**The Role of Eucalyptus Pre-treatment on Co-Pyrolysis with PE Wastes**

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**Highlights**

* Co-Pyrolysis of pre-treated eucalyptus blended with PE Wastes.
* Comparison of different eucalyptus pre-treatments on its pyrolysis.
* In general acid hydrolysis was the most effective pre-treatment.

**1. Introduction**

*Eucalyptus globulus* waste was selected for this study, because this species has been largely used in pulp and paper industry in Iberian Peninsula, which has generated high amounts of wastes. Pyrolysis has been widely applied to biomass for the production of bio-oils. Though, bio-oils yields up to 60-75% have been reported [1], the produced bio-oils have some adverse characteristics, like: high contents of solids, ash, oxygen-containing compounds and water and chemical instability, which prevents them from being directly used in fuel conventional engines. Though the quality of the bio-oils may be improved after upgrading catalytic processes, the overall costs are economically prohibitive. In contrast, polyethylene (PE) wastes pyrolysis produce liquids contents up to 85%, containing mainly hydrocarbons suitable to be used in conventional engines after minor upgrading [2]. Thus, co-pyrolysis of biomass and plastics may help to solve the problems associated to bio-oils disadvantages. As a different approach, eucalyptus waste was pre-treated before pyrolysis by auto-hydrolysis and acid hydrolysis to start molecular gradation and easing pyrolysis chemical bonds break-down. These pre-treatments removed hemicellulose and produced added-value products, like: oligosaccharides with applications in the food and pharma industries. Pre-treatments remaining solids were blended with different contents of PE wastes and co-pyrolysed to be converted into pyrolysis liquids to be used as biofuels or as raw materials.

**2. Methods**

Eucalyptus was pre-treated by different processes: acid hydrolysis and auto-hydrolysis. In acid hydrolysis, eucalyptus wastes were pre-treated at 130°C with an aqueous solution of 1.5 % H2SO4, using a liquid/solid ratio of 7 (w/w) at 130°C. While, in auto-hydrolysis only water was used, the same liquid/solid ratio was tested, but at temperatures of 190° and 210°C. The liquid fraction and the solid residue (cellulolignin), obtained after these pre-treatments, were separated at room temperature using a hydraulic filter press (up to 200 bar). The solid was washed with water, pressed again and dried at 45°C. Untreated eucalyptus and pre-treated by all these processes were blended with of PE wastes and co-pyrolysed. Eucalyptus content changed from 0 to 100 wt%. Co-pyrolysis experimental work was carried out in an autoclave at the following conditions: 400ºC, 30 minutes and nitrogen initial pressure of 0.6 MPa. Gases, liquids and solids were analysed according to previous work [3].

**3. Results and discussion**

There was a significant decrease in hemicellulose content after all treatments, thus yielding cellulose enrichment. As expected auto-hydrolysis pre-treatment at 210°C was more effective than that done at 190°C. Specifically, hemicellulose was completely removed for auto-hydrolysis at 210°C, thus lignin content increased around 30%, together with an increase in the cellulose content, in relation to pre-treated material. Regarding the acid hydrolysis, extractives and soluble ash were removed from the solid phase, together with hemicellulose (near to 85% removal). Thus, there was an increase in the lignin and glucan fractions, that accounted for more than 40 %, each, of the recovered solid material (dry basis). Acid hydrolysis and auto-hydrolysis at 210°C led to the recovery of hemicellulose as soluble saccharides (mainly monomeric pentoses) that can be upgraded by fermentation. While, auto-hydrolysis at 190°C led mainly to soluble oligosaccharides that are directly marketable added-value products. As such, a more integrated upgrade approach can be obtained to yield synergies between the thermochemical and biochemical routes. Though no great changes were observed in Figure 1, in general, acid hydrolysis was the most effective pre-treatment, as it led to the highest contents of liquids, to the highest conversions and to the lowest solids contents. Both auto-hydrolysis led to similar liquids yields, while the lowest liquids contents were obtained for untreated eucalyptus. However, with the rise of PE content, the effect of eucalyptus pre-treatment decreased, because PE is easier to pyrolyse than biomass.



**Figure 1.** Effect of eucalyptus content and type of pre-treatment on products yields obtained by co-pyrolysis at 400ºC, and 30 min. Solid lines refer to pre-treated eucalyptus and dashed lines to untreated eucalyptus.

**4. Conclusions**

Eucalyptus pre-treatments weakened initial macromolecular structure and eased pyrolysis. Acid hydrolysis was the most effective pre-treatment, leading to the recovery of hemicellulose as soluble saccharides and to the highest pyrolysis liquids. As PE was easier to pyrolyse, the effect of pre-treatment on co-pyrolysis was more important with lower contents of PE wastes.

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