
THERMAL DECOMPOSITION OF BLACK LOCUST AND WHEAT STRAW UNDER TORREFACTION

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Abstract

In this work the torrefaction of two typical Hungarian biomass materials, wheat straw and black locust wood was studied. Three different torrefaction temperatures were applied: 225, 250 and 300°C with one hour isothermal period. The untreated and torrefied biomass materials were characterized by thermogravimetric analysis (TGA) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) techniques. The alkali ion contents of the samples were determined by ICP-OES technique. It was found that the thermal treatment at 225°C for 1 hour modifies the thermal decomposition mechanism of the cellulose content of the sample, indicating chemical changes in the cellulose structure. At 250°C the hemicellulose content of the analyzed biomass materials partially decomposes. Furthermore, the most labile lignin groups (terminal CH₂OH) also start to decompose. At 300°C torrefaction temperature the major part of hemicellulose and cellulose decomposes. The degree of the cellulose decomposition highly correlates with the alkali ion content of the samples.

Keywords: Torrefaction, Pyrolysis, Biomass, Cellulose, Lignin

1. Introduction

In Hungary the energy content of the most abundant agricultural and forest byproducts is utilized by direct combustion. Greenhouse gases (carbon dioxide, methane and nitrogen oxides) are produced during the combustion of the fuels. The alternative energy sources and new methods of their application can reduce the CO₂ content of the air. Intensive research is carried out to develop thermal processes, which are suitable for the realization in the industrial scale. In energetic applications, the raw biomass has several disadvantages due to the high oxygen content, low energy density and high moisture content. These disadvantages can be reduced by torrefaction, which is a mild thermal pretreatment between 200 and 300°C for the conversion of biomass in an inert atmosphere [1]. The purpose of the pretreatment from a chemical point of view is the removal of water and the acidic groups of hemicelluloses or the whole hemicellulose fraction with minor degradation of cellulose and lignin in the biomass [2, 3]. During the process, water and a part of the volatiles are released, causing a decrease in mass, but an increase in the energy density, this way reducing the storage and transportation costs [4, 5, 6]. In order to maximize the effectiveness of the energy extraction, we need to characterize the biomass materials as much as possible.

In this work the torrefaction of black locust and wheat straw was studied, which are typical biomass products or by-products in Hungary. Thermoanalytical and pyrolysis methods were applied to provide information about the composition and the thermal behavior of these woody and non-woody biomass samples.

2. Materials and Methods

2.1 Materials

In this study a black locust wood and wheat straw, a non-woody biomass were studied. The samples were dried at 105°C for 8 hour in an oven to about 6% moisture content prior to the torrefaction experiment. The untreated samples were ground by a cutting mill to <1mm particle size. The torrefaction experiments were carried out in a tube furnace in inert (nitrogen) atmosphere using flow rates of 20 ml min⁻¹. About 2.5 g samples were treated in a glass sample holder. The torrefaction experiments were performed at 225°C, 250°C, and 300°C with one hour isothermal period.

2.2 Methods

ICP-OES

About 2 g of biomass samples were ashed at 550°C in a furnace according to EU standard method CEN/TS 14775:2004. The ashes were fused at 920 °C with a fusion blend (Li₂B₄O₇:LiBO₂, 2:1) and digested by 25 cm³ 33% nitric acid. The potassium, sodium, calcium and silicon contents of the samples were determined by a Spectro Genesis ICP-OES (Spectro

Analytical Instruments) with axial plasma observation. The amounts of the ashes have been determined using a CEN/TS 14775 EU standard method.

TGA

The untreated and torrefied biomass materials were characterized by thermogravimetric analysis (TGA) and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) techniques. The thermogravimetric analyses were performed using a modified Perkin-Elmer TGS-2 thermobalance. About 6-8 mg of the biomass samples were measured in inert (argon) atmosphere using flow rates of 140 ml min⁻¹. The samples were flushed for 45 min by the carrier gas before the experiments to achieve an inert atmosphere. The samples were heated in a platinum sample pan at a rate of 10°C min⁻¹ from 25°C to 225°C 250°C or 300°C and the isothermal period was 1 hour.

Py- GC/MS

Approximately 1.2 mg samples were pyrolyzed at 550°C for 20s in helium atmosphere using a Pyroprobe 2000 pyrolyzer interfaced to an Agilent 6890A/5973 GC/MS. The pyrolysis products were separated on a DB-1701 capillary column. The GC oven was programmed to hold at 40°C for 4 min then increase the temperature to 280°C (hold for 5 min) at a rate of 6°C min⁻¹. The mass range of *m/z* 14-500 was scanned by the mass spectrometer in the electron impact mode at 70 eV.

3. Results and Discussion

3.1. TGA results

Figure 1 shows the thermogravimetry (TG) and derivative thermogravimetric (DTG) curves of wheat straw and black locust under torrefaction at different temperatures. The decomposition profiles during torrefaction in the thermobalance are somewhat similar to the thermal decomposition under dynamic conditions since the samples were heated at 10 °C min⁻¹ heating rate up to the isothermal temperatures during torrefaction. Comparing the mass loss rate curves, some differences can be observed between the two samples. The main DTG peak of the black locust at 300°C heat-treatment can be attributed to the decomposition of cellulose, and the shoulder at about 220°C (17 minutes) originates from the hemicellulose decomposition. The cellulose content of wheat straw starts to decompose at lower temperature, therefore the decomposition peak of hemicellulose is not separated from that of cellulose. Under torrefaction at 300°C the decomposition rate of wheat straw is higher than that of black locust, and reaches its final weight after 25 min isothermal period. The weight loss rate of black locust is lower at this temperature and even after the 1 hour isothermal period the rate of decomposition is still not negligible.

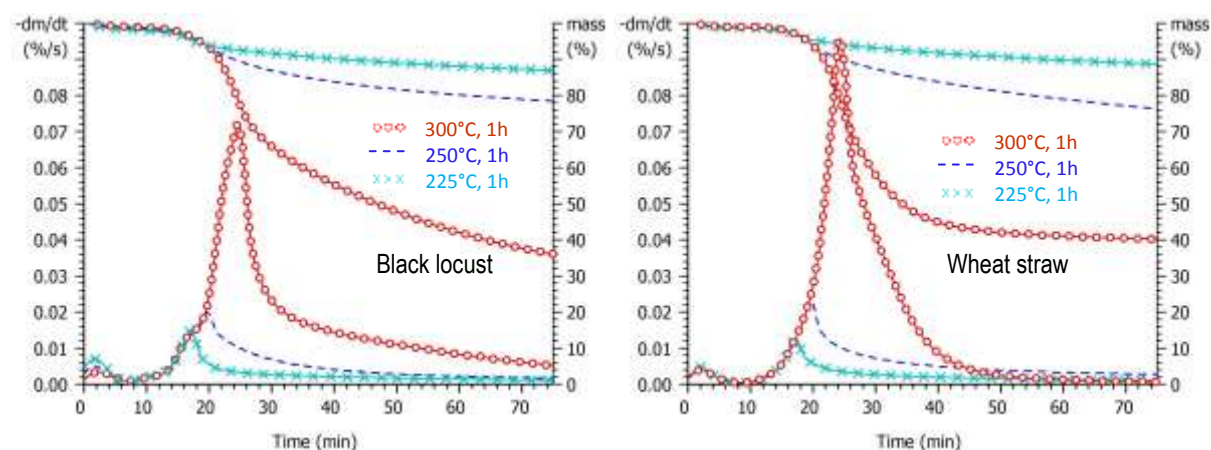


Figure 1. Mass loss and rate of the decomposition of black locust and wheat straw under torrefaction in the thermobalance at different temperatures.

The reason of the different thermal behavior of these two biomass materials could be interpreted by its different alkali ion contents, which have been determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) method. Table 1 summarizes selected data of ICP-OES characterization of the black locust and wheat straw samples. As the table shows wheat straw sample contains more than an order of magnitude more K⁺ than the black locust sample, and its Na⁺, Ca⁺ and Si contents are also significantly higher. The presence of alkali ions catalyzes the thermal degradation of cellulose [7-9]. The reason of the promoted decomposition rate of wheat straw under torrefaction is most probably the catalyzed decomposition of its cellulose content.

Table 1 The amounts of ash and a few inorganic components in black locust and wheat straw samples

	Ash content (% m/m)	Si content (% m/m)	Ca ²⁺ content (% m/m)	K ⁺ content (% m/m)	Na ⁺ content (% m/m)
Black locust	0.54	* N. D.	0.085	0.12	* N. D.
Wheat straw	5.25	1.066	0.137	1.69	0.008

* N. D.: Not determined, below the detection limit

3.2. Pyrolysis results

Pyrolysis-gas chromatography/mass spectrometry has been applied to reveal the changes in the pyrolysis product distribution of the samples after torrefaction. The pyrolysis temperature of 550°C was chosen on the basis of the TGA results. It showed that the thermal decomposition of the woody and non-woody samples ended by this temperature. Figure 2 presents the Py-GC/MS chromatograms of untreated and torrefied black locust samples. The main peaks indicated by red arrows point to the product compounds of increased and decreased yields, when the torrefied biomass samples have been pyrolyzed.

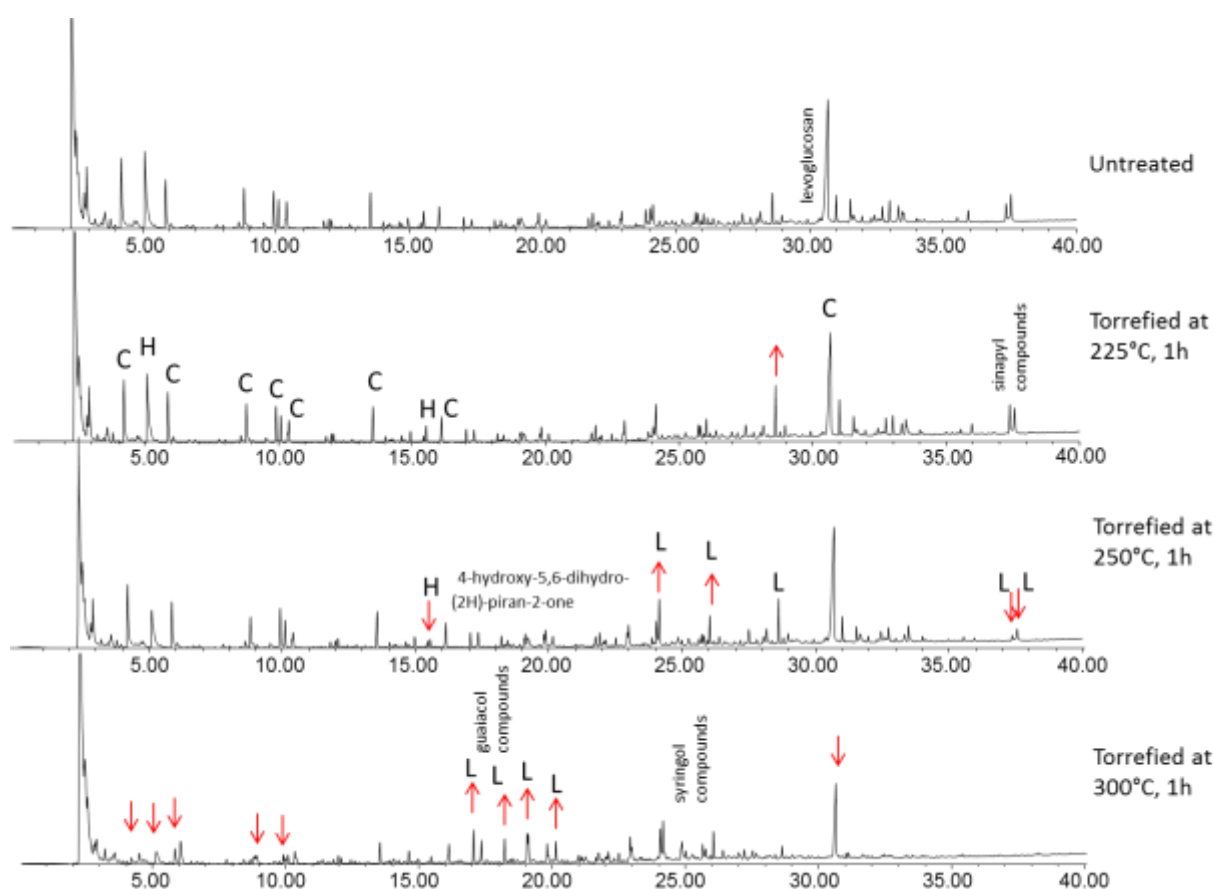


Figure 2. Pyrograms of untreated and torrefied black locust samples (Py-GC/MS)
C: Cellulose-; L: Lignin-; H: Hemicellulose decomposition products

The main route of cellulose decomposition under inert atmosphere is the depolymerization, which leads to the formation of 1,6-anhydro-β-D-glucopyranose (levoglucosan). This is the main decomposition product in the pyrogram of the untreated black locust sample. The yield of levoglucosan and smaller cellulose decomposition products (e.g. hydroxyl acetaldehyde and hydroxyl propanone) decreased significantly after the thermal treatment at 300°C indicating the partial decomposition of cellulose at this temperature. The 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one is a typical pentose marker of hemicellulose decomposition. As the pyrograms of black locust show, the yield of this pentose marker is decreased from the samples torrefied at 250°C and 300°C showing that the hemicellulose content of biomass decomposed to a high extent at these temperatures.

The yield of the syringol and sinapyl compounds is increased at 225°C. At 250°C the syringol compounds are increased to a small extent, while the sinapyl compounds mostly disappeared. At 300°C the major decomposition products of lignin are mostly guaiacol and syringol compounds, while the sinapyl compounds disappeared at this temperature. These observations indicate that under thermal treatment at 250°C the most labile terminal CH₂OH lignin functional groups start to decompose, while the decomposition of these functional groups are almost complete at 300°C.

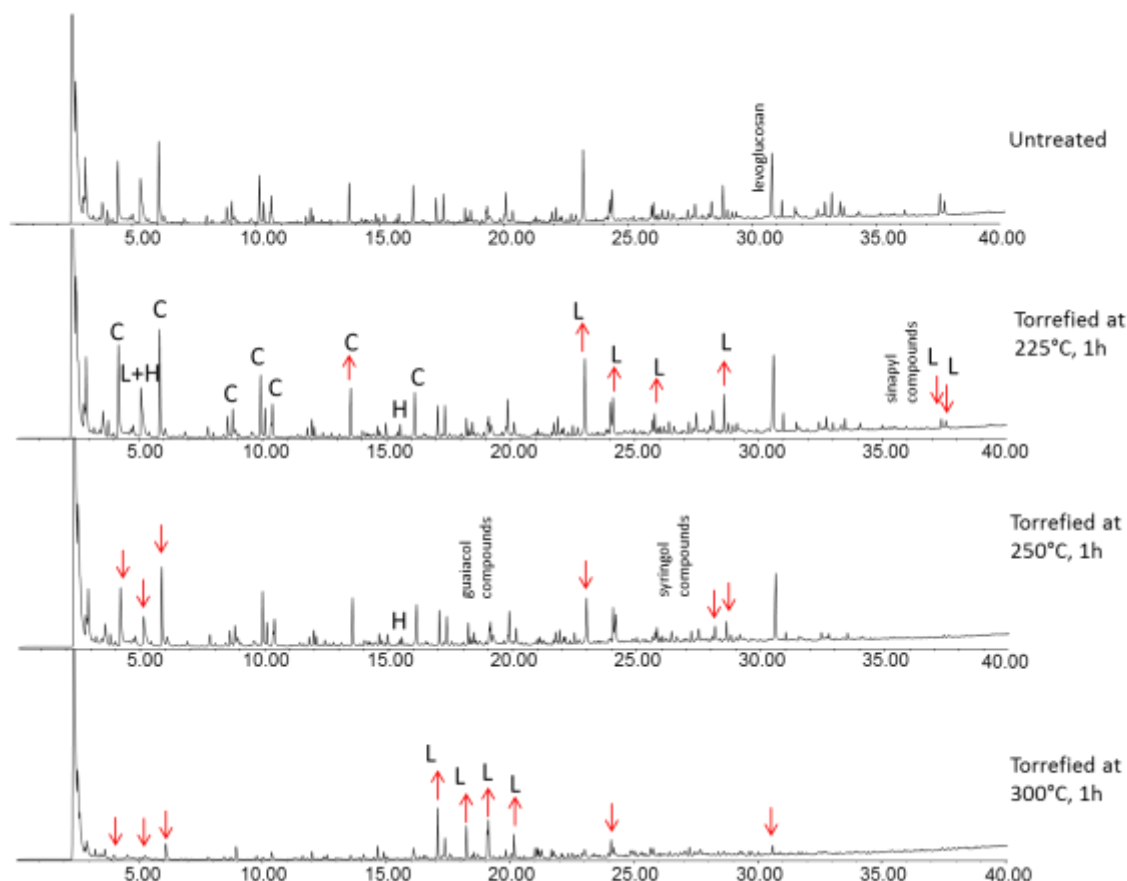


Figure 3. Pyrograms of untreated and torrefied wheat straw samples (Py-GC/MS)
C: Cellulose-; L: Lignin-; H: Hemicellulose decomposition products

Figure 3 presents the Py-GC/MS chromatograms of untreated and torrefied wheat straw samples. Some differences in the pyrolysis pattern can be observed between the black locust wood and the wheat straw samples. By comparing the pyrograms of the untreated samples we find that in case of wheat straw the levoglucosan yield is smaller, while the amount of smaller molecular weight products of cellulose is higher than from wood. These results can be explained by the higher inorganic content and hence by the catalyzed decomposition of cellulose in the wheat straw sample. At 250°C the hemicellulose content of the analyzed biomass materials partially decomposes, and the most labile lignin groups (terminal CH₂OH) also start to decompose at this temperature. In the pyrogram of wheat straw torrefied at 300°C the lignin decomposition products became dominant indicating the decomposition of the major part of cellulose at this temperature. At 300°C the main decomposition products of lignin are mostly guaiacol compounds showing that the methoxyl groups of the syringol moieties were partially cleaved during torrefaction. We can conclude that at 300°C the cellulose and lignin degradation is more intensive in the wheat straw samples than in the black locust samples. It can be explained by the well-known observation that the decomposition mechanism of both cellulose and lignin is changed by the higher presence of the alkali ions [7-11].

4. Conclusions

The thermal decomposition of untreated and various thermally treated (torrefied) biomass samples were measured by TGA and Py-GC/MS analytical methods. The alkali ion contents of the samples were determined by ICP-OES system. We concluded that the alkali ions exhibit substantial impact on the low-temperature (225-300°C) thermal treatment of the biomass similarly as during the pyrolysis at higher temperatures. The influence of the alkali ion content is reflected in the fast weight loss during torrefaction of wheat straw at 300°C, which can be attributed apparently to the degradation of cellulose

molecules. The intensity of acetic acid, the most significant pyrolysis product of hemicellulose, changes similarly with the torrefaction temperature in case of wood and wheat straw, which shows that the alkali ions have negligible influence on the scission of acetate side groups. The most labile lignin groups (terminal CH₂OH) start to decompose at 225°C in wheat straw and at 250°C in the black locust sample. The relative amount of syringol decomposition products reduces significantly after 300°C thermal treatment of wheat straw, while those are still significant decomposition products of the black locust torrefied at 300°. The reduced yields of syringol derivatives and the increased amounts of guaiacol products prove the cleavage of methoxyl groups. These results demonstrate that the alkali ions promote the scission of both aliphatic and aromatic functional groups of lignin during torrefaction of biomass samples.

5. Acknowledgement

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6. References

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