CHALLENGES IN UNDERSTANDING THE SIMULTANEOUS AQUEOUS EXTRACTION AND HYDROLYSIS OF SPRUCE HEMICELLULOSES

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The aqueous extraction of hemicelluloses has gained an increasing interest with new emerging applications for hemicelluloses in the modern forest-based biorefinery concept. The extraction kinetics play a key role in their industrial utilization as both the reaction rate of the dissolution itself and the hydrolysis kinetics influence the recovery of the desired products. Pressurized hot water extraction of spruce sapwood was investigated in the temperature range 120 °C-170 °C using a large liquid-to-solid ratio in an intensified cascade reactor system. The results show a complex dependence of the final product on various parameters. A significant temperature dependence of the extraction rate was observed, albeit low influence of the changes in pH. Moreover, a clear dependence of the hydrolysis rate on the temperature and pH was observed. The molar mass of the extracted hemicelluloses was clearly influenced by the internal diffusion limitations, which are dependent on the chip size.

Keywords: hemicellulose, aqueous extraction, hydrolysis

INTRODUCTION

Lignocellulosic feedstock is becoming a viable option for industries valorizing carbohydratesand in many cases the products can compete with traditional crude oil or natural gas based products.[1] Biofuels such as bio ethanol and higher alcohols produced with the help of catalysis arise growing interest.[2] In the production of alcohols and other value added products from sugar monomers, the hydrolysis of oligomeric hemicellulose to sugar monomers is currently one of the most crucial issues.[3-7] In addition to the growing interest towards utilizing hemicelluloses based sugar monomers, the utilization of the hemicellulose oligomers is a growing field and new applications are emerging continuously. Various industrie sin the field of fine chemicals, biocomposites, cosmetics, and alimentary products a reutilizing hemicelluloses in an increasing degree.[8-10] Applications related to films, hydrogels, coatings and hybrid thermoplastics are being developed and taken into use. Examples include new drug delivery methods, such as neutral and ionic hydrogels, barriers against oxygen and water vapor for the packaging industry, papermaking related binders and some medicinal and nutritional health products.[8,11-13]

Acetylgalactoglucomannan (AcGGM), the main hemicellulose in softwoods, can be utilized *e.g.* for the applications described above, due to its biological and physico-chemical properties. The extraction of the AcGGM from wood, however, requires deep going quantitative knowledge of the kinetics and the solid-liquid reactions involved.[8-9,14-17] The best solvent for extracting unmodified AcGGM, according to current knowledge, is neutral or slightly acidic water. Quantitative studies on the pressurized hot water extraction (PHWE) of hemicelluloses found in literature have mainly focused on hardwoods, due to their current use in industry, while the information related to softwoods is rather limited.[14,16,18-19] The main challenges related to the effective industrial use of AcGGM are the

controlled extraction and the ability to control the hydrolysis of the oligomers, as the desired products are not necessarily monomeric sugars but rather oligomers of a certain molecular weight. The ability to tailor the product obtained in the extraction process would give a considerable advantage in industrial production and even pave the way for new applications.[14,20]

The extraction rate of a compound and its dependence on different parameters is often studied in a systematic fashion by varying one parameter, while keeping the rest at a constant level. This gives the possibility to quantitatively determine the influence of a single parameter on the reactions involved in a reliable fashion.[18,21] The combinatory influence can then be combined in, for example, kinetic modeling, where the model is then able to predict precisely the overall behavior of the system.[14,22-23]This approach was also used in the current study, and the temperature and particle size were changed stepwise while striving to keep the conditions otherwise constant. Sampling and analysis was performed at 5 points of time during the extraction.[14]

EXPERIMENTAL

The kinetic PHWE experiments were performed with a cascade reactor system, in the current study (Fig. 1). The main advantage, compared to traditional digesters, is the possibility to control the reaction conditions very precisely and rapidly, which is the basis for reliable kinetic experiments. Moreover, the system allows the sampling of both the solid and liquid phase during the reaction. The system includes online monitoring and recording of the pressure and temperatures inside each reactor chamber, which enables a detailed interpretation of the data. Numerous samples were analyzed for sugar composition, molar mass, and pH. The sugar compositions and the overall amount of extracted hemicelluloses were analyzed employing acid methanolysis and the well-established GC method.[24-25] The molar mass of the extracted hemicelluloses was determined by HPSEC-MALLS with an RI-detector.[26-27] The analysis contributes to understanding the overall mass balance of the different reactions including the possible degradation of the monomers. The total volume of the reactor was 4.3 dm^3 and each cascade chamber was 0.2 dm^3. The flow-rate used in all of the experiments was 150 dm^3 h^{-1}. A solid-to-liquid ratio of ~180 was used, in order to avoid the interference of thermodynamic limitations and severe mixing was applied in order to overcome any eventual external mass transfer limitations. The temperature in the experiments was between 120-170 °C, which has been shown to be the most relevant range for PHWE. The raw material, fresh spruce (*Piceaabies*) sapwood, and the samples were stored at -18 °C in order to avoid contamination and decay.Sapwood was used in the experiments as pulpwood is the main raw material for the chemical industry and it contains mainly sapwood. Two well defined chip sizes were used in the experiments, a 1.25-2 mm sieved fraction and hand-made 10*10 mm chips. The total amount of wood used in each experiment was 25 g dry weight, 5 grams per chamber.

RESULTS AND DISCUSSION

The cascade reactor system performed well, enabling an accurate control of the reaction conditions and sampling. The reaction was initiated and stopped rapidly; the desired reaction temperature was reached in about 3-4 min and the quenching took 1 min. The overall dissolution rate of the hemicelluloses was highly temperature dependent, as displayed in Figure 2.

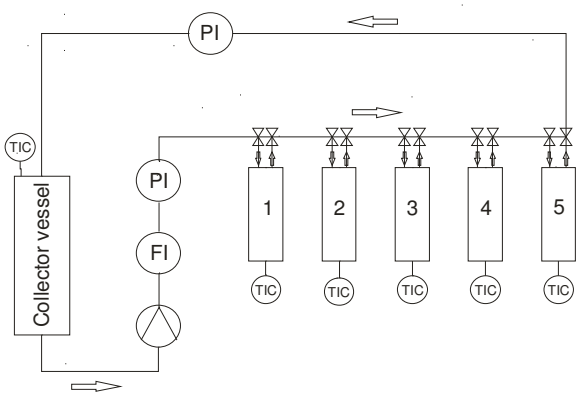

Figure 1: A simplified scheme of the reactor setup. The reactor chambers are numbered from 1 to 5

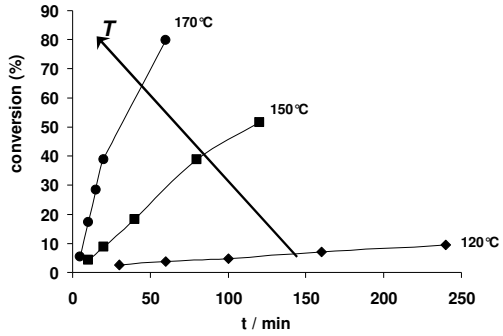

Figure 2: Conversion of hemicellulose extraction as a function of time at different temperatures with 10*10 mm cubic blocks

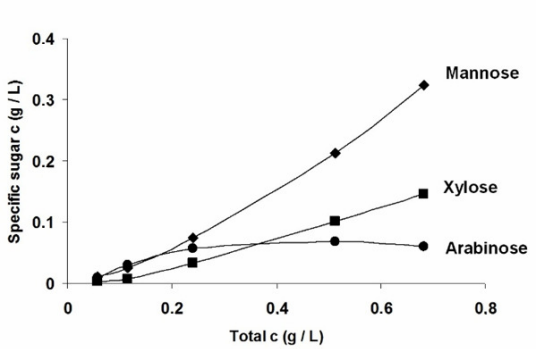

Figure 3: Concentration of different sugars as a function of total concentration for an experiment performed at 150 °C with 10*10 mm cubic blocks

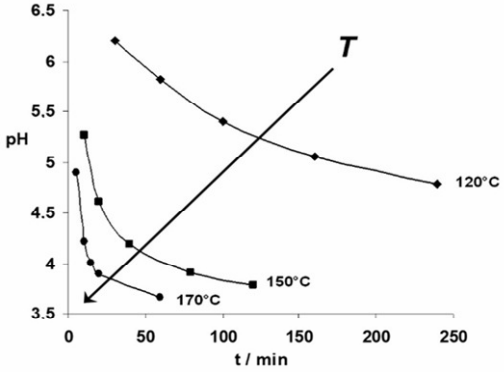

Figure 4: The pH as a function of time for different temperatures (chip size 10 mm cubic)

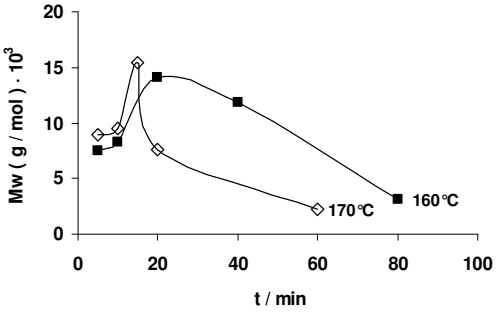

Figure 5: Mean molar mass during the extraction at 160 °C (open symbols) and 170 °C (solid symbols) with 10 mm cubic blocks

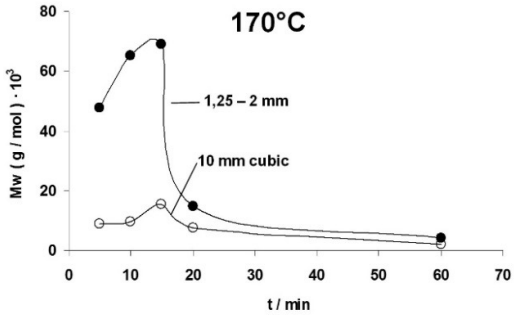

Figure 6: Mean molar mass during the extraction at 170 °C for two different chip sizes

A conversion of 80% was reached after 60 min at the highest temperature, while only 10% was obtained after 240 min at 120 °C. The conversion was calculated as per cent of the total amount of hemicelluloses in the wood material, i.e. at 100% conversion all of the hemicelluloses are in the liquid phase. Also variations in the reaction rates of different hemicelluloses fractions were noticed. It was clearly visible (Fig. 3) that, for example, arabinose was extracted rapidly in the early stages of the experiments, while the extraction rate of mannose even increased during the reaction. This could be utilized in practice for influencing the selectivity of extraction by applying temperature profiling.

The pH changed throughout the reaction and a systematic correlation with the conversion was observed, e.g. increasing conversion led to lower pH. The lowest pH obtained in the performed experiments was about 3.6 (Fig. 4). The liberation of acetic acid is the main reason for the decrease in pH.

Significant temperature dependence was shown for the degradation of the oligomers,

which can be considered as a possibility for optimizing this phenomenon depending on the desired product. Figure 5 shows that the hydrolysis is significantly stronger at 170 °C than at 160 °C as higher average molar masses are obtained at 160 °C than at 170 °C, especially at the later stages of the extraction. The chip size influenced clearly the molar weight of the final hemicelluloses. Figure 6 displays experiments performed with the two different fractions, 1.25-2 mm and 10*10 mm cubic. The results clearly demonstrate that the internal diffusion limits the extraction of the larger molecules, especially with the larger chips.

The following conclusions can be drawn from the above mentioned experiments. The extraction rate of spruce hemicelluloses is increased by temperature and the pH decreases significantly with conversion. The hydrolysis rate is increased at higher temperatures. Larger hemicelluloses can be obtained from smaller chips and sugars are released with different rates from the wood chips.

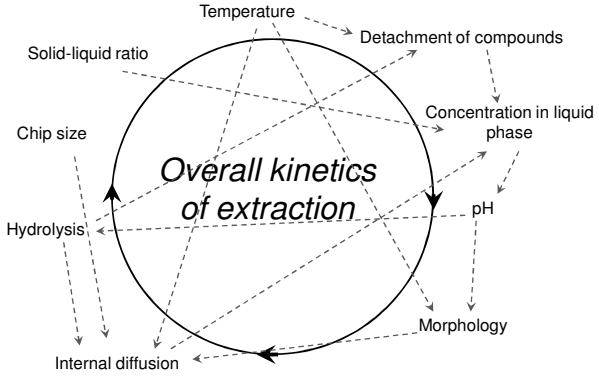

Figure 7: A schematic representation of correlations between different parameters in spruce hemicellulose extractions. The arrows represent the influence of one parameter on another one

There are clear trend lines in these observations. However, the overall extraction of hemicelluloses from wood and its dependence on the experimental parameters is much more complex, due to the fact that no single parameter can be varied without influencing simultaneously other parameters, severely complicating the interpretation of the data.

Still some conclusions could be made. The temperature enhances the detachment of the hemicelluloses from the wood matrix and increases the overall rate. However, it is not sufficient for the oligomers to be only detached in order for them to move into the liquid phase, since they also need to diffuse out from the chip. This is significantly hindered, especially for the larger molecules, by the morphology of the wood matrix. This is clearly demonstrated by the experiments performed with different chip sizes. It is known from the production of pulp that both the temperature and pH influence the morphology of the chips. This leads to the fact that the pH, which changes throughout the extraction and depends on the conversion, also influences the conversion and properties of the final product, i.e. the molar mass. The experiments show that hydrolysis occurs also inside the chips, and not only in the liquid phase, therefore if the large hemicelluloses are not liberated from the chip "in time" they are hydrolysed to smaller fractions. Moreover, temperature also commonly influences internal diffusion. The solid-liquid ratio influences the concentration in the liquid phase, and subsequently pH. This has a direct impact on hydrolysis, which in turn influences the internal diffusion as the smaller fractions are better able to diffuse out from the wood matrix. The correlation of the factors mentioned here is by no means a complete list, but demonstrates the complexity involved in the overall extraction process and especially the quantitative investigation of it. Figure 7 demonstrates some of the correlations involved.

The aim of the current article is not to give detailed quantitative answers to the factors influencing the extraction of hemicelluloses, but rather to bring attention to the complexity and challenges involved. This applies both to the experimental planning as well as data evaluation, which can easily be performed too simplistically if the various aspects are not considered. This is visible also from the literature where somewhat contradictory results occur for example for the influence of pH on the overall extraction rate.[14,28]

In order to be able to evaluate the influence of one parameter on the overall reaction and the obtained product, considerably more experiments are needed. Mathematical modeling is also a useful tool in order to evaluate the influence of a single parameter, as well as their correlations.

CONCLUSION

The aqueous extraction of spruce hemicelluloses is a complex issue as the temperature, pH, as well as external and internal mass transfer phenomena influence both the overall rate and the obtained hemicellulose properties. The decoupling and quantitative assessment of the parameters is a key issue in understanding and modeling the phenomenon, as well as in implementing it in industrial production in order to obtain the desired products for further processing in an effective way. One of the major challenges involved is the interlinking of the parameters in the complex system, *i.e.* a single parameter can not be varied without influencing the others.

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