

## *Final Report of Project*

# *“Study of the Chemical Processes of Biomass Utilization”*

*(OTKA K 72710/KM2, 2008-2012)*

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### *Topic 1: Study of the Thermal Reaction of Solid Biomass Materials*

Such chemical reactions were studied in inert and reactive atmosphere that take place during the heating of solid biomass materials of plant origin.

#### **Task 1/A: Thermal Investigation of Biomass Fuels**

Biomasses for energy production were investigated which included

- Products from energy plantations: black locust, willow and poplar as well as energy grass, sorghum, and Ethiopian mustard
- Agricultural by-products: various straws, corncob, cornstalk, and rice husk
- Sewages sludge (which is also regarded as a biomass in the technical literature).

In a main part of the work the kinetics of the thermal decomposition processes was studied. This research aimed at obtaining knowledge on the course of these processes and at finding kinetic models that can be developed into submodels of industrial modeling in the future. One should note here that the study of small samples under well-controlled conditions cannot provide directly data for large-scale industrial applications, but can serve as a basis for further developments. Such models were employed that reflected the complexity of the biomass materials. Special care was taken to keep the number of the unknown parameters at a moderate level and to evaluate series of experiments in a wide range of experimental conditions. It was tested how the model can predict experiments far from the range of experimental conditions used in the determination of the model parameters. The paper dealing with these latter aspects was in the list of the “most read articles” of *Energy & Fuels*, which is an ACS journal. (Here is an [internet link](#) for the top of this list archived in 2011.)

A model was developed for wood combustion under well-controlled experimental conditions in the kinetic regime. This model described the mass-loss and was built from three submodels:

- (i) The decomposition of cellulose in the presence of oxygen was found to be a self-accelerating that was described by autocatalytic-type kinetics;
- (ii) The decomposition of the rest of the biomass was described by a distributed activation energy model (DAEM) reflecting the very high number of different reacting species in a biomass;
- (iii) The burn-off of the char produced in the above reactions was approximated by a successive n-order reaction.

The model took into account that the rate of these process depend on the oxygen concentration.

This model describes the mass-loss during combustion in the kinetic regime with higher precision than the existing models. However, it is much more complex. A relatively fast and precise numerical computational method was also given. In our opinion the rapid development of the computer hardware and software will make possible to use submodels with such complexity in two and three dimensional industrial reactor models. Presently an advanced personal computer can calculate one million solutions in ca. 100 minutes by this model at arbitrary temperature – time functions.

Beside the reaction kinetic investigations, principal component analysis was also employed in this task. Concerning the thermal behavior, a relationship was found between the TGA results and the heating value.

### **Task 1/B: Investigations connected to high-yield, environment-friendly charcoal production and to the novel application possibilities of the charcoals**

Investigations were carried out in cooperation with Norwegian, US and Chinese teams. Our task in this work was the reaction kinetic evaluation and modeling.

The study of the chemical processes during charcoal formation overlapped with the studies on the thermal decomposition reactions outlined at the previous task. Another work obtained knowledge on cellulosic samples that were pretreated by a pressurized heating for a subsequent activated carbon production.

Charcoals can easily be gasified by carbon dioxide due to their reactivity and high specific surface. A detailed kinetic study was published in *Energy & Fuels* on this topic, and another is expected to be submitted in next January. As in Task 1/A, efforts were taken to determine the unknown parameters and validate the models at a wide range of experimental conditions. For this purpose the recent work included modulated and “constant reaction rate” (CRR) temperature programs. The results of these experiments were evaluated together with the linear T(t) experiments by the method of least squares.

The modulated and CRR temperature programs were also employed in a detailed study on the combustion properties of torrefied woods. This type of fuel is produced from biomass feedstock by a heating at 220-280°C. Torrefied woods have several advantageous properties including a hydrophobic nature; open air storage possibility without rotting; and an increased heating value. The model outlined at the previous task (in page 1) was employed for the description of their combustion kinetics in the kinetic regime. 36 different experiments were evaluated simultaneously by the method of least squares to get reliable results. The corresponding paper was submitted to *Energy & Fuels* this week.

### **Task 1/C: Study of Feedstocks, Solid Products and Intermediates for Topics 2 and 3**

From the results of this task we would like to draw attention to the results of three specific works as follows.

Corn fiber, which is the residue of the corn wet-milling process, was studied as a feedstock for the isolation of the hemicelluloses and the production of ethanol. The results indicate that the applied analytical methods are suitable for studying changes in the composition of the variously treated corn fibers.

Fundamental research was carried out to enhance the second generation bioethanol production from lignocellulosic biomass materials. The effects of the pretreatments on the raw materials were studied by pyrolysis – gas chromatography – mass spectrometry and thermogravimetry – mass

spectrometry. It was found that both the steam pretreatment and the alkali treatment change the chemical structure of the lignocellulosic materials. Relations have been found between the functional group composition of lignin and the efficiency of the polyethylene-glycol addition during the enzymatic hydrolysis of the steam pretreated samples.

The alkaline pretreatment of the industrial hemp breaks up the strong fibers of hemp, which can be utilized as cellulosic fiber in composite materials as well as raw material for the second generation bioethanol production. The chemical composition and the thermal stability of the hemp samples undergone by various alkaline treatments (NaOH, KOH) have been studied by thermogravimetry-mass spectrometry. It was concluded that the alkaline treatment removes certain functional groups of the hemicellulose component of hemp, while the residual alkali ion content has significant effect on the thermal decomposition mechanism. Relations have been found between the thermal decomposition parameters, the altered composition of hemp, as well as the alkali ion content by using principal component analysis.

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## ***Topic 2: Studies in the Field of Bioethanol Production***

Besides corn and other grains there is a remarkable potential of hemp and sweet sorghum in Hungary, which have high yields. These plants and their residues/byproducts (hemp hurds, sweet sorghum bagasse) can be used as raw materials for sucrose (saccharose) or cellulose based biofuel ethanol production. Polysaccharides in lignocellulosic biomass can be converted to sugars in chemical or enzymatic way after physical and/or chemical pretreatment. Monomer sugars can be fermented to ethanol after hydrolysis or in simultaneous saccharification and fermentation process.

Steam pretreated sweet sorghum bagasse and hemp hurds substrates were subjected to enzymatic hydrolysis in the 1<sup>st</sup> year of the project. Pretreatment was carried out at the Department of Chemical Engineering, Lund University, Sweden. Enzymatic degradation was performed using commercial enzyme preparations from Novozymes, Denmark. Surfactant was applied in order to enhance the efficiency of enzymatic hydrolysis which allows reducing the amount of enzyme needed in the process as well. The dosage of additive was optimized to achieve high-degree degradation of polymers and low enzyme adsorption on the substrates during the hydrolysis.

Performance of enzymatic degradation of the two agricultural/industrial by-products, sweet sorghum bagasse and hemp hurds, in the presence of additives was further investigated in the 2<sup>nd</sup> year of the project. Data available in the literature and our previous results showed that not only surfactants but polymers can be used to intensify the enzymatic degradation of lignocellulosic materials. Therefore besides Tween 80 (polysorbate 80, nonionic surfactant and emulsifier) which was used in previous experiments, PEG (polyethylene glycol, produced by the interaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers, molecular mass below 20,000 g/mol) was tested as well. The applied loading of PEG was equal to the one determined for Tween 80 on the two substrates at the optimal parameters for the enzymes (50°C, pH 4.8), what resulted in the highest degradation yield of cellulosic polymer and lowest enzyme adsorption. In order to investigate if the surfactant or the polymer has an effect on the optimal temperature of the enzymatic hydrolysis by changing the surface properties of the solid lignocellulose substrate or the features of the enzyme protein molecules, the effect of the additives on degradation was studied at various temperatures. The degradation yields calculated from the chemical composition, i.e. cellulose and hemicellulose contents of the substrates and the concentration of the monomer sugars in the hydrolysis supernatants were used for the evaluation of the experiments.

The effect of additives (Tween 80, PEG 4000) on the enzyme adsorption during degradation of the water insoluble fraction (washed fibers) of steam pretreated sweet sorghum bagasse and hemp hurds was studied at various temperatures in the 3<sup>rd</sup> year of the project. Though some enzyme cost reduction has been achieved during the last decade as a result of improved efficiency of commercially available enzyme preparations, it is still significant. Therefore lowering the amount of enzymes needed for the hydrolysis and/or recycling of them in the process remained in the focus of the research in this area.

Significance of non-productive bonding of enzyme proteins on the lignin content of the substrates was investigated. Besides the above mentioned agricultural/industrial residues pure cellulose (Avicel) and delignified pinewood cellulose consisting of low hemicellulose content (Solka Floc) were used as model substrates in the experiments. Adsorption studies were carried out for the total protein content and for certain enzyme components. Protein concentration and standard activity measurements were performed; furthermore gel electrophoretic analysis was applied to detect the enzyme adsorption during the hydrolysis.

The aim of the study was to examine the effect of the additives on cellulase protein adsorption regarding i) the quality of additive, ii) the nature of substrate, iii) the temperature of degradation. Furthermore, we investigated if the performance of enzymatic hydrolysis clearly correlates to the degree of protein adsorption on the substrates used.

In the 4<sup>th</sup> year of the project sweet sorghum based technologies were modelled using Aspen Plus flow-sheeting software by solving the mass and energy balances. Sweet sorghum deteriorates rapidly after the harvest; therefore juice must be squeezed immediately. The juice is fermented only during the harvest (juice period). The bagasse produced during juice extraction is dried in a superheated steam dryer and used as feedstock right after the juice period (bagasse period). It is wetted, impregnated with SO<sub>2</sub> and pretreated in a continuous steam-explosion unit. Hydrolysis of the solid fraction and ethanol fermentation are carried out simultaneously (SSF) applying commercial cellulase preparation. In both periods on-site yeast propagation is implemented. Ethanol fermentation of juice and SSF of pretreated bagasse take place in the same fermentors. As the fermenting organism is ordinary baker's yeast pentoses are not converted. Ethanol is concentrated by distillation. Stillages derived from juice and bagasse are separated into thin and thick stillage. The former is digested anaerobically and biogas is produced, while the latter is dried and incinerated with the biogas to generate heat and power. Our model calculations proved that the heat demand of the process can be covered by incinerating the biogas, the pressed sludge and dried thick stillage, hence external energy source is not required.

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### ***Topic 3: Modified Lignocellulosic Fibers from Agricultural Wastes***

The work aimed at producing special substances with sorption and ion exchange capacities. Following the project's work plan, a detailed literature search was carried out in the first year to learn about the state of art on the retreatment methods of biomass raw materials and the modification possibilities of cellulose fibers. Based on the literature data raw materials were selected and purchased (sunflower husk, rapeseed pellet and starch-free wheat grain) and an experimental plan was prepared.

From the second year the manufacture of cation exchange materials from biomass was studied using a solid phase thermochemical reaction with citric acid. A pure cellulose model substance (Solka Floc) was involved in the experiments for the comparison of the results. The sorbent

materials obtained were qualified, tested (copper ion sorption, capacity, etc.). During our measurements the effects of particle size, the initial water content, water addition, temperature and time on the reaction were investigated. We found that the copper sorption capacities of the *cellulose* citrate produced from rapeseed pellet was similar to the ones of the *starch* citrate determined earlier, though the cellulosic substance was prepared by a *simple* preparation scheme from *raw* biomass, while the starch-based product was manufactured from *pure* starch under *optimized* reaction parameters.

Afterwards the manufacture of adsorbents suitable for sorption of inorganic pollutants was studied using an experimental design. The thermochemical reaction between the rapeseed pellet and the citric acid was optimized by a 2p type factorial experimental design. The optimal citric acid concentration, temperature and reaction time were determined.

Moreover the effects of pretreatments on the adsorption effectiveness were investigated: combination of solvent extraction, acidic or alkaline pretreatment steps and modification with citric acid were carried out using rapeseed pellet and starch-free wheat grains and finally materials having ion exchange capacity were obtained. The capacities were determined for three metal ions (copper, zinc and nickel) separately, from aqueous solution in batch experiments. The highest effectiveness for all the three cations was found in case of rapeseed pellet applying solvent extraction, alkaline pretreatment and reaction with citric acid.

Studying the adsorption behavior, progress curves of the adsorption of zinc and copper ions for the rapeseed and wheat modified with citric acid for 24 hours, while adsorption isotherms were recorded from copper, zinc and nickel solutions, in batch mode of operation.

Adsorbents suitable for removal of organic pollutants were manufactured from rapeseed pellet and starch-free wheat applying epichlorohydrin and colin-chloride as reactants. The ratio of the reaction components was varied and the products were ranked by sorption of methylene blue. We found that much higher (tenfold) sorption capacity product was obtained from rapeseed than from wheat grains. The best product – manufactured using 0.045 : 0.015 : 0.3 : 0.83 mol ratio of epichlorohydrin: colin-chlorid: NaOH: water – was found to bond 48 % of methylene blue under the experimental conditions.

The results were published in international journals. A PhD dissertation was also written and defended from the results. Concerning the utilization possibilities of the results, we found that the product from rapeseed pellet (extracted with solvent, pretreated with alkaline solution, and modified with citric acid), is suitable for column applications after removal of the easily dissolved compounds. The capacity of the particles (after shaping) was found similar (2.79 mmol H<sup>+</sup>/g) to one of a commercially available product: Purolite C104 ion exchange (2.90 mmol H<sup>+</sup>/g).

## SELECTED PUBLICATIONS

### *Publications in international journals:*

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***PhD Theses:***

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