Final report

for TNN123499 project entitled

„Conversion of waste into fuel by thermal methods”

1. Background

Utilization of renewable energy sources to a greater extent is promoted in the last decades due to environmental pollution issues and climate change, and became even a more urgent in the current energy crisis. Among the renewable energy sources, biomass is the only source of carbon and therefore could provide a renewable alternative to fossil-based solid or liquid fuels or to several fossil-based industrial feedstock.

The main objective of this project was to gain information about the thermal decomposition processes taking place under thermal conversion of biomass into solid or liquid fuel. Understanding the thermal decomposition processes may help to optimize the process conditions in order to improve the quality of the product and the feasibility of the recycling method.

A wide range of biomass materials was selected for the project to cover the diversity of the area. The samples studied in the project are summarized in Figure 1. The project was performed in the framework of a bilateral cooperation with the Thailand Institute of Scientific and Technological Research, therefore, typical Thai and Hungarian biomasses were also selected for the study.

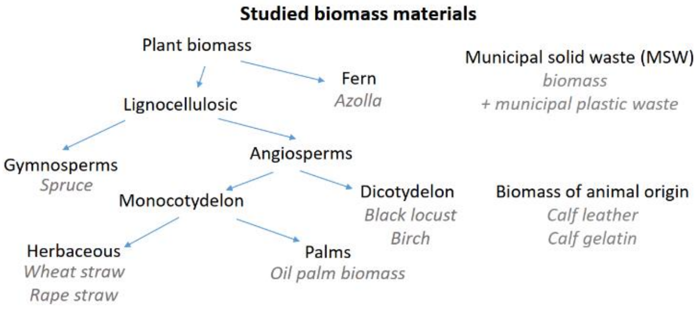

Figure 1: Materials selected for research in the project

2. Results

2.1 Thermal conversion of plant biomass

2.1.1 Effect of torrefaction

Low-temperature pyrolysis, the so-called torrefaction is considered a promising way to generate renewable fuel from biomass. A major aim of torrefaction is to upgrade the quality of the solid biomass by decreasing the moisture content and increasing the energy density, hydrophobicity and grindability. The goal of our work was to clarify the influence of inorganic ion contents on the thermal degradation process during torrefaction. Therefore, the majority of the water-soluble inorganics were removed by washing, then the thermal degradation properties and composition of the raw and washed samples were compared. The hemicellulose, cellulose and Klason lignin contents of the washed and untreated raw and torrefied, black locust wood, rape straw and wheat straw samples were compared. The relative amount of hemicellulose changed similarly with the increase of torrefaction temperature in the series of untreated and hot-water washed samples. Furthermore, the tendencies were found similar in case of both the black locust and rape straw samples, indicating that contrary to cellulose the impact of the alkaline ions on the thermal stability of hemicelluloses is marginal. The thermal stability of cellulose raised by about 50°C in the straw samples and by about 30°C in the wood sample as an effect of washing. The char yields of the washed samples were found significantly lower than that of the native samples. These observations confirm that alkali ions have catalytic effects on the decomposition mechanism of cellulose and lignin even under mild thermal conditions.

With the aim of understanding the structural changes in the hemicellulose, cellulose, and lignin components taking place during torrefaction, comparative Py−GC/MS analysis of untreated and variously torrefied Norway spruce stem wood, stump, and bark materials has been performed. The intensities of the most characteristic pyrolysis products evolved from the untreated and torrefied samples have been compared. The results of the Py-GC/MS analysis demonstrated that the yields of acetic acid and other compounds of low molecular mass were reduced in the pyrolyzates of each torrefied sample, confirming the scission of the most labile acetate groups from the hemicellulose chains even at 225 °C. This effect is important with regard to lowering the acidity of the pyrolysis oil by applying torrefaction as a pretreatment prior to the pyrolysis of raw biomass, as the high acidity of bio-oil is one of its main drawbacks.

The results are summarized in papers published in the *Journal of Analytical and Applied Pyrolysis*[1] and *Energy & Fuels*[2].

2.1.2 Lignin as a methylating agent in thermal reactions of biomass

Lignin is a biopolymer with high molecular weight, one of the main components of a lignocellulosic biomass. The building blocks of lignin are methoxyphenyl moieties (e.g. guaicyl, syringyl), whose number of methoxy groups depends on the biomass type. The methylating activity of lignin during certain thermal treatments has been reported in our previous studies, when the direct methylation of various thermal decomposition products was observed in the pyrolyzates of biomass–plastic mixtures.

In the present project the detailed analysis of the thermal decomposition products revealed the methylating activity of lignin on other components of the biomass.

The lipid content analysis of oil palm empty fruit bunch (EFB) showed that the biomass had considerable amounts of fatty acids, which were in the form of glycerides and free acids. During the torrefaction of EFB biomass, the free fatty acids evaporated; however, a portion of the glycerides was methylated and thus fatty acid methyl esters (FAMEs) formed during the thermal treatment. The kinetics of FAME formation was independent of the fatty acid chain length, which was determined on the basis of the condensate yield ratios.

A series of torrefaction at six temperatures between 210–360 °C showed that the growth of FAME formation was the highest between 270–300 °C, while nearly the maximum FAME yields were measured in the condensates of EFB collected at 330 and 360 °C. Therefore, torrefaction at and above 330 °C depleted the sources of fatty acids in the solid residues.

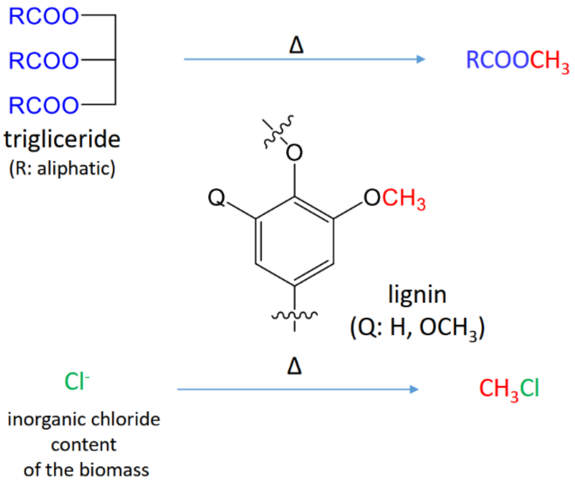

Figure 2: Methylation by lignin in thermally induced reactions of biomass pyrolysis

Pyrolysis of a model mixture, consisting of EFB lipid extract and beech lignin (MWL), proved that FAMEs formed by the interaction of the lipid and lignin contents of the biomass. In addition, TG/MS results confirmed that the fatty acid moieties were methylated by the methoxy side groups of lignin. Demethylation lowered the thermal stability of lignin and the evolution temperature of phenolic products; moreover, enhanced the char formation. The evolution of 4-methylguaiacol and 4-methylsyringol decreased, while the release of guaiacol and syringol increased in comparison with the thermal degradation of native lignin.

Py-GC/MS measurements of raw and torrefied EFB showed that the remainder of triglycerides produced further amounts of FAMEs. The thermal pretreatment up to 300 °C increased the accessibility of the components and the conversion of FAMEs calculated on raw EFB base during flash pyrolysis. It means that a prolonged heating of biomass is advantageous for FAME formation.

The *in situ* FAME formation revealed in our work provides an opportunity to develop the process of biomass pyrolysis. The interaction of lignin with triglycerides, which can be naturally present or as an additive in a pure or waste material, produces FAMEs, which are utilizable as a fuel. In addition, the related lignin demethylation increases the char yield; hence, the FAME formation improves the solid product as well.

Methyl chloride was detected during thermal decomposition of rape and wheat straw samples which was explained by the reaction of inorganic chlorine with the methyl groups of lignin. The relative intensity of methyl chloride measured by TG/MS was halved from the samples torrefied at 250 and at 275 °C, and it disappeared from the samples after torrefaction at 300 °C, indicating the scission of methoxy groups of lignin during torrefaction. We concluded that most of the methoxy groups of straw lignins were probably cleaved during torrefaction at 275 and 300 °C, and at the same time the initial chlorine content of the straw samples decreased. Therefore, the severely torrefied straw samples produced only small amount of methyl chloride during thermal decomposition.

The results are summarized in Figure 2 and were published in the *Journal of Analytical and Applied Pyrolysis*[1,3].

2.1.3 Comparison of torrefaction and hydrothermal treatment

The impact of torrefaction and hydrothermal carbonization (HTC) was studied on *Azolla filiculoides*, as an aquatic biomass feedstock for renewable energy sources. The torrefied azolla and the hydrochar prepared at the same temperatures (260, 280, 300 °C) were studied and compared in order to reveal the effects of dry and wet thermal treatments. The comparison of torrefied and HTC treated azolla samples showed that the HTC process resulted in a significantly higher degree of decomposition than torrefaction at the same temperatures. Based on both TGA and Py-GC/MS results, torrefaction at 300 °C degraded the sample somewhat less than HTC at 260 °C. Torrefaction mainly decomposed the thermally less stable carbohydrate components of azolla, while hydrothermal treatment affected also other constituents of the biomass, thus, leading to a higher extent of degradation. Scanning electron microscope (SEM) images revealed more intense morphological changes as a result of HTC comparing to torrefaction. Torrefied samples treated up to 280 °C visibly kept the original structure of the biomass, while hydrochars and sample torrefied at 300 °C had a porous structure.

The analysis of the pyrolysis products showed that the sources of aromatic products were the thermally most stable parts of azolla during both torrefaction and HTC. The yield of nitrogen-containing compounds were slightly reduced in the pyrolyzate of torrefied samples; however, the sources of these compounds were significantly eliminated during HTC. The intensity of carbohydrate products was decreased gradually with increasing treatment temperatures from torrefied samples; however, HTC reduced strongly the carbohydrate content of the samples. The amount of phytosterols decreased to the greatest extent during both treatments. The aliphatic compounds were mainly preserved after torrefaction, while HTC strongly decreased the sources of these products, which can be explained by the hydrolysis of fatty acid esters.

The results have been summarized in a paper published in the *Journal of Analytical and Applied Pyrolysis*[4].

2.1.4 Study on biocarbon yield and properties

The solid product of biomass pyrolysis, the so-called biocarbon, biochar or charcoal, has various applications besides heating and barbequing, like biochar for soil amendment, activated carbon for flue-gas cleaning, or substitution of the fossil carbon source by renewable biocarbon in metallurgical processes.

Each application requires a large amount of carbonaceous material with certain properties; therefore, both obtaining high char yield and achieving required properties are desirable. The primary goal of this work was to investigate the effect of carbonization conditions on the yields and the composition of the solid products. The second objective of this work was to study the composition and evolution profiles of the volatile content in detail, as these are critical indicators of thermal and environmental stability of biocarbon.

Slow pyrolysis of spruce and birch was performed using various heating programs and conditions in a horizontal quartz tube reactor heated by an electric furnace. The effects of feedstock and carbonization conditions on the yield of biocarbon, liquid and gaseous products were studied. Increased char yield was observed when staged pyrolysis program, low purging flow rate or covered sample holder were applied. Spruce produced more charcoal than birch due to the higher lignin content of softwood. The thermal properties, volatile matter (VM) content and the evolution profiles of volatiles from the biocarbons were characterized by TG/MS. The composition of volatiles was analyzed in detail by Py-GC/MS. The amount and the evolution profiles of the main gaseous products were similar from spruce and birch biocarbons prepared under the same conditions. The relative amount of aromatic and polyaromatic compounds in the VM content drastically decreased with increasing carbonization temperature. Biocarbons prepared by staged pyrolysis using 700 °C final temperature had lower VM content and released less water above 800 °C, indicating that probably less hydroxy groups remained in the biocarbon samples prepared by staged carbonization. The detailed analysis of the residual volatiles provided insights into the structure of the biocarbon, thereby revealing information about the carbonization mechanism. Understanding the composition of the volatiles facilitates the selection and development of the appropriate biocarbon for industrial applications of special needs.

The composition of the condensates collected during carbonization reactions were characterized by GC/MS. It was concluded that the composition of the condensates was primarily determined by the feedstock, the different final temperatures (400, 500, and 700 °C) and other experimental conditions (flow rate, staged heating program) does not modify the composition notably.

The results of the study were summarized in a paper published in the *Bioresource Technology*[5].

2.2 Characterization of oil palm biomass materials

The palm oil industry produces large amounts of biomass by-products, such as palm empty fruit bunch (EFB), mesocarp fiber (MF), and kernel shell (KS). The thermal behavior, the organic biopolymer and inorganic composition of three oil palm biomass wastes have been determined. The analysis of biopolymer and inorganic content showed that the composition of KS and MF were rather similar, like their thermal behavior. Their hemicellulosic and cellulosic components degraded in fairly separated two steps. KS and MF were also similar in the extent of the carbohydrate contents (ca. 20% each) and in the ratio of lignin subunit types (S, G, H) present in the pyrolyzates. KS possessed the highest lignin content and it had relatively low amount of ash. However, EFB contained more cellulose (ca. 30%) and extractive components. Moreover, the S/G lignin product ratio was higher in the pyrolyzate of EFB. In comparison with KS and MF, the EFB biomass had lower thermal stability. EFB contained the highest amount of potassium (2.26%), while MF and KS had moderate and low alkali contents, respectively. The alkali ions affected the decomposition of all three biopolymer components, namely cellulose, hemicellulose and lignin, resulting in an enhanced char formation. The catalytic effect was observed as the evolution of the related products from EFB shifted to lower temperatures by 20–30 °C. In addition, the formation of typical depolymerization products of xylan hemicellulose (4-hydroxy-5,6-dihydro-2*H*-pyran-2-one) and cellulose (levoglucosan) was hindered during the pyrolysis of EFB, while these compounds were detected in considerable yields from KS and in somewhat lower amounts from MF. The enhanced char formation was revealed by the highest fixed carbon content of EFB measured by TGA. Based on the results and

observations, EFB supposed to be treated separately from KS and MF during a conversion process with the aim of specific utilization, especially in the case of a multi-stage thermal treatment.
The results were published in the *Journal of Analytical and Applied Pyrolysis*[6]

2.3 Thermal decomposition of leather

Investigation of the thermal decomposition reactions of tanned leathers and tannins can contribute to the understanding of tanning chemistry, the identification of tannins in modern and historical leathers and the development of thermal conversion method for waste leather.
The thermal decomposition of tanned leathers as well as hydrolysable (chestnut, valonea, tara) and condensed (quebracho, mimosa) tannins were studied using both slow and high heating rates. Calf gelatin was chosen as a reference material. The comparison of the thermal decomposition temperatures of the vegetable tanning agents and vegetable tanned leathers showed that the lower the thermal stability of the tanning agent, the higher the stability of the tanned leather. This means that tannins with higher reactivity can establish stronger chemical bonds with collagen producing more stable leather from a thermochemical point of view. Resorcinol and orcinol were identified as marker compounds of the condensed tannins among the pyrolysis products of leathers tanned with mimosa and quebracho. Specific pyrolysis products were not found for hydrolyzable tannins; however, the yield of phenol and pyrogallol was higher in the pyrolyzates of leathers tanned with hydrolyzable tannins. The effect of aging on leather was demonstrated by various thermal methods. Correlation was found between the thermal denaturation parameters assessed by micro-DSC and the lower thermal stability and the maximal decomposition rate determined by TGA. The oxidation of collagen was confirmed by higher yields of 2-pyrrolidone and succinimide, which are thermal decomposition products of oxidized proline and hydroxyproline residues identified by Py-GC/MS.
The results of this work were published in the *Journal of Analytical and Applied Pyrolysis*[7,8].

2.4 Thermo-catalytic studies on a mixture of plastic waste and biomass

The effects of various catalysts on the composition of volatile pyrolysis products of a plastic waste and biomass mixture (1:1) were studied, by pyrolyzing the mixture sample using slow and fast heating rate. Various zeolite catalysts (β- and Y-zeolites, ZSM-5 and FCC) and nickel-molybdenum (NiMo) catalyst on alumina support were applied to find suitable catalysts for upgrading the quality of the thermal decomposition products of the waste mixture. The rate of evolution of the decomposition products under slow pyrolysis was measured by TG/MS. The composition of the pyrolyzates was analyzed in detail by Py-GC/MS method. One of the main advantages of the application of zeolite catalysts was that acetic acid content of the oil originating from the biomass part was reduced by 40–60% during the fast pyrolysis of the mixture. The influence of all applied catalysts was more pronounced on the plastic content of the sample than on biomass. The pyrolysis experiments revealed that the catalysts promoted the cracking reactions of the evolved hydrocarbons; furthermore, the formation of aromatic products was enhanced remarkably in the presence of all zeolite catalysts. β-zeolite and ZSM-5 catalysts were found the most effective in cracking hydrocarbons to gaseous products and in aromatization, while the highest CO_2 formation was obtained by FCC from the biomass part of the studied waste mixture. NiMo catalyst promoted the H_2 production from the plastic part; furthermore, slight aromatization and cracking effects were also observed.
The results were published in the *Journal of Thermal Analysis and Calorimetry*[9].

Publications from the project results

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[3] B. Babinszki, E. Jakab, V. Terjék, Z. Sebestyén, I. S.Czirok, J. Bozi, L. Attanatho, Y. Thanmongkhon, Zs. Czégény; In situ formation of fatty acid methyl esters via thermally assisted methylation by lignin during torrefaction of oil palm biomass, J. Anal. Appl. Pyrolysis 168 (2022) 105720.

[4] B. Babinszki, E. Jakab, Z. Sebestyén, M. Blazsó, B. Berényi, J. Kumar, B.B. Krishna, T. Bhaskar, Zs. Czégény; Comparison of hydrothermal carbonization and torrefaction of azolla biomass: Analysis of the solid products, J. Anal. Appl. Pyrolysis 149 (2020) 104844.

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[8] Z. Sebestyén, E. Badea, C. Carsote, Zs. Czégény, T. Szabó, B. Babinszki, J. Bozi, E. Jakab; Characterization of historical leather bookbindings by various thermal methods (TG/MS, Py-GC/MS, and micro-DSC) and FTIR-ATR spectroscopy, J. Anal. Appl. Pyrolysis 162 (2022) 105428.

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