

Thermal decomposition of mixtures of biomass and high density polyethylene in atmospheres with different oxygen concentration

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The study of the behavior of the thermal decomposition of mixtures of biomass and thermoplastic materials is of interest for its use in the determination of residence times of the solid in the processes of thermal recovery of industrial and urban wastes such as pyrolysis, gasification or combustion. These processes allow the obtainment of combustible gases and/or energy, with the reduction of landfilling as an added advantage. One of the first issues that can be encountered when implementing these processes in a commercial reactor is the knowledge of the thermal degradation behaviour of the materials under different conditions.

One of the materials present in significant quantities in municipal solid waste is polyethylene. Numerous studies on the thermal decomposition of polyolefines and, in particular, polyethylene have been carried out, especially in vacuum or inert atmosphere [1-9]. Thermogravimetry is the most commonly used technique for the determination of kinetic parameters, although the experimental conditions utilized are very different, involving broad ranges of temperature, sample amount, heating rates, reaction atmospheres and pressures. Most authors describe thermal decomposition by a power law equation and perform isothermal and/or dynamic experiments.

The degradation of polyethylene generates a mixture of gases, oils and waxes with a wide distribution of molecular weights. No solid residue is formed that, by its combustion or gasification, can be used for supplying energy to the global process. Taking this into account, the study of the thermal decomposition of mixtures can be interesting. The addition of a second material such as biomass, that generates char, can be very effective for obtaining an economically advantageous process. Taking this into account, the type of atmosphere and the heating rate are variables that influence on the char yield and should be studied.

In this work, an experimental study on the thermal decomposition of mixtures of pinewood sawdust and high density polyethylene in different atmospheres has been carried out. In order to analyze the effect of the mixture, experiments with pure polyethylene and pure sawdust have also been carried out under the same conditions.

The experimental work has been performed in a SETARAM 92 thermobalance. The initial amount of sample used in the experiments with mixtures was approximately 2 mg of pinewood sawdust and 2 mg of pure ultrahigh density polyethylene (Hostalen GH4765 from Hoechst) to assure no diffusion problems. Taking into account the low thermal conductivity of the materials, this sample amount is small enough to avoid temperature profiles in the sample, and it can thus be considered isothermal. The particle size of the polyethylene samples was 200 - 300 μm , while the particle size of the sawdust was 297-630 μm . A flow of 80 SPT ml min^{-1} of nitrogen, air or mixtures of nitrogen and air with different oxygen concentrations was continuously introduced downwards in the chamber. The thermocouple was located below the sample pan at a distance of 5 mm. Dynamic experiments were carried out at four different heating rates: 5, 12, 25 and 50 $^{\circ}\text{C min}^{-1}$. The oxygen concentrations tested were 0% (nitrogen), 4%, 10.5%, 16% and 21%.

Pyrolysis of pure polyethylene starts at around 370 $^{\circ}\text{C}$, reaching its maximum rate above 390 $^{\circ}\text{C}$. The heating rate influences the process. The solid conversion increases as the heating rate increases. The kinetic parameters have been obtained from the experiments and a comparative study of these results with the results obtained by different authors [1-9] has been made. In the case of the thermal decomposition of mixtures in an inert atmosphere, the presence of a more reactive solid at low

temperatures (? 200 °C) such as biomass does not affect significantly the behaviour of polyethylene during thermal decomposition. In this case, two different steps can be clearly distinguished: the thermal decomposition of sawdust, which starts at approximately 200 °C, is almost complete at 360 – 370°C, and is followed by the pyrolysis of polyethylene.

The increase of the oxygen concentration clearly influences the behaviour of the thermal degradation of the mixture. The two steps that can be observed when an inert atmosphere is used change drastically depending on both the oxygen concentration and the heating rate. When low heating rates are used, these two steps are still observed, although higher solid conversions are obtained at a given temperature. For oxygen concentrations as low as 4% the thermal degradation of polyethylene starts at much lower temperatures than in nitrogen so the degradation of the two materials overlap.

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