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Effect Of Experimental Conditions On Pyrolysis Of Plastics Mixed With Forestry Biomass

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Pyrolysis studies are being carried out with several waste materials with the goal of producing liquids that could be re-utilised in different end-use applications. The main aim of this work is to increase liquid yields produced by pyrolysis of various blends of plastics and biomass wastes. Polyethylene (PE), polypropylene (PP) and polystyrene (PS) were used as the plastic wastes component. Forestry residue pine was used as the biomass component. The presence of biomass waste decreased the liquid fraction but increased the gas fraction of the products, due to the high percentage of volatiles of the pine.

Introduction

As most plastics are not biodegradable, their deposition in landfills is not a desirable solution from an environmental standpoint. There is also a lot of controversy about the incineration of these wastes, due to the release of toxic and greenhouse gases. Another disadvantage of the traditional incineration of these wastes is that it completely destroys all its organic matter which could be otherwise valuable for different applications. Besides that, the biomass residues, that can be found in forests and that accumulate on the ground, posing a risk of fuel for forest fires, can also be processed in order to recover its organic content in a useful form.

One of the promising ways of taking profit of the energy value of these wastes is by pyrolysis. It involves breaking down the molecular structure of these wastes under moderate pressure and temperature conditions, in order to produce a mixture of hydrocarbons in the three physical states. The liquid fraction, "bio-oil", has properties and composition similar to the petroleum derived fuels and can be used as raw material for the petrochemical industry and the gas fraction can also be used to provide energy for the process.

Several authors have studied plastics pyrolysis and have demonstrated the potentialities of this technology to process plastic wastes (Kaminsky et al, 1997; Scott et al, 1990; Conesa et al, 1997; Williams et al, 1997). Pyrolysis of a mixture containing polyethylene (PE), polypropylene (PP) and polystyrene (PS) in different blendings, showed that total conversion in all tests was higher than 80%, the main product being liquid (at normal conditions of temperature and pressure) with yields around 75% (w/w) and gas yields were always lower than 10%, though products yields depended on the nature of plastic input (Kaminsky et al, 1997). Williams et al (1997) and Fortuna et al (1997) studied waste tyres pyrolysis obtaining around 33% of solid residue, 35% of oil fraction, 12 % of scrap and 20% of gases. In general plastic waste pyrolysis allows the production of higher liquid products yields than those obtained with tyres pyrolysis. Therefore, some authors studied the pyrolysis of mixtures of plastics and tyres wastes and observed that the use of plastic wastes favoured tyres pyrolysis and allowed increasing liquid yields, whilst higher contents of tyres wastes favoured the formation of solid compounds (Pinto et al, 2001).

In the present work, plastic wastes were blended with biomass (pine) residues with the aim of studying the experimental conditions that maximized liquid yields. A mixture of PE, PP and PS, the major plastic components of the Municipal Solid Wastes was used in the present study. Pine was the biomass species selected for this work, because it is the most abundant variety in Portuguese forestry.

Experimental Part

All pyrolysis experiments were conducted in a 1 liter stainless Hastelloy C276 alloy autoclave (by Parr Instruments), with furnace and reaction mix temperature control, agitation control, and pressure sensors. Installation description and experimental procedures were already described (Pinto et al, 1999). The following range of experimental conditions was studied: waste particle size lower than 3 mm; run temperature - 350 to 450°C; reaction time - 5 to 30 minutes; initial pressure - 0.2 to 1.0 MPa.

The gaseous fraction was analyzed on a Gas Chromatograph (GC) to identify and quantify the major gas components produced with the several pyrolysis reaction conditions. The liquid fraction was distilled to give three fractions: the lighter hydrocarbons (first distillate, boiling point (bp) <150ºC), the heavier hydrocarbons (second distillate, 150ºC<bp<270ºC), and the residue (third distillate, bp>270ºC). The first two distillates were analyzed by GC. The distillation curve of the liquid fraction was also compared to the ones of gasoline and diesel. The remaining solid fraction was weighted and extracted with dichloromethane (DCM) and tetrahidrofuran (THF) in a soxhlet extractor (by ASTM D5369-93(2003)). The dried solid product was weighted to give the effective pyrolysis yield of solids. The extracted liquids were subsequently analyzed by GC.

Discussion of Results

In the first set of trials a waste mixture with the following composition was studied: 30% (w/w) of Pine, 39% of PE, 12% of PS and 19% of PP. The results presented in Figure 1 were obtained at a fixed initial pressure of 0,41 MPa, a fixed reaction temperature of 420ºC, while reaction time varied between: 5 and 30 minutes. It can be seen in Figure 1 that an increase in reaction time did not seem to change significantly the yields of the desired fractions (liquids and gases). So, it is of no good to use reaction times higher than 15 minutes, this value having been chosen for subsequent experiment sets. A lower reaction time was not selected, due to the error associated with this parameter when reaction times lower than 10 minutes are used in this specific equipment. In future, a different type of reactor should be used to allow the use of lower reaction times without increasing the level of errors in this parameter.

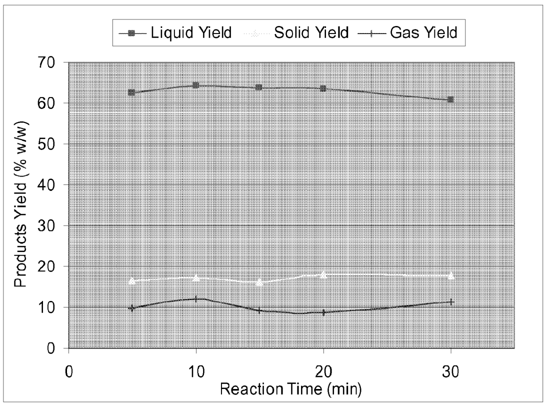

Figure 1: Variation of the three fractions yields at five different reaction times with reaction temperature: 420ºC, initial pressure: 0,41 MPa and mixture composition: 30% Pine, 39% PE, 12% PS and 19% PP.

In the second set of trials, whose results are shown in Figure 2, the experimental conditions were: waste mixture with the composition mentioned before, fixed initial pressure of 0,21MPa and fixed reaction time of 15 minutes, while the pyrolysis temperature was varied between 350ºC, and 450ºC.

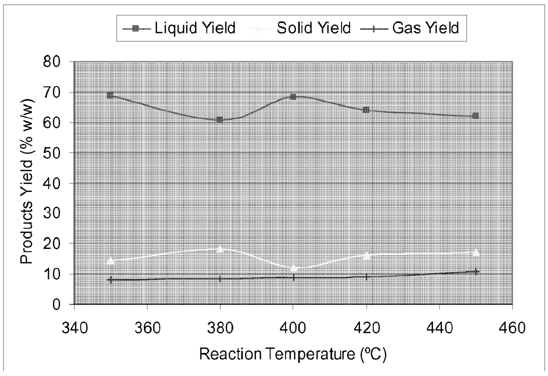

Figure 2: Variation of the three fractions yields at five different reaction temperatures with optimized reaction time: 15 min, initial pressure: 0,41 MPa and mixture composition: 30% Pine, 39% PE, 12% PS and 19% PP.

It can be observed in Figure 2 that an increase in reaction temperature seems to decrease liquid yields and to favour the release of gaseous compounds. The lowest liquid yields were obtained at 380ºC, at which maximum solid yields were also obtained. The results presented in Figure 2, led to selection of 400ºC for the next experiment sets. Results reported by Pinto et al (2001), obtained during pyrolysis of mixtures of plastics and tyres wastes, also showed that the effect of temperature on liquid yields led to sinusoidal curves.

The third set of trials was conducted at a fixed reaction time and temperature (15 min and 400ºC, respectively), using the same waste mixture composition used in the previous sets, and varying the initial pressure from 0,21 to 1,03 MPa. As it can be seen in Figure 3, an increase in the initial pressure did not seem to affect much gas and solid yields. On the other hand, the increase of initial pressure up to 0,62 MPa led to a decreasing tendency on liquids formation. The results presented in Figure 3 led to the selection of the value 0,41 MPa for the subsequent experiment sets.

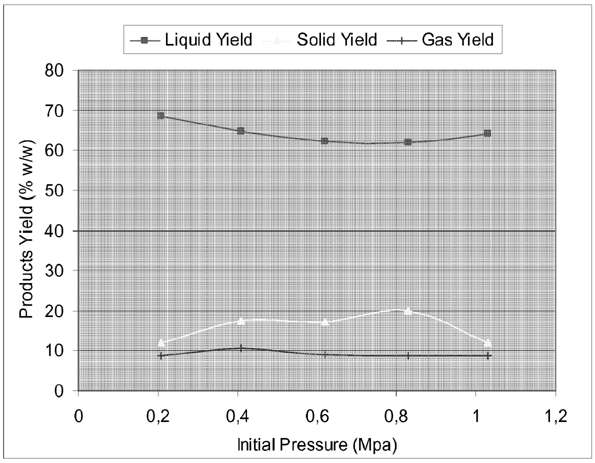

Figure 3: Variation of the three fractions yields at five different initial pressures with optimized reaction time: 15 min, optimized reaction temperature: 400ºC and mixture composition: 30% Pine, 39% PE, 12% PS and 19% PP.

The fourth set of trials was conducted at the selected values of initial pressure, reaction time and reaction temperature (0,41 MPa, 15 min and 400ºC, respectively). The pine content in the wastes blend was increased from 0 to 100%. Plastic waste composition was kept constant in all experiments (in a 100% plastics total: 56% of PE, 17% of PS and 27% of PP). The results obtained are shown in Figure 4. It can be clearly seen that the pine content in waste mixture was the parameter that most affected products yields. The increase in pine percentage led to an overall decrease in the effective liquid yield, while both the solid residue and gas fraction increased almost linearly with the pine percentage. While plastics pyrolysis led to a liquid yield of around 80% (w/w), being solid and gas yields lower than 10% each, when only pine was pyrolysed the liquid yields decreased to values around 33% (w/w), being this value lower than that of solid yields, which was the main product obtained.

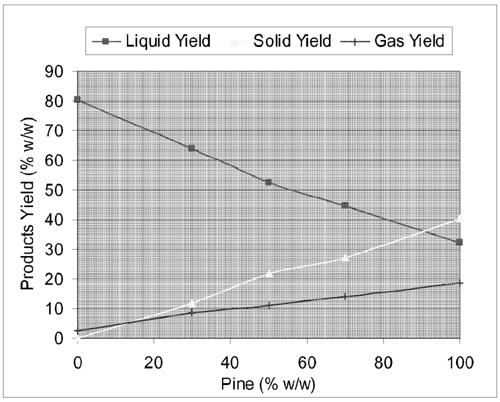

Figure 4: Variation of the three fractions yields at five different mixture compositions with optimized reaction time: 15 min, optimized reaction temperature: 400ºC and optimized initial pressure: 0,41 MPa.

In Figure 5 is presented an example of the obtained gas chromatograms showing the major components present in the gas fraction, which are alkanes: methane and propane, and CO2 and CO from oxidation of pine volatiles due to the oxygen content of pine, besides the nitrogen that was used as the inert gas to pressurize the autoclave.

In Figure 6 is shown an example of a chromatogram of the first distillate liquid sample, showing that the liquid fractions are a complex mixture of several compounds. The results obtained so far have shown that liquid fractions composition were most affected by pine content in wastes, being this parameter the one that most affected not only liquid yields , but also liquid composition and properties.

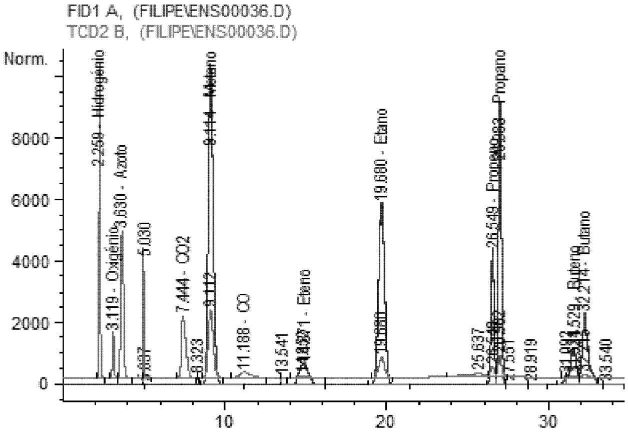

Figure 5: Chromatogram of the gas fraction obtained by pyrolysis of a mixture of pine and plastic wastes.

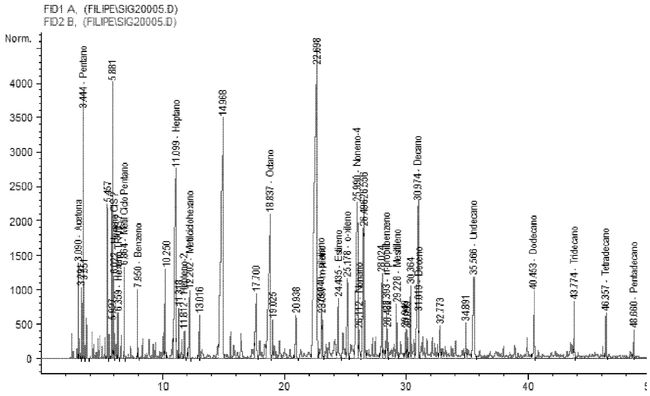

Figure 6: Example of a chromatogram of the first distillate liquid sample.

Conclusions

Pyrolysis technology has proven to be a possible way of converting plastics and biomass wastes into economical valuable products.

The experimental condition that seems to have the greatest influence in the pyrolysis products yields is the biomass percentage in the feed mixture. When using an average feed composition of 30% (w/w) of pine and 70% of plastics, liquid fraction yields above 60% were obtained, as well as gas yields in the range of 10%.

Further work is in progress to fully analyse liquid fractions compositions and to determine the effect of experimental conditions on them in order to further optimise the pyrolysis process.

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