As an objective we produced and characterized nitrogen- and high carbon-containing charcoals from protein- and lignocellulosic-based secondary raw materials.
The thermal characterization of bovine leathers was performed using thermogravimetry/mass spectrometry (TG/MS), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), principal component analysis (PCA), complemented by ICP-OES measurements, and nitrogen and ash content determination. Calf parchment was used as a reference (not-tanned) material. The nitrogen content of the samples was determined by a research group at the Department of Applied Biotechnology and Food Science of the Budapest University of Technology and Economics. The ICP-OES revealed information regarding the preparation of the samples. The identified inorganic elements (i.e., chromium, alkali and alkaline earth metals, and sulfur) originate from various fabrication steps like liming, tanning, and finishing. The ash content refers to the inorganic part of the samples, which is affected by the tanning methods. Dumas method was used to determine the nitrogen content, which provided data for calculating the protein content of the samples. Higher protein content corresponds to a lower tannin content in all investigated leathers. The thermal stabilization effect of the tanning was confirmed by TG/MS measurements using slow and controlled decomposition. The carbonaceous residue and the nitrogen content proved to be good indicators of the tannin content, too. According to the TG/MS data, the yield of hydrogen cyanide and acetonitrile was the highest during the thermal decomposition of chromium-tanned leather. In order to investigate this behavior in detail, parchment samples with increasing chromium content were prepared and analyzed by TG/MS and Py-GC/MS. It was found that the chromium sulfate content of the samples induced a catalytic effect on the hydrogen cyanide, acetonitrile and propionitrile formation, while the evolution of ammonia reduced with increasing chromium content. It was concluded that chromium sulfate promoted the release of water from collagen; hence decreased the hydrolysis of the polypeptide bonds, which caused the reduced evolution of ammonia. It is worth mentioning that the superior thermal stabilization conferred by chromium salts was for the first time explained by the promotion of water release and inhibition of peptide bond cleavage. It is important to note that the applied chrome tanning agent released sulfur dioxide in the 300–500 °C temperature range in spite of the fact that anhydrous chromium sulfate decomposes at 700 °C in inert atmosphere. Consequently, the decomposing carbonaceous matrix of leather or parchment promoted the decomposition of chromium sulfate, which evolved oxygen beside sulfur dioxide. The released oxygen dehydrogenated certain CH-NH groups in the polypeptide chain resulting in the increased formation of water, hydrogen cyanide and other nitriles. In addition to the enhanced fragmentation, the char yield was also increased in the presence of chromium sulfate. The pyrolysis product distribution of the samples was analyzed by Py-GC/MS technique at 400 and 600 °C. The relative intensity of diketopiperazines, as the typical cyclic dimer products of collagen, was reduced in comparison with the compounds of smaller molecular mass in the presence of metal tanning agents and at higher pyrolysis temperature. Principal component analysis was performed to identify differences in the pyrolysis products distribution. PCA calculations revealed that both vegetable tanning and chromium-tanning specifically modify the composition of the pyrolyzates. The score plots showed that leathers tanned with vegetable tannin or mixed vegetable and inorganic tanning agent separated from the chromium-tanned sample and from the parchment. An MSc student, István Sándor Czirok was involved in the laboratory work that is the basis of his MSc thesis. The title of his thesis is “Thermal characterization of leathers tanned by vegetable tannins and chromium salts”. In June of 2021, the thesis was successfully defended at the Eötvös Loránd University. István Sándor Czirok joined to this project as a PhD student. His PhD work is dedicated to the thermal decomposition of collagen based biomass materials. In 2022, he was successfully admitted to the Hevesy György Doctoral School of Chemistry at the Eötvös Loránd University. During his PhD work, the supervisors are Zsuzsanna Czégény and the principal investigator of this project. The results on the characterization of tanned leathers and parchment have been orally presented at the International Symposium on Feedstock Recycling of Polymeric Materials in 2021 (ISFR 2021). In 2023 first paper of his PhD work was successfully published in the Journal of Analytical and Applied Pyrolysis entitled “Thermal characterization of leathers tanned by metal salts and vegetable tannins”.
Charcoals were produced from the leathers in a laboratory scale furnace under nitrogen atmosphere at 400, 500 and 700 °C. A BSc student was involved in this part of the project. TG/MS was applied in order to characterize the raw materials and the charcoals. It was observed that the yields of the carbonaceous residues are decreasing by the increasing treatment temperature. The charcoal yield was the lowest from the chromium tanned leather. The reason could be that the chromium tanning agent was applied in the lowest concentration during the tanning procedure, while the vegetable tanning agents, used in higher concentration, produce also charcoal during thermal decomposition. The nitrogen content of the leather and charcoal samples was determined. The chromium tanned leather has the highest nitrogen content among the raw materials. Therefore, it is reasonable that the carbonaceous residue of this leather has 1.5 times higher nitrogen content than the other charcoal samples formed at all three carbonization temperatures. The specific surface area of

the produced charcoals has been determined by BET (Brunauer - Emmett - Teller) method. Charcoals formed from the vegetable tanned leathers have the highest specific surface area. According to the TG/MS measurements, the maximal thermal decomposition rate of the charcoal samples is decreasing with increasing production temperature. The temperature of this parameter is increasing with increasing carbonization temperature. Charcoals from the chromium tanned leather become less hydrophobic comparing to the others. At around 800 °C carbon reacted with the chromium oxide forming metal chrome and carbon dioxide. In January of 2022 the BSc thesis with the title "Production of charcoal samples from leathers and their characterization using thermoanalytical methods" was successfully defended at the Budapest University of Technology and Economics.

We continued the leather research on four historical leather bookbindings dated between the 17th and 19th century. The study has been performed to obtain information about the thermal stability, composition and molecular structure of four historical leather bookbindings in comparison with a modern leather sample. The goal of this study was to identify correlations between their thermal, structural and chemical properties and deterioration mechanisms by using thermal analysis and decomposition methods and infrared spectroscopy (FTIR-ATR). The TG/MS study revealed that the maximum thermal decomposition rate of the historical samples depended on the deterioration profile of leather. The TG/MS analysis proved that the historical samples have higher amount of adsorbed water compared with the modern leather pointing to their higher polarity. Micro-DSC analysis allowed classifying the historical samples as "leather-like", "parchment-like", or "gelatin-like" samples demonstrating that the leather underwent various deterioration processes over time. The occurrence of oxidation reactions were indicated by the significantly higher yield of carbon dioxide measured during the pyrolysis of historical leathers. Py-GC/MS results allowed us to characterize the composition of the historical leathers. The smaller yield of the pyrolysis products attributed to vegetable tannins detected in the chromatograms of historical leathers was related to the degradation of tannins, while the higher amount of 2-pyrrolidone and succinimide confirmed the oxidation of proline and hydroxyproline amino acid residues in historical leathers. Leather de-tanning and collagen gelatinization were clearly evidenced by both micro-DSC and FTIR-ATR, as well. A paper has been published in the Journal of Analytical and Applied Pyrolysis with the title "Characterization of historical leather bookbindings by various thermal methods (TG/MS, Py-GC/MS, and micro-DSC) and FTIR-ATR spectroscopy".

Crab exoskeleton chitin sample was studied in cooperation with the Surface Chemistry Group of the Budapest University of Technology and Economics. We prepared nitrogen-containing carbon catalyst support from the chitin-based sample. A multi-technique investigation into the conversion of crab shell to porous carbon adsorbent was reported in a paper published in the Journal of Thermal Analysis and Calorimetry. Thermogravimetry and pyrolysis-gas chromatography/mass spectrometry studies were used to reveal the thermal degradation of this natural polymer and follow the decomposition process through the identification of the products. The complex degradation mechanism of this biomass is reflected by the high number of volatile degradation species. Depolymerization of chitin polymer occurs already at 320 °C forming 1,6-anhydro-2-acetamido-2-deoxyglucose monomer and furan derivatives by dehydration. N-containing heterocycles are also released at lower temperature, but their formation becomes significant only at 500 °C. The relative nitrogen/phosphorous intensity data indicate that 84 and 59% of the initial N-content is retained in the char after 350 and 500 °C pyrolysis, respectively. Based on these results, the carbonaceous residue of the crab shell still contains a significant amount of nitrogen and is a potential support of transition metal catalysts. We may conclude that crab shells have a high potential as precursor of nitrogen-containing biocarbon. Paper has been published including the results in the Journal of Thermal Analysis and Calorimetry.

PVC and leather were mixed in different ratios in order to study the effect of the components on the thermal decomposition of each other in the mixture. The amount of the carbonaceous residues of the PVC-leather mixtures was lower than the expected value so chemical reactions take place between the components during the thermal degradation. By mixing the two components the fragmentation decomposition mechanism becomes preferred. The first step of the PVC decomposition (dehydrochlorination) was shifted to a lower temperature range by 20-30 °C in the PVC-leather mixtures compared to the pure PVC. The leather part of the mixtures promotes the elimination of benzene. Mass spectrometric curve of toluene proves that the second thermal decompostion step of the PVC was also affected by the added leather. These phenomena can be observed in case of adding the vegetable tanned leather as well. Evolution of acetonitrile from the amino acid chain is slightly hampered by the presence of the PVC. Oral presentation has been given in this topic and our future work will be the investigation of this mixture.

In order to get a better understanding on the thermal decomposition of the lignocellulosic biopolymer fraction, hemicellulose separated from beech wood was studied by an MSc student. The title of the prepared MSc thesis

was “Thermochemical characterization of torrefied hemicellulose”. In June of 2020, the thesis was successfully defended at the Budapest University of Technology and Economics. The beech wood hemicellulose, xylan was heated to different torrefaction temperatures (200, 225, 250, 275 and 300 °C) under inert atmosphere. The sample preparation and the thermal stability of these torrefied hemicellulose samples were characterized by thermogravimetry. Thermal decomposition process was influenced by the relatively high Na^+ content remained in the xylan sample after the separation procedure. Another objective of this project is to produce biocarbon of high fix carbon content from wood for the possible application in the metallurgical industry. Slow pyrolysis of spruce and birch was performed at various heating programs and conditions. The effects of feedstock and carbonization conditions on the yield of biocarbon, liquid and gaseous products were studied. The composition of volatiles was analyzed in detail by Py-GC/MS. Increased char yield was observed when staged pyrolysis program, low purging flow rate or covered sample holder were applied.
The effects of various catalysts on the composition of volatile pyrolysis products of a plastic and biomass mixture waste were studied. Various zeolite catalysts (β-and Y-zeolites, ZSM-5 and FCC) and a nickel-molybdenum catalyst on alumina support were applied. It was found that various zeolite type catalysts and an alumina supported NiMo (nickel-molybdenum) catalyst increase the formation of hydrocarbons of smaller molecular mass. The TG/MS results revealed that under gradual heating the catalytic effect was more pronounced on the plastic part than on the biomass component. The significant cracking effect of catalysts was proved by the remarkable decrease in the amounts of alkenes and alkadienes. β-Zeolite and ZSM-5 had the most remarkable cracking and aromatization effects during the thermal decomposition. One of the main advantages of the zeolite catalysts on the decomposition of the biomass part was the reduction of acetic acid by 40–60% in the oil. Moreover, enhanced formation of the lignin-derived aromatic compounds was observed. Both the decreased acidity and the increased aromatic content improve the oil quality. The share of aromatic hydrocarbons increased by 70% in the presence of β-zeolite, by 40–45% when Y-zeolite or ZSM-5 catalysts were applied. Each tested catalyst upgraded the quality of the oil to a different extent. The alumina supported NiMo catalyst was effective in promoting the H_2 production from the plastic components. Slight aromatization and cracking effect were observed, as well. The results of on-line analysis proved that testing and comparing the efficiency of various catalysts, by focusing on the primary pyrolysis processes and products, could be applied as a novel way for optimization of the utilization of waste components by catalytic pyrolysis. Regarding this part of the project paper has been published in the Journal of Analytical and Applied Pyrolysis.

Within the framework of the OTKA PD 132438 project 9 paper were published in referred Journals, 1 PhD has been started, 1 MSc and 2 BSc thesis were written and 5 conference oral presentations were held.