University of West Hungary

Thesis of Ph.D. Dissertation

THERMAL CHANGES OF FLAVONOLS AND WOOD

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I. Object and aim of study

Wood is often exposed to the effect of heating during its processing like steaming, drying, and the production of chipboard. In this case the temperature does not exceed 200 °C and the thermal treatment most often – except drying – does not take long, maximum for 1-2 hours.

On the effect of heating complex chemical and physical-chemical processes take place in wood. These processes are influenced by the anatomical and the chemical structure of the examined wood, as well as the applied temperature-range, the time of heat treatment and heating rate. These factors basically modify how heat can get into the wood. Short-timed treatment causes only surface changes.

The thermal degradation of wood has been studied for ages in details, but only a few examinations have been carried out on changes at mild-temperature. The mild-temperature treatment (100-200 °C) results in the change of colour and spectral properties of wood.

Woods having bigger extent of discolouration are more resistant to enviromental-biological effects. Lignin and extractives – first of all flavonoids – play the most important role in the colour change of wood. As the quality and quantity of flavonoids are peculiar to the kind of timber, the wood colour considerably depends on the kind of timber as well. Extractives are sensitive to enviromental effects (e.g. temperature, light), thus external conditions influence the colour of wood. It is evident that the colour change due to heating is in connection with chemical processes. The examination of the chemical properties of extractives can give useful advise to avoid colour changes during wood-processing.

My research project is:

- to investigate the processes produced by thermal treatment in two different kinds of wood,
- to characterize the thermal degradation of wood by means of changes of flavonoids in wood,
- to examine the thermal and spectral properties of characteristic flavonoids in wood,
- to find out if structural factors influence the thermal stability of flavonols (number and position of various hydroxyl-groups, glycosidic linkage),
- to support degradation processes with different spectroscopic methods (UV-VIS, MALDI-MS).

II. Materials and methods

For experiments two different kinds of wood were chosen: black locust ((*Robinia pseudoacacia L.)* having specific and large quantity of extractives and poplar (*Populus nigra L.*) containing slight amount of flavonoids. The resistance of the two examined wood was very different. The flavonoid content of black locust could be extracted by acetone-water 1:1 solution, thus it became suitable for studying effect of flavonols. As the representative of extractives the two most characteristic flavonols of hardwood, the robinetin, quercetin and their homologe compounds (fisetin, kaempferol, myricetin) and glycosides (rutin, myricitrin) were examined.

The colour changes during heating were monitored by MINOLTA CM-2002 spectrophotometer. Results were given in CIELAB ($L^*a^*b^*$) colour measurement system. From wood-samples were made 30×30×5 mm-sized sample. 10^{-2} mol/dm^3 concentration of metanolic solution of flavonoids were used for measurements, which were impregnated into silica gel surface. High-powered drying-box was used for the thermal treatment. The samples were heated for 120 minutes at four different temperatures in the range of 140-190 °C.

PERKIN ELMER Thermal Analyzer were used for thermogravimetrial (TG) and differential scanning calorimetrial (DSC) investigations. A heating rate of 10, 20, 40 °C/min and low sample masses (1-3 mg) were applied. The measurements were done in nitrogen and air atmosphere, and the used temperature range was between 40-500 °C.

Spectrophotometric measurements were carried out with a Shimadzu UV-3101PC type UV-VIS-NIR Scanning Spectrophotometer with using 10 mm quartz cuvette or reflection supplement. The UV-VIS absorption spectra were recorded in the range of 200 to 500 nm. The spectra were evaluated by version 3.9 of UV-2101/3101 PC Personal Spectroscopy Software. The solutions of flavonoids ($7{,}0 \cdot 10^{-5}$) were prepared in abs. ethanol by direct weighing for investigations of properties of flavonoids in solution. The solutions were made after heating of solid samples. For measuring light absorption on inert (silica gel) surface $2{,}0 \cdot 10^{-3}$ mol/dm^{-3} concentration of methanolic solution of flavonols were used. The TLC sheets were covered evenly with flavonoid solution, than the heat treatment was carried out in drying-box.

Finnigan LASERMAT 2000 MALDI-TOF Spectrometer was used for mass-spectrometric measurements. The solutions of flavonoids were prepared in 70:30 volumetric mixture of acetonitril and distilled water. The flavonoid concentrations were about 10^{-2} mol/dm^3. The spectra were recorded of samples dried up from solution without adding a matrix.

III. Summary of the results of the research

During the investigation of the processes produced by thermal treatment in wood of *Robinia pseudoacacia, Populus nigra* and in chosen model-compounds of flavonoids the following were established:

1. The examination of the colour changes of hardwood due to heating showed that changes depend on the time and temperature of heating. Character of colour changes of wood can be classify on the type of chemical structures of wood flavonoids. Extent of colour change is most significant of wood containing robinetin or flavonoids with similar chemical structures.
2. It was identical in character of the colour change caused by heating with spectral properties in dependence on time and temperature, too. The results indicate that the measuring of the brightness-difference change can detect the chemical change of wood well, in spite of the fact that any process of concrete chemical compounds can not be ordered to change.

3. Thermogravimetrial (TG) curves of wood showed that black locust containing large amount of flavonoids decompose at higher temperature than poplar and extracted black locust. To add robinetin to sample of extracted black locust the TG curve was the same as the curve of original wood sample. The results of thermal analysis proved that flavonoids influence the thermal changes of wood.
4. It was established that the colour changes of quercetin and robinetin caused by heat treatment were different (it derives from their dissimilar chemical structure), which indicate various processes, too. The colour changes of flavonol homologes were analogous with the two model-compounds.
5. The examination of the thermal behaviour of flavonols established that the chemical structure is closely related to thermal stability even in case of small differences existing between flavonol homologes. It was found that the number and position of various hydroxyl-groups play an important role in the thermal properties of flavonol compounds:

5.1. It was determined from the studying of the homologe-compounds that thermal stability of the molecule increases with the OH-group number on the B ring. The most stable were robinetin and myricetin having three hydroxyl-groups on the B ring (they are decomposed at higher temperature and also the degree of mass decrease is lower).

5.2. The comparison of flavonols forming one another structural isomer indicated that also the position of hydroxyl-groups influences the thermal decay of molecules. Here it is also valid that compounds containing more OH-groups on the B ring are more thermal stable. In case of compounds having the same B ring, the presence of OH-group in the 5^{th} position increases the decomposition temperature further.

5.3. I have come to the conclusion that the thermal stability of flavonoid glycosides are the smallest. Molecules are decomposed at lower temperature with the cleavage of glycosidic bond.

6. Such peculiarity of flavonols was observed during my DSC investigations, which had not been described earlier in the literature. During the thermal heating and the following cooling reversible structural rearrangement take place in crystal structure of molecules. However, the verification of this supposition demands further investigations.
7. The investigations of spectral changes of heated quercetin and robinetin on silica gel surface supported the results of colour changes well. The processes taking place at lower and higher temperature diverge basically from one another. It was proved by the two kinds of measurement methods that the process mechanism of the two model-compounds was different.

8. The spectra of heated quercetin and robinetin recording on inert surface refered to formation of quinoidal stucture. The quinoidal structure conduces to dimerization which has been proved by mass spectrometric measurements. The results of flavonols supported the rapid colour changes of wood containing extractives due to heating.

IV. Proposals for utilization of the results

The consequences of my research lead to some new scientific results in wood-chemistry, which can be served as explanations of the chemical processes proceeded during the change of the physical properties of heat treated wood. Beside physical properties also dynamical-mechanical features of wood change during the heat treatment, thus in what follows it will be suitable to examine these parameters and wettability, too.

The investigations of the thermal degradation processes of flavonoids on silica gel surface, the results have provided explanation of colour changes on wood surface. Further examinations are demanded for kinetic and structural interpretation of changes. The comparative analysis of different flavonoid structures are recquired.

The results of this study have provided data to new research and development tendency, to the theoretical and practical basis of the production of „thermowood”.

V. Publications and pesentations

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