

Improved bio-oils from *in situ* co-pyrolysis of grape seeds and polystyrene

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Highlights

- Co-pyrolysis process results as a simple and economic way to improve bio-oil.
- A particular-designed fixed-bed reactor eases positive synergetic effects during co-pyrolysis process.
- Co-pyrolysis process enhances liquid fraction yields and improves physical and chemical properties of bio-oil.

1. Introduction

The effective use of renewable sources to produce energy rises as an important goal to reduce the environmental impact caused by fossil fuels exploitation. The use of lignocellulosic biomass becomes one of the best promising alternatives since it is the only carbon-containing renewable source that can produce similar products to fossil fuels using pyrolysis process and it does not compete with food market. Unfortunately, the properties of the pyrolytic bio-oils as fuels are very poor and different upgrading strategies need to be implemented. Among all strategies, co-pyrolysis of biomass and plastics wastes such as Polystyrene (PS), polyethylene (PE), and/or waste tires (WT) emerges as a promising way to achieve this goal [1]. Thus, the present work develops a new and low-cost strategy based on the *in situ* co-pyrolysis of biomass and plastic wastes that allows the user to obtain an advanced bio-oil to be used directly or to be processed in bio-refineries.

2. Methods

The biomass used in the present study was grape seeds (GS), dried up to moisture levels lower than 2 wt. % and PS was selected as a plastic residue. As it can be observed in Table 1, the lower oxygen content and the higher heating value associated to PS, should lead to a liquid phase with improved properties in a co-pyrolysis process of both feedstock, based on the rule of mixtures. Moreover, previous thermogravimetric tests carried out at similar heating rates than those used in the fixed bed reactor have shown that there is a mutual region where radical interactions of both feedstock could take place (see Figure 1), which could favor the presence of synergetic effects.

Table 1. Feedstock (GS and PS) characterization.

	GS	PS
Ash	4.6	0.1
Volatile matter	69.5	97.7
Fixed Carbon	25.9	0.45
Ultimate analysis (wt. %)		
C	57.6	90.3
H	6.3	9.1
N	2.4	0.3
S	0.2	0.0
O (by difference)	33.7	0.3
LHV (MJ/kg)	22.2	42.1

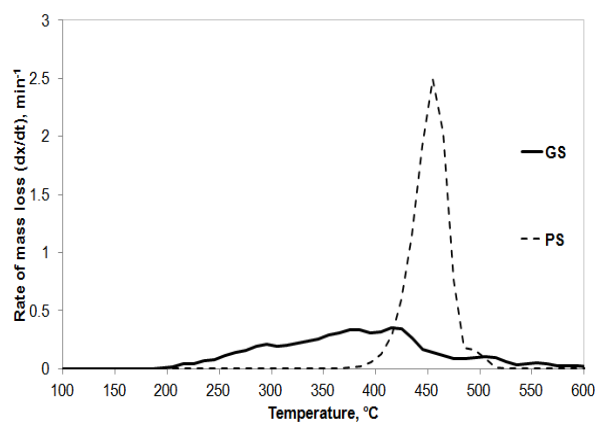


Figure 1. Simulated-rate of mass loss of Grape seeds and Polystyrene at heating rate 100 °C/min

Co-pyrolysis experiments were carried out in a Stainless steel fixed-bed reactor. This reactor has been specifically designed to carry out this process having the peculiarity that incorporates a vertical mobile liner to ensure the high heating rates needed for the process. The reactor was heated externally with an electrical resistance at approximately 100 °C/min to the final pyrolysis temperature of 550 °C. Liquid and solid yields were obtained by weight, while the gas yield was calculated by the gas composition. Different feedstock mixtures (up to 40 wt. % of PS) were studied and the influence of this variable on the bio-oil properties was also analysed.

3. Results and discussion

Obtaining a well-defined phase distribution in the resulting bio-oil is decisive to ensure the viability of the process since liquid fractions obtained from pyrolysis of both feedstock are immiscible. Thus, co-pyrolysis of GS jointly with PS lead to obtain a well-defined two-layer liquid, allowing the user to obtain not only an easy separation but also an improvement of the properties of the organic phase. Experiments have shown that adding different amounts of PS in the feeding (5, 10, 20 and 40 wt. %) results in a positive synergetic effect, obtaining higher amounts of the liquid fraction than those obtained based on the rule of mixtures (see Table 1). Moreover, it is possible to improve the physical and chemical properties of the liquid, reflected by a less viscous and a non-corrosive liquid (values of pH between 5.4-6.1). In reference to this, the resulting liquid also presents less oxygen content (values between 6.3-15 wt.%) and a higher heating value (values between 30-38 MJ/kg). These findings are remarkable since represent a deoxygenation rate of more than 50 % and an increment in the heating value up to 40 %.

Table 1. Properties of the organic phase of different pyrolysis and co-pyrolysis experiments.

Property	GS	PS	GS/PS (95/5) ¹	GS/PS (90/10) ¹	GS/PS (80/20) ¹	GS/PS (60/40) ¹
Liquid yield	33.3	90.2	37.4 (36.1) ²	49.3(39.0) ²	56.0 (44.7) ²	69.5 (56.1) ²
Water content (wt. %)	1.6	<1	<1	<1	<1	<1
pH	6.1	3.8	5.6 (5.9) ²	6.1 (5.8) ²	5.4 (5.6) ²	5.7 (5.1) ²
O (%)	15.4	2.2	15.0 (14.7) ²	14.8 (14.1) ²	8.1 (12.8) ²	6.3 (10.1) ²
HHV (MJ/Kg)	27.5	40.8	30.8 (28.2) ²	33.4 (28.8) ²	37.9 (30.2) ²	38.3 (32.9) ²

¹ Mixtures were prepared in wt. %.

² Theoretical values calculated from each individual feedstock and their respective mass ratio, assuming that there are no interactions among the pyrolytic vapor molecules.

4. Conclusions

The results have shown the great potential of GS to carry out the co-pyrolysis process with PS to produce a liquid bio-oil that can be considered as a high quality renewable vector. Thus, maximizing liquid yields and improving the organic fraction properties by optimizing the operational conditions jointly with a further and more extensive bio-oil characterization are the close next steps for the development of advanced bio-oils.

References

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Keywords

Bio-oil, co-pyrolysis, biomass, Polystyrene.