

# Low-Cost strategies for the production of bio-oils derived from the pyrolysis of lignocellulosic biomass

O. Sanahuja-Parejo

osanahuja@icb.csic.es

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SUPERVISORS: T. García (Instituto de Carboquímica) and M.S. Callén (Instituto de Carboquímica)

## OBJECTIVES AND NOVELTY

The use of lignocellulosic biomass in thermochemical processes has attracted a great deal of interest in recent years, as it is possible to obtain value-added products that can be potentially complementary and/or considered as an alternative to those obtained from fossil fuels. The use of this biomass would result in a reduction both on the environmental impact caused by the exploitation of fossil fuels and in the waste generated waste. Moreover, it would also be expected to decrease the foreign dependence on non-producer countries, a fact that could minimize the well-known supply problems and current increasing prices. Among all the thermochemical existing processes for the treatment of biomass, pyrolysis has stood out in recent years. The development of this technique is advancing considerably as it is a process capable of producing liquid, solid and gaseous biofuels in a simple step. However, most of the studies carried out are limited to laboratory scale, under ideal operating conditions, and studies on relevant scales are quite limited.

In this context, this thesis addresses the environmental problems arising from the necessary reduction in the use of fossil fuels, using lignocellulosic biomass (grape seeds (GS)). In addition, this thesis also focuses on solving the problem of the elimination and energy recovery of certain waste with high environmental impact, such as waste tyres (WT) and polystyrene (PS). Unfortunately, the scope of biomass pyrolysis is limited and only a low-quality biofuel can be obtained, which cannot be standardised and has very limited applicability. In this sense, several strategies have been proposed throughout this report to improve its quality, differentiating between *in situ* and *ex situ* strategies. The *in situ* strategy is focused on the co-pyrolysis of biomass with polymeric residues together with the incorporation of low-cost heat carriers, based on calcareous sorbents, with catalytic properties. On the other hand, the *ex situ* strategy evaluated the catalytic cracking of bio-oil vapours using bifunctional ZSM-5 zeolites (impregnated with different amounts of magnesium) with hierarchical porosity. Thus, during this thesis, different experimental facilities have been used, from laboratory-scale fixed-bed reactors to a pilot plant equipped with an Auger reactor.

## RESULTS

A thermogravimetric analysis (TGA) was conducted for the selected materials (GS, PS and WT) and their respective mixtures (GS/WT and GS/PS),

with the aim of assess their thermal behaviour under pyrolytic conditions. The study evidenced that the radicals released during the pyrolysis process of these mixtures coexist in a temperature range favouring potential interactions. Furthermore, these analyses allowed establishing the optimal reaction temperatures for the complete decomposition of both feedstocks at 550 °C (GS/WT) and 600 °C (for GS/PS), respectively.

The next step was the experimentation in a fixed bed reactor, where the influence of the ratio of a heat carrier with catalytic properties (CaO) in the co-pyrolysis of GS (80 wt%) and WT (20 wt%) was studied. Although the organic phase decreased mainly due to the dehydration effect of CaO, the quality of this fraction was improved. In all cases, this fraction was practically dehydrated and the oxygen content decreased drastically reaching the lowest oxygen content (4.6 wt%) for the ratio 1:1 and, reaching an HHV of 41 MJ/Kg. Other properties such as total acid number (TAN) or pH were also improved and associated with the decarboxylation of biomass-derived fatty acids. The sulphur content derived from the thermal decomposition of WT decreased with catalyst content, which was associated with the ability of the CaO to hydrodesulphurise. The amount of catalyst also affected the composition of the organic phase. The higher the catalyst content in the feedstock, the higher the aromatics content in the bio-oil, reaching the maximum aromatics production for the 1:1 ratio (15.7 area%). The same trends were observed for cyclic hydrocarbons. Finally, a considerable increase of ketones at higher amounts of CaO due to decarboxylation reactions via fatty acid ketonisation mechanisms at the basic sites of the catalyst also stood out. On the other hand, the positive effect of CaO was also evidenced in the production of more valuable and environmentally friendly gas stream. Thus, CO<sub>2</sub> and sulphur components were significantly reduced due to the CO<sub>2</sub>-capture and desulphuration effects associated to this solid, and the production of both H<sub>2</sub> and CH<sub>4</sub> increased due to water gas shift and methane reforming reaction.

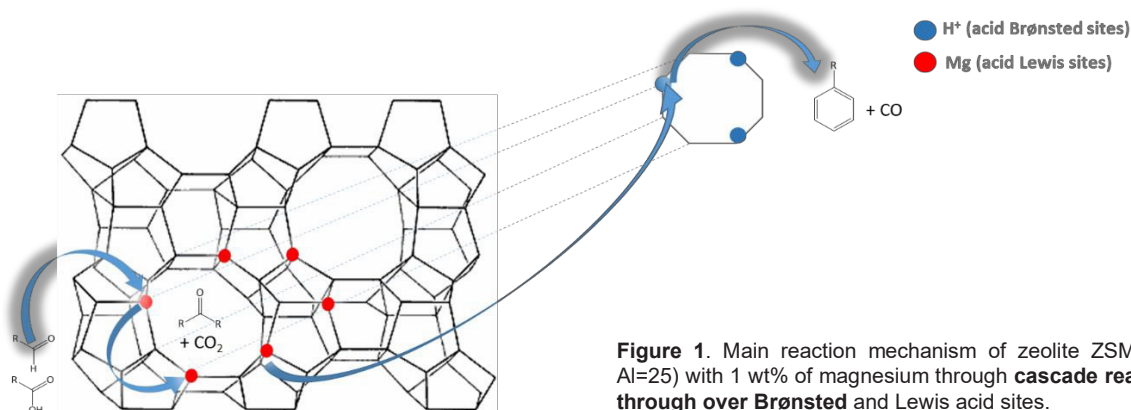
Once this optimal feedstock:catalyst ratio was selected, the influence of the amount of WT on the catalytic co-pyrolysis of GS/WT in the fixed bed reactor was studied. Although similar trends were observed in the products quality, these effects were enhanced by increasing the WT content in the feedstock mixture. Particularly, using 40 wt% of WT in the feeding, an increase in aromatics (28.2 area %), linear paraffins (8.6 area %) and cyclic hydrocarbons (26.3 area %) was observed.

The following step, in view of the excellent results obtained in the fixed bed, was to study the influence of the properties and composition of different catalysts based on calcareous sorbents, using the pilot plant equipped with an Auger reactor. In this case, it could be observed that the trends in the products and in the quality and composition of the bio-oil were similar than those explained above. However, these effects were promoted by the use of this kind of reactor, reaching a practically fully deoxygenated organic fraction (reaching values of 95% of deoxygenation). Particularly, the most promising results were obtained using high-purity CaO, where the aromatisation of the organic fraction was maximized (reaching up to 70 area %).

Subsequently, catalytic co-pyrolysis experiments with GS and PS were carried out. The influence of different amounts of PS in the feedstock mixture and the influence of the addition of the CaO were studied in the fixed bed reactor. The results obtained in terms of product yields and bio-oil quality followed the same trends than those obtained with WT and were enhanced at when higher amount of PS was added to the feeding. That is, an improved organic phase in terms of lower oxygen content and higher calorific value (39 MJ/Kg), an increase of valuable aromatics and a subsequent decrease of undesired oxygenated compounds were also obtained, reaching the maximum of aromatics in the GS/PS (80/20) mixture. The same experimentation was carried out in the pilot plant and the same trends were observed as in the fixed bed. Nonetheless, a higher positive synergetic effect was evidenced using this technology obtaining an organic phase with oxygen contents lower than 1 wt%. It has also been possible to establish the optimum conditions for scaling up the process, i.e. using a 20 wt% of plastic waste together with a feedstock:catalyst ratio of 1:1. Finally, it has been possible to establish the main reaction mechanisms of catalytic co-pyrolysis, highlighting particularly the hydrodeoxygenation of phenols to produce aromatics, which was enhanced by the addition of larger quantities of plastic or catalyst to the feedstock mixture, and the ketonisation of fatty acids in the basic active sites of the catalyst, which was favoured at high catalyst ratios.

Another objective was the develop the *ex situ* upgrading of bio-oil vapours by catalytic cracking of

the vapours on magnesium-impregnated hierarchical acid zeolites. The zeolites were first synthesised in the laboratory. Subsequently, bio-oil catalytic cracking tests were carried out using a laboratory-scale fixed-bed reactor and it was observed that the ZSM-5 zeolite with Si/Al=25 ratio impregnated with 1 wt% magnesium improved the bio-oil both in terms of high deoxygenation rate (68 %) and high aromatic content (increased 11.36 %). A great characterisation of the catalysts was carried out to identify the key parameters. Thus, different techniques were used (XRD, XPS, porosity and acidity, N<sub>2</sub> adsorption isotherms, TEM, high resolution TEM, TPD-NH<sub>3</sub>, Py-DRIFTS and (<sup>1</sup>H, <sup>27</sup>Al, <sup>29</sup>Si)-MAS-NMR) and the different active sites and their position in the zeolites were identified. Firstly, the Brønsted acid sites as H<sup>+</sup> species in the exchange positions, within the internal structure of the zeolite and on the external surface. Secondly, the medium-strength Lewis acid sites associated with (Mg<sup>2+</sup>+OH<sup>-</sup>)<sup>+</sup> species in exchange positions and close to the extraframework AlO<sub>4</sub><sup>-</sup> species that were mainly found in the microporous structure. Fourthly, MgO nanoparticles inside the crystal structure, produced by condensation of (Mg<sup>2+</sup>+OH<sup>-</sup>)<sup>+</sup> in exchange positions. And finally, the amorphous MgO nanoparticles finely dispersed on the external surface of the zeolite. By comparing, on the other hand, the composition of the gas obtained by GC and the composition of the organic phase of the obtained liquid (GC-MS), it could be shown that the upgrading mechanisms were taking place through different types of parallel reactions, the balance of which depends on the amount and distribution of the different active sites. The three main types of mechanisms that have been identified are decarbonylation of phenols at the Brønsted acid centres, decarboxylation of phenolic compounds through the MgO nanoparticles and cascade reactions as shown in Fig.1. (first an aldol condensation reaction of ketones to aldols at the high-strength Lewis acid sites of the microporous structure, and then a dehydration of these compounds at the Brønsted acid sites on the outer surface of the zeolite to obtain aromatic compounds). Thus, the above-mentioned zeolite with these species significantly improved the bio-oil by cascade reactions.



**Figure 1.** Main reaction mechanism of zeolite ZSM-5 (Si/Al=25) with 1 wt% of magnesium through **cascade reactions through over Brønsted and Lewis acid sites.**

## CONCLUSIONS

The development of both in situ and ex situ upgrading strategies has shown a positive impact on the production of an improved bio-oil with a high potential to be considered a renewable energy vector. Particularly, the co-pyrolysis process with natural catalyst such as CaO in an auger pilot plant can be considered an efficient process to improve both bio-oil yield and quality, where a practically dehydrated and deoxygenated organic fraction can be obtained. On the other hand, the development of the catalytic cracking of bio-oil using hierarchical Mg-load zeolites has shown new insights into the bio-oil upgrading, where high rates of deoxygenation and aromatisation can be obtained in a simple step. Thus, these strategies are promising in order to enhance the incorporation of bio-oils in the energy market or for its use directly as drop-in fuels.

## RELATED PUBLICATIONS

<sup>[1]</sup> Sanahuja-Parejo O, Veses A, Navarro MV, et al (2018) Catalytic co-pyrolysis of grape seeds and waste tyres for the production of drop-in biofuels. *Energy Convers Manag.* 171:1202–1212.

<sup>[2]</sup> Sanahuja-Parejo O, Veses A, López JM, et al (2019) Ca-based catalysts for the production of high-quality bio-oils from the catalytic co-pyrolysis of grape seeds and waste tyres. *Catalysts.* 9(12):992.

<sup>[3]</sup> Sanahuja-Parejo O, Veses A, Navarro MV, et al (2019) Drop-in biofuels from the co-pyrolysis of grape seeds and polystyrene. *Chem Eng J.* 377:120246.

<sup>[4]</sup> Sanahuja-Parejo O, Veses A, López JM, et al (2020) Insights into the production of upgraded biofuels using Mg-loaded mesoporous ZSM-5 zeolites. *ChemCatChem.* 12(20):5236–5249.

<sup>[5]</sup> Veses A, Sanahuja-Parejo O, Navarro MV, et al (2020) From laboratory scale to pilot plant: Evaluation of the catalytic co- pyrolysis of grape seeds and polystyrene wastes with CaO. *Catal Today.* 379:87-89. Full Thesis can be downloaded from <https://hdl.handle.net/10261/284904>