CHEMICAL ENGINEERING TRANSACTIONS
VOL. 65, 2018

A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eliseo Ranzi, Mario Costa
Copyright © 2018, AIDIC Servizi S.r.l.
ISBN 978-88-95608- 62-4; **ISSN** 2283-9216

DOI: 10.3303/CET1865036

Co-Pyrolysis of Pre-Treated Biomass and Wastes to Produce Added Value Liquid Compounds

Filomena Pinto*, Filipe Paradela, Florbela Carvalheiro, Luís C. Duarte, Paula Costa, Rui André

LNEG, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, PORTUGAL
filomena.pinto@lneg.pt

It is imperative to find novel environmental friendly liquid fuels to be used in the long distance transportation sector. Pyrolysis of wastes may have an important role in the near future to attain this goal. Biomass pyrolysis has also been widely studied by several researchers, but besides the potentialities of such technology, the bio-oil obtained still has to overcome some challenges related to its unsuitable properties to be used in conventional combustion devices. On the contrary, plastics pyrolysis produces oils, whose main compounds are hydrocarbons, thus they can be used in conventional engines without complex and high cost upgrading processes. Thus, co-pyrolysis of plastics blended with biomass may be a suitable option to produce alternative liquid fuels from wastes. The biomass selected for this study was *Eucalyptus globulus* wastes, because it has been mostly used in the pulp and paper industry in Iberian Peninsula, which has produced high amounts of wastes. On the other hand, PE (polyethylene) was the plastic chosen, because of the huge wastes amounts generated per year. With the aim of facilitating biomass pyrolysis and to increase the production of liquid compounds with suitable properties to be used as fuels, an alternative to the conventional biomass pyrolysis was studied. First eucalyptus wastes were pre-treated by diluted acid hydrolysis, which removed the hemicellulose fraction, produced added value sugar-based compounds and upgraded the remaining solids to better conditions for pyrolysis. Several pathways were studied, including untreated and pre-treated eucalyptus, blended with different contents of PE wastes. The best technical option is the co-pyrolysis of pre-treated eucalyptus mixed with PE, as the highest liquids yields were produced. However, this process needs to be further studied and the economic viability of the overall process still needs to be proven.

1. Introduction

Modern societies face the challenges of sustainable use of resources and suitable management of the produced wastes, together with the need of finding alternative environmental friendly fuels to substitute fossil fuels. The use of biomass and residues such as: plastics, tyres, packaging and also RDF (residual derived fuel) for the production of liquid biofuels and/or raw materials may help to fulfil these challenges.

Pyrolysis technology has been widely applied for the energy recovery of biomass and plastic wastes, whenever mechanical or physical recycling cannot be applied. Plastics pyrolysis has been widely studied (Marcilla et al., 2009) and it has been shown that plastics are easily converted into mixtures of liquid hydrocarbons (Kumara et al., 2012) to be used as fuels and/or as raw material for different industries (Kaminsky and Zorriqueta, 2007). Total conversions of around 90 wt% can be achieved at moderated conditions of pressure and temperature with liquid yields of about 80 wt% (Costa et al., 2007).

Biomass pyrolysis has also been widely studied, especially fast pyrolysis for the production of liquid biofuels. Yields from 60-75% have been reported, depending on experimental conditions used and on biomass type (Bridgwater, 2012). However, the bio-oil obtained from pyrolysis of biomass residues has undesirable properties such as: chemical instability and high contents of solids, ash, oxygen-containing compounds and water, which makes difficult its direct use in conventional engines. Thus, in order to improve bio-oil quality, expensive downstream thermal catalytic processes and the use of hydrogen are needed to upgrade bio-oil into diesel oil and gasoline, or to produce chemical raw material (Bridgwater, 2012). Although these processes

Please cite this article as: Pinto F., Paradela F., Carvalheiro F., Duarte L., Costa P., Andre R., 2018, Co-pyrolysis of pretreated biomass and wastes to produce added value liquid compounds, Chemical Engineering Transactions, 65, 211-216 DOI: 10.3303/CET1865036

can improve the quality of the oil, the amount of hydrogen required and the total associated costs may make them economically unattractive (Pinto et al., 2016). On the contrary, the pyrolysis oils obtained from pyrolysis of other wastes, like plastics, tyres and RDF do not present the mentioned disadvantages, as they contain mainly hydrocarbons, thus they are suitable to be used in conventional engines after minor upgrading. By the right manipulation of the composition of biomass and plastics wastes blends it may be possible to obtain bio-oils with more suitable compositions (Paradela et al., 2009.

In an alternative approach, biomass pre-treatments (prior to pyrolysis) are proposed to be used to minimize bio-oil shortcomings. Processes such as auto hydrolysis and diluted acid hydrolysis are able to remove the hemicellulose fraction into the liquid stream and potentially to upgrade the remaining solid to better conditions for pyrolysis. Previous results showed that these pre-treatments also enable the recovery of added-value products, particularly sugar-based, such as marketable oligosaccharides with potential applications in the food and pharma industries and monosaccharides that can be upgradable by fermentation in the biorefinery framework (Branco et al., 2015; Moniz et al., 2016). The remaining solids obtained after pre-treatments are rich in carbon and poor in oxygen, containing mainly glucan and lignin at higher mass percentages than the values found in the initial biomass. These solids were processed directly by thermochemical processes with significant advantages, as hydrothermal pretreatments weakened the initial macromolecular structure of biomass and thus facilitated the following conversions. These solids can be directly processed by thermochemical processes or alternatively, they could be mixed with the wastes mentioned (plastics for instance) to be converted into pyrolysis liquids to be used as biofuels or as raw materials for various industries. This paper analysis several pyrolysis pathways of pre-treated and untreated biomass wastes blended with plastic wastes with contents from 0 to 100 wt% to select the best pathway to increase the added value products obtained from biomass and to increase bio-oil production.

2. Experimental Part

2.1 Feedstocks

The biomass selected for the presented study was residues of *Eucalyptus globulus*. Due to its fast growth and high productivity, it has been the main tree species used in the pulp and paper industry in Iberian Peninsula. Its production and use generates high amounts of biomass residues, including bark, leaves, branches and stumps. The eucalyptus used in this work was collected in Mortágua (Portugal), milled to pass a screen of 6 mm, and stored as a uniform lot in plastic containers at room temperature. Its chemical composition (dry weight basis) is: glucan 36.1 %; hemicellulose 23.8 % (including xylose as the main sugar at an overall content of 13.9 %); Klason Lignin 26.7 %, ash, 3.9 %, protein 2.8 % and 8.2 % of extractives and others.

PE (polyethylene) wastes were selected for this study due to the huge amounts generated per year. The aim was to try to improve and diversify these wastes valorisation. PE wastes were recycled materials with particle sizes between 2 and 3 mm diameter. PE wastes C/H ratio was around 6.0, while that of eucalyptus was about 8.6. PE HHV (high heating value) was 46.4 MJ/kg daf and eucalyptus HHV was 21.4 MJ/kg daf.

2.2 Pre-treatment experimental work

The effects of H_2SO_4 concentration (0 - 2 wt%) and reaction time (isothermal period, 0 - 240 min.) on biomass pre-treatment were studied according to the Doehlert uniform design (Doehlert, 1970). Eucalyptus biomass was mixed with H_2SO_4 aqueous solutions in a liquid to solid ratio of 7 wt. Dilute acid hydrolysis assays were performed in autoclave (AJC, Portugal) at 130 °C, in universal Schott flasks. The hydrolysate (liquid fraction) and the solid residue (cellulolignin), obtained after hydrolysis, were separated using a hydraulic filter press (up to 200 bar) at room temperature. The recovered solid was washed with water. The hydrolysate composition was determined by HPLC as described by Branco et al. (2015), and modelled by linear multiple regression to second-order polynomial models. The optimal conditions were obtained using the Microsoft Excel® Solver tool based on the best-fit equations using a constrained model.

2.3 Co-pyrolysis experimental work

Raw and pre-treated eucalyptus wastes were pyrolysed. In some pyrolysis experiments these two types of biomass wastes were previously mixed with PE wastes in contents that changed from 0 to 100 wt%. PE is easier to pyrolyse than eucalyptus, thus its presence allowed to maximise liquid yield.

Pyrolysis experimental work was carried out in a 1 L autoclave, built of Hastelloy C276, by Parr Instruments. The autoclave was loaded with the waste mixture selected. Afterwards, the autoclave was purged and pressurised to the pre-set value of nitrogen. Then, it was heated and kept at the reaction temperature during the reaction time previously settled. Authors previous work (Paradela et al., 2009) has suggested the following range of conditions for eucalyptus and PE wastes mixture: run temperature of 400 °C, reaction time of 30 minutes and initial pressure of 0.6 MPa.

At the end of the reaction time, the autoclave was cooled down to room temperature and gases were measured, collected and analysed by gas chromatography (GC) to determine the contents of CO, CO_2, H_2, CH_4 and other gaseous hydrocarbons (C_xH_y). Solid and liquid products were weighted. Solids were extracted in a Soxhlet extractor, first with n-hexane and then with tetrahydrofuran to determine the amount of liquids soaked in solids. Liquids were distilled to obtain three fractions: one with a distillation point lower than 150 ºC, other that distillated between 150 and 270 ºC and the liquid residue. Hydrocarbon content in the two lighter fractions were analysed using a Hewlett Packard 6890 Gas Chromatograph.

3. Results and Discussion

3.1 Eucalyptus pre-treatment

The pre-treatment conditions were optimized aiming to remove hemicellulose from the solid biomass and to produce a monosaccharide-rich hydrolysate that could later be used as fermentation media. This framework requires a careful adjustment of the operational conditions, once these two aims can be conflicting. As conditions favouring hemicellulose removal, induce sugar degradation into fermentation inhibitors, most noteworthy furfural (Gírio et al., 2012). As such, the use of a statistical experimental design is of paramount importance, as well as the correct choice of the target variable to be optimized. In this work, the target variable chosen was the difference between the concentration of total monosaccharides present in the hydrolysate (directly correlated to the removal of hemicellulose) and the concentration of potential fermentation inhibitors, furfural, 5-(hydroxymethyl)furfural (HMF), acetic acid and other aliphatic acids.

Figure 1 presents the response surface obtained for the tested experimental domain. Acid concentration was the most relevant operational variable favouring hemicellulose removal, but also monosaccharide degradation (p-value < 0.001). On the other hand, reaction time had lower impact. This model enabled the identification of the best operational conditions (130 ºC, 1.5 % H_2SO_4 and 130 min), that were then validated experimentally. These conditions are relatively mild and easily obtained in industrial conditions. Under these conditions, a liquid phase containing 27 g/L of total sugars was obtained, as well as solid phase to be used for pyrolysis assays. Regarding the solid phase, extractives and soluble ash were removed, together with hemicellulose (close to 85% removal). This induced a relative increase in the lignin and glucan fractions, that accounted for more than 40 %, each, of the recovered solid material (dry basis), thus yielding a biomass material with lower oxygen content. These results agreed with those found in literature (Gírio et al., 2012). The potential energy integration with the pyrolysis process, as the preliminary pinch analysis points out, allows significant reductions on pre-treatment operational costs.

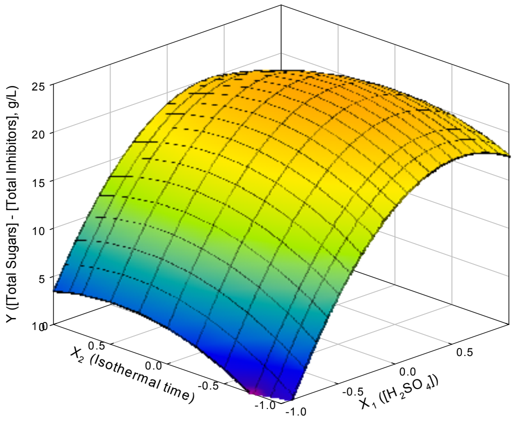


Figure 1: Total sugars minus total inhibitors concentration as a function of acid concentration and reaction time for the pre-treatment process (Multiple R = 0.984, adjusted R2 = 0.949, p-value < 0.001). Independent variables axes are represented as coded variables.

3.2 Co-pyrolysis results

Untreated eucalyptus wastes were blended with different amounts of PE wastes and afterwards co-pyrolysed. Liquid, gases and solid products yields obtained are shown in Figure 2 (dashed lines). Also, the conversion of initial feedstock into gaseous and liquid products is presented. Figure 2 shows that the rise of PE content in the blend favoured the formation of liquid products, while the formation of gases and solids both decreased. Thus, the conversion increase with the rise of PE content is due to the formation of liquid products. These results fairly agree with those found in literature, though obtained for other biomass types (Pinto et al. 2016) and also show that for the conditions tested, PE conversion into liquids was easier than biomass.

Pre-treated eucalyptus wastes were also mixed with PE wastes before co-pyrolysis and the results obtained are also presented in Figure 2 (solid lines). As expected the effect of rising PE content in the feedstock blends was similar to that obtained with raw biomass, as the increase of liquid yields and the decrease of gases and solid yields was observed with the rise of PE. The increase of feedstock conversion into liquids and gases was also observed. However, the use of pre-treated biomass led to higher liquid yields and to lower solids than the values obtained with untreated eucalyptus. When no PE wastes were pyrolysed, the rise observed in liquid yields was around 30 % higher than the corresponding value obtained with untreated eucalyptus. This increase was around 24 % for the blend with 25 % of PE. In Figure 2 can be observed that as the amount of PE increased, the effect of pre-treated eucalyptus on liquid yield diminished, because PE pyrolysis was easier than eucalyptus. Figure 2 also shows that pre-treated biomass led to lower gas yields than untreated eucalyptus. The results obtained so far clearly showed that the pre-treatment favoured biomass pyrolysis and the formation of liquid compounds, which agree with the hypothesis that the pre-treatment weakened biomass initial structure and promoted chemical bonds break down.

Gaseous compounds analysis by GC showed that the rise of PE content in the blend led to the increase of CH_4 and total hydrocarbons (C_xH_y) contents, while both CO and CO_2 were observed to decrease. No clear trends were observed for H_2 release, whose concentration was kept low (below 5 % v/v) for all the tests done, probably because hydrogen is needed to stabilise the radicals initial formed after cracking reactions. These general tendencies were observed for both untreated and pre-treated eucalyptus, though different concentrations were obtained. In general pre-treated eucalyptus led to lower H_2 contents, probably because as biomass cracking was favoured, more radicals were formed which might have consumed more hydrogen for their stabilisation.

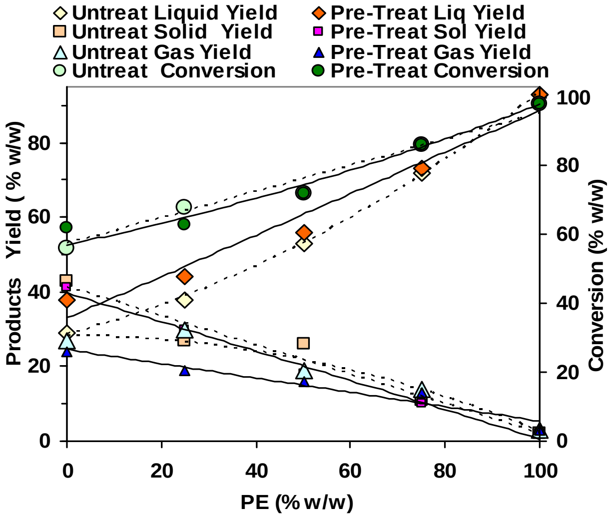
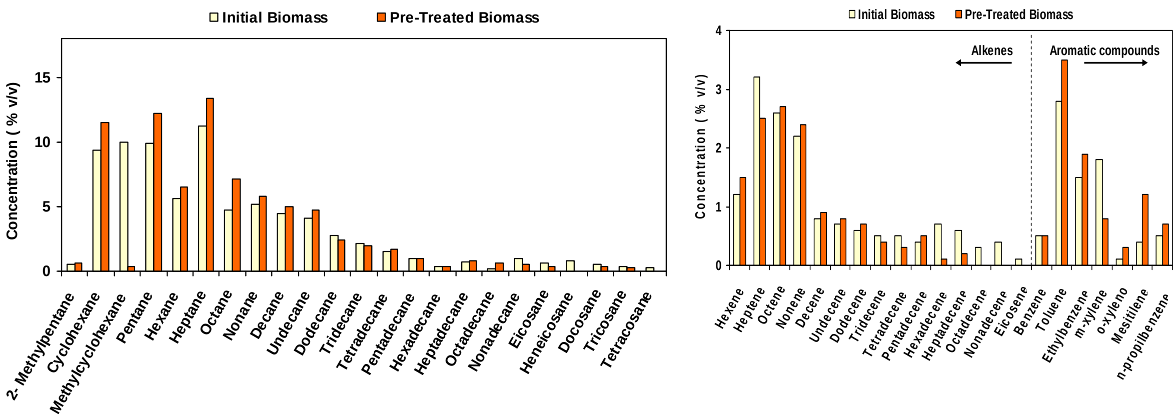


Figure 2: Effect of eucalyptus content on wastes blends on co-pyrolysis products. Solid lines refer to pre-treated eucalyptus and dashed lines to initial and untreated eucalyptus.

The liquid fraction with distillation temperature bellow 270 ºC was analysed by GC. For the blends with higher PE content than biomass, the chromatographic profile was similar to that obtained for PE pyrolysis (Costa et al. 2007). The liquid fraction contained mainly linear alkanes and alkenes with a wide range of carbon numbers, between C_5 and C_{24} for alkanes and C_5 and C_{20} for alkenes (Figure 3). These results agree with those reported by other authors (Marcilla et al. 2009). The linear alkanes presented in higher concentrations, in the liquid pyrolysis product were between pentane and undecane. Alkenes detected in higher contents were those between hexene-1 and nonene-1. In general, alkanes and alkenes concentration decreased with the rise of the number of carbon atoms (Figure 3). The aromatic compounds analysed with the highest contents were toluene, ethylbenzene and m-xylene, which agrees with information reported in literature (Costa et al. 2007). No great changes were observed with pre-treated biomass (Figure 3), due to the reduced amount used (25% w/w). When more biomass was used in the feedstock blends, other compounds were detected, mostly with oxygen atoms, like acids, alcohols, ketones, etc. The full characterization of such compounds was not yet possible, due to their huge number and small concentrations. Liquid yields were reduced with the rise of eucalyptus and lower contents of alkanes and alkenes were obtained.


(a) *Alkanes*

(b) Alkenes and aromatic compounds

Figure 3: Effect of eucalyptus treatment on liquids composition obtained by co-pyrolysis of the blend with 75 wt% of PE. (a) Alkanes. (b) Alkenes and aromatic compounds.

3.3 Integrated process of auto hydrolysis and co-pyrolysis

Different pathways were analyzed considering untreated and pre-treated eucalyptus:

I) Pyrolysis of untreated eucalyptus
II) Pyrolysis of pre-treated eucalyptus
III) Pyrolysis of untreated eucalyptus blended with PE
IV) Pyrolysis of pre-treated eucalyptus blended with PE

To improve the versatility of the global process, it was also considered to blend untreated and pre-treated eucalyptus with PE wastes, as plastics are easier to pyrolysis than biomass and the products obtained by plastics pyrolysis are richer in hydrocarbons.

The pre-treatment process removed the hemicellulose fraction and the remaining solid rich in lignin showed to be suitable for co-pyrolysis. As the pre-treatment process weakened the initial macromolecular structure of eucalyptus the following cracking reactions that occurred during pyrolysis were facilitated, which led to higher contents of liquid products. Therefore, the results obtained so far have shown that the use of pre-treated eucalyptus improved biomass pyrolysis and its conversion into liquid products. Besides, this pre-treatment led to the production of added value products, mainly sugar-based compounds. These compounds may be used as raw material in several industries.

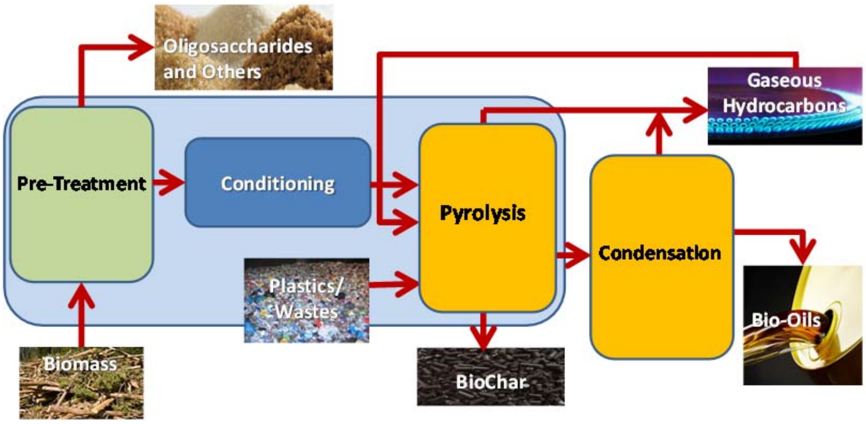


Figure 4: General concept for converting eucalyptus and PE wastes into valuable products.

The technical analysis of these pathways showed that pyrolysis of pre-treated eucalyptus blended with PE is the most promising one. Though, this process has the highest overall cost, the market price of the added value compounds produced by auto hydrolysis may be enough to compensate the rise of operation costs. Thus, in Figure 4 are shown the general concept for converting eucalyptus and PE wastes into valuable products, considering pathways IV) Pyrolysis of pre-treated eucalyptus blended with PE. Between pre-treatment and pyrolysis, a conditioning operation was considered to adjust biomass characteristics to those required by pyrolysis, namely moisture content. Though the technical advantages of the general concept presented in Figure 4, this subject needs to be further analysed focusing on the overall economic analysis. Suitable energy integration between biomass pre-treatment and pyrolysis process would significantly reduce the overall operational costs.

4. Main Conclusions

Biomass pre-treatment under mild acidic conditions enabled the recovery of a sugar-rich stream with low concentrations of sugar degradation products. This hydrolysate is an added-value stream that can be easily converted by fermentation. The pre-treated biomass was enriched in lignin and glucan and presented a lower oxygen content which favoured its use as feedstock for pyrolysis. The initial biomass macromolecular structure was weakened by the pre-treated process, which favoured chemical bonds breakdown occurring during pyrolysis, thus leading to higher production of liquid products.

Co-pyrolysis of pre-treated eucalyptus bended with PE wastes is a technical viable option, as PE wastes are easier to pyrolysis than biomass and the products obtained by plastics pyrolysis are richer in hydrocarbons. Besides, the versatility of the global process is increased.

The better properties presented by the bio-oil produced from pre-treated biomass, together with the recovery of the valuable sugar-rich hydrolysate, suggest a higher economical potential of this valorisation strategy that must be explored further.

Acknowledgments

This article is a result of the project BIOFABXXI - POlisboa-01-0247-FEDER-017661, supported by Operational Programme for Competitiveness and Internationalization (COMPETE2020) and by Lisbon Portugal Regional Operational Programme (Lisboa 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF).

The authors thank Céu Penedo and Belina Ribeiro for their technical support.

Reference

Branco P.C., Dionisio A.M., Torrado I., Carvalheiro F., Castilho P.C., Duarte L.C., 2015, Autohydrolysis of *Annona cherimola* Mill. seeds: Optimization, modelling and products characterization, Biochemical Engineering Journal, 104, 2-9, DOI:10.1016/j.bej.2015.06.006.

Bridgwater A.V., 2012, Review of fast pyrolysis of biomass and product upgrading, Biomass and Bioenergy, 38, 68-94, DOI: 10.1016/j.biombioe.2011.01.048.

Costa P., Pinto F., Ramos A.M., Gulyurtlu I., Cabrita I., Bernardo M.S., 2007, Kinetic study of polyethylene pyrolysis, Energy & Fuels, 21, 5, 2489-2498, DOI: 10.1021/ef070115p.

Doehlert, D. H., 1970, Uniform shell designs, Applied Statistics, 19, 231-239, DOI: 10.2307/2346327.

Gírio F.M., Carvalheiro F., Duarte L.C., Bogel-Lukasik R., 2012, Deconstruction of the hemicellulose fraction from lignocellulosic materials into simple sugars, p 3-37. In da Silva SS, Chandel AK (ed), D-Xylitol DOI:10.1007/978-3-642-31887-0_1. Springer-Verlag, Berlin.

Kaminsky W., Zorriqueta I.-J.N., 2007, Catalytical and thermal pyrolysis of polyolefins, Journal of Analytical and Applied Pyrolysis, 79, 368–374, DOI: 10.1016/j.jaap.2006.11.005.

Kumara S., Panda A.K., Singh R.K., 2011, A review on tertiary recycling of high-density polyethylene to fuel, Resources, Conservation and Recycling, 55, 893– 910, DOI: 10.1016/j.resconrec.2011.05.005.

Marcilla A., Beltrán M.I., Navarro R., 2009, Evolution of products during the degradation of polyethylene in a batch reactor, Journal of Analytical and Applied Pyrolysis, 86, 14–21, DOI: 10.1016/j.jaap.2009.03.004.

Moniz P., Ho A.L., Duarte L.C., Kolida S., Rastall R.A., Pereira H., Carvalheiro F., 2016, Assessment of the bifidogenic effect of substituted xylo-oligosaccharides obtained from corn straw. Carbohydrate Polymers,136, 466-473, DOI: 10.1016/j.carbpol.2015.09.046.

Paradela F., Pinto F., Gulyurtlu, I., Cabrita, I., Lapa, N., 2009, Study of the co-pyrolysis of biomass and plastic wastes, Clean Technologies and Environment Policy, 1, 115-122, DOI: 10.1007/s10098-008-0176-1.

Pinto F., Costa P., Miranda M., 2016, Production of liquid hydrocarbons from rice crop wastes mixtures by co-pyrolysis and co-hydropyrolysis, Fuel, 174, 153–163, DOI: 10.1016/j.fuel.2016.01.075.