

CO-PYROLYSIS OF VARIOUS LIGNINS WITH POLYCARBONATE

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The co-pyrolysis of bisphenol A polycarbonate with lignins of various origin and obtaining procedures (Klason annual plants, Organosolv hardwood and Lignoboost softwood lignin) were comparatively studied with a focus on product yield and oil composition. Similarities and differences among studied lignins were observed and discussed. Lignoboost lignin gave the highest oil yield and the lowest amount of residue. Organosolv hardwood yielded significant amounts of syringol, methylsyringol and isovanillic acid, while Lignoboost lignin yielded more guaiacol and its methyl- and ethyl-derivatives. Residual acetic acid and sulphur compounds from the obtaining procedures were found for Organosolv hardwood and Lignoboost lignin.

Keywords: co-pyrolysis, Klason, Organosolv, Lignoboost, polycarbonate

INTRODUCTION

Lignocellulosic biomass, such as agricultural and forestry residues or energy crops, etc., is the cheapest and most abundant form of biomass, which supplies about 14% of the world's energy needs.^{1,2} Lignin is a major component of wood, together with cellulose and hemicellulose, representing about 4-35 wt% of most biomass, 16-25 wt% of hardwoods and 23-35 wt% of softwoods.³ It is the second largest source of organic raw material⁴ and the most abundant aromatic natural polymer.⁵ Vast quantities of lignin are available as a waste by-product of the pulp and paper industry and other forest product industries (such as lumber milling). Lignin is also a major by-product of the growing second-generation biofuel industry. Lignin presents strong interest due to the fact that it is one of the few naturally produced aromatic chemical precursors; therefore it has been proposed as an alternative source of chemicals or hydrocarbon fuels^{6,7} for saving coal and petroleum.

Pyrolysis of biomass has received strong interest in recent decades, when the awareness on limited amounts of fossil resources asked for alternative solutions based on renewable materials. Many kinds of biomass species have been subjected to pyrolysis conditions to produce fuels, solvents and chemicals,^{8,9} but the challenge is the economical separation of products for the chemicals and the liquid fuels markets. Pyrolysis was proved to be a simple thermochemical way to transform lignin into low molecular weight

compounds.^{10,11} However, due to its complex composition and to its highly branched, three-dimensional phenolic structure, lignin pyrolysis leaves significant amounts of residue and the produced oils are rich in oxygen-containing compounds.

Co-pyrolysis of biomass with synthetic polymers was considered as a possibility to enhance the liquid production from biomass and to decrease the oxygen content of the pyrolysis oils, since polyolefins contain about 14 wt% hydrogen.¹²⁻¹⁵ Synthetic polymers could act as a hydrogen source in thermal coprocessing with organic natural materials with less hydrogen content, such as coal or biomass.¹⁶ The synergistic effects observed for co-liquefaction of coal-plastic mixtures lead to an increase in oil yields.¹⁷ Biomass has low C content of 47-51 wt% and high O content of 42-46 wt%, while synthetic polymeric materials, such as waste plastics or tires, have very high C content – of about 84 wt%, and low O content – of about 1.5 wt%. Coprocessing of synthetic polymers with biomass could balance the C, O and H in the feedstock, with strong effects on the properties of degradation products. Biomass has lower thermal stability compared to plastics and thus it could affect their radical degradation mechanism by promoting the degradation of synthetic macromolecules.¹⁸ In the co-pyrolysis, the yields and composition of the products strongly depend on the treatment method, processing conditions,

type of biomass and of synthetic polymers.

We previously described the recent knowledge acquired on the thermal degradation of lignin as an approach to obtain valuable chemicals or hydrocarbon fuel¹⁹ and we reported on the thermal behaviour of organic materials, such as keratin waste²⁰ or various lignin based materials.^{21,22} We also published our results on the co-pyrolysis of pine cones with synthetic polymers,²³ of LignoBoost lignin with various synthetic polymers²⁴ and of vegetable cooking oil with polycarbonate.²⁵ Here, we present a study on the thermal co-pyrolysis of various lignins with bisphenol A polycarbonate, which showed promising results due to the similar phenolic nature of the starting materials.

EXPERIMENTAL

Three lignin powder samples of different origin and obtained by different procedures were considered for this study, as following: lignin separated by Klason method from the straw of common wheat annual plant (Klason annual plants), Organosolv lignin extracted with acetic acid from birch wood (Organosolv hardwood) and LignoBoost lignin precipitated from the black liquor resulted from softwoods in kraft mills (LignoBoost softwood). The samples were used as received, without preliminary drying. Bisphenol A polycarbonate (PC) was considered as a representative synthetic polymer for co-pyrolysis due to its phenolic structure, based on our previous results.²⁴

Pyrolysis was performed in a semi-batch tubular glass reactor, which is schematically shown in Fig. 1. Amounts of 0.5 g of lignin and polycarbonate mixtures in 1:1 wt ratio were used for degradation. Two furnaces were considered for independent heating of different zones of the reactor. Firstly, the upper part of the reactor, containing a layer of about 0.03 g quartz wool, was heated at 300 °C. Then the bottom part of the reactor, containing the pyrolysis sample, was

gradually heated by 10 °C min/min up to the final degradation temperature of 500 °C. The set-up allows controlled conditions for catalytic upgrading of the pyrolysis products; however this will be subject of another study, where the present results will stand as reference. The volatile degradation products were cooled in an ice trap that separated the condensable (liquid) and non-condensable (gas) fractions.

Co-pyrolysis of lignin with PC gives an aqueous phase and an oil one. Water comes both from the humidity of the lignin and from the thermal degradation of the lignin structure. The oil phase contains the liquid products from degradation of PC that solubilizes the tar from lignin. Since pyrolysis of lignin gives mainly polar, oxygen-containing compounds, some of them distribute between water and oil phase. Diethyl ether was added to the co-pyrolysis liquid products to extract most of the organic compounds from the aqueous phase. Diethyl ether was also used to remove the pyrolysis oil from the cold parts of the reactor and from the glass lines. The aqueous phase was separated by density from the ether one and it was washed several times with diethyl ether for advanced extraction of organic compounds; its final amount was considered for calculation of the product yield. Since high amounts of diethyl ether were used in the procedure, the final fraction was partially concentrated under vacuum at room temperature, before analysis by gas chromatography.

GC-MSD analysis was performed on a 6890N Agilent gas chromatograph coupled with a 5975 inert XL Agilent mass selective detector, working at 70 eV, over an HP5-MS (30 m × 0.25 mm × 0.25 μm) column packed with (5%-phenyl)-methylpolysiloxane. The following parameters were used: injector – 230 °C; split ratio – 10:1; flow rate – 1 ml min⁻¹; temperature program – 40 °C (2 min), 10 °C min⁻¹ up to 250 °C (7 min); sample amount – 0.2 μl. Qualitative identification of the compounds was performed based on NIST database of MS spectra.

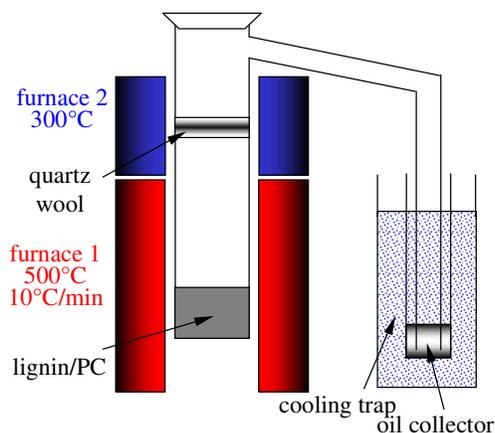


Figure 1: Set-up for two-stage co-pyrolysis of lignin with polycarbonate

RESULTS AND DISCUSSION

Lignoboost lignin gave different yields of products from the co-pyrolysis with PC, compared to Klason annual plants and Organosolv hardwood lignins, which gave similar results, as shown in Fig. 2. Due to their phenolic structures prone to crosslinking, lignins and polycarbonates leave high amounts of solid residue after pyrolysis. This was also valid for the co-pyrolysis of Klason annual plants and of Organosolv hardwood with PC (~46 wt%), while less residue (31 wt%) remained from Lignoboost lignin with PC. Also, the co-pyrolysis of Klason

annual plants and Organosolv hardwood with PC produced a similar amount of oils (~36 wt%), but the former yielded slightly more gases (16 wt% compared with 13 wt%) and less aqueous phase (2 wt% compared with 4 wt%). Lignoboost lignin increased the oil yield to 48.5 wt%, the yield of aqueous phase being also higher (9 wt%).

The distribution of compounds in co-pyrolysis oils is described by the NP-gram curves (NP stands for normal paraffins) drawn in Fig. 3, based on the GC-MSD chromatograms shown in Fig. 4; the amount of main compounds in co-pyrolysis oils is shown in Fig. 5.

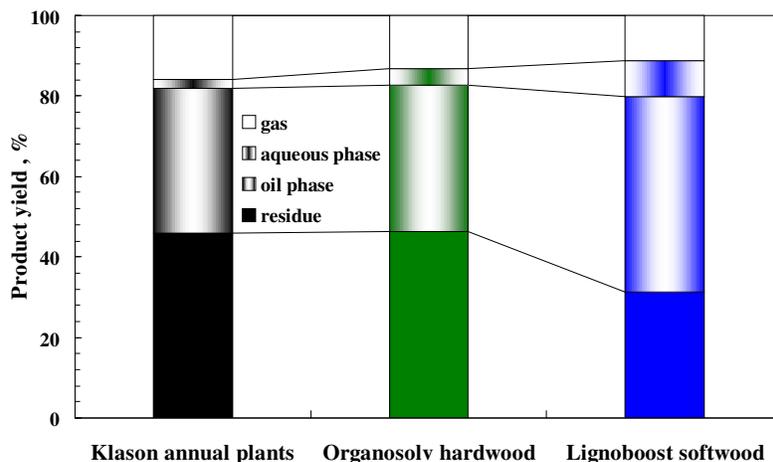


Figure 2: Product yield from co-pyrolysis of various lignins with bisphenol A polycarbonate

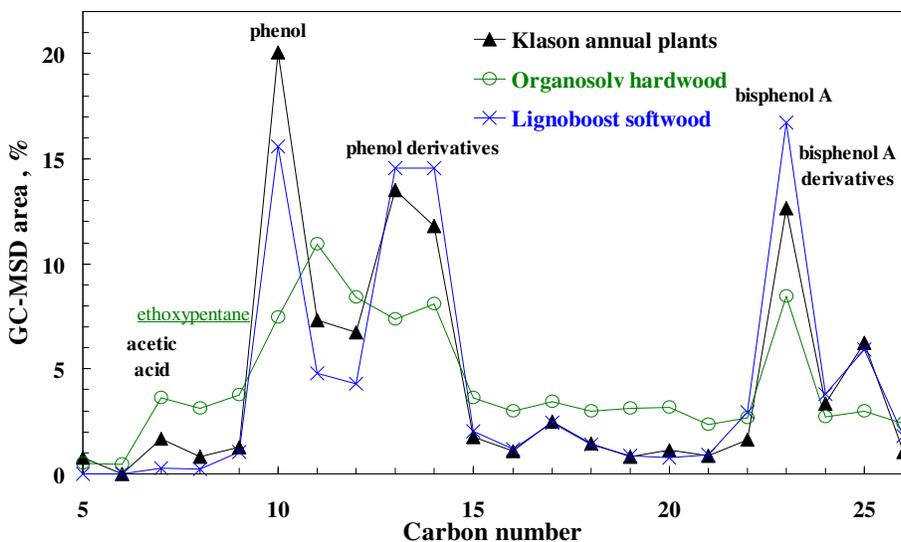


Figure 3: C-NP grams of co-pyrolysis oils from various lignins and bisphenol A polycarbonate

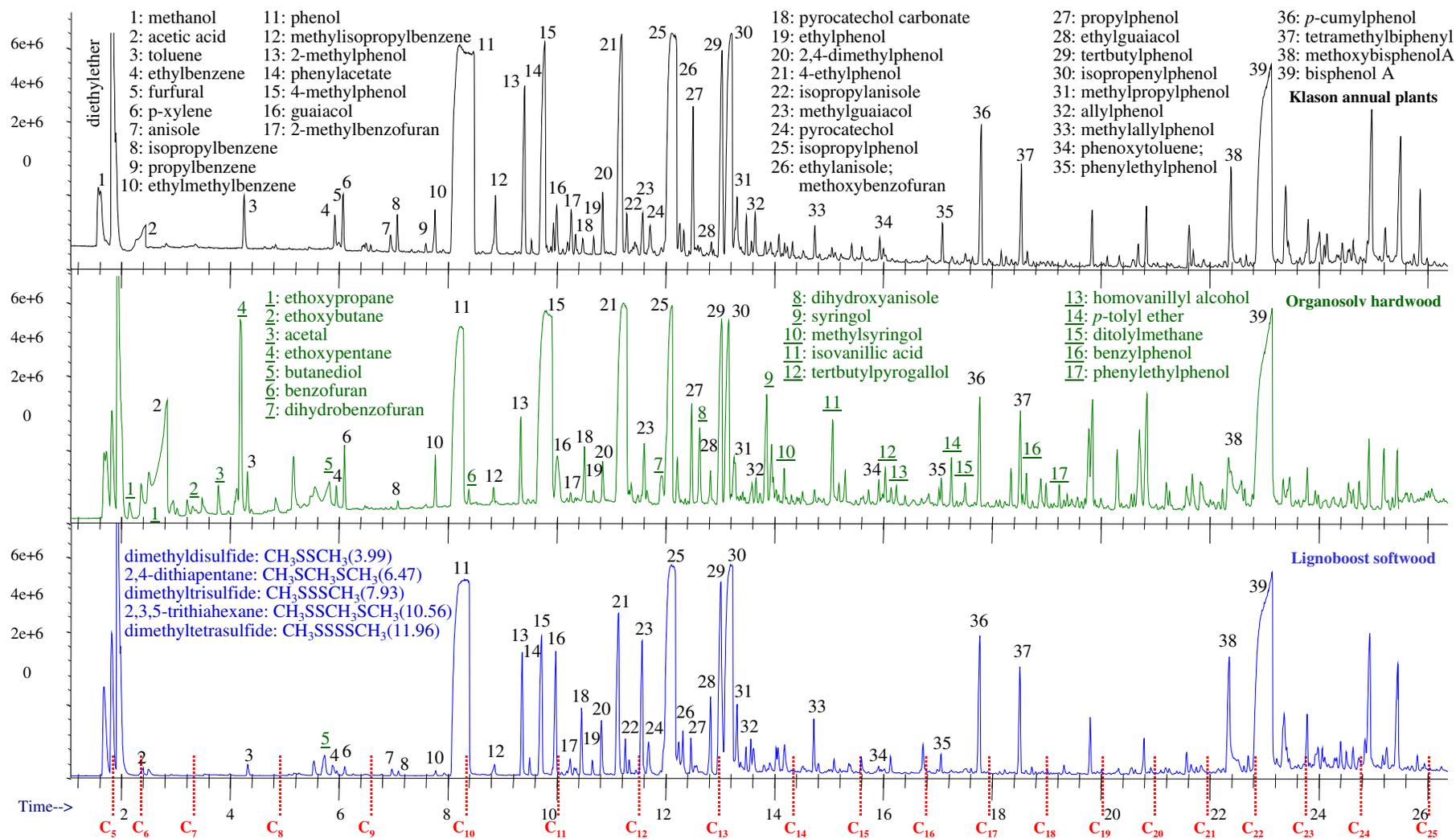


Figure 4: GC-MSD chromatograms of co-pyrolysis oils from various lignins and bisphenol A polycarbonate

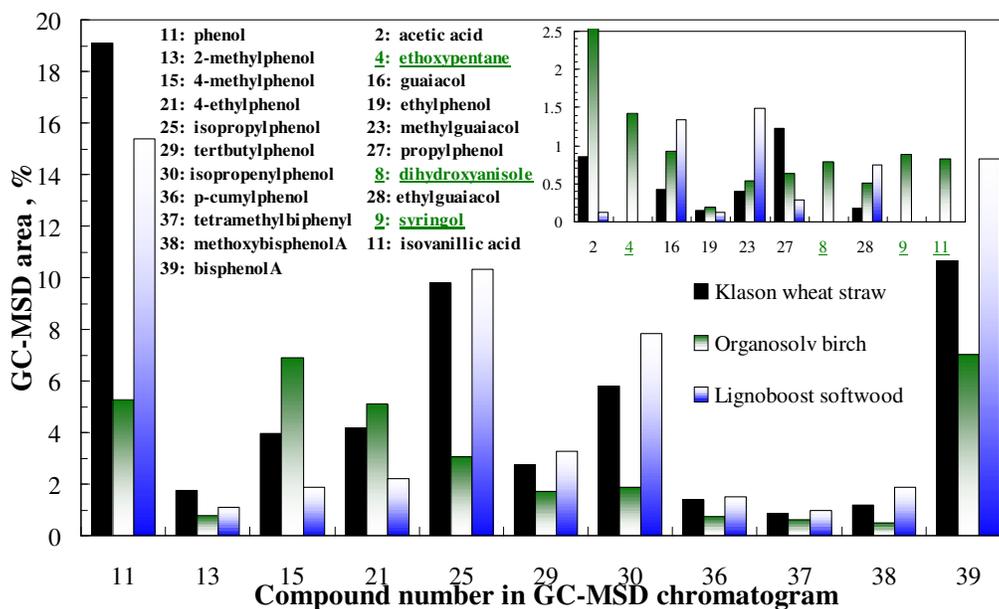


Figure 5: Amount of main compounds in co-pyrolysis oils from various lignins and bisphenol A polycarbonate

Co-pyrolysis oils from Klason annual plants and from Lignoboost lignin with PC had a similar distribution of compounds, with four main peaks in the NP-gram, at nC_{10} , nC_{13} - nC_{14} , nC_{23} and nC_{25} , but with slight changes of the amount of compounds corresponding to each peak. These stand mainly for phenol, phenol derivatives, bisphenol A and bisphenol A derivatives, respectively. The co-pyrolysis of Organosolv hardwood with PC resulted in a more uniform distribution of compounds, with higher amounts in the nC_7 - nC_8 and nC_{16} - nC_{21} ranges of the NP gram. Especially the acetic acid at nC_7 was found in high amounts (2.5%, Fig. 6), compared with the other samples (0.9% for Klason annual plants and lower for Lignoboost lignins), and this is caused mainly by the residual acetic acid delignification agent used in the Organosolv process. The peaks at nC_{13} - nC_{14} , nC_{23} and nC_{25} were similar with those for Klason annual plants and Lignoboost lignin, but they were much smaller, while the peak at nC_{10} was shifted to nC_{11} .

As expected from the structure of the starting materials, the main compounds obtained from the co-pyrolysis of lignins with PC are phenol and bisphenol A, together with their derivatives. In terms of GC-MSD peak area percent, phenol (compound 11, at nC_8 , in Fig. 5) represented 19.1% and bisphenol A (compound 39, at nC_{23}) was 10.9% of the total

area of the chromatogram for co-pyrolysis of Klason annual plants with PC, the following compounds, in decreasing order of the peak area, being isopropylphenol (compound 25, at nC_{13} – 9.8%), isopropenylphenol (compound 30, at nC_{14} – 5.8%), 4-ethylphenol (compound 21, at nC_{12} – 4.2%), 4-methylphenol (compound 15, at nC_{11} – 3.9%), tertbutylphenol (compound 29, at nC_{14} – 2.7%), 2-methylphenol (compound 13, at nC_{11} – 1.8%), p-cumylphenol (compound 36, at nC_{17} – 1.4%), propylphenol (compound 27, at nC_{13} – 1.2%) and methoxybisphenol A (compound 38, at nC_{22} – 1.2%), the other compounds having a peak area below 1% from the total area of the chromatogram.

Organosolv hardwood yielded some additional compounds upon co-pyrolysis with PC, from which ethoxypentane (compound 4, at nC_8), dihydroxyanisole (compound 8, at nC_{13}), syringol and methylsyringol (compounds 9 and 10, at nC_{14}) and isovanillic acid (compound 11, at nC_{15}) were found in the highest amounts – Fig. 5. However these compounds were not found in significant amounts in the co-pyrolysis oils of PC with Lignoboost lignin. Organosolv hardwood yielded the highest amounts of 4-methylphenol (compound 15, at nC_{11}) and 4-ethylphenol (compound 21, at nC_{12}), to the detriment of phenol or its heavier derivatives and bisphenol

A (Fig. 5), but it gave high amounts of compounds in the 19.5-21 min range of the retention time (nC₁₉-nC₂₀ in Fig. 4), which were found to be diaromatic degradation products of bisphenol A.

Lignoboost lignin decreased the amounts of 4-methylphenol and of 4-ethylphenol, but increased the amounts of guaiacol (compound 16, at nC₁₁) and its methyl- and ethyl-derivatives (compounds 23 and 28, at nC₁₃ in Fig. 5). Small amounts of sulphur containing compounds, listed in Fig. 4, were found in the co-pyrolysis oils of PC with Lignoboost lignins; they originate from the Kraft pulping that provides the black liquor from which lignin is obtained by the Lignoboost process.

CONCLUSION

This study presents a part of our results on the co-pyrolysis of natural polymers with synthetic ones. Lignins of various origin and obtaining procedures and bisphenol A polycarbonate were considered due to their phenolic structure. Co-pyrolysis was performed at 500 °C, but the volatile degradation products were passed through a layer of quartz wool maintained at 300 °C. The interactions at high temperatures between PC and lignins were more favourable for Lignoboost, leading to higher oil yields (with about 13 wt%) and reduced amounts of residue (10-15 wt%). The composition of co-pyrolysis oils depended on the starting lignins. However phenol, bisphenol A and their derivatives were the most important compounds in all cases.

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REFERENCES

¹ A. Faaij, *Mitig. Adapt. Strateg. Glob. Change*, **11**, 343 (2006).
² C. Di Blasi, *Prog. Energ. Combust. Sci.*, **34**, 47 (2008).

³ A. V. Bridgwater, *Therm. Sci.*, **8**, 21 (2004).
⁴ R. J. A. Gosselink, E. de Jong, B. Guran and A. Abächerli, *Ind. Crop. Prod.*, **20**, 121 (2004).
⁵ J. H. Lora and W. G. Glasser, *J. Polym. Environ.*, **10**, 39 (2002).
⁶ S. Karagöz, T. Bhaskar, A. Muto and Y. Sakata, *Fuel*, **84**, 875 (2005).
⁷ G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, **106**, 4044 (2006).
⁸ S. Yaman, *Energ. Convers. Manage.*, **45**, 651 (2004).
⁹ T. Sonobe and N. Worasuwannarak, *Fuel*, **87**, 414 (2008).
¹⁰ D. Vamvuka, *Int. J. Energ. Res.*, **35**, 835 (2011).
¹¹ J. E. G. van Dam, M. J. A. van den Oever, W. Teunissen, E. R. P. Keijzers and A. G. Peralta, *Ind. Crop. Prod.*, **19**, 207 (2004).
¹² V. I. Sharypov, N. Marin, N. G. Beregovtsova, S. V. Baryshnikov, B. N. Kuznetsov *et al.*, *J. Anal. Appl. Pyrol.*, **64**, 15 (2002).
¹³ N. Marin, S. Collura, V. I. Sharypov, N. G. Beregovtsova, S. V. Baryshnikov *et al.*, *J. Anal. Appl. Pyrol.*, **65**, 41 (2002).
¹⁴ V. I. Sharypov, N. G. Beregovtsova, B. N. Kuznetsov, L. Membrado, V. L. Cebolla *et al.*, *J. Anal. Appl. Pyrol.*, **67**, 325 (2003).
¹⁵ V. I. Sharypov, N. G. Beregovtsova, B. N. Kuznetsov, S. V. Baryshnikov, V. L. Cebolla *et al.*, *J. Anal. Appl. Pyrol.*, **76**, 265 (2006).
¹⁶ C. Vasile and M. A. Brebu, *Cellulose Chem. Technol.*, **40**, 489 (2006).
¹⁷ A. Sinag, M. Sungur and M. Canel, *Energ. Fuels*, **20**, 1609 (2006).
¹⁸ E. Jakab, G. Varhegyi and O. Faix, *J. Anal. Appl. Pyrol.*, **56**, 273 (2000).
¹⁹ M. Brebu and C. Vasile, *Cellulose Chem. Technol.*, **44**, 353 (2010).
²⁰ M. Brebu and I. Spiridon, *J. Anal. Appl. Pyrol.*, **91**, 288 (2011).
²¹ M. Brebu, G. Cazacu and O. Chirila, *Cellulose Chem. Technol.*, **45**, 43 (2011).
²² M. Brebu and I. Spiridon, *J. Anal. Appl. Pyrol.*, <http://dx.doi.org/10.1016/j.jaap.2013.05.016>.
²³ M. Brebu, S. Ucar, C. Vasile and J. Yanik, *Fuel*, **89**, 1911 (2010).
²⁴ M. Brebu and I. Spiridon, *Polym. Degrad. Stabil.*, **97**, 2104 (2012).
²⁵ N. M. M. Mitan, M. Brebu, T. Bhaskar, A. Muto, Y. Sakata *et al.*, *J. Mater. Cycles. Waste. Manag.*, **9**, 62 (2007).