Simulation of the mashing process – Model based assistance for progress, monitoring and control of the depolymerisation of natural polymers using the example of the mashing process

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Initial Situation:

Many basic processes as well as single process steps of life sciences consist of a combination of solution processes of suspended solids and degradation of natural macromolecules. In the area of food and feed-processing industry, pharmacy and biotechnology they are usually based on enzymatic catalyzed degradation processes. In general the basic procedures of these applications are comparable and they are the result from the particulate solution of disperse raw material (e.g. malt, flour, powder) or a linked transport-reaction-process. They are a result of the process and substrate-dependent activity of an enzyme and of mass transfer properties of the single particles in a suspension. Examples are the lipolytic activity in a cleaning process, HFCS-production from corn meal, the enzymatic degradation of lignin during wood processing, the enzyme-catalyzed protein denaturation of leather finishing, the polymer hydrolysis of biogas production or bioethanol production as well as the mashing process of beverage production.

Against this background it becomes clear, that by enzyme-catalyzed depolymerisation processes related to various applications not only technological factors have to be considered, but also the complete system of depolymerisation processes, enzyme kinetics and mass transfer linked to each other have to be investigated.

The impact of a complex cascade on the interpretation of the process technology, in which the individual phenomena are not the important one, is not possible without a model-based analysis.

The objective of the project consists in the research of mechanisms of enzymatic activity and the influencing mass transfer during depolymerisation processes. As a research object the starch degradation during the mashing process is chosen. The results are combined in a simulation tool which can be used in breweries or linked industries, e.g. the production of wort based beverages or ethanol, for process planning and especially optimization.
Research Results:

Within the project the dependence of starch degradation on molecular weight depend enzyme kinetics as well as mass transfer of reactants has been studied and a population dynamics model for enzyme kinetics of starch degradation has been developed. In addition, practical-applicable temperature-time profiles of real matrix systems in mashing and brewing trials (barley malt mash) and their influence on the starch degradation have been investigated, resulting in a transfer of the results to applications in practice.

In the studies the influence of mass transfer phenomena on enzymatic starch conversion was investigated. The water uptake and starch polymer leaching of particulate starch are evident for starch gelatinization and were described by mass transfer correlations. A successful development of a mechanistic and predictive model of enzymatic starch conversion needs to take into account the involved mass transfer mechanisms. For this reason the necessary diffusion coefficients were examined experimentally. The mass transfer resistance is doubtlessly within the primary starch particle. Intensification of convective mass transfer in the liquid phase of starch suspension has negligible effects. Likewise, the comminution of starch raw material, with comminution machines used usually in the brewery, has only a minor effect on the mass transfer. Coupling of these results with the developed population balance model offers a description of the enzymatic starch conversion in more detail.

Furthermore a population balance model describing the evolution of the chain length- and amount of branching distribution for starch has been developed. The model is based on literature data about the mechanisms of the three most important enzymes (α-amylase, β-amylase, and limit dextrinase) and the process parameters (pH, ion-concentration, and temperature). E.g., the dependence of the activity of amylase in the pH-range 3-9 is modeled excellently. This population balance model can serve as a basis for model-based control and optimization. For unbranched and branched starch a numerical method has been developed. Therefore, complex depolymerization processes can be simulated fast and accurately. The method was about 1000 times faster than the kinetic Monte-Carlo method for short-chained and unbranched saccharides. A user friendly tool has been developed for the depolymerization of unbranched starch. An identifiability-study and a parameter estimation from experimental data imply that the missing model parameters can be estimated with a low number (< 10) of measurement of chain length-distributions. This is a significant improvement compared to current methods which require circa 5 time profiles for around 10 monodisperse initial conditions.

Determining the enzyme kinetics of starch degradation (amyolysis) of the single amylolytic enzymes in pure starch by the molecular weight of the starch degradation products measured by means of field-flow fractionation system was not realizable. Thus, the focus was put on the experimental setup for the measurement of temperature-time profiles in practical matrix systems (barley malt mash) and their influence on starch degradation. With the results, it is possible to control the starch degradation by the mashing parameters (time and temperature, mashing procedure) and the malt modification (Kolbach index). For the first time, this could be detected analytically using AF4 method to track the molecular size distribution of the starch degradation products. The molecular weight distribution of starch degradation products in beer depends on the mashing-in-temperature as well as raw material quality (modification).

Regardless of the proteolytic modification the molecular weight distribution of starch degradation products in beer by using a high-short-mashing-procedure (mashing-in-temperature of 63°C) compared to lower mashing-in-temperatures of 45°C or 55°C increases significantly. The overall level of the molecular weight distribution using an undermodified malt (Kolbach index 36 %) is significantly higher than by the use of a protein solution level of 41 % Kolbach index. The degree of modification and the spectrum of polysaccharides achieved by process management showed great influence on the resulting beer characteristics (especially palativeness).

By due consideration of all results it can be confirmed, that dealing with enzyme catalyzed depolymerisation processes in various applications not only technological variables should be considered, but the enzyme kinetics as well as mass transport of reactants have to be investigated coupled.

The developed model describing the individual phenomena in combination with the experimental results allows a detailed understanding of the process technology. The complexity of the experimental setup of enzyme-substrate reactions demands further research in this field. However, further development based on the developed model linked to the knowledge of mass transport should be continued.

Economic Value:

More than 1000 SMEs of the malting and brewing industry will benefit from the obtained results during the project. Until today the mashing process cannot be simulated or controlled inline. The developed simulation model can serve as a basis for model-based control and optimization of the starch degradation during the mashing process. A further development of the model opens up the possibility of process control and allows individual management of single brews or
batches of raw material to manage the mashing process in an economical way. Furthermore, important knowledge about interaction of mass transfer processes and enzymatic degradation can be provided. This allows, for example, the optimization of the energy-intensive grinding processes (step before mashing). The results are very useful for process optimization in the brewing industry and linked industries or for similar processes of life science applications. Results on starch gelatinization, which is fundamental for enzymatic degradation, promise an optimization of the temperature-time profiles during the mashing process in consideration of variable raw material quality.

Due to the insufficient reproducibility of the measurement system caused by unsolved pure starch as well as the enormous reaction rate of the enzymatic starch degradation of < 1 min, if the starch is in solution, temperature-time profiles of enzyme kinetics of single amylolytic enzymes could be detected with limited success. Here, additional support and further research is necessary. However, within the project, temperature-time profiles of practical matrix systems (barley maltmaries) and their influence on starch degradation could be analyzed successfully. With these results the adaption of starch degradation managed by the mashing parameters (time and temperature) as well as the modification of malt (Kolbach index) can be carried out and thus the degradation of starch can be controlled in detail. In addition, a new method for detecting the molecular size distribution of starch degradation products in mash and beer was developed which can be directly applied in practice.

The degree of polysaccharide degradation can be influenced by the management of the mashing procedure and as a result the beer quality can be significantly improved (especially the full-bodied).

The developed population balance model for enzymatic depolymerization of branched starch can be used and validated for the obtained data of the real matrix systems. The practical results and the developed analytical method (AF4 / aFFF) for detecting the molecular size distribution in mash and beer can be directly applied in practice. The research findings enable the brewing industry to achieve an optimization of the recipe or an adaptation of the technology to get significant quality improvements and potential to control the process more efficient.

Publikationen (Auswahl):

- FEI Schlussbericht 2015
- Henke, S.; Sommer, K.;: About the influence of mass transfer phenomena on starch gelatinization during mashing. ASBC Annual Meeting (2014), Chicago.
Weiteres Informationsmaterial:

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