

CATALYTIC CONVERSION OF BIOMASS- DERIVED FURFURAL INTO VALUE-ADDED CHEMICALS

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Abstract Lignocellulosic biomass represents the most promising substitute for fossil resources and their ever-growing conversion to fuels and chemicals. It can be processed in various ways, thus yielding a variety of products. The most preferable technique is hydrolysis, which can transform cellulose and hemicellulose into second-generation biofuels and platform chemicals, such as furfural. Heterogeneously catalyzed liquid-phase hydrotreatment of furfural will be presented as one of the potential routes for converting furfural to bio-based functionalized furans, lactones, furfuryl ethers and alkyl levulinates. Development and optimization of these processes involved thorough investigation of reaction conditions and the nature of catalysts on the activity and selectivity towards the desired products and their detailed analytical characterization.

Keywords:

circular economy, biomass, catalysis, furfural, hydrotreatment.

1 Introduction

In recent history, the modern lifestyle has placed consumption and the availability of resources at the core of its nature. Those resources come mostly from fossil fuels, which have a very long regeneration time; with such intense consumption, they will be depleted in a short time. These trends have led to a linear economy, with one-time consumption of goods and their assumed destruction or exhaustion upon completed usage. However, a more responsible approach is circular economy, which replaces the concept of “consumer” with that of “user”. Users get the benefit of utilizing the good, after which it is returned to the circle for additional applications.

The concept of cycling is visualized in Figure 1. Explaining the benefits of the circular economy through four concepts: 1. The power of the inner circle refers to minimizing the use of materials in circular economy with respect to that of linear economy. This is visualized with the tighter circle, which would lower the need for refurbishing, remanufacturing and changing the properties of the used material for further usage, while increasing the savings on additional materials, labor, capital, energy and externals such as greenhouse gases, water, toxicity, etc.; 2. The power of longer cycling refers to maximizing the length of each cycle and/or the number of consecutive cycles. This could be done through repair, reuse, or remanufacturing, which would avoid new resources being directed to the manufacturing of a brand new product; 3. The power of cascaded use refers to expanding reuse across various other industries, with minimal change to product’s nature; 4. The power of pure inputs refers to fact that purity of materials increases collection and redistribution efficiency, while maintaining product quality (The Ellen MacArthur Foundation, 2012).

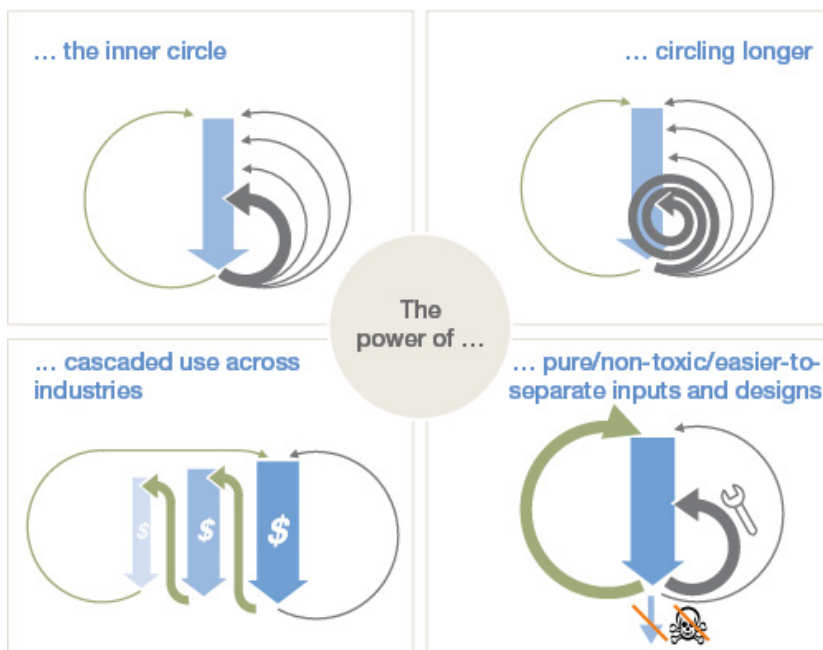


Figure 1: Four core values of circular economy (The Ellen MacArthur Foundation, 2012).

Since fossil fuels are not being replenished as fast as they are being utilized, proper replacement is needed. The most suitable substitute is lignocellulosic biomass. Since this type of biomass is not edible (therefore does not compete with the food sector), is easily regenerated, and could be utilized with the application of minor changes to existing technologies, it is considered the most valuable feedstock in the biorefinery concept. Lignocellulose is composed of cellulose (40-50 %), hemicellulose (25-35 %), and lignin (15-20 %), depending on its source (Alonso *et al.*, 2012). It mostly refers to the biomass obtained from agricultural waste residues (rice straw, wheat straw, corn stover, hulls, plant residues, etc.) or urban biomass (branches, leaves, forest residue, construction/demolition wood). In these terms, Slovenia represents a high-potential location for versatile biorefinery, as it is third in Europe (after Finland and Sweden) in terms of relative forest coverage (Area of Wooded Land, 2019). In addition, Slovenia has strong existing chemical, agricultural and wood-processing industries; therefore, there is more incentive to utilize existing raw materials, while providing new value-added products to the market.

With such ubiquitous potential sources of raw material, as well as its miscellaneous composition, biomass can be processed in a variety of ways while also producing diverse types of products. Some of those processes include harsh conditions used for pyrolysis, gasification, or liquefaction, while a preferable route is through hydrolysis (Figure 2.). With such systems, small, adaptable biorefineries are sought for extraction of a wide assortment of products acquired from every part of the lignocellulosic biomass: extractives, cellulose, lignin, and hemicellulose. One such refinery is Tanin Sevnica d.d. Tanin valorizes the hemicellulosic part of the forest by wood processing of residual biomass. After hemicellulose isolation and subsequent hydrolysis to C5 cyclic sugars (xylose, mannose, glucose, galactose), acid-catalyzed dehydration of pentoses produces furfural (Figure 3.) (Li *et al.*, 2016).

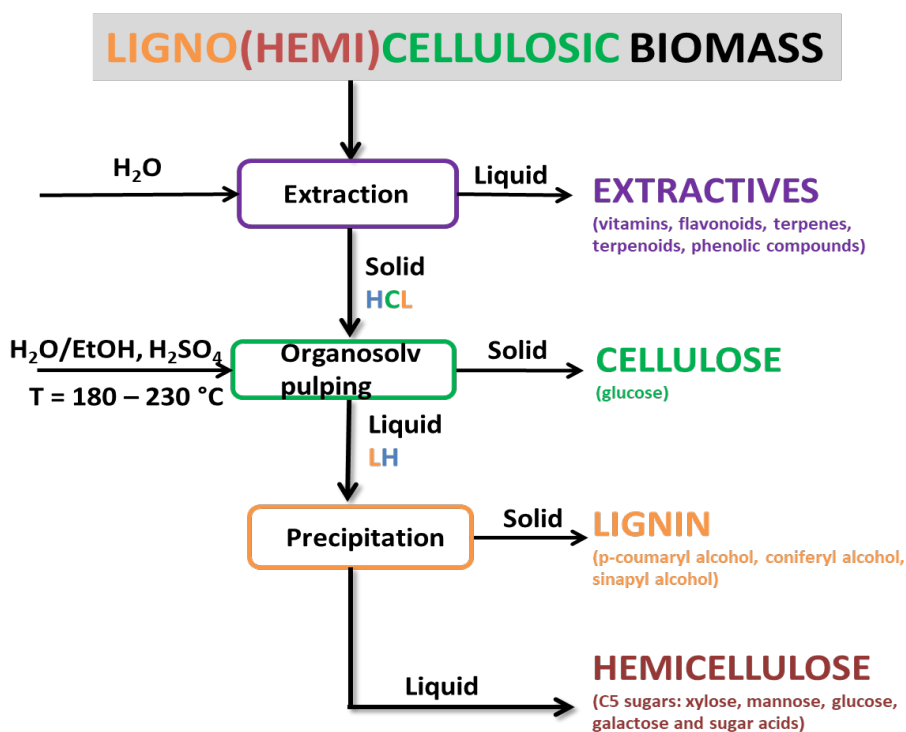


Figure 2: Scheme of lignocellulosic hydrolysis.

Furfural is a bio-based model compound that can be further upgraded to a wide array of value-added, bio-based chemicals and biofuels. Its functionalities (furan ring and aldehyde group) allow numerous possible reactions: reduction, oxidation, decarbonylation, acetalization, aldol condensation, etherification, esterification, hydrogenolysis, ring-opening, etc. Numerous reviews have been published on catalytic upgrading of furfural over various metal catalysts (Sharma *et al.*, 2013; Šivec *et al.*, 2019); however few report thorough experimental study of the influence of reaction conditions on catalyst activity and selectivity, followed by multiscale modeling.

This study had the aim of developing a potential reaction mechanism for furfural hydrotreatment over molybdenum-based catalysts. Optimization of reaction conditions was carried out in a batch reactor involving three different MoO_3 catalysts and a MoO_2 catalyst. The results were compared to those of Ni and Pd supported on alumina support. All collected samples were analyzed by gas chromatography for identification and quantification of the products, which were later used for constructing the reaction mechanism.

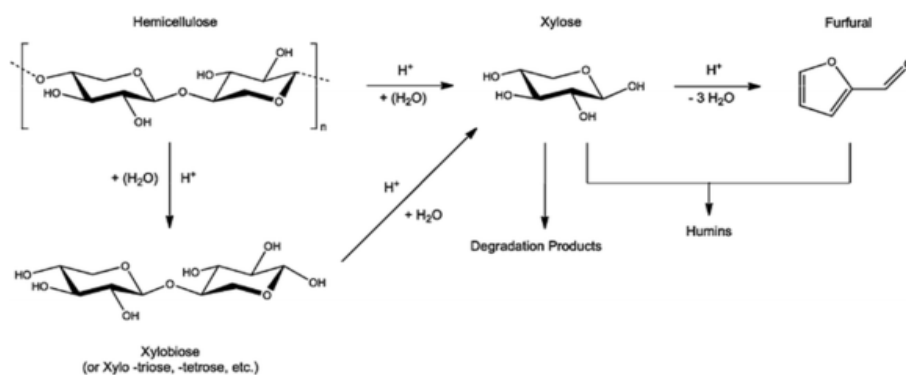


Figure 3: Scheme of hemicellulose hydrolysis to xylose and subsequent dehydration to furfural.

2 Experimental Part

All experiments were performed in a 300 mL stainless steel autoclave, equipped with the magnetically driven Rushton turbine impeller (Figure 4.). Hydrotreatment experiments on furfural were done at temperatures of 150-200 °C and a hydrogen pressure of 5 MPa for 5 hours, over various catalysts. The catalysts in use involved

three MoO₃ provided by three different manufacturers (ABSCO Ltd., Fluorochem, Honeywell-Fluka, and Sigma-Aldrich), MoO₂, and alumina-supported Ni and Pd. The gaseous phase was continuously analyzed by an Agilent 490 Micro Gas Chromatographer, while liquid phase samples were collected and analyzed later by Shimadzu Ultra QP2010 Gas Chromatographer with Mass Spectrophotometer for identification, and a Flame Ionization Detector for quantification.

3 Results

After screening all the catalysts under these reaction conditions, all the products were analyzed by gas chromatography, and the potential reaction mechanism was proposed, as in Figure 4. The results suggested that isopropanol hydrogenates furfural to furfuryl alcohol even at room temperature without the presence of the catalyst, but in rather minor quantities. However, in the presence of the catalyst, furfuryl alcohol (FAL) was observed in more significant quantities, which then allow the metal's activity to further upgrade FAL, thus leaving concentrations of furfuryl alcohol at lower amounts. Alumina-supported nickel and palladium catalysts showed higher activity compared to that of MoO_x, regardless of the reaction conditions. It was observed that, in addition to FAL, Ni/Al₂O₃ catalyzed the hydrodeoxygenation reaction, thus producing 2-methylfuran (MF), while Pd/Al₂O₃ further hydrogenated the furan ring, thus producing tetrahydrofurfuryl alcohol (THFA).

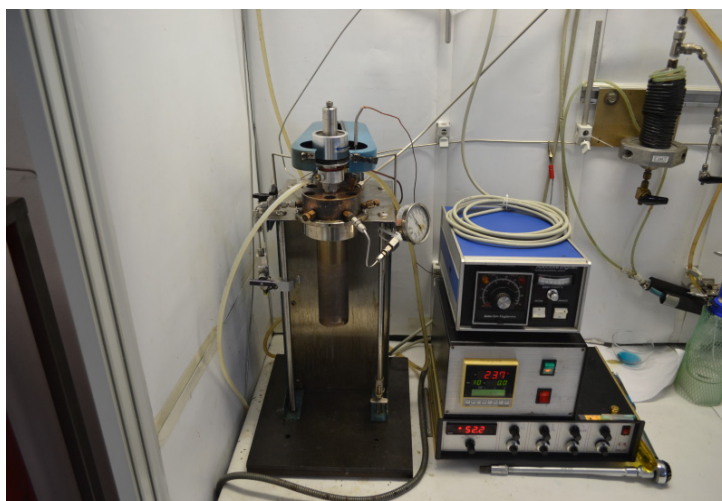


Figure 3: High pressure mixing reactor with stainless steel autoclave.

There were no significant differences in activity or selectivity among the four molybdenum oxide catalysts, regardless of their differences in manufacturing or oxidation state. It was observed that furfural undergoes the acetalization reaction at room temperature with isopropanol, thus forming di-isopropoxymethylfuran, which is reversible back to furfural. Yet again, furfural undergoes hydrogenation from isopropanol, yielding furfuryl alcohol. It was observed that, under medium temperatures (175 °C), the major product is isopropyl furfuryl ether, with minor concentrations of the ring-opening product, isopropyl levulinate (IPL). At higher temperatures, IPL becomes the major product, while an additional reaction took place. While hydrogenating furfural, isopropanol converts to acetone, which then undergoes aldol condensation with furfural, thus forming furfuryl acetone.

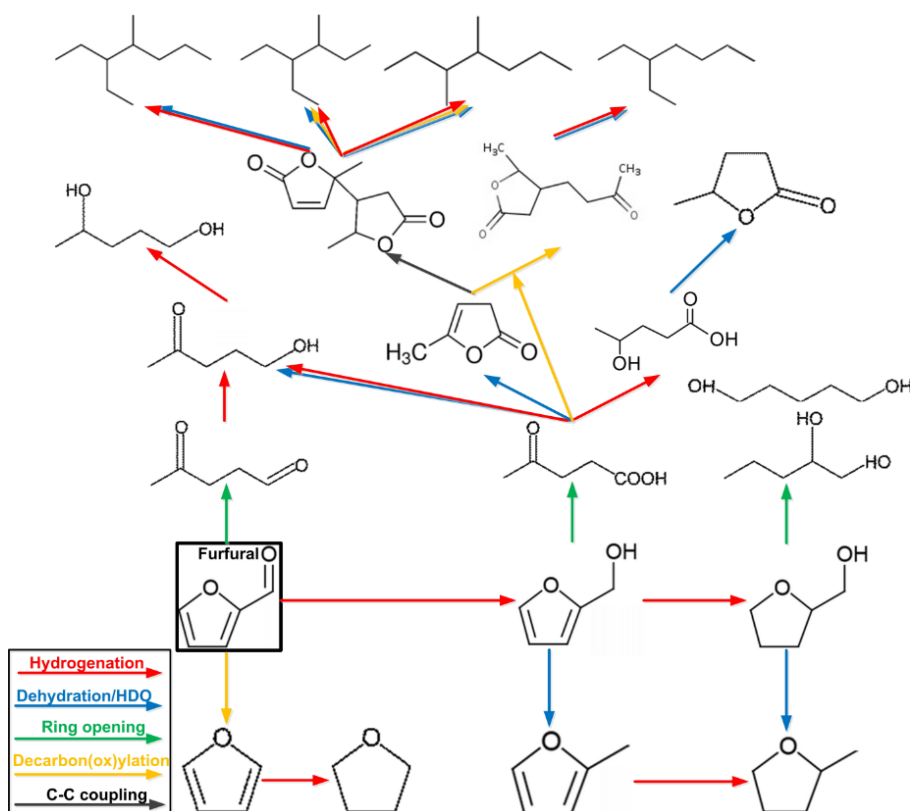


Figure 4: High pressure mixing reactor with stainless steel autoclave.

4 Conclusions

The modern lifestyle, current technological advances, and the latest environmental policies require a shift from linear economy to circular economy. In such a system, products manufactured and used will be more efficiently designed, require less material input, will be used longer, will permit use in different niches with minor adjustments, and lastly, will pose less harm to the environment while being used and upon their discarding.

Biomass represents the most promising substitute for fossil energy, which currently represents the principal source for fuels and chemicals, as well as the greatest reason for climate change and pollution. Lignocellulosic biomass can be fragmented to its constituent components, lignin, cellulose, and hemicellulose, and then further upgraded to various value-added chemicals. Hemicellulose can undergo hydrolysis to produce pentane sugars, which can be dehydrated in the presence of an acid catalyst to furfural. In the presence of secondary alcohols, furfural can easily be converted to furfuryl alcohol, and then further upgraded to various value-added chemicals, depending on the nature of the catalyst. Ni and Pd catalysts catalyze hydrodeoxygenation and hydrogenation reactions, respectively. Molybdenum oxide catalysts had lower activity and selectivity, while producing furfuryl acetone and the ring opening product, isopropyl levulinate. Consequently, IPL could be used in this way as a fragrance and flavonoid additive, or further upgraded to fuel additive compounds.

Further studies should involve process optimization and subsequent microkinetic and DFT modeling in order to better understand, describe, and predict the behavior of the catalytic system. Thorough characterization of the catalysts is also beneficial in order to correlate activity and selectivity to the nature of the catalyst. Additionally, bifunctional/bimetallic catalysts should also be investigated to potentially lower the number of reaction steps needed, and/or the required time and energy.

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