

Production of Liquid Compounds by Co-Pyrolysis of Different Pre-Treated Biomasses Mixed With Plastic Wastes

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As an innovation to conventional biomass pyrolysis to produce liquid biofuels, different types of biomass wastes were pre-treated by autohydrolysis, prior to pyrolysis. Eucalyptus forestry waste, corn cobs agricultural residue, and miscanthus (an energy crop) were autohydrolysed. Autohydrolysis led to valuable sugar-rich stream that may be used in fermentation and to solids rich in lignin that were pyrolysed. Pyrolysis of autohydrolysed eucalyptus led to an increase in liquids yields of 24 % in relation to untreated eucalyptus, as autohydrolysis weakened initial macromolecular structure and thus helped chemical bonds breakdown during pyrolysis. However, similar pyrolysis liquid yields were obtained by autohydrolysed or untreated corn cobs and miscanthus, thus feedstock composition is an important issue. Nevertheless, the production of added value products by autohydrolysis may still justify this pre-treatment. Otherwise, more severe pre-treatments of these biomasses might improve co-pyrolysis as it happened with eucalyptus. As polyethylene (PE) is easier to pyrolyse than biomass and greatly favours the production of liquid hydrocarbons, autohydrolysed and untreated biomass was mixed with PE wastes to be used in co-pyrolysis. The rise of PE content in the blend clearly favoured the production of liquid products of pre-treated and untreated biomass. 75 %wt. of PE in the blend led to liquid yields of 72 %wt. for untreated eucalyptus and of 82 %wt. for autohydrolysed eucalyptus.

1. Introduction

Biomass pyrolysis is a widely studied subject with the aim of developing alternative liquid biofuels for long distance transportation sector. Though it is possible to reach bio-oil yields up to 75 % by flash pyrolysis, bio-oils have some adverse properties, like high contents of solids, ash, oxygen and water, which have hindered direct use in conventional engines. Moreover, due to the chemical instability, bio-oils aging may bring storage problems (Bridgwater 2012). As plastics are easier to pyrolyse and favour the production of hydrocarbons (Uzoejinwa et al., 2018), co-pyrolysis of biomass and plastics helps to dilute the undesirable characteristics of liquids produced from biomass pyrolysis. Several authors have presented the advantages of co-pyrolysis of biomass mixed with plastics in relation to conventional biomass pyrolysis (Uzoejinwa et al. 2018). The use of plastics may improve the overall conversion and the quality of the products without the need of catalysts or high hydrogen pressure. Johansson et al. (2018) also stated that the use of plastic waste significantly affected the composition of woody biomass pyrolysis products, as reactive oxygenated compounds like ketones, aldehydes and acids were suppressed, whilst more stable alcohols and esters of hydrocarbons were produced. However, the use of plastics may bring some challenges related to chlorine content in the plastic waste, the increase of oils viscosity and the need of different process conditions, due to different properties of the materials. Tests done in a pilot scale pyrolysis installation showed that the presence of plastics improved the efficiency of pyrolysis process, oil yield increased and the pyrolytic water was reduced, due to the lower oxygen content in the feedstock (Johansson et al., 2018). Xue et al. (2015) also stated that as plastic contains high levels of hydrogen and lower oxygen than biomass, plastics can supply hydrogen to the co-pyrolysis reaction medium and regulate the carbon, hydrogen and oxygen content in the feedstock, thus improving the quality of the bio-oil produced (Chen et al., 2016). Xiong et al. (2015) stated that due to PE presence in biomass blends the bio-oil improved, having high hydrogen and lower oxygen contents.

On the other hand, biomass flash pyrolysis requires very small particle sizes, which means high operating costs for biomass preparation. In fact, flash pyrolysis requires very high biomass heating rates, thus very small particle sizes, and very high cooling rates of pyrolysis bio-oils are needed. Hence, an unconventional procedure to prepare biomass for flash pyrolysis was tested. First, biomass was pre-treated using a hydrothermal pre-treatment (autohydrolysis) which weakened biomass initial macromolecular structure, thus it may help pyrolysis process. Autohydrolysis usually removes and converts the hemicellulose fraction into valuable compounds, i.e. oligosaccharides, with possible applications in the food and pharma industries. Next, the pre-treated solids with increased content of glucan and lignin were used as feedstock for pyrolysis process. There is only some information available about pyrolysis studies of pre-treated biomass. Hao et al. (2017) studied the effect of using autohydrolysed pre-treated pine on pyrolysis oils properties, and observed that during autohydrolysis, decomposition of hemicellulose and cleavage of lignin ether bonds occurred, thus the pre-treatment led to reduction of carboxyl acids and of condensed phenolic hydroxyl groups in the heavy oils generated by pyrolysis. At the pyrolysis temperature of 600 °C there was also the removal of condensed hydroxyl groups and methoxy groups from the bio-oil, which is useful for using the bio oil as a fuel.

There is little information available about co-pyrolysis studies of pre-treated biomass blended with plastics. In previous pre-treatment studies under mild acidic conditions it was found that pre-treated eucalyptus favoured this biomass pyrolysis, as the initial macromolecular structure was weakened. As plastics are easier to pyrolyse than biomass and may also supply hydrogen to reaction medium, co-pyrolysis of eucalyptus mixed with PE wastes showed that the overall conversion and liquid products formation were favoured (Pinto et al., 2018). In the present study autohydrolysis was used to pre-treat different biomass wastes such as energy crops (miscanthus), forestry biomass (eucalyptus) and agricultural residues (corn cobs) to compare pyrolysis of untreated with pre-treated biomass. To improve pyrolysis bio-oils properties and hydrocarbons content, untreated and pre-treated biomass solids were mixed with polyethylene (PE) wastes before pyrolysis. PE wastes were chosen, to try to improve the valorisation of these wastes, which are produced annually in high amounts. Furthermore, PE wastes are easily pyrolysed, leading to liquid yields of about 80 %wt., containing mainly linear liquid alkanes. Hence, PE may favour biomass pyrolysis process by providing a liquid medium to improve mass and energy transfer. PE content on biomass blends ranged between 0 and 75 %wt. to study the effect of PE content on liquid yield.

2. Experimental part

2.1 Feedstocks

Three different types of biomass were chosen for this study: *Eucalyptus globulus* residues (a forestry biomass), corn cobs (an agricultural residue) and miscanthus (an energy crop). *Eucalyptus globulus* has been largely used in the pulp and paper industry in Iberian Peninsula, and its forestry management and industrial uses produce a significant amount of residual biomass, namely stumps, leaves and small branches. Corn cobs are the main residue from corn production that can be either collected in the fields or at industrial sites. Miscanthus is a high yielding energy crop that grows fast and produces a crop every year without the need for replanting. Miscanthus is a common energy crop due to its fast growth, low mineral content, and high biomass yield. It can be cropped yearly without the need for replanting.

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

2.2 Biomass pre-treatment

Biomass autohydrolysis was carried out in a 2 L stainless steel, stirred, reactor (Parr Instruments). Water was the only added reactant in a liquid/solid ratio of 7 (w/w). The reaction was carried out under non-isothermal conditions, as upon reaching the desired temperature (190 °C or 210 °C), the reactor is rapidly cooled down. The hydrolysate (liquid fraction) and the pre-treated solid biomass obtained were separated at room temperature using a hydraulic filter press (up to 20 MPa). The recovered solids were washed with water, pressed again and dried at 45 °C and then used in co-pyrolysis tests. Biomass feedstock, pre-treated solid biomass and hydrolysates were chemically characterized as described before (Moniz et al., 2018) and the results are shown in Table 1.

2.3 Co-pyrolysis experimental work

Each untreated and pre-treated biomass was blended with PE wastes and the mixture was co-pyrolysed in an autoclave built of Hastelloy C276, by Parr Instruments. PE content on biomass blends varied from 0 and 100 %wt. The autoclave was purged and pressurised with nitrogen to 0.6 MPa. Next, the autoclave was heated and kept at the reaction temperature of 400 °C during 30 min, according to authors' previous work, (Pinto et al.,

2018). Afterwards, the autoclave was cooled down to room temperature. Gases were collected, measured and analysed by gas chromatography (GC) to determine the contents of CO, CO₂, H₂, CH₄ and other gaseous hydrocarbons, referred as C_nH_m. Solid and liquid products were weighted and analysed. Solids were extracted in a Soxhlet extractor, using n-hexane, toluene and tetrahydrofuran (THF) to determine the amount of liquids soaked in solids. Liquid fractions were analysed by GC (Hewlett Packard 6890) and GC-MS - gas chromatography/mass spectrometry (LECO Instruments, PEGASUS III series 3104).

3. Results and discussion

3.1 Biomass pre-treatments

Table 1 presents the structural composition and ash content of untreated and pre-treated biomass. All pre-treated solids presented a significant removal of hemicellulose. As expected, the most severe autohydrolysis eucalyptus pre-treatment (carried out at 210 °C) was more effective in hemicellulose reduction than the one carried out at 190 °C. Specifically, hemicellulose was completely removed for autohydrolysis at 210 °C, thus inducing an increase in the lignin content close to 30 %. Corn cobs autohydrolysis pre-treatment led to lower hemicellulose removal than those observed for eucalyptus and consequently to an increase in lignin content of around 16 %. On the other hand, miscanthus was the biomass whose autohydrolysis pre-treatment led to lower alterations, as the decrease in hemicellulose was only 18 %, while the rise of lignin content was only around 14 %. Autohydrolysis pre-treatments of all biomasses studied led to significant increases in glucan and reductions in extractives and others. Autohydrolysis also led to reduction in ash content, due to the solubilisation of some inorganic compounds. Eucalyptus autohydrolysis at 190 °C and 210 °C led to ash reductions of around 50 % and 62 %, respectively, while a decrease of 23 % was observed for corn autohydrolysis. Autohydrolysis of miscanthus led to ash reduction of about 44 %.

Table 1: Structural composition and ash content of untreated and pre-treated biomass (dry basis, %wt.).

	Glucan	Hemicellulose	Klason Lignin	Extractives and others	Ash
Untreated Eucalyptus	42.3	27.6	26.4	1.1	2.6
Autohydrolysis Eucalyptus (190 °C)	55.4	12.5	29.6	1.2	1.3
Autohydrolysis Eucalyptus (210 °C)	64.2	0.0	34.2	0.7	1.0
Untreated Corn Cobs	35.7	33.3	14.6	15.1	15.1
Autohydrolysis Corn Cobs	44.2	25.7	16.9	12.3	12.3
Untreated Miscanthus	41.3	27.4	23.1	6.4	6.4
Autohydrolysis Miscanthus	50.0	22.6	26.4	0.0	0.0

Although all pre-treatments yield a significant mass loss of the feedstock, the removed components can be effectively upgraded in the biorefinery framework. Autohydrolysis at 210 °C led to the recovery of hemicellulose as soluble saccharides (mainly monomeric pentoses) that can be upgraded by fermentation. Autohydrolysis at 190 °C yielded mainly soluble oligosaccharides that are directly marketable added-value products.

3.2 Co-pyrolysis products yields

In Figure 1 is shown the effect of eucalyptus pre-treatment on co-pyrolysis gases and liquid yields and on total conversion. As expected, the increase of PE content in the blend led to higher liquids yields and conversions, because PE is easier to pyrolyse than biomass. These results agree with those found in literature (Pinto et al. 2018). The comparison between co-pyrolysis products yields obtained with pre-treated eucalyptus and untreated eucalyptus showed that higher liquids yields were obtained when pre-treated eucalyptus was used, being this effect only significant for PE blends lower or equal than 50 %wt. The increase in liquids yields was around 24 % for PE content till 25 %wt. in pre-treated eucalyptus blends. When PE content increased to 50 %wt. the rise in liquids yields was only 14 %. As PE is easier to pyrolyse than biomass, when the amount of PE was higher than 50 %wt., the effect of pre-treated eucalyptus on liquid yield was negligible. On the other hand, it was observed a reduction in gases yields when pre-treated eucalyptus was co-pyrolysed. As this decrease was compensated by the rise in liquid yields, no significant changes were observed in conversions obtained with untreated and pre-treated eucalyptus. The comparison between liquids yields and conversion obtained by co-pyrolysis of eucalyptus autohydrolysed at 190 °C or at 210 °C shows that no great variations were observed. In fact, only when pre-treated eucalyptus was pyrolysed alone it was observed that the autohydrolysis eucalyptus at 210 °C led to an increase of around 20 % in liquids yield, to which corresponded an increase of about 16 % in total conversion.

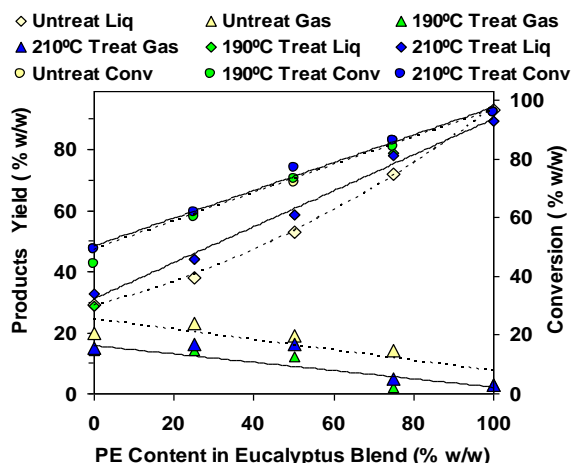


Figure 1: Effect of eucalyptus autohydrolysis at 190 °C and 210 °C on co-pyrolysis gaseous and liquid products and on total conversion. Solid lines refer to pre-treatment and dashed lines to untreated biomass.

As no great differences in co-pyrolysis results were obtained with eucalyptus autohydrolysed at 190 °C or at 210 °C, corn cobs and miscanthus co-pyrolysis were only evaluated for the biomass pre-treated by autohydrolysis at 190 °C. Co-pyrolysis products yields and conversion of blends of PE with pre-treated and untreated corn cobs are shown in Figure 2 (a). Once again, the rise of PE content in the feedstock favoured the formation of liquids and total conversion, though there was a decrease in the formation of gaseous compounds. In contrast to what happen with eucalyptus pre-treatments, the results obtained with corn cobs showed that no great differences were obtained when pre-treated or untreated corn cobs were studied. These results fairly agree with the milder changes of corn cobs structural composition after pre-treatment in comparison with eucalyptus pre-treatment (Table 1). In fact, the small changes in liquid and gases yields obtained for co-pyrolysis of untreated and pre-treated corn cobs are generally within experimental error, consequently no significant changes were observed in total conversion.

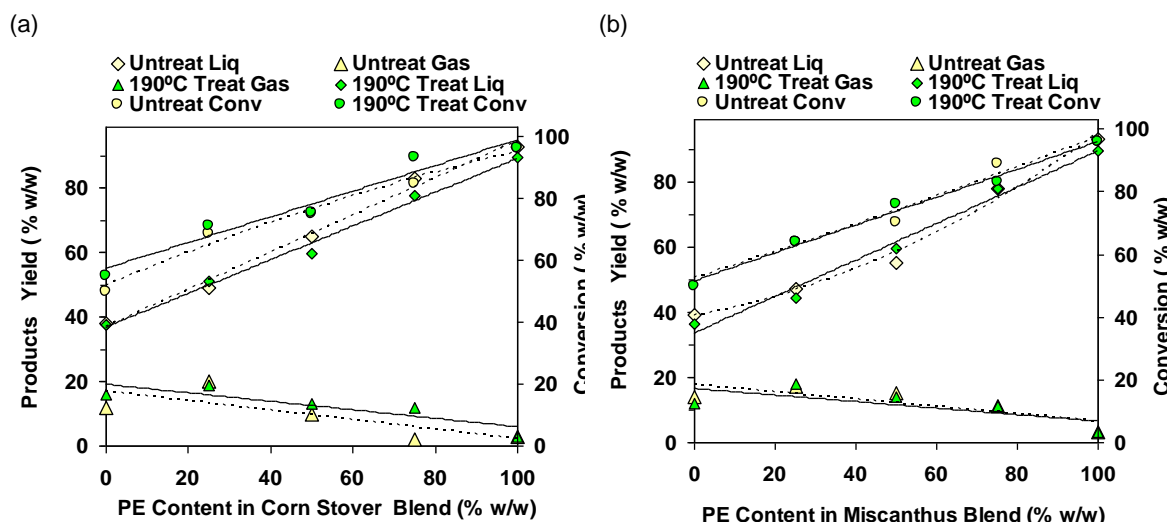


Figure 2: Effect of autohydrolysis pre-treatment at 190 °C of (a) corn cobs and (b) miscanthus on co-pyrolysis products and on total conversion. Solid lines refer to pre-treatment and dashed lines to untreated biomass.

In Figure 2 (b) may be analysed the effect of miscanthus autohydrolysis pre-treatment at 190 °C on co-pyrolysis products yields and on total conversion. Similar trends were obtained for miscanthus and as expected, the increase of PE content on miscanthus blends either untreated or pre-treated led to the increase of liquids yields and total conversion. Again, no significant differences were obtained on products obtained by co-pyrolysis of untreated and pre-treated miscanthus, which again agrees with the slighter changes in structural composition

(Table 1). Though the autohydrolysis at 190 °C of corn cobs and miscanthus did not seem to have significantly affected pyrolysis process, the results obtained showed that this biomass pre-treatment prior to pyrolysis may still be interesting, because the pyrolysis process did not seem to be negatively affected, while the pre-treatment allowed obtaining added value compounds. These biomasses pre-treatment by autohydrolysis at higher temperature or by acid hydrolysis might lead to greater changes in structural composition and thus might favour pyrolysis process. However, the economical evaluation of the overall process is needed to guarantee that the integration of autohydrolysis with pyrolysis is beneficial.

Gases GC analysis showed that under all tested conditions CO₂ and CH₄ were the compounds formed with the highest contents. Only very small contents of CO were analysed, thus CO₂/CO ratio was always higher than 3.0, which may mean that decarbonylation reactions were not favoured, while decarboxylation reactions were more probable. The rise of PE content on biomass blends led to the decrease of the total amount of carbon oxides (CO+CO₂), as only biomass contains oxygen. Gaseous hydrocarbons content decreased with the rise of the number of carbon atom, thus methane content was always higher than C₂, C₃ and C₄, C₄ were the gaseous hydrocarbons formed in the lowest contents. The contents of gaseous alkanes were always higher than those of gaseous alkenes. No clear tendencies were obtained in relation to the effect of the type of biomass or the use of pre-treated or untreated biomass on gas composition.

Regarding the liquid phase, its complete characterisation is difficult and analyses are still in progress, due to the high number of compounds and their small concentrations. GC and GC-MS analysis of liquids showed that the main compounds were mostly linear alkanes and alkenes with a large range of carbon numbers, most of them in small concentrations (Figure 3).

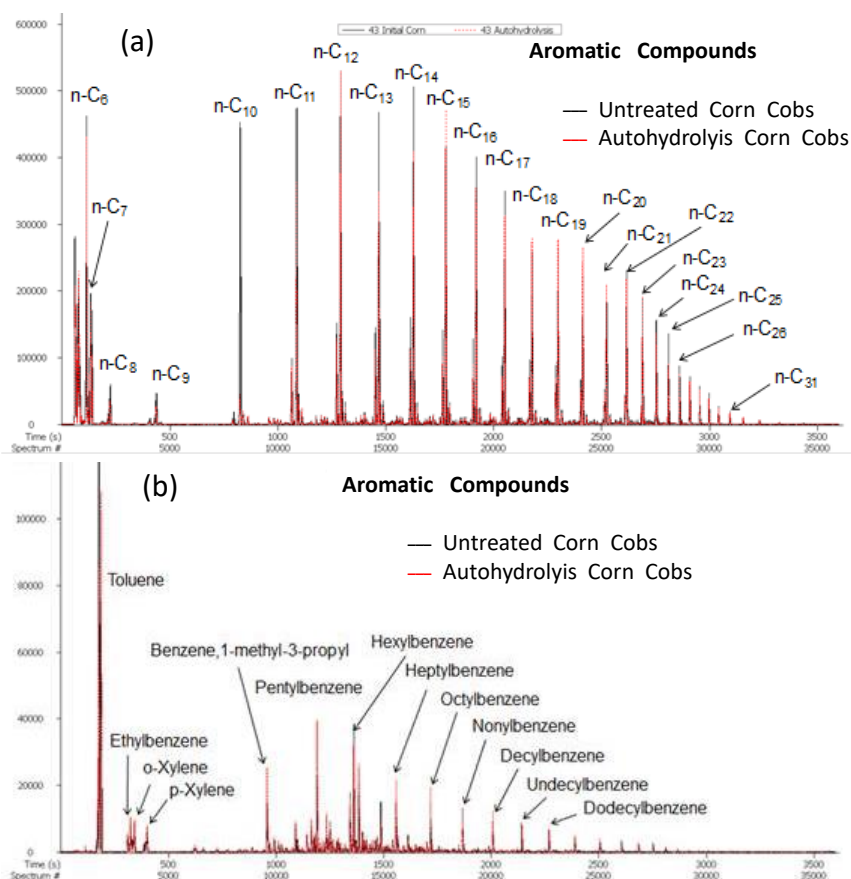


Figure 3: GC-MS analysis of liquids obtained by co-pyrolysis of 50:50 blend of PE and corn cobs. (a) Alkanes and alkenes and (b) aromatic compounds.

Due to the impossibility of presenting the GC-MS analysis of all liquids obtained by co-pyrolysis of different untreated and pre-treated biomasses, in Figure 3 are only presented the results obtained for corn cobs. For all the feedstocks studied, alkanes up to C₃₁ and alkenes till C₂₃ were analysed. In general, untreated biomass led to lighter alkanes. Alkanes with higher contents were among C₁₀ and C₁₇, whilst alkenes with the highest

concentrations were typically between C₁₂ and C₁₅. Several aromatic compounds were also analysed, mainly toluene, pentylbenzene and hexylbenzene. Moreover, other compounds with oxygen atoms, like alcohols, ketones, acids, etc. were also detected, due to biomass decomposition, but it was not possible to quantify all these compounds. The rise of PE amount in feedstock led to the formation of higher amounts of hydrocarbons, especially alkanes. It was not possible to find any relevant tendencies in relation to the effect of using pre-treated or untreated biomass on co-pyrolysis liquids composition.

4. Conclusions

The use of PE wastes mixed with biomass clearly favoured the production of liquids and increased the overall conversion, because PE is easier to pyrolyse than biomass, hence mass and energy transfer was favoured and PE cracking might also have supplied some hydrogen to reaction medium.

Pre-treatment of eucalyptus wastes by autohydrolysis favoured co-pyrolysis process and increased liquids yields of 24 %, because the removal of hemicellulose, protein and extractives weakened initial structure and favoured molecular break-down. Co-pyrolysis of autohydrolysis eucalyptus at 190 °C or at 210 °C led to similar results, though autohydrolysis at 210 °C led to greater alterations in structural pre-treated eucalyptus.

The results obtained showed that the effect of autohydrolysis pre-treatment on co-pyrolysis process is dependent on the feedstock type, as the results obtained for corn cobs and miscanthus showed that the use of pre-treated biomass did not increase liquid yields and conversion. However, the integration of autohydrolysis with co-pyrolysis may still be economical advantageous, due to the production of added value compounds by autohydrolysis. This subject needs to be further studied and the techno-economic analysis is needed.

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