Effect of Experimental Conditions on Co-Pyrolysis of Pre-Treated Eucalyptus Blended with Plastic Wastes

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Eucalyptus has been largely used in the pulp and paper industry in Iberian Peninsula, due to its fast growth and high productivity. This eucalyptus utilisation has generated high amounts of wastes, including leaves, branches and stumps. Hence, these wastes were selected for the co-pyrolysis studies to produce liquid fuels or raw materials. As an alternative to the conventional biomass pyrolysis, biomass was pre-treated under mild acidic conditions to obtain valuable sugar-rich stream to be used in fermentation and the solids rich in lignin were mixed with PE (polyethylene) wastes to be used in co-pyrolysis. The pre-treatment process seems to have weakened initial macromolecular structure of eucalyptus wastes and thus might have helped chemical bonds breakdown during co-pyrolysis. The results obtained so far have shown that PE presence seems to have favoured the biomass conversion. The effect of experimental conditions using Response Surface Methodology (RSM) was studied. There was a good agreement between theoretical and experimental data. The highest liquid yield (78 % wt) was obtained at 380 ºC and for the reaction time of 20 min. These conditions led to the lowest gases yield (7 % wt) and also to the lowest solids yield (14 % wt).

1. Introduction

Modern societies need to find alternative liquid fuels to fulfil the needs for long distance transportation sector. Pyrolysis has been studied to attain this objective. Pyrolysis technology has been widely applied for converting biomass into liquid biofuels, especially fast and flash pyrolysis and there is huge information available. Bio-oil yields from 60 - 75 % have been reported (Bridgwater, 2012). Liquids produced by biomass pyrolysis have some unfavourable characteristics, namely: high contents of solids, ash, oxygen-containing compounds and water and chemical instability. Thus, they are not suitable to be used as fuel in conventional engines without expensive upgrading processes that use specific catalysts and hydrogen pressure (Bridgwater, 2012). Though the quality of the oil may be improved, the associated costs may make the upgrading processes economically unattractive (Pinto et al., 2016).

Thus, an alternative to the conventional biomass pyrolysis was studied. First eucalyptus wastes were pre-treated under mild acidic conditions, which removed the hemicellulose fraction and produced valuable compounds, like oligosaccharides with possible applications in the food and pharma industries and monosaccharides that can be upgraded by fermentation. The solids obtained after this pre-treatment were richer in carbon and lignin and were used in pyrolysis tests. As the hydrothermal pre-treatment weakens biomass initial macromolecular structure, pyrolysis process is expected to be facilitated.

Co-pyrolysis of pre-treated eucalyptus solids blended with polyethylene (PE) wastes was studied, with the aim of solving the problems related to the undesirable properties of bio-oils produced from biomass pyrolysis. This may also solve the problems related to the seasonality of some biomass wastes. Plastic waste contains high levels of hydrogen and reduced oxygen as compared to biomass (Xue et al., 2015). Thus, plastics can supply hydrogen to the co-pyrolysis reaction medium and adjust the carbon, hydrogen and oxygen content in the feedstock, improving the quality of the bio-oil produced (Chen et al. 2016). Brebu et al. (2010) also stated that the possible synergistic effects observed during pine pyrolysis with synthetic polymers were due to the fact that polyolefin polymers could supply hydrogen that could promote thermal conversion of the biomass, thereby

increasing the pyrolysis liquids. Liquids produced by plastics pyrolysis contain mainly hydrocarbons, suitable to be used as fuels and as raw materials for several industries, after minor upgrading. Thus, plastics presence helps to dilute the undesirable characteristics of liquids produced from biomass pyrolysis. Co-pyrolysis of biomass blended with plastics has shown to be a promising option for future industrial application, due to its attractive performance/cost ratio (Abnisa and Daud, 2014).

There is huge information about pyrolysis of biomass or plastics, but co-pyrolysis of biomass mixed with plastic wastes is a less studied subject, however some works have already been published about this subject (Abnisa and Daud, 2014). Some authors have studied the effect of experimental parameters (Xue et al., 2015), namely reaction time and run temperature and pressure, on the formation of liquid products by co-pyrolysis of biomass and plastics (Costa et al. 2014). However, the use of pre-treated biomass brings new challenges, as the pre-treatment weakens chemical bonds and facilitates biomass pyrolysis, it is expected that low severe conditions may be use. Thus, this paper studied the effect of experimental conditions used during co-pyrolysis of pre-treated eucalyptus blended with PE wastes, namely pyrolysis temperature and reaction time. The range of experimental conditions selected was done having in mind previous knowledge (Paradela et al., 2009). To reduce the experimental effort, Response surface methodology (RSM) approach was used to optimize the experimental conditions to achieve bio-oils.

2. Experimental part

2.1 Feedstocks

Eucalyptus globulus was chosen for this study, because if has been largely used in the pulp and paper industry in Iberian Peninsula, which has generated high amounts of this biomass residues, not all of them properly valorised. Eucalyptus residues with a particle size below 6 mm were used in this study. This biomass chemical composition (in dry weight basis) is: glucan 36.1 %; hemicellulose 23.8 % (including xylose as the main sugar at an overall content of 13.9 %); Klason Lignin 26.7 %, ash, 3.9 %, protein 2.8 % and 8.2 % of extractives and others. Eucalyptus wastes C/H ratio was around 8.6 and HHV (high heating value) was 21.4 MJ/kg daf (dry and ash free).

Eucalyptus wastes were pre-treated under mild acidic conditions, using H_2SO_4 aqueous solutions with a liquid/solid ratio of 7 (w/w) at 130 °C. During this pre-treatment, extractives and soluble ash were removed, as well as around 85 % of hemicellulose. A monosaccharide-rich hydrolysate that could later be used as fermentation media was produced. This liquid phase contained around 27 g/l of total sugars. A relative increase in the lignin and glucan fractions was observed in the solids that account for more than 40 %, each, of the recovered solid material (dry basis). These solids also presented a lower oxygen content which might favour its use as feedstock for pyrolysis.

PE wastes were also chosen for the co-pyrolysis studies because of the high amounts produced per year, with the aim of improving and diversifying these wastes valorisation. PE wastes were pellets of recycled materials with particle sizes in the range of 2 and 3 mm diameter. PE wastes C/H ratio was around 6.0, while HHV was 46.4 MJ/kg daf.

2.2 Co-pyrolysis experimental work

Pre-treated eucalyptus wastes were blended with 50 % wt of PE wastes and the mixture was co-pyrolysed in an autoclave built of Hastelloy C276, by Parr Instruments. The autoclave was purged and pressurised with nitrogen to 0.61 MPa. Afterwards, the autoclave was heated and kept at the reaction temperature during the reaction time previously settled. The range of experimental conditions, presented in Table 1, was selected according to authors' previous work, (Costa et al., 2007; Paradela et al., 2009). At the end of the reaction time, the autoclave was cooled down to room temperature. Gases were collected, measured and analysed by gas chromatography (GC) to determine the contents of CO, CO_2, H_2, CH_4 and other gaseous hydrocarbons, referred as C_nH_m. Solid and liquid products were weighted and analysed. Solids were extracted in a Soxhlet extractor, first with n-hexane, then with toluene and finally with tetrahydrofuran (THF) to determine the amount of liquids soaked in solids. Hydrocarbon content in liquid fractions was analysed using a Hewlett Packard 6890 Gas Chromatograph.

2.3 RSM methodology

Previous studies showed that the pressure was the parameter that least affected the results of co-pyrolysis of mixtures of pre-treated eucalyptus with 50 % wt of PE. On the other hand, it was decided to use relatively low run pressures to control capital and operation costs. Thus, the optimisation of co-pyrolysis experimental

conditions was focused on studying the effect of run temperature ant reaction time. The ranges of values used are presented in Table 1.

RSM approach was selected to obtain a model for liquids yield obtained from co-pyrolysis of pre-treated eucalyptus mixed with PE. The two experimental parameters were x_1: reaction temperature and x_2: reaction time. The low, medium and high levels of these parameters (-1, 0 and 1) were tested according to Table 2 data. The repetitions of the central point (0, 0, 0) allowed to estimate the repeatability of the experiments.

Table 1: Range of experimental conditions

Level		Temperature (ºC)	Time (min)
Low	-1	380	20
Medium	0	415	50
High	1	450	80

Table 2: Low, medium and high levels of the X_i parameters (-1, 0 and 1) tested

X_1	X_2	Temperature (ºC)	Time (min)
-1	-1	380	20
1	-1	450	20
-1	1	380	80
1	1	450	80
0	0	415	50
0	0	415	50
0	0	415	50
0	0	415	50

3. Results and discussion

3.1 Theoretical products yield calculated by RSM methodology

RSM methodology was used to evaluate the effect of pyrolysis temperature and reaction time on products yields, using Table 2 range of these experimental parameters, to obtain the system response for the dependent variable that is liquid yield. To attain this aim, a linear polynomial model was fitted to the experimental results, using the least squares method, accounting for the effect of the individual parameters together with their interactions. This was accomplished by minimising the differences between experimental values and the ones predicted by the model with the optimised coefficients. This fitting led to Equations (1), (2) and (3) that allow the calculations of the theoretical yields of liquids, gases and solids, respectively, in % daf.

$$\text{Liquids Yield (\% daf)} = 64.6 - 10.8x_1 - 3.3x_2 + 0.6x_1x_2 \tag{1}$$

$$\text{Gases Yield (\% daf)} = 13.4 + 3.8x_1 + 2.2x_2 - 0.1x_1x_2 \tag{2}$$

$$\text{Solids Yield (\% daf)} = 17.9 + 1.5x_1 + 1.5x_2 - 0.8x_1x_2 \tag{3}$$

RSM methodology supplied a significant amount of information about the effect of run temperature and reaction time on products yields, considering that run pressure is kept constant, as the same initial pressure was used in all experiments. Figure 1 shows the response surfaces derived from the models. Figure 1 (a) shows the effect of run temperature and reaction time on liquids yields. Similar plots were drawn to analyse the interactions of these parameters in the other products yields (gases and solids), Figure 1 (b) and (c).

The effect of run temperature on liquids yield, Figure 1 (a), for the total interval of reaction time, while pressure is considered constant may be analysed. Pyrolysis temperature was the parameter that most affected pyrolysis process. The rise of run temperature decreased the formation of liquids and the same effect was obtained with

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the increase of reaction time. The combination effect of run temperature and reaction time was a milder one and so it is not appreciable in Figure 1 (a), which agrees with the relatively small coefficient of equation (1).

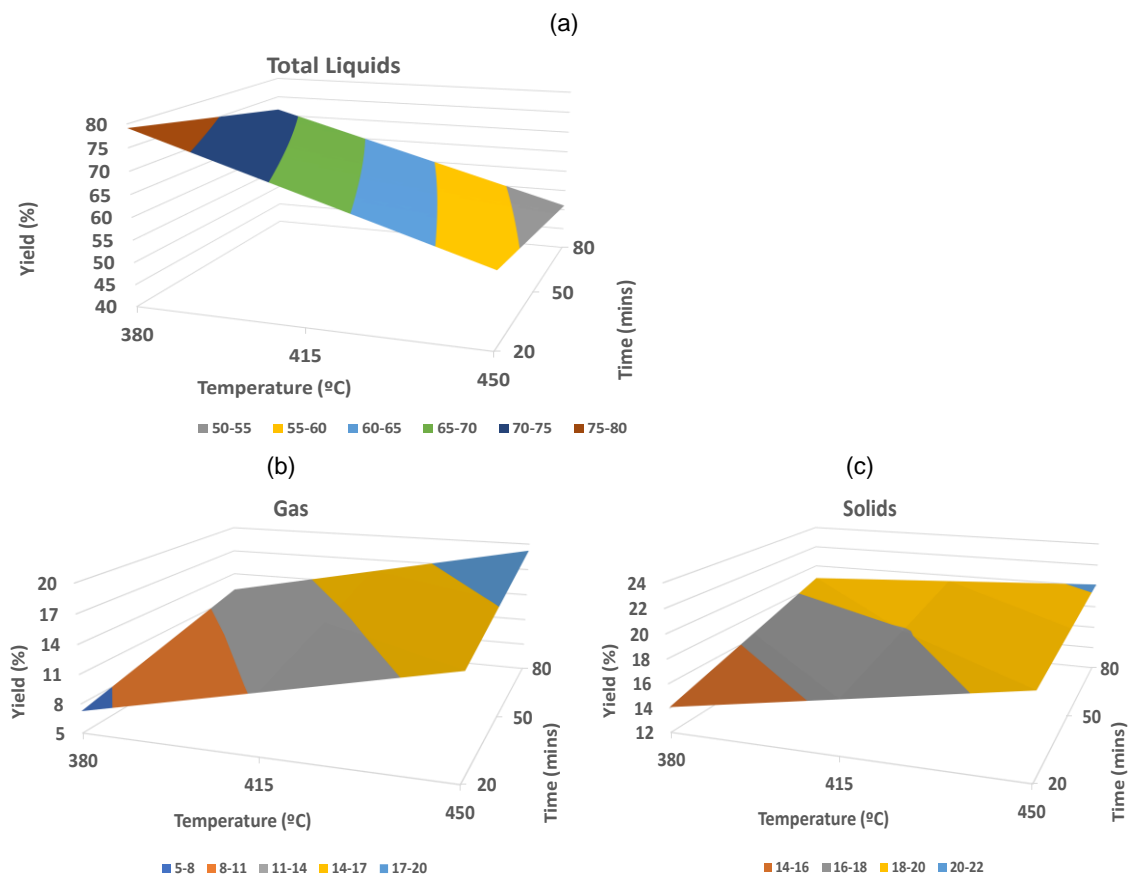(a)

(b)   (c)

Figure 1: Response surfaces obtained with the linear model for the liquids yields (a), gases yields (b) and solids yields (c). Surface colours indicate different yields ranges.

On the contrary, the increase of both run temperature and reaction time had a positive effect in the formation of gases Figure 1 (b), probably because as both parameters led to liquids destruction, their conversion into smaller molecules seems to have been favoured. A similar figure was drawn for solids yields, Figure 1 (c), which also shows that the formation of solids increased with the rise of run temperature and reaction time, though a smaller effect than that of gases release was observed. Thus, it is expected that the increase of both these parameters might have promoted liquids molecules destruction and the radicals initially formed were partially converted into gaseous molecules, while others might have reacted between themselves by recombination reactions, originating heavier molecules than the original liquid ones.

Co-pyrolysis main objective is the production of liquid compounds that may be converted into liquid fuels or may be used as raw material in several industries. Thus, the optimization of co-pyrolysis system was done to maximize the production of liquids. Hence, the optimal run temperature and reaction time conditions were obtained by the maximization of equation (1), to which corresponded the highest yields visually identified in the response surfaces graphics, Figure 1(a). The highest theoretical liquids yield (79.1 % wt) was obtained at 380 ºC and for the reaction time of 20 min. The lowest gases and solids yields were obtained at these conditions.

3.2 Experimental products yields

The theoretical yields calculated by equations (1) to (3) were compared to the yields obtained experimentally. Figure 2 shows this comparison for liquids, gases and solids. In general, there was a good agreement between theoretical and experimentally yields as shown in Figure 2. The main discrepancies corresponded to the central point, but its influence was not so important because four experiments were done with these conditions.
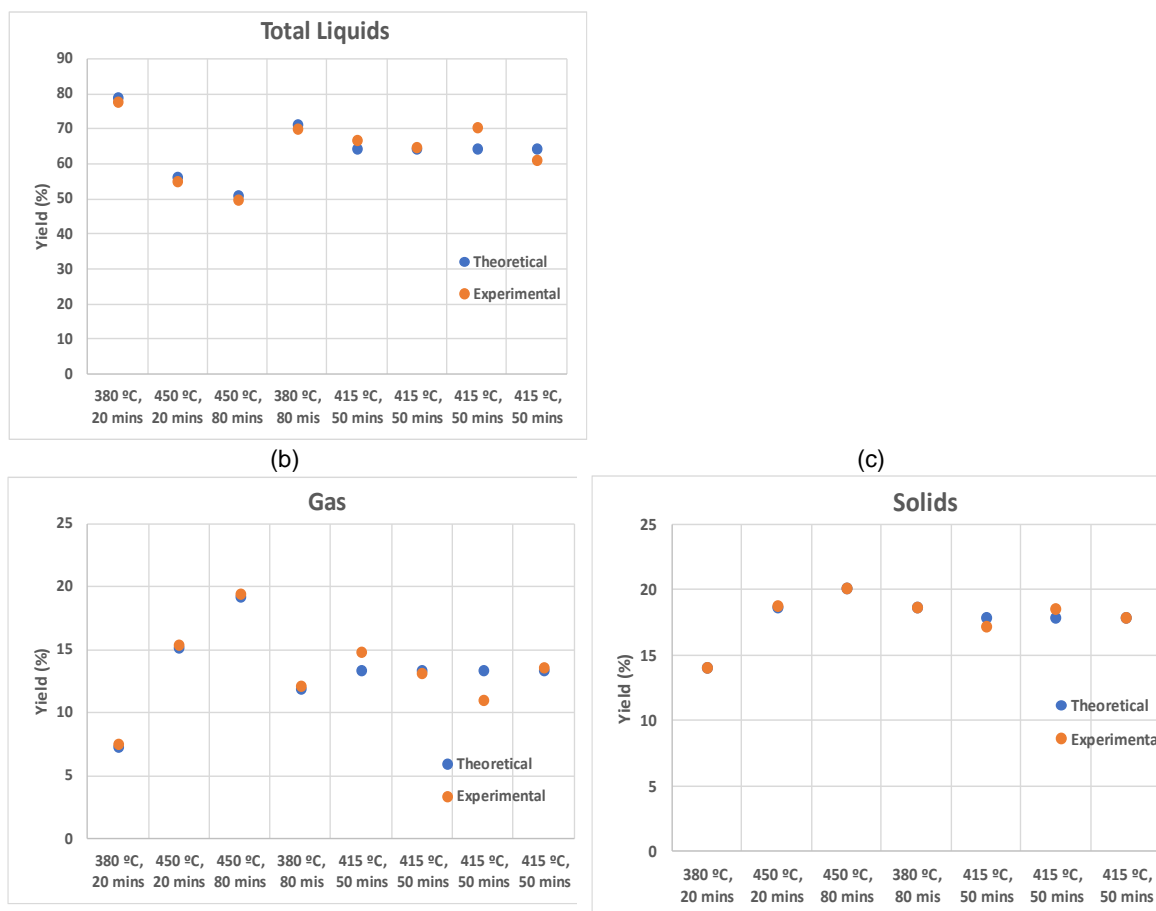
(a)

Figure 2: Experimental and theoretical yields for (a) liquids, (b) gases and (c) solids.

Experimental results also showed that the highest liquid yield was obtained at 380 ºC and for the reaction time of 20 min. This yield (78 % wt) showed a good agreement with the theoretical value of 79.1 % wt. The selected condition of temperature and reaction time, respectively 380 ºC and 20 min, led to the lowest gases yield (7 % wt) and also to the lowermost of solids (14 % wt). This data is in good agreement with theoretical yields.

3.3 Co-pyrolysis gases and liquids analysis

Gases GC analysis showed that for all conditions studied alkanes contents were much higher than alkenes. Hence, CH_4 and C_2H_6 were formed with the highest contents. Gaseous hydrocarbons content decrease with the rise of the number of carbon atom, thus methane content was always higher than ethane and this value was higher than propane concentration. In general, CH_4/C_nH_m ratio was lower than 1, varying from 0.9 till 0.6. CO_2 contents were always higher than CO ones, being CO_2/CO ratio between 2.4 and 2.9, which means that decarboxylation reactions were more probable than decarbonylation ones. No clear tendencies were obtained in relation to the effect of run temperature or reaction time on gases composition. More data would probably be needed to observe meaningful tendencies. However, the rise of reaction time seems to have favoured the formation of hydrocarbons (CH_4 and C_nH_m). The increase of run temperature seems to have promoted the formation of heavier gaseous hydrocarbons (C_nH_m).

GC analysis showed that liquid fraction contained mainly linear alkanes and alkenes with a large range of carbon numbers, alkanes till C_{26} and alkenes up to C_{17} were detected. In general, there was a decrease in liquids alkanes and alkenes concentration with the rise of the number of carbon atoms. Alkanes present with higher concentrations, in the liquid pyrolysis product were between C_6 and C_{12}, while alkenes compounds with the highest contents were usually between C_8 and C_{11}. Aromatic compounds, especially benzene, toluene and ethylbenzene were also quantified. Besides hydrocarbons other compounds, mostly with oxygen atoms, like acids, alcohols, ketones, etc. were also detected, but not quantified, probably coming from eucalyptus decomposition. The complete characterisation of liquid compounds was not possible, because of the high number of compounds and their small concentrations. In general, alkanes and alkenes with lower number of

carbon atoms and aromatic compounds were favoured by the rise of temperature. The increase of reaction time also seems to have favoured the formation of aromatic compounds and of lighter alkanes and alkenes. However, more information is needed to draw more strong tendencies.

4. Conclusions

The use of pre-treated eucalyptus wastes favoured this biomass pyrolysis, as the initial macromolecular structure was weakened. The presence of PE wastes was also a good option, because plastics are easier to pyrolyse than biomass and may also supply hydrogen to reaction medium, which favours the overall conversion and the formation of liquid products.

RSM methodology was a good option to study the effect of experimental conditions on co-pyrolysis of treated eucalyptus mixed with PE, as it allowed decreasing the number of experiments.

Theoretical results agreed well with experimental ones. The highest liquid yield of 79.1 % wt. was predicted by the theoretical model at 380 ºC and for the reaction time of 20 min, which is in accordance with the experimental value of 78 % wt. obtained at the same experimental conditions.

Gaseous products main components were CH_4, C_nH_m and CO_2, though minor contents of H_2 and CO were also determined. CH_4/C_nH_m ratio varied between 0.9 and 0.6 and CO_2/CO ratio ranged from 2.4 to 2.9. Liquid compounds GC analysis showed the presence of mainly linear alkanes and alkenes, though oxygen compounds were also detected, mostly coming from eucalyptus breakdown.

Acknowledgments

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