	0.0129	0.0027	0.0096
CO / CO_2	7.97	5.07	6.32	4.02	5.20	3.31
H_2 / H_2O	0.91	0.10	0.74	0.08	0.62	0.07

Acknowledgements

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