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Catalytic co-pyrolysis of grape seeds and waste tyres for the production of drop-in biofuels

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ABSTRACT

Catalytic co-pyrolysis of grape seeds and waste tyres was performed in a fixed-bed reactor using calcined calcite as a catalyst. The organic phase obtained was analysed for its further application as a potential and stable drop-in fuel. Remarkable positive effects were achieved after the joint incorporation of both waste tyres and calcined calcite to grape seeds in the process. More specifically, the addition of considerable amounts of waste tyres (between 20 and 40 wt%) with a constant ratio of feedstock to calcined calcite of 1 were considered the optimal experimental conditions to promote positive synergistic effects on bio-oil yields and its characteristics as a fuel. Thus, when the proportion of waste tyres in the feed reached 40 wt%, the organic phase yield was considerable improved, reaching up values higher than 73 wt%, significantly greater than those obtained from conventional pyrolysis (61 wt%). Moreover, oxygen content was reduced to 4.2 wt%, minimizing any problems related to corrosivity and instability. HHV was enlarged from 15.3 up to 27.3 MJ/kg, significantly increasing the value of the resulting bio-oil. pH values and specially total acid number were also improved reaching values down to 1 mg KOH/$g_{\text{bio-oil}}$ in all cases. Additionally, a more valuable chemical composition was achieved since the production of aromatic and cyclic hydrocarbons was maximized, while a significant reduction in phenolic compounds was achieved. Moreover, bio-oil sulphur content was drastically reduced in comparison with the pyrolysis of waste tyres by itself from 0.6 down to 0.2 wt%. The role of calcined calcite was directly related to the promotion of dehydration reactions of acids and phenols in order to generate hydrocarbons. On the other hand, radical interactions between the biomass and waste tyres pyrolysis products played a fundamental role in the production of more valuable compounds. Finally, the CO_2 capture effect produced a more environmentally friendly gas while maintaining its calorific value.

1. Introduction

The appropriate use of renewable sources is considered crucial to meet the challenge of reducing the environmental impact caused by the extraction of fossil fuels and their processing in present-day refineries. Lignocellulosic biomass is one of the most promising alternatives for reducing fossil fuel dependence, because: (a) it is the only carbon-containing renewable source that can produce biofuels that are similar to fossil fuels; (b) it is considered inexpensive [1]; and (c) it does not compete with food production. Among all the possible techniques that can be used to enhance the value of lignocellulosic biomass [2], fast pyrolysis is an attractive alternative because it is the only thermo-chemical process that can produce a liquid biofuel in a simple one-step process. Additionally, solid and gas fractions are produced. These fractions can be used as energy sources to cover the thermal requirements of the process [3,4]. In fact, the success of any biomass pyrolysis process lies in the exploitation of all by-products. In this regard, the application of an autothermal system, where gas and char fractions are used as an energy source for the process and for power generation, seems an appropriate solution [5,6].

Biomass pyrolysis can be defined as the thermal degradation of biomass in the absence of oxygen at moderate temperatures (450–600 °C). The potential of this technology allows a liquid fraction (bio-oil) yield of 60–70 wt% to be achieved depending on the experimental conditions and reactor type [7]. After the process, the organic fraction of bio-oil, which can be easily separated, becomes the most valuable product, since it is considered a potential source of second-generation biofuels [8]. However, bio-oil quality needs to be improved in order to be used in current power generation infrastructures and/or further processed at state of the art bio-refineries [9–11]. Bio-oils consist of a complex mixture of hundreds of organic compounds, mainly reactive oxygenated compounds, which make them unstable and give them lower heating values in comparison to currently available commercial liquid fuels. Moreover, bio-oils are highly acidic in nature,

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mainly due to the presence of carboxylic acids, and can cause severe problems of corrosion. For these reasons, bio-oils face a great challenge in order to be considered as a real alternative to fossil fuels able to replace commercial liquid fuels, such as gasoline or diesel. Therefore, the most cost-effective solution lies on the development of drop-in fuels, where biomass pyrolysis liquids would be added to those obtained from fossil fuels in existing refineries [12–14]. Thus, the short-term objectives for the production of second-generation biofuels are focused on obtaining a more stable and deoxygenated bio-oil, which could be mixed with current conventional fuels [15–17] as is already the case with first-generation biofuels.

The most promising alternatives for the production of drop-in biofuels from pyrolysis, owing to their lower cost and simplicity, are those performed *in situ* during the process. Two different approaches emerge as the best potential solutions. First, the incorporation of different low-cost and/or regenerable cracking catalysts, also known as catalytic pyrolysis [18–21] and, second, the co-feeding of different polymers/plastic residues such as polyethylene (PE), polypropylene (PP), polystyrene (PS) or waste tyres (WTs) [22–25] to the process. The state of the art of these technologies has been described in numerous reviews [6,26–30] and there is consensus that catalytic co-pyrolysis, where both solutions are simultaneously implemented, is a much promising technology than the catalytic pyrolysis of biomass on its own. The level of success of this technology would lie in the occurrence of favourable synergistic effects caused by radical interactions during feedstock devolatilization, resulting in a bio-oil (the organic fraction) without phase separation. In this sense, it is worth of mention that those liquid organic fractions separately obtained from the pyrolysis of either polymer residues or lignocellulosic biomass are not miscible [4]. Thus, their direct processing cannot be performed in a bio-refinery. Moreover, the proportion of plastic-derived material in the feedstock should be considered a key factor in order to ensure the feasibility of any large-scale catalytic co-pyrolysis process.

All catalytic co-pyrolysis research conducted to date has shown very promising results in obtaining an improved liquid fraction, not only in terms of higher liquid yields but also better fuel properties [26,30]. The resulting bio-oil not only presents a lower oxygen content, and consequently a higher heating value, than those obtained by conventional pyrolysis, but also lower acidity and water content. Moreover, a pronounced increase in aromatic hydrocarbon composition can be obtained. Additionally, lower coke formation on the catalyst surface is observed, mainly due to the promotion of hydrogen transfer reactions enhanced by the higher hydrogen content of the plastic-type residues [26]. More specifically, Dorado et al. [25] tested several types of biomass and plastic-derived residues for the production of drop-in fuels, and concluded that certain combinations of plastic/biomass blends favour the production of particular aromatic products (toluene, xylene and ethylbenzene) in the presence of H-ZSM5. Similar tendencies were observed by other authors [31,32] where the catalytic co-pyrolysis of pine wood and LDPE with zeolitic catalysts enhanced the production of toluene and xylenes. Similarly, studies focusing on the catalytic co-pyrolysis of biomass model components (cellulose, hemicellulose or lignin) with waste tyres using SBA-15, MCM-41 and HZSM-5 [22] catalysts were conducted in a lab-scale reactor, showing an increase in the aromatic fraction yield. In line with this, Rezaei et al. [33] studied hierarchical mesoporous Y and Al-SBA-15 for the catalytic co-pyrolysis of yellow poplar and PE. The authors revealed a high selectivity to aromatic hydrocarbons production attributed to the effective pore structure, large channels, and high acidity of the catalysts as well as the high H_2 evolved from PE pyrolysis. However, it should be pointed out that, as in the case of biomass catalytic pyrolysis, catalysts deactivation as a result of coke deposition on the zeolite-based catalysts [26] and the formation of polycyclic aromatic hydrocarbons are still important challenges which need to be resolved. In addition, all these tests were conducted mainly through zeolitic materials entailing an extra-cost associated to the addition of new or regenerated catalyst. Hence, the application of low-cost catalysts such as CaO, that has already shown promising results in the catalytic pyrolysis of biomass [5,19] could emerge as a promising alternative, enhancing positive synergistic effects in the catalytic co-pyrolysis process.

Among all available lignocellulosic biomass, agricultural residues such as grape seeds (GSs) rise as a worldwide available biomass. For the moment, GSs have been barley studied at pyrolysis processes despite its high-energy content that makes it a potential renewable feedstock for energy production [34]. For instance, Xu et al. [34] demonstrated that the organic phase obtained after the pyrolysis process could be an attractive fuel with significant energy content. In addition, Brebu et al. [35] also studied the pyrolysis of GSs and the co-pyrolysis process of GSs and polyethylene, concluding that interactions between both materials were leading to positive effects on both liquid yields and bio-oil composition. As shown, the number of works using GSs as feedstock is limited and a wider range of studies using this raw material needs to be conducted.

On the other hand, regarding the plastic waste-to-energy conversion, WTs valorisation could play a crucial role since WTs wastes represent a great annual generation. Moreover, since WTs pyrolysis has been successfully conducted [36–38] and the positive effect on their addition to the pyrolysis of biomass has been also demonstrated [23,39], the catalytic co-pyrolysis of GSs and WTs with CaO as catalyst could be an attractive, novel and low-cost solution for the production of drop-in fuels ensuring both the sustainability and feasibility of the process.

In this work, we present the findings of the study of the catalytic co-pyrolysis of GSs and WTs using CaO as a catalyst. This strategy is a new, simple and low-cost alternative for the obtention of high quality bio-oils to be used as drop-in biofuels. In order to accomplish this aim, a study was made of the effect of two different variables, the GSs-to-WTs ratio and feedstock (GSs + WTs)-to-catalyst ratio, on pyrolysis products, and the influence of these variables on the characteristics of the liquid product (bio-oil) was more extensively analysed. In addition, synergy effects between both feedstocks, in the presence and absence of catalyst, were assessed based on the rule of mixtures.

2. Materials and methods

2.1. Biomass, waste tyres and catalyst

The biomass used in the present study was GSs (*Vitis vinifera*), obtained from the north-east area of Spain. The fresh biomass was previously dried in order to reduce moisture levels to below 2 wt%, and then used directly. Granulated WTs with a particle size of between 2 and 4 mm were supplied by a Spanish WTs recycling company (Gesneuma S.L.U.). WTs were composed of rubber without the steel thread and the textile netting (moisture content of 0.9 wt%).

Table 1 summarizes the main properties of both feedstocks. The lower heating value (LHV) was measured experimentally with an IKA C-2000 calorimetric bomb using the Spanish (UNE) standard procedure UNE 164,001 EX. Proximate analysis of the received feedstock was determined according to UNE-EN ISO 18134-3 for moisture, UNE-EN ISO 18122 for ash proportion, and UNE-EN ISO 18123 for volatile matter. Fixed carbon was determined by difference. Ultimate analysis of the feedstock was determined in a Thermo flash 1112, according to UNE EN 5104, and oxygen content was determined by difference. At this point, it is worth mentioning that great differences were detected between both feedstocks. Table 1 shows that while GSs were characterized by a remarkably high oxygen content (33.7 wt%), implying a relative low LHV (22.2 MJ/kg), the composition of the WTs was characterized by an important source of carbon with low oxygen content, implying heating values similar to or even higher than those obtained from fossil fuels (% C: 87.9 wt%, % H: 3.3 wt% and LHV: 37 MJ/kg, respectively).

Calcined calcite (90% CaO, Calcinor) was used as the catalyst in this