APPLICATION REPORT

High pressure reactor
Pretreatment Techniques for Biorenewable Sources

Biomass pretreatment technologies
Overview of pretreatment techniques

The fields of application for Berghof highpreactor are chemical reactions proceeding at increased temperature and pressure demand with a maximum at 260°C/200bar which can be found in various sectors of chemical engineering. Ideal reaction conditions are realized due to the modern and diverse design of highpreactor. In the present series of highpreactor Application Reports an overview on selected research topics is given. The intention is not to provide exhausted scientific information but an introduction to various topics for our customers. All application reports are based on scientific articles published mainly by Berghof highpreactor users. Original literature is cited at the end for further reading.

Overview

The use of alternative energy sources to substitute successively fossil fuels attracted much attention in the last decades. With respect to sustainability and green chemistry, researchers try to gain access to organic feedstock as a renewable energy source. But, for an economic use of biomass as a fuel (see also application report “Biofuels”) special pretreatment techniques are necessary.

Biomass, mostly lignocellulosic biomass is composed of cellulose, hemicellulose and lignin being the primary building block of plant cells. Cellulose can be defined as a linear polymer whose D-glucose subunits (7.000-15.000) are bound by β-1,4 glycosidic bonds. The polymers are linked together by hydrogen and Van der Waals bonds holding the linear chain

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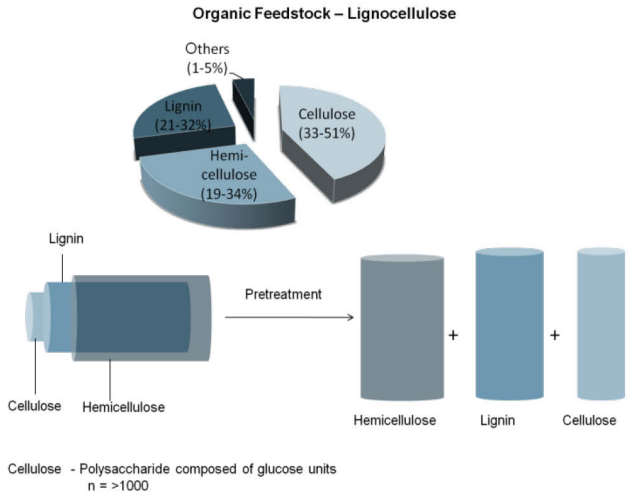
firmly together. Cellulose is packed in microfibrils which are covered by hemicellulose and lignin.
Lignin is a complex, large molecule structure building up the cell wall of plants and acting as a scaffold permitting structural rigidity and preventing against vermin.

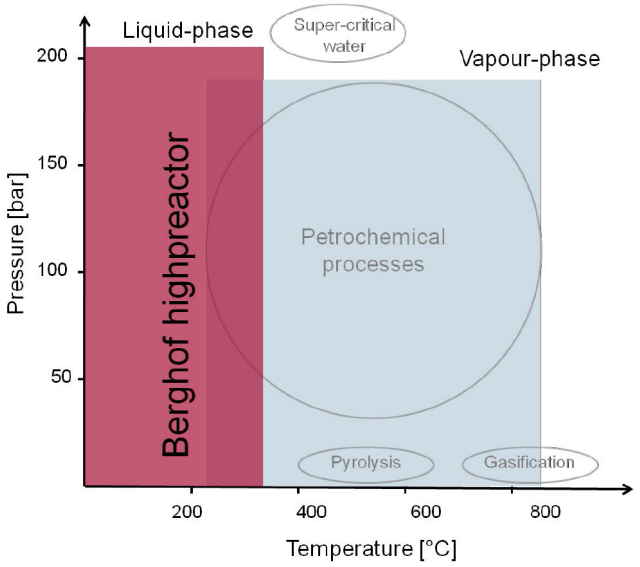
Hemicellulose consists of shorter chains of 500-3.000 different sugar units which are branched.



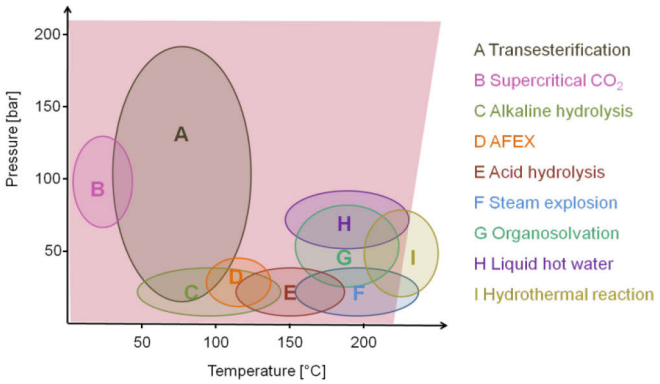
Lignocellulose as a basic raw material for biofuel production

The pretreatment of biomass aims to break down the lignin structure and to disrupt the crystalline structure of cellulose into their monomers for achieving an economical yield of fermentable sugars.

Moreover, lignin is one of the most abundant renewable biomass next to cellulose arising as a residue from pulp and paper as well as biofuel industries. It is assumed that more than 70 million tons of lignin is produced as a by-product from the papermaking industry. The development of new wood-based end products increases the market potential for lignin. Additionally, considering the efforts to reduce the fossil-fuel dependency by producing fuels based on biomass, will extraordinarily increase the quantity of lignin and expand its market. The development of new raw material pre-treatment techniques and marketable lignin-based materials can be expected to be a possible field of application for Berghof highpreactor (please also compare with the given application examples illustrated below).

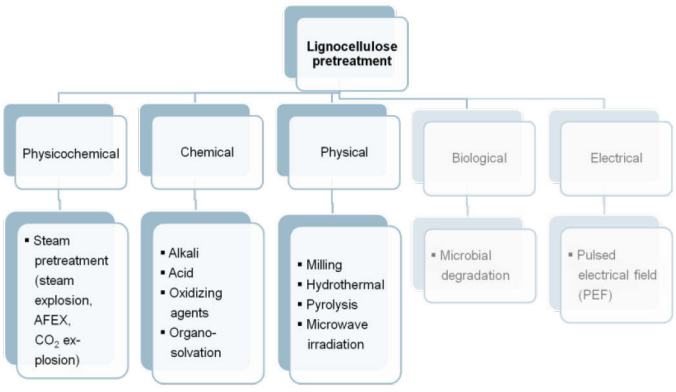


Application of Berghof highpreactor in the range of 260 °C / 200 bar



Berghof highpreactors are suitable for a broad range of synthesis

Hemicellulose is easily hydrolysable by dilute-acid hydrolysis (0.5-1.5 %) under moderate conditions (160-230 °C; 10 bar). Hydrolysis of lignocellulose is impeded by physicochemical and structural factors which require more extreme techniques.



Pretreatment techniques

The pretreatment of biomass plays a crucial role e.g. in the ethanol and paper production obtaining lignin with consistent, uniform, and stable properties. Berghof highpreactor can be used in the wide field of developing new efficient pretreatment techniques.

1 Physicochemical pretreatment

1.1 Steam Explosion

One possibility to treat lignocellulosic raw material is the so-called steam explosion. It is normally initiated at 160-260 °C at corresponding pressure of 5-50 bar. The biomass-water vapour-mixture is held for some seconds or minutes to promote the hemicellulose hydrolysis. Afterwards, the sample is immediately exposed to atmospheric pressure leading to an explosive decompression.
The steam explosion can be described as a thermomechanochemical process where lignocellulosic structures are disrupt aided by steam (thermo), shear forces (mechano), and the hydrolysis of glycosidic bonds (chemical). The reaction is carried out in reactors enabling the application of high pressure and temperatures, e.g. highpreactor. The reactor is equipped with a drain valve ejecting the material by the induced force.

The lignocellulosic structures are penetrated by steam under pressure leading to condensation of the steam and wetting of the material. Following, acetyl groups of the hemicellulose fraction hydrolyse by forming organic acids which in turn catalyze the depolymerization of hemicellulose. Depending on the reaction condition, e.g. high temperatures and pressures, the degradation of sugars into furfural and 5-hydroxymethylfurfural (HMF) can be promoted. During the sudden pressure release, the moisture within the lignocellulosic structures evaporates immediately. The expansion of the vapor exerts shear forces on the structures leading to the breakdown of the lignocellulosic structures.

Steam explosion pre-treatment is very cost-effective (low energy consumption, no recycling) and starts to become a favored pretreatment technique.

1.2 Ammonia Fibre Explosion (AFEX)

The AFEX-process is very similar to the previously described steam explosion. Biomass is exposed at alkaline pH to liquid ammonia at 90-120 °C for several minutes. Afterwards, the pressure is suddenly released. Mostly, ammonia loadings of 1 kg ammonia per 1 kg dry weight biomass are used.

The AFEX technique solubilizes lignin while hemicelluloses and cellulose remain intact. But, the pretreatment technique was shown not to be effective for biomass with lignin content higher 25 %. A major advantage is that in comparison to other methods no by-products with inhibitory effects are formed during the treatment. However, due to remaining residues of lignin fragments on the cellulosic surface subsequent water washing is necessary what increases the amount of waste water. Liquid ammonia, used during the process, can be recovered and reused to 99 %. Here, the cost for ammonia and the recycling of the reagent are a major drawback.

1.3 Carbon Dioxide Explosion

An alternative method presents the carbon dioxide explosion using supercritical carbon dioxide. In comparison to steam explosion and AFEX lower temperatures are required. The size of carbon dioxide molecules is comparable to that of water or ammonia. Accordingly, they penetrate small pores which are also accessible to water and ammonia.

Lignocellulosic biomass is kept at pressure of 74 bar at around 31° C under supercritical CO2 for minutes to hours. The carbon dioxide pressure is released explosively which increases the surface area of the substrate for further conversion. The explosive steam treatment causes the liquid to be acidic which catalyzes the hydrolysis of hemicellulose.

Supercritical carbon dioxide is an attractive reagent for performing biomass pretreatment due to its availability at low costs, non-toxicity, non-flammability, easy recovery, and environmental acceptability. But, it is assumed that the process of carbon dioxide explosion is too expensive for industrial application.

2 Chemical pretreatment

2.1 Alkaline hydrolysis

Lignocellulosic biomass can be treated with alkaline agents, mostly NaOH, KOH, $Ca(OH)_2$ (lime), and NH_4OH. The effect depends on the lignin content of the material. Pretreatment is performed at low temperatures (50-150 °C), moderate pressure and high concentration of the base in hours or days rather than seconds and minutes.
The mechanism for alkaline pretreatment is similar to Kraft paper pulping technologies where intermolecular ester bonds cross-linking to other components as hemicelluloses are hydrolysed (saponification). This efficiently increases the accessibility of enzymes to cellulose. At high base concentrations decarboxylation of end groups and hydrolytic reactions can take place, causing, most likely, degradation and loss of carbon.

It was found that using NaOH causes swelling of the lignocellulosic material leading to

- → an increased internal surface area,
- → a decreased degree of polymerization,
- → a decrease in cristallinity,
- → separation of structural linkage between lignin and carbohydrates,
- → and disruption of lignin structures.

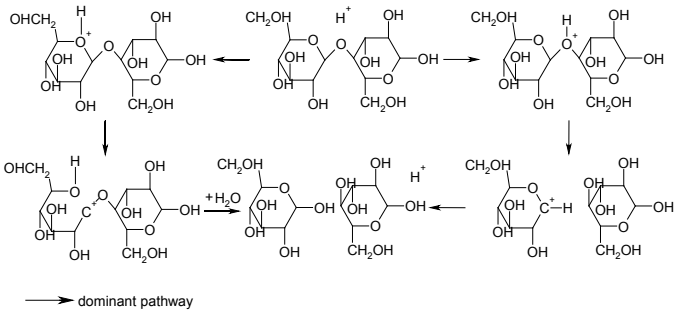
In comparison to other techniques, alkaline treatment causes less sugar degradation and many of the used salt can be regen-

erated. Nevertheless, it is assumed that alkaline pretreatment is more effective on agricultural residues than on wood material.

2.2 Acid hydrolysis

Acid hydrolysis is the traditional method for lignocellulosic fermentation. The breakdown of cellulose into glucose followed by the conversion of glucose to HMF and other degradation products is catalyzed. The main catalyst is the hydrogen ion which can easily access to the pores of the microfibrils. The basic mechanism of the hydrolysis proceeds in three steps.

(1) A proton from the acid interacts rapidly with the glycosidic oxygen linking two sugar units by forming a conjugate acid.
(2) Cleavage of the C-O bond and breakdown of the conjugate acid to the cyclic carbonium ion (half-chair conformation)
(3) Rapid addition of water leads to the formation of free sugar and a proton.



Acid hydrolysis pathway

Mostly, H_2SO_4 is applied, while HCl, HNO_3 and H_3PO_4 were also reported. Hemicellulose is removed easily when H_2SO_4 is added which enhances the digestibility of cellulose. For acid hydrolysis treatment two possible operation procedures exist:

→ High temperature (>160°C) and dilute acid (0.5-1.5%).
→ Low temperature (<160°C) and concentrated acid (30-70%).

In both cases the lignocellulosic biomass is treated within minutes or hours depending on the feedstock.

The main drawback of concentrated acids is their extreme corrosivity which makes the use of non-metallic constructions or special metallic alloys essential. Berghof highpreactor are characterized by heavy-walled, several millimeter thick PTFE inserts and linings offering effective protection against the most corrosive materials such as acids and bases. Due to this outstanding characteristic the use of expensive alloys can be avoided.
The recovery of the concentrated acid is an energy-consuming process. Furthermore, during the neutralization process large amounts of gypsum will be produced. A commercial application of this process is unlikely due to high investment and maintenance costs. In contrast, dilute acid pretreatment is the more commonly applied method.

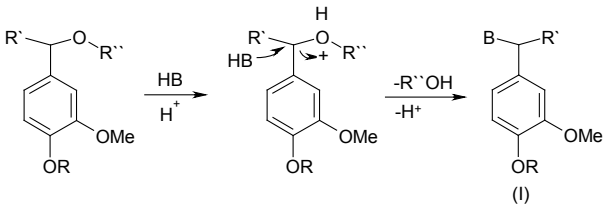
2.3 Organosolvation

Organosolvation is a promising chemical pretreatment strategy. Lignocellulosic raw material is treated with an organic solvent mixture (alcohol, esters, ketones, glycols, organic acids, phenols, esters) and acid catalyst (HCl, H_2SO_4, oxalic, salicylic acid) to break the crystalline structure of lignocellulose *i.e.* to solubilize lignin and to hydrolyse hemicellulose. The usage of catalysts enables a more selective delignification with a less degraded lignin for further technical applications.

The reaction conditions vary in dependence on the biomass. Typically, the reaction is performed at 180-200 °C within 30-90 min. The delignification process combines the following reactions:

→ Solvolysis, i.e. cleavage of lignin macromolecule via cleavage of α-aryl ether bonds (I).
→ Solvation, i.e. association of the lignin fragment with the surrounding solvent.
→ Dissolution, i.e. transport of the lignin-solvent-complex into bulk fluid.

The most easily hydrolysed bonds are α-aryl ether bonds. In comparison, β-aryl ether linkages are more resistant. The linkages are cleaved by nucleophilic substitution using acid catalyst.



R, R`= H, Me
R`` = neighbouring lignin unit
B = OH, OMe (basic species)

Organosolvation

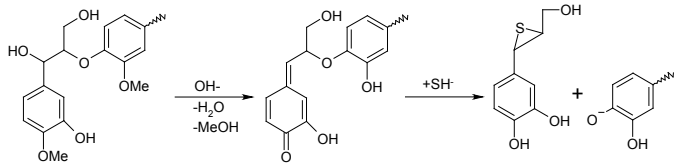
Used solvents have to be drained from the remaining cellulose, evaporated, condensed and recycled to reduce the costs of the process. Additionally, residual solvent can have an impact on further enzyme hydrolysis and fermentation.

The treatment of wood with organic solvent mixtures either alone or in combination with an acid or alkaline catalyst under high temperatures and pressure obtains so-called organosolv lignin. Firstly, raw material is treated with diluted acids to hydrolyse the hemicellulose fraction. Following, the residues are treated under organosolv conditions for the delignification of pretreated lignocellulose. Using this technique, lignin retains its original structure, has a low sulphur level, and especially has a low molecular weight which makes it attractive for synthesizing new compounds (see also application report “Biomass derived Chemicals and Products”).

It is expected that due to the outstanding properties of lignin, obtained by organosolv techniques, have a great potential to replace materials and chemicals derived from crude oil. But nevertheless, further research has to be done to improve and promote this technique (e.g. applicability to a wider variety of biomass, efficient utilization of the structural complexity of the lignin macromolecule).
Berghof highpreactor are a useful tool to perform chemical reactions also with highly corrosive liquid media. Its complete PTFE-lining effectively protects against acids and bases. Thus, safe and easy working conditions can be assured.

2.4 Kraft process

The Kraft process is used in the papermaking industry to separate lignin from cellulose fibres.
The process includes cooking (150-170 °C, 1-2h) of wood chips with NaOH and Na_2S, known as white liquor which breaks the lignin-cellulose bonds. The produced pulp is washed to recover the so-called black liquor (organic from the wood and residual inorganic chemicals) and afterwards bleached for subsequent treatment.
During cooking, lignin undergoes degradation into its fragments which are soluble in strong basic reagents. The main chemical reaction is the cleavage of ether bonds by nucleophilic sulfide or bisulfide ions.



Kraft process

3 Physical pretreatment

3.1 Hydrothermal pretreatment

Hydrothermal treatment of lignocellulosic material mainly includes liquid hot water (autohydrolysis) where pressure is needed to keep the water in liquid state at elevated temperatures.
Hemicellulose is hydrolysed within minutes at temperatures between 200 °C-240 °C and pressure above the saturation point. The reaction mechanism is similar to the acid hydrolysis technique. The reaction is catalyzed by hydronium ions (H_3O^+) coming from auto-ionization of water. Elevated pressure and temperatures between the boiling point (100°C, 1bar) and the critical temperature (374 °C, 221 bar) causes break down of water hydrogen bonds resulting in a change of the properties. Subcritical water is less polar and behaves more like an organic solvent. Due to the increased solubility of organic materials and gases the water itself can act as a solvent, reagent and catalyst. At these elevated temperatures the pK_a of water is affected such that the pH at 200°C is nearly 5.0. Therefore, hemicellulose can be easily depolymerized by selective hydrolysis of glycosidic linkages and acetyl groups. However, not only hemicelluloses´ carbohydrates are dissolved, but also the surface of cellulose is enlarged being more accessible for enzymatic hydrolysis.

Comparison of Water and Supercritical Water

Paramter	Water	Supercritical Water
T [°C]	25	374
p [bar]	1	221
ε*	78	20
ρ [g/cm^3]**	0.997	0.375
logK_a***	10^{-7}-10^{-6}	10^{-20}-10^{-18}

*Dielectric constant

**Density

*** Acid dissociation constant

The application of liquid hot water is a promising technique with low operational costs. The addition of further chemicals or acids and their recycling is not required. However, under subcritical conditions, water changes its properties and behaves more like an acid. The performance of the reaction with Berghof highpreactor with PTFE-lining is recommended.

To sum up, Berghof highpreactor can be used in the wide field of biomass pretreatment techniques. Its modern design enables the performance of various chemical reactions under preselected conditions. The complete PTFE-lining permits synthesis with highly corrosive media, implying an easy and safe handling.

Simpliest handling and safe working due to mature reactor concept

Sustainability and green chemistry will continue to be a hot topic in politic and society. Researchers are appealed to find novel renewable energy sources, new organic feedstock and to improve existing techniques. Berghof highpreactor have a high potential being applied in R&D of various sectors to support the ongoing research.

4 Literature Overview

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