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A step towards the de

The organosolv process

Biorefinery technologies are being developed at the Energy Research Centre of the Netherlands (ECN) to produce fuels, chemicals, materials, and energy from biomass. One of these technologies is the organosolv process which aims to fractionate lignocellulosic biomass into its major components (cellulose, hemicellulose, and lignin). Downstream of the organosolv process, these fractions can be converted into second generation biofuels, and chemicals such as ethanol, furfural and phenolics (a component in resins and glues). The cellulose fraction can also be used for material applications such as paper. This article presents the organosolv technology and gives results from experimental and simulation studies.

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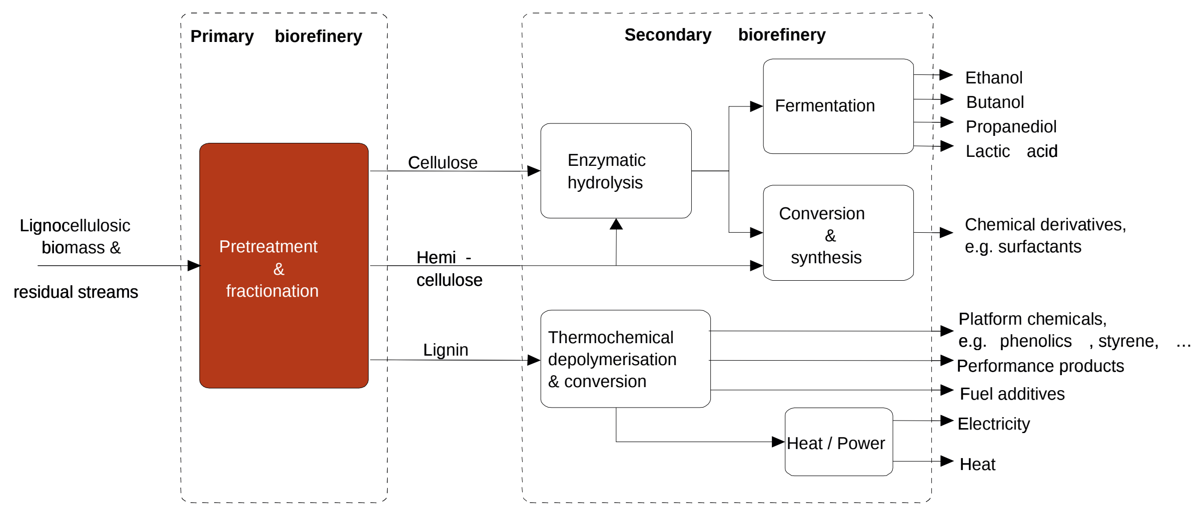
ECN is a research institute which focuses on topics like energy saving, clean fossil fuels, and sustainable energy including solar, wind, and biomass. The mission of ECN is to “develop high-level knowledge and technology for a sustainable energy system and to transfer them to the market”. Main drivers for this development are the need to reduce greenhouse gas emissions by substitution of fossil fuel sources and their products and to enhance supply-security. The group Transportation Fuels and Chemicals (part of the unit Biomass, Coal and Environmental Research) is developing technologies for the production of fuels and chemicals from biomass.
The work focuses on the conversion of lignocellulosic biomass such as wood and straw.

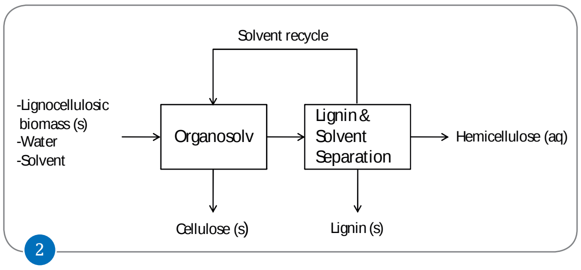
Lignocellulosic biomass

Lignocellulosic biomass consists of two major types of bio-polymers: (1) carbohydrates, in the form of hemicellulose (a branched co-polymer of C5 and C6 sugars) and cellulose (a linear crystalline polymer of the C6 sugar glucose) and (2) lignin (a highly branched, random co-polymer of phenyl propane units). Hemicellulose, cellulose and lignin have many potential applications of which some examples are given in the biorefinery concept in Figure 1. Cellulose and hemicellulose can be converted into sugars from which a wide range of products can be produced (bio)chemically including for example bio-ethanol for fuel purposes and furanics such as furfural. Alternatively, the cellulose fraction can be used for material applications such as paper. The lignin fraction is a potential source of aromatics that can be applied e.g. as phenolics in resins or as raw material for production of aromatic ethers as octane enhancers in transportation fuels. Valorization of all three fractions is crucial to maximize the use of the renewable carbon present in the biomass feedstock and to improve the economic profitability of a lignocellulosic biorefinery.



1 Concept of a lignocellulosic biomass refinery [1]

velopment of a Biorefinery



2 Organosolv process scheme

The Primary Biorefinary

The first challenge in developing a lignocellulosic biomass refinery is separating the biomass constituents in the primary biorefinery, see Figure 1. A possible technology for this purpose is the organosolv process, which uses an organic solvent to extract lignin from the biomass [2, 3]. This is one of the few technologies that yields hemicellulose, cellulose and lignin of sufficient quality for further processing into fuels and chemicals. Other fractionation technologies result either in an impure lignin stream or in lignin degradation. During the organosolv process the lignocellulosic biomass is suspended and heated in a mixture of an organic solvent, water and possibly a catalyst. The use of many different organic solvents for this process has been reported [2]. The ECN organosolv process uses ethanol or acetone. Typical reaction times range from 30 to 120 minutes at temperatures between 160 and 210°C. Optimum conditions depend on the feedstock.

During the reaction the lignin fraction of the biomass dissolves and the hemicellulose, the most reactive of the carbohydrate fractions, hydrolyses to soluble sugars and derivatives (e.g. furfural). Process conditions are chosen in such a way that cellulose, the most recalcitrant fraction, is not affected and can be separated as a solid by filtration.

The lignin is then precipitated by changing the organic solvent-water ratio (e.g. by evaporation of the organic solvent) The resulting lignin is typically >90% pure, low in ash and sulphur-free. The organic solvent is then recycled.

A simplified process scheme for the organosolv process is shown in Figure 2.

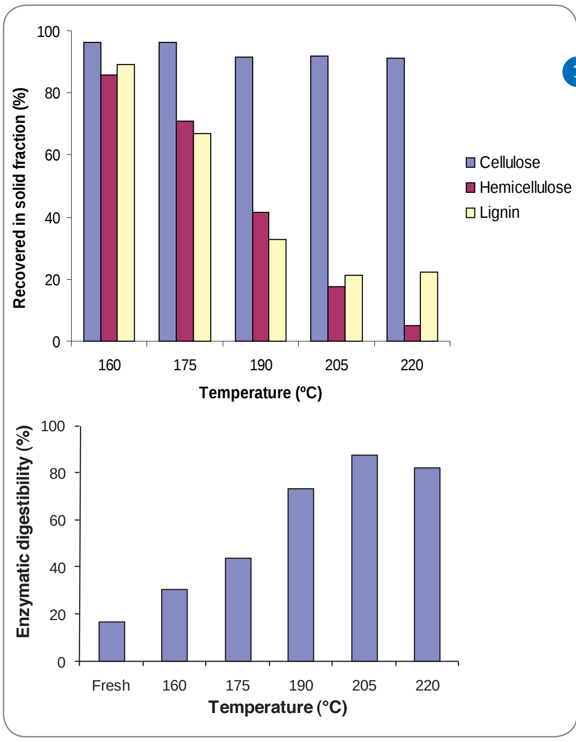
Research at ECN

Experimental

At ECN, the organosolv process has been studied extensively on lab-scale using (agricultural) residues and energy crops. Organosolv was found to be most suitable for specific hardwoods such as willow and herbaceous crops such as wheat straw.

Some important process parameters were identified:

- Type and concentration of organic solvent.
- The type of organic solvent determines to a large extent both process effectiveness as well as process design (e.g., pressure and safety). The organic solvent to water ratio governs the selectivity of the process towards the desired products due to effects on lignin solubility (delignification) and pH (hemicellulose hydrolysis).
- Liquid to solid (L/S) ratio.
- The liquid to solid ratio influences the product yields and concentrations. A higher L/S ratio leads to a higher degree of lignin extraction but at the cost of lower product concentrations.
- Pretreatment severity; combination of temperature, residence time and acidity (catalyst dose).
- More severe pretreatment leads on the one hand to improved fractionation, but on the other hand to potential degradation of the products as well as increased costs due to, among others, larger constraints on the used materials for the equipment.



3 Influence of temperature on acetone-based organosolv fractionation of wheat straw (60 min, L/S= 10 L/kg, 60:40% w/w acetone:H_2O, no catalyst used) [4]

Figure 3 shows some results of a parametric study on acetone-based organosolv fractionation of wheat straw as an example [4]. In this study 50:50% w/w acetone-water mixture were used during 1 h at 205 °C and no catalyst) [4].

The composition of the fractionated wheat straw was determined as well as the enzymatic digestibility of the resulting solid cellulose towards glucose. It was found that an increase of reaction temperature results in a more pure cellulose due to increased removal of hemicellulose and lignin. In addition, the enzymatic digestibility of the

Simplified process scheme for organosolv fractionation of wheat straw

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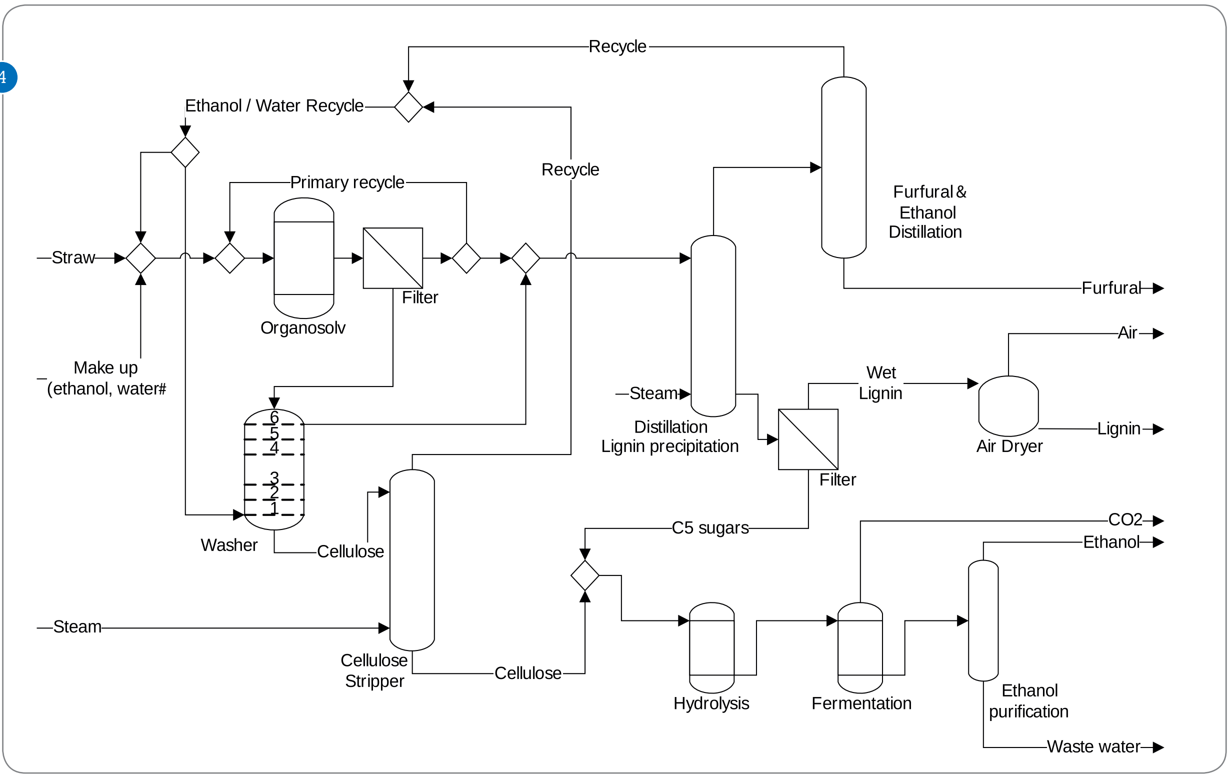

cellulose increases with temperature. Optimum results obtained within this study were 82% hemicellulose hydrolysis, 79% delignification, 93% cellulose recovery, and 87% enzymatic digestibility of the cellulose fraction (compared to 16% for untreated wheat straw)

Conceptual design organosolv process

The experimental results obtained on lab-scale served as a starting point for a conceptual design and economic evaluation using Aspen Plus simulation software. In the conceptual biorefinery, as shown in Figure 4, wheat straw is fractionated using the organosolv process (reaction conditions: 200 °C,60 min, solvent: aqueous ethanol (60% w/w), 5 L/kg dry biomass). After the reaction, the pulp (cellulose) is filtered off, washed with recycled aqueous ethanol and stripped with steam to recover solvent. Subsequently, the cellulose is fed to the enzymatic hydrolysis reactor. During the enzymatic hydrolysis the cellulose is converted into glucose, which is then co-fermented with hemicellulose sugars to bioethanol. The organosolv liquor is sent to a distillation tower where the lignin is precipitated and separated from furfural (a derivative of C5 sugar xylose) and ethanol. The lignin is filtered from the resulting liquor and dried. The remaining aqueous stream with the C5 sugars is fed to the enzymatic hydrolysis reactor. Ethanol and furfural are separated by distillation to recycle ethanol and obtain furfural as a product.

Thus far, the process simulation work resulted in the following preliminary conclusions:

- A high degree of ethanol recycling (>> 95%) is required for an energetically and economically viable process.
- Addition of water for lignin precipitation should be minimized to avoid dilution of product streams and high energy consumption of the distillation step that is required for solvent recycling.
- The most energy-consuming process steps are the ethanol distillation steps for recycling and the organosolv reactor (heating of the incoming streams).
- Heat integration of the unit operations is required to make the process energetically viable.

After process optimization and heat integration, the simulated solvent recycling degree was 99.9% and the corresponding energy consumption of the biorefinery was 20 % of the energy content of the wheat straw input (based on the lower heating value). Currently, the economic evaluation of the organosolv process is being made.

Conclusions and perspectives

Organosolv is a promising technology to fractionate lignocellulosic biomass with sufficient quality of all major fractions for direct application or further processing. The technology can be used to produce: (1) (hemi) cellulose sugars for downstream conversion to fuels and chemicals, (2) cellulose for material applications such as paper, and (3) a high purity lignin fraction for the use in resins or other applications. Research at ECN has shown that organosolv is especially suited to lignocellulosic biomass like hardwood and straw. System modeling of a conceptual organosolv process showed that the process can potentially be energetically feasible. Current research at ECN is focused on development of a continuous organosolv reactor, scale-up, and application tests of the organosolv fractions.

References

For references see *www.npt.nl* at *Inhoudsopgaven*.