Furans from biomass

Production, applications and techno economic potential

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1. Introduction

Lignocellulosic biomass consists of polymeric sugars which can be converted into furans by rearrangement to fructose and elimination of water; mainly to hydroxylmethylfurfural (HMF) and furfural, which can be seen in Figure 1.

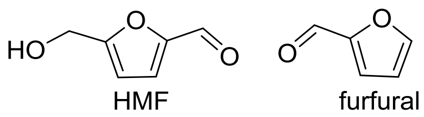

Figure 1: Chemical structure of hydroxylmethylfurfural (HMF) and furfural.

These compounds can serve as platform chemicals that can be chemically modified and used in many applications within the chemical industry to everyday products. Examples of products where derivatives from HMF and furfural are found are paints and varnishes, fuels, plastics and composites. Since the starting material is bio based, these products have great potential in becoming substitutes for these types of products that now are fossil based.

HMF can be produced from lignocellulosic biomass containing hexoses (C6) such as fructose and glucose by treating it with an acid at elevated temperature. Interesting examples of products that can be generated from HMF are dimethyl furan (DMFu) which can be used as a biofuel and caprolactone, a building block for plastics (polyester). These can be seen in Figure 2.

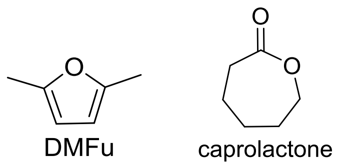

Figure 2: Chemical structure of dimethyl furan (DMFu) and caprolactone.

Furfural is derived from pentoses (C5) such as xylose and arabinose. Furfural can be used to produce furfuryl alcohol or methyltetrahydrofuran (MeTHF). Furfurylalcohol can be used in pressure impregnation of wood, and is commercialized by the Norwegian company, Kebony. MeTHF is a useful and wide spread solvent in the chemical industry. Another interesting potential application for MeTHF is as a biofuel replacing fossil gasoline or diesel.

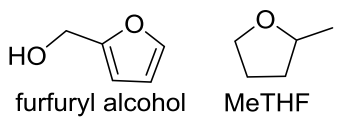

Figure 3: Chemical structure of furfuryl alcohol and methyltetrahydrofuran (MeTHF).

Another compound that could be produced from the same type of process as HMF is levulinic acid, Figure 4. Levulinic acid is formed together with formic acid. Levulinic acid can be transformed to γ-valerolactone that serves as a precursor to MeTHF. [1]

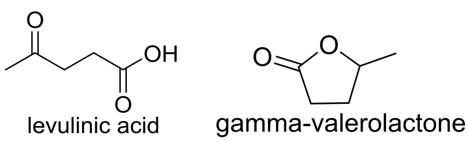

Figure 4: Chemical structure of levulinic acid and γ-valerolactone.

2. Process

2.1 Starting material

A variety of biomasses can be used for production of C6 and C5 rich streams. Hydrothermal treatment of lignocellulosic biomass such as hardwood and softwood or residues from the forest- and agricultural sector can generate streams enriched in sugars. However, this kind of streams often contain C6 and C5 sugars, sugar degradation products and lignin that will limit the use. This could be handled by fractionation using different techniques such as simulated moving bed chromatography, different filtration techniques, extraction and/or distillations. Different types of biomass will result in higher amounts of either C5 or C6 sugars due to the nature of different biomasses

There is also an opportunity to use already processed streams from the pulping industry such as fiber reject or pre-hydrolysates. The advantage of using these types of materials is that they usually have a low value and even could be considered as waste with a cost related to handling and destruction/landfill. Using these already processed streams as starting materials will lower the raw material cost and also contributing to a more effective use of the biomass. On the other hand, already processed streams often are complex mixtures that could complicate the process/downstream handling and give lower yields.

2.2 Production of HMF and furfural

The production of HMF or furfural is often done by letting an acid, sulfuric acid or hydrochloric acid, catalyze the formation of HMF from fructose or furfural from xylose respectively under elevated temperatures. Under certain conditions both HMF and furfural are unstable chemicals that could be difficult to isolate without formation of degradation products resulting in lower yields. To maximize the yield of HMF and prevent it from degrading, an organic solvent can be used in a two phase system to extract the HMF when formed. This two phase system usually increases the yield by minimizing the degradation [2].

2.2.1 Commercial production

The production of furfural at commercial scale is done by some companies. International Furan Company (IFC) is one of them, producing furfural with headquarters in the Netherlands and the biggest production site, named Central Romana in the Dominican Republic. The raw material for the production is mainly agro-wastes as corn cobs, sugar cane bagasse and cereal byproducts. The furfural is converted to furfuryl alcohol in Belgium at the company TransFuran Chemicals with an annual production of 40 000 ton furfuryl alcohol per year. [3] [4] [5]

Another producer of furfural is Illovo Sugar Company in South Africa. It is a big sugar producer from sugar cane and they use the agricultural byproducts for production of specialty chemicals, for example furfural and furfuryl alcohol. [6]

The production of HMF at commercial scale was first done in 2013 by AVA Biochem in Switzerland. They produce 300 ton of HMF per year. [7]

2.3 End products

Figure 5 shows a schematic picture of production routes from biomass via HMF and furfural to useful end products. Some of the end products are also describes below.

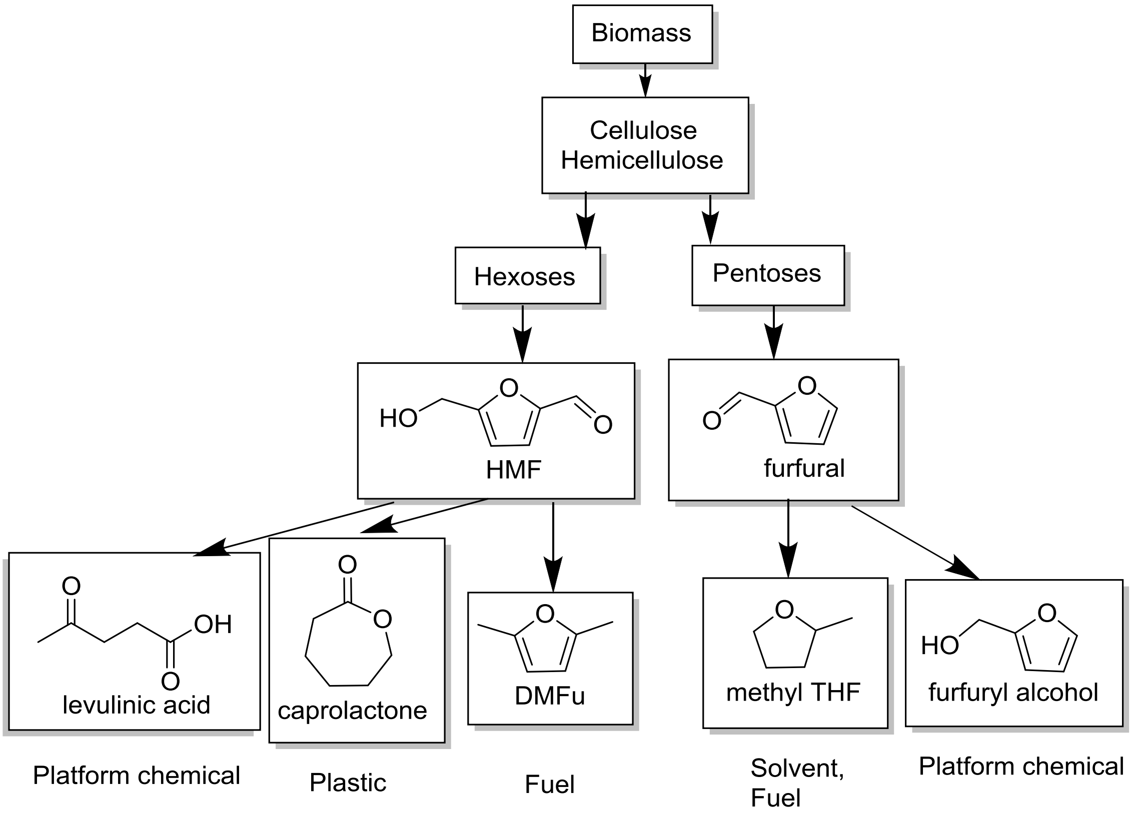

Figure 5: Scheme of starting material and some of the end products from HMF and furfural.

2.3.1 Dimethyl furan

Dimethyl furan (DMFu) can be used as a biofuel on its own or as an additive in gasoline or diesel. A lot of research has been made around the optimal fuel mixture for DMFu for different types of engines. [8]

The production of DMFu has been investigated in laboratory scale and there have been suggested ways of having production on industrial scale. One way to do this would be by having a plant with HMF and DMFu production separately. The proposed technology would use 300 ton fructose per day as starting material and use a copper-ruthenium-carbon catalyst in the DMFu production. This would lead to a price for HMF of 1.07 dollar per kilo and for DMFu of 2.02 dollar per liter. [9]

2.3.2 Caprolactone

Caprolactone can be polymerized into polyesters and have many application areas. Perstorp has a product branch called CAPA which consists of caprolactones in a variety of combinations. The usages for those are for example coatings, adhesives, elastomers, bioplastics and foams. [10]

2.3.3 Levulinic acid

Levulinic acid (LA) is one of the degradation products in the production of HMF. Due to higher stability of levulinic acid as compared to HMF, LA could be easier to produce in large scale. LA can be used in many applications, for example polymer resins, animal feed, , fuels, antifreeze products, herbicides, in the flavoring and fragrance industry and textile dyes,. [11]

One suggested route for LA production contains two process steps, the initial step generates HMF followed by production of LA. This two-step process has proven to give relatively good yields, over 60 %. If using cellulosic waste materials as paper mill sludge or agricultural residues the production cost could be as low as 0.088-0.22 dollar per kilo LA. [1] This process is called the Biofine process, which is a commercially available process. For example, a plant in Caserta, Italy has been built according to this technique. [12]

2.3.4 Formic acid

Formic acid (FA) is a byproduct in the production of levulinic acid. FA can be used as a decalcifier, leather tanning agent or deicing agent. Furthermore, FA is used in many chemical production routes/products.

2.3.5 Methyltetrahydrofuran

MeTHF is an organic solvent that has come to be known as a more environmentally friendly solvent than for example tetrahydrofuran. It can be produced from furfural or levulinic acid and degrades in sunlight and air. It has been proven to be a good solvent for many organic reactions and also have potential to be used as a biofuel. [13]

2.3.6 Furfuryl alcohol

Furfuryl alcohol can be derived from furfural and is used as starting material for several chemical compounds. It can be used as intermediate in the pharmaceutical industry and its polymers have good mechanical and thermal properties. [14] It can be used to produce a resin used in the foundry industry as a polymeric binder for foundry sands. It is also used for wood treatment to produce acid-resistant coatings and as a flavour ingredient. [6]

3. Summary

Furans as furfural and HMF can serve as starting chemicals for a number of compounds with different applications. The production from biobased materials is under development to get more efficient productions routes. However, some factories with commercial production have been around for a long time. There are a lot of potential in these materials and the more research on alternative starting materials and cost efficient production routes that is done, the bigger potential these materials have on the market.

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