Biorefineries

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Production of Platform Chemicals and Synthesis Gas from Biomass

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One hundred and fifty years after the beginning of coal-based chemistry and fifty years after the start of petroleum-based chemistry, industrial chemistry is entering a new age. In the 21st century, utilization of renewable raw material will gain importance in the industrial conversion of chemical substances. Partial or even complete re-adjustment of whole economics to renewable raw materials will require entirely new approaches in research, development, and production.[1] One approach is the development of biorefinery technologies and systems. Biorefining involves the transfer of efficiency and logic from the fossil-based chemistry and substance conversion industry as well as energy production to the biomass industry.[2] The US National Renewable Energy Laboratory (NREL) published the following definition:[3] "A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new domestic biobased industry."

It is estimated that in 2025, up to 30% of raw materials for the chemical industry will be produced from renewable sources (biomass).[4] To achieve this goal, it is necessary to develop new biorefinery platform technologies, such as those listed here:

1) lignocellulosic feedstock conversion (LCF) biorefinery, (LCF pretreatment—efficient separation of the LCF into lignin, cellulose, and hemicellulose),
2) advancement of thermal, chemical, and mechanical processes (e.g. new decomposition methods, gasification (syngas) and liquification of biomass),
3) advancement of biological processes (biosynthesis; e.g. decomposition of starch and cellulose using bacteria),
4) the combination of substance conversion processes (e.g. biotechnological and chemical processes),
5) cereal whole-crop biorefinery concepts,
6) green biorefinery concepts, and
7) the intensification of research and development of phase III biorefineries (feedstock mix→process mix→product mix).[2]

Whereas functional products from renewable resources (fiber composite materials, starch- and protein-derived products) are already available today on the market,[5] current chemical research is focused on the production of platform chemicals and synthesis gas to design consistently structured compounds as chemical building blocks.[6]

The US Department of Energy submitted a list of 12 potential biobased platform chemicals obtained by screening of around 300 substances. Selection criteria were biomass precursors (carbohydrates, lignin, fats, and proteins), process platforms, building blocks, secondary chemicals, intermediates, products, and final application.[7] The reported platform chemicals can be produced from sugar biologically and chemically. The building-block chemicals can subsequently be converted into a multitude of high-value biobased chemicals and materials. Building-block chemicals, as considered for this analysis, are molecules with multiple functional groups that reveal the potential to be transformed into new families of useful molecules. The 12 sugar-based building blocks are 1,4-diacids (succinic, fumaric, and malic), furan-2,5-dicarboxylic acid, 3-hydroxypropionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol, and xylitol/arabinitol.[7]

One method for the degradation of hyperfunctionality in carbohydrates is acid-catalyzed processes for the selective removal of functional groups and formation of defined building blocks. 5-Hydroxymethylfurfural (HMF) is a bifunctional aromatic building block, which can be produced preferentially from inulin by acid-catalyzed intramolecular dehydration (Scheme 1).[8]

Schiwek et al. suggested that HMF can be converted into furan-2,5-dicarboxylic acid (FDCA) by selective oxidation.[9] FDCA can be used as a replacement for terephthalic acid in the production of polyethyleneterephthalate and polybutyleneterephthalate. Furthermore, the reduction of HMF can lead to products such as 2,5-dihydroxymethylfuran and 2,5-bis(hydroxymethyl)tetrahydrofuran, which can serve as alcohol components in the production of polyesters, providing completely biomass-derived polymers when combined

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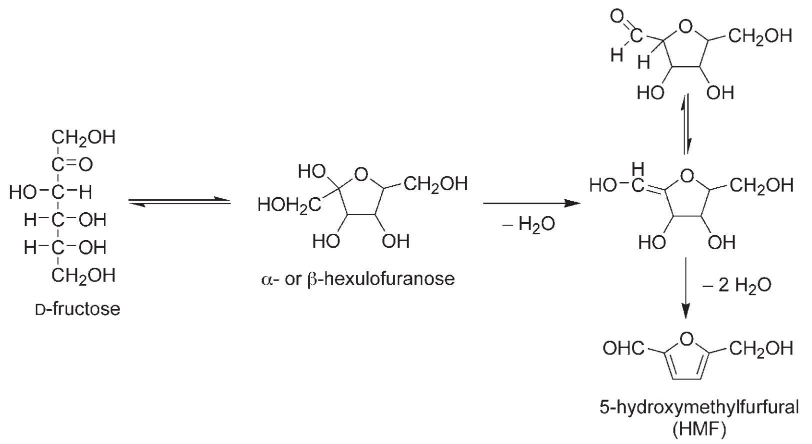


Scheme 1. Synthesis of 5-hydroxymethylfurfural from fructose.

with FDCA. In addition, HMF can serve as a precursor in the synthesis of liquid alkanes, for example, for use in diesel fuel.[10]

Thus, it would be desirable to develop an efficient industrial process for the production of HMF. A disadvantage of the known HMF production technologies starting from fructose in homogeneous aqueous sulfuric acid solution is the formation of unwanted by-products caused by fragmentation, condensation, additional dehydration, and reversion. By using acidic ion-exchangers and dimethyl sulfoxide (DMSO) as reaction media, it is possible to suppress side reactions. However, product recovery by distillation of DMSO is very expensive.

Román-Leshkov et al.[11] recently reported that selective intramolecular dehydration at fructose concentrations in the range of 10–50 wt% led to high yields of 5-hydroxymethylfurfural (80% HMF selectivity, 90% fructose conversion) in a biphasic reaction, in which both the organic and aqueous phase are modified. The acid catalyst (hydrogen chloride or an acidic ion-exchanger) modified with a polar aprotic molecule (DMSO) and/or 1-methyl-2-pyrrolidone (NMP) is located in the aqueous phase together with a hydrophilic polymer poly(1-vinyl-2-pyrrolidone) (PVP) for suppression of side products. The formed HMF is continuously extracted in an organic phase of methyl isobutyl ketone (MIBK) modified with 2-butanol to support HMF separation. Usually, the separation works at a ratio of $[HMF]_{aq}/[HMF]_{org} = 1:10$ and depends on the composition of the individual phases. It was determined by simulation that the separation of the solvent MIBK by vacuum distillation at a concentration of 10 wt% HMF needs 40% less energy compared to conventional processes using DMSO.

Thus, it is possible to produce HMF in high yields from carbohydrates. However, further experimental work should be directed on the investigation of the conversion of low-cost carbohydrate sources, such as glucose and xylose, accessible from lignocellulosic biomass.[2,7]

The synthesis of sugar alcohols as platform chemicals from cellulose as starting material is also a subject of investigation. The hydrolysis of cellulose is carried out under drastic reaction conditions as a result of its crystallinity, its high degree of polymerization, and the poor accessibility of chain ends. Mineral acids, bases, supercritical water, and enzymes are used for the degradation of cellulose.[12] Corresponding problems of these methods are low activity and/or selectivity, difficult separation of the products and catalysts, corrosion, and generation of a large amount of neutralization waste.

Consequently, heterogeneous (Pt and Ru) catalysis should represent a modern environmentally friendly method for cellulose degradation.[13] Recently, Dhepe, Fukuoka, and co-workers reported the possibility of direct conversion of cellulose into sugar alcohols using a series of heterogeneous catalysts, such as $Pt/\gamma\text{-}Al_2O_3$, $Pt/SiO_2\text{-}Al_2O_3$, and ultrastable Y zeolite in water. Sugar alcohols were obtained in yields of approximately 30% at an initial H_2 pressure of 5 MPa, reaction temperatures of 463 K, and a reaction time of 24 h. The space–time yield of the reaction—that is, the mass of cellulose per mass of catalyst per hour—of 0.09 is very low. However, the catalysts can be reused after washing with water in up to three more cycles.[14]

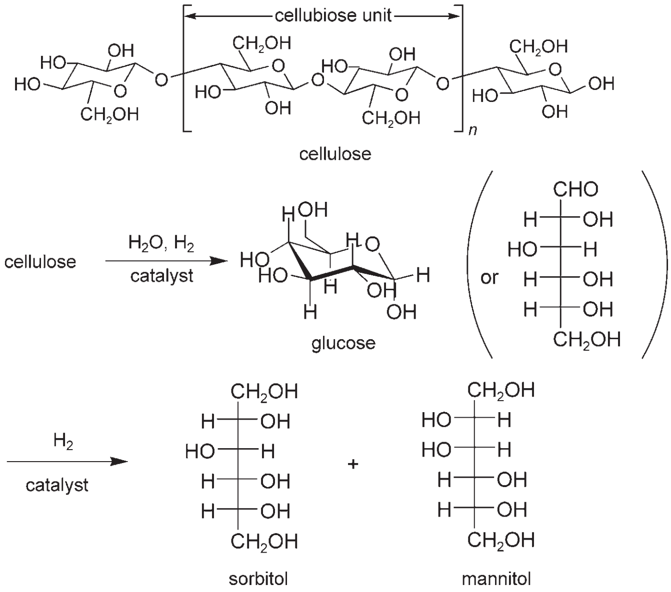
Sorbitol and mannitol were formed in a molar ratio of 4:1 or higher. For the formation of mannitol, an epimerization reaction of sorbitol has been proposed and proved experimentally (Scheme 2). In the overall reaction, the hydrolysis is discussed as a rate-determining step because the reduction of glucose gives an almost stoichiometric amount of sorbitol (using Pt or Ru catalysts).

Using catalysts that produce hydrogen under these reaction conditions, such as the H-shape of Y zeolite or the H-shapes of Zeolithe Socony mobil as well as Moredenite, the corresponding yields of glucose out of sugar are reduced to only 3%. In situ formation of hydrogen and its adsorption on the intrinsic acid sites of the surface of the supporting material is suggested.

Sorbitol is applied not only in sweeteners but also as a platform chemical for the synthesis of isosorbide, 1,4-sorbitan, glycerol, glycols, and lactic acid[7] and is also a potential platform chemical for the production of liquid hydrocarbons.[10]

The "two-platform concept" is one that considers both the synthesis of defined functional platform chemicals (sugar platform) and the production of synthesis gas (syngas platform) from biomass.[2] Syngas can be converted into methanol and subsequently into a variety of derivatives. Furthermore, hydrocarbons used as fuels are accessible via Fischer–Tropsch technology.[15]

The production of Fischer–Tropsch liquids from biomass is not viable from an economic point of view and thus represents a challenge for research and development.[7] The production of synthesis gas in conventional Fischer–Tropsch plants require either an O_2 plant or a large Fischer–Tropsch reactor to process the synthesis-gas stream by dilution with air/nitrogen, thereby increasing the capital costs of such facilities. About 50% of the costs of producing Fischer–Tropsch liquids from biomass are capital costs, 50% of which result from biomass gasification, gas

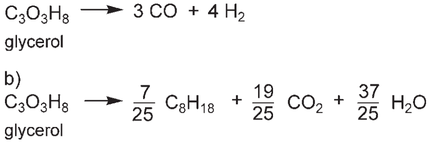


Scheme 2. Catalytic conversion of cellulose into sugar alcohols.[11]

cleaning, and synthesis-gas processing.[16] The company CHOREN (Freiberg, Germany) is producing fuels from renewable resources via syngas and Fischer–Tropsch synthesis (10000 tons per year).[17]

Dumesic and co-workers have proposed a new approach that may allow the operation of a small-scale Fischer–Tropsch reactor to produce undiluted H_2/CO gas mixtures.[18] As a starting material they used glycerol, which is obtained as a by-product in biodiesel manufacturing (there is a large surplus of it on the market). The combination of both processes, a) endothermic ($350\ kJ\,mol^{-1}$) production of synthesis gas and b) exothermic ($412\ kJ\,mol^{-1}$) Fischer–Tropsch conversion, overall results in an exothermic process with an enthalpy of $-63\ kJ\,mol^{-1}$, which approximately corresponds with the calorific value of glycerol (Scheme 3).

The production of synthesis gas was carried out using 30 wt% aqueous glycerol solution and Pt catalysts on various carrier materials, such as Al_2O_3, CeO_2/ZrO_2, MgO/ZrO_2. Pt-Al_2O_3 revealed to be the most stable supported catalyst for this oxidation, and the process conditions were thus precisely investigated using this catalyst by varying temperatures from 573 to 623 K and pressures from 1 to 20 bar. Besides the primary reaction (synthesis of CO/H_2), also the secondary reaction (synthesis of CO/CO_2) was investigated. Finally, an overall carbon balance of 10% was achieved regarding the conversion of glycerol into synthesis gas. The final product stream contained unconverted glycerol and small amounts of ethylene glycol, methanol, hydroxypropanone, and ethanol. The authors concluded that their route to produce synthesis gas could be combined with related processes.



a)

$$\underset{\text{glycerol}}{C_3O_3H_8} \longrightarrow 3\,CO + 4\,H_2$$

b)

$$\underset{\text{glycerol}}{C_3O_3H_8} \longrightarrow \frac{7}{25}\,C_8H_{18} + \frac{19}{25}\,CO_2 + \frac{37}{25}\,H_2O$$

Scheme 3. Production of octane from glycerol via synthesis gas.

An important challenge for industrially relevant biorefinery technologies is the efficient synthesis of chemically unified basic chemicals with the capacity to form a "family tree" of derivatives. It is necessary to combine the biomass degradation processes closely with processes to build the intermediates and final products. Therefore, biological and chemical processes have to be combined and new catalysts (heterogeneous, enzymatic) for these processes have to be developed.

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