COMBINATION OF ANALYTICAL PYROLYSIS AND FRACTIONATION OF TECHNICAL LIGNIN AS A TOOL FOR IMPROVEMENT OF ITS ANTIOXIDANT PROPERTIES

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The modern biorefinery concept is aimed at the elaboration of sustainable processes with the most profitable utilization of all products obtained at the technological cycle. Lignins separated as by-products in the result of lignocellulosic chemical processing are recognized as an important component of polymer systems. The presence of sterically hindered phenolic hydroxyl groups in lignin macromolecule opens the possibility of its application as antioxidant for composites, e.g. polyurethanes (PU), which are considered as one of the most versatile polymeric materials. In the present work, the object of investigations was lignin obtained as a by-product of wheat straw processing for pulp and fuel ethanol production (CIMV pilot plant, France). However, high heterogeneity of CIMV lignin negatively influences its applicability that can be avoided by fractionation. Three soluble fractions were isolated from CIMV lignin by a sequential extraction with dichlomethane (A fraction), methanol (B fraction) and mixture of both the solvents (C fraction) and characterised in terms of their composition and structure using analytical pyrolysis (Py-GC/MS). It was found that volatile products from A fraction pyrolysis was highly enriched with aliphatic compounds originated from waxes and parafinics of wheat straw. The lignin component of this fraction contained the highest amount of syringyl sub-structures in comparison with parent lignin and both other soluble fractions. The B fraction was characterized with the highest amount of lignin guaiacyl sub-structures and carbohydrate admixtures as well. The C fraction was the most condensed among others that coincided with its lowest functionality in terms of phenolic hydroxyl groups. Application of Py-GC/MS method opened an opportunity to found some novel correlations "structure-activity" needed for understanding and tuning of antioxidant properties of lignins.

Antioxidant properties of parent lignin and its fractions was assessed in the tests with free radicals $ABTS^{\bullet+}$ and $DPPH^{\bullet}$. It was shown that radical scavenging activities of B and C fractions in the $DPPH^{\bullet}$ assay were some higher than those for both parent lignin and A fraction. It was shown that increasing ratio between content of syringyl and guaiacyl substructures and the extent of conjugation of lignin macromolecule (Py-GC/MS data) enhanced lignin radical scavenging capacity. The compositional heterogeneity (the presence of lipophillic extractives) had negative impact on the lignin radical scavenging capacity. The antioxidant activity of the fractions under investigation was tested by their influence on thermo-oxidative destruction of PU films The data of TGA method (oxidative conditions) clearly testified the antioxidant effect of all three fractions with the most prominent activity for B fraction. The shifting of the exothermal maxima connected with oxidizing of volatiles products of PU destruction and char combustion to the higher

temperature region by 20-30K and 30-40K was registered. The action of lignin-based antioxidants manifested itself also in increasing the temperature of 50% mass loss by PU from 637K (control PU sample) up to 673K (PU with lignin-based antioxidants).

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