Transformation of renewable resources into value added chemicals

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1. ABSTRACT-

A renewable resource is a natural resource with the ability to reproduce through biological or natural processes and replenished with the passage of time. Renewable resources are part of our natural environment and form our ecosystem. The synthesis of chemicals by using renewable resources is presently the most widely envisioned approach. However, the platform molecule value chain is in competition with well optimized cost effective synthesis routes from fossil resources to producechemicals that have already in a market. The plants are also able to elaborate energy storage products such as lipids, sugars, and starches.In this review article, carbohydrate has taken as a renewable feedstock and various product obtained from it is discussed.

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2. INTRODUCTION-

The development of environmental benign and efficient synthetic methods is the central goal of current research in chemistry. This field of chemistry has come to known as ‘Green Chemistry’ which has become the forefront. In this regard, catalysis is a key technique for their contribution towards “Greener” chemistry. One of the ways in which processes can be made greener is to use renewable resources to replace non-renewable starting material. This is one of the basic principle of the green chemistry. Using starting materials derived from growing plants, rather than irreplaceable materials like petroleum and natural gas is one way in which we seek use renewable resources. The interest in biomass conversion to chemicals increased rapidly during the last some years within industrial companies and Academic level with the support of international and national agencies. Biomass is an abundant and the only sustainable carbon resource, and biomass refinery processes must be developed in the next few decades to produce energy and materials which will replace the ones produced from the diminishing fossil-based resources. Chemical manufacturers worldwide became interested in renewable feedstocks for producing bulk and specialty chemicals.[1-3] Furthermore, due to the rapid increase in the oil price, we face a new situation where the market price of the crude is higher than that of biomass derived pure molecules such as sucrose or glucose. The cost of platform molecules derived from carbohydrates or vegetable oils is fairly stable compared to that of fossil fuels and even trend to decrease steadily with time. Nature produces more than 150 billion metric tons of biomass per year by using photosynthesis but out of that only 4% are used by humans for food and non food purposes.Carbohydrates are the most abundant renewable resources available, and now days they are viewed as a feedstock for the Green Chemistry. The synthesis of chemicals by conversion of platform molecules obtained by depolymerisation and fermentation of biopolymers is presently the most widely envisioned approach. Successful catalytic conversion of these building blocks into intermediates, specialties and fine chemicals will be examined. However, the platform molecule value chain is in competition with well-optimized, cost-effective synthesis routes from fossil resources to produce chemicals that have already in a market.Fermentation is also an important process used for conversion of biomass into some important chemical compound. On an industrial scale, glucose is produced from starch by enzymatic hydrolysis, corn being the main source of glucose. Another important source of glucose for chemical production is woody biomass. Improvement of processes for harvesting and processing wood cellulose could result in a glucose source much less expensive than corn. Advances in woody biomass processing, along with enhancements in corn production, will make glucose an easily available raw material for the production of chemicals. Biomass is not only converted to food but also valuable products like medicinal drugs, flavors and fragrances.The need to decrease greenhouse gas emissions suspected to have a detrimental effect on the global climate by employing renewable carbon available from biomass. Today these fossil resources supplyapproximately 86% of energy and 96% of organic chemicals,but in as soon as two decades petroleum production is unlikely to meet the growing needs of humanity and natural gas resourceswill be increasingly inaccessible.Moreover, consumers andgovernments concerned about CO_2 emissions and other environmental impacts are demanding renewable power and products.With advances in conversion technology, plentiful biomassresources have the potential to regain their central position asfeedstocks for civilization, particularly as renewable carbonsources for transportation fuels and chemicals.Today these fossil resources supplyapproximately 86% of energy and 96% of organic chemicals,but in as soon as two decades petroleum production is unlikelyto meet the growing needs of humanity and natural gas resourceswill be increasingly inaccessible.Moreover, consumers andgovernments concerned about CO_2 emissions and other environmental impacts are demanding renewable power and products.With advances in conversion technology, plentiful biomass resources have the potential to regain their central position asfeedstocks for civilization, particularly as renewable carbonsources for transportation fuels and chemicals. According to Bozell and Petersen two different strategies can be selected to achieve biomass conversion to chemicals

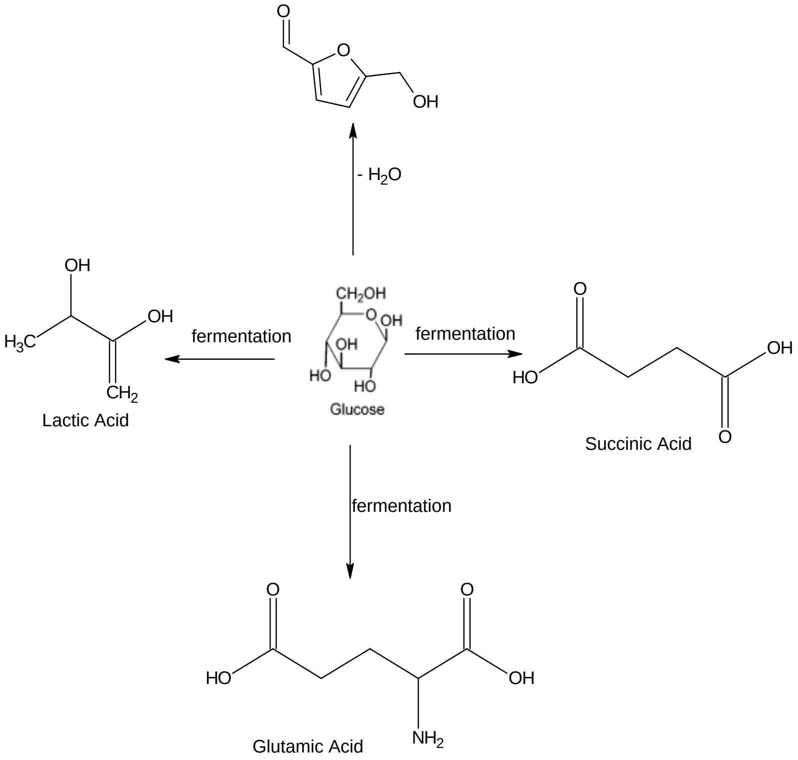
[4-5]

1. A target-driven approach employing process analysis methodology designed to find the most efficient synthetic routes to produce a given chemical starting from well-identified plat-form molecules. This approach may result in an uneconomical production of chemicals with respect to well-optimized, conventional synthesis routes from hydrocarbons.
2. A process driven approach whereby biomass is converted by one or more catalytic processes (hydrogenation, hydro-genolysis, oxidation, etc.) yielding a family of valuable products.[6-9] This approach is not intended to duplicate chemicals currently produced from fossil resources and could be more effective to find rapidly new valuable bioproducts. Section 3 will provide examples of the catalytic conversion of platform molecules to pure isolated chemicals.Vegetable oils and animal fats also as an important source of so many important chemicals like fatty acids and fatty amines. From terpenes like pinene, limonene, careen and camphene we get many important value added chemicals.

3. Conversionviaplatform molecules

3.1 Glucose Platforms

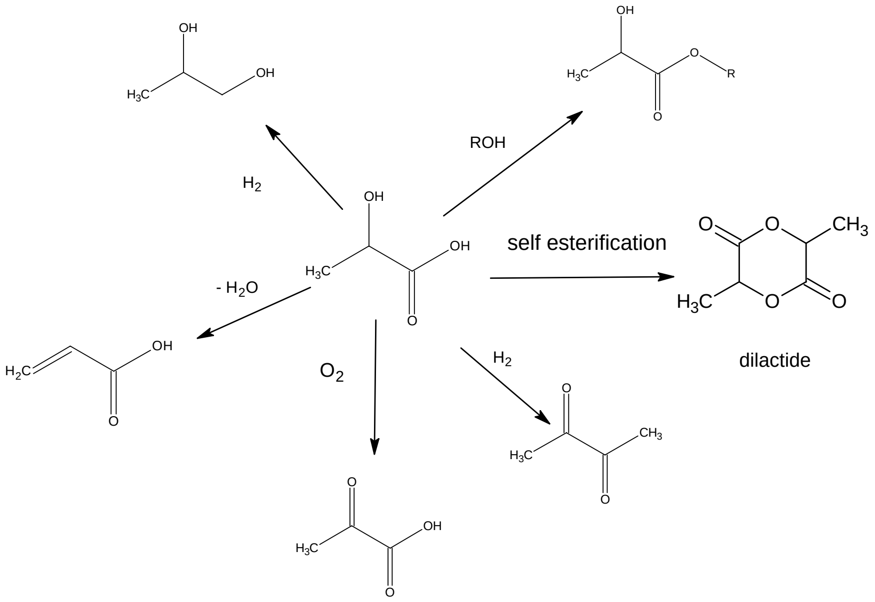
Generally, glucose is obtained from sucrose, starch, cellulose and lactose.Glucose is a simple monosaccharide found in plants. It is one of the three dietary monosaccharides, along with fructose and galactose that are absorbed directly into the bloodstream during digestion. It is an important carbohydrate in biology because cells use it as the primary source of energy and a metabolic intermediate.[10-12] Glucose is one of the main products of photosynthesis and fuels for cellular respiration. Another important source of glucose for chemical production is woody biomass. On an industrial scale, glucose is produced fromstarch by enzymatic hydrolysis, corn being the main source of glucose. So many important chemicals like lactic acid, succinic acid 3-hydroxy propionic acid and itaconic acid are obtained by glucose fermentation. Molecular level understanding of acid-catalysed conversion of sugar molecules to platform chemicals such as hydroxymethyl furfural (HMF), furfuryl alcohol (FAL), and levulinic acid (LA) is essential for efficient biomass conversion.[13-15]



Glucose and its various derivatives

3.1.1. Lactic Acid Platform

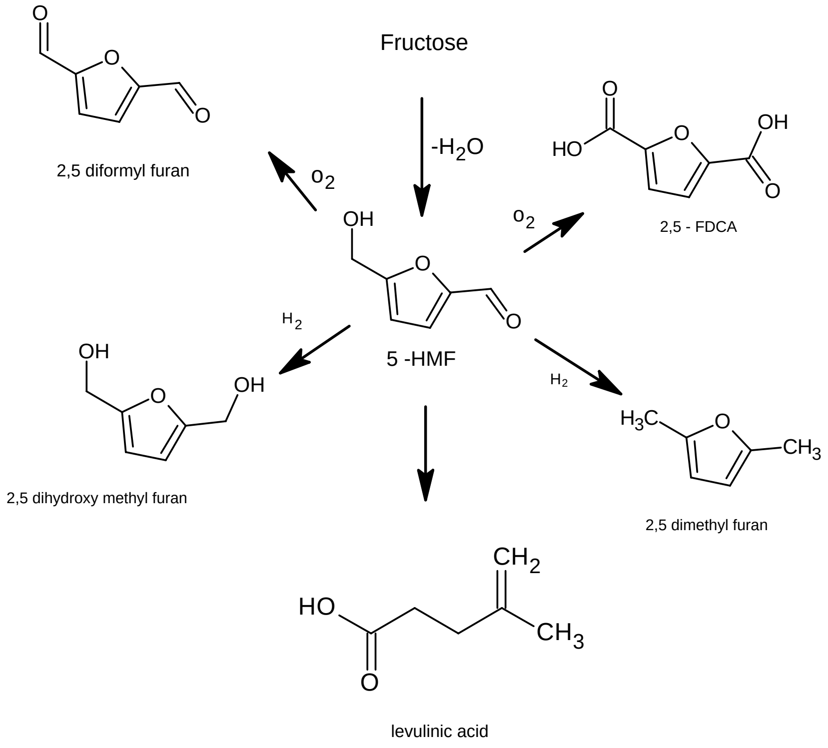
Lactic acid i.e. 2-hydroxypropionic acid can be produced by chemical synthesis or by fermentation of different carbohydrates such as glucose (from starch), maltose (produced by specific enzymatic starch conversion), sucrose (from syrups, juices, and molasses), lactose (from whey), etc. [16] However, lactic acid is commercially produced today mainly through the fermentation of glucose. An important step in the lactic acid production is the recovery from fermentation broth. The conventional process for the recovery of lactic acid is still far from ideal. Indeed, it involves the precipitation of calcium lactate after the separation of micro-organisms and the conversion of the salt to lactic acid by addition of sulfuric acid. The dilute lactic acid produced is then submitted to purification.The production of lactic acid is around 350 000 t/year, and the worldwide growth is believed by some observers tobe 12-15% per year.[17]Lactic acid exists in two optically active isomeric forms,L(+) andD(-). It is utilized in the food chemical, pharmaceutical, and cosmetic industries. Lactic acid is a bifunctionalcompound bearing a hydroxyl group and an acid function,being amenable to numerous chemical conversions to usefulproducts. The chemistry of lactic acid has been reviewed byHolten,[18-19]and several reviews have summarized its uses andreactions.[19-24]



3.1 2-Hydroxymethyl furfural (5-HMF) platform

Furan derivatives, such as 5-hydroxymethylfurfural (HMF) and furfural, obtained from renewable biomass-derived carbohydrates have potential to be sustainable substitutes for petroleum-based building blocks used in production of fine chemicals and plastics. furan derivatives, such as furfural and 5-hydro-xymethylfurfural (HMF), can be produced from renewable biomass resources by acid-catalyzed dehydration of pentoses and hexoses, respectively.[26-27] These compounds have the potential to be sustainable substitutes for building blocks derived from petrochemicals in the production of plastics and fine chemicals. 5-HMF and its derivatives levulinic acid, 2,5-bis(hydoxymethyl)-furan (2,5-BHF), 2,5-diformylfuran (2,5-DFF) and 2,5-furandicarboxylic acid

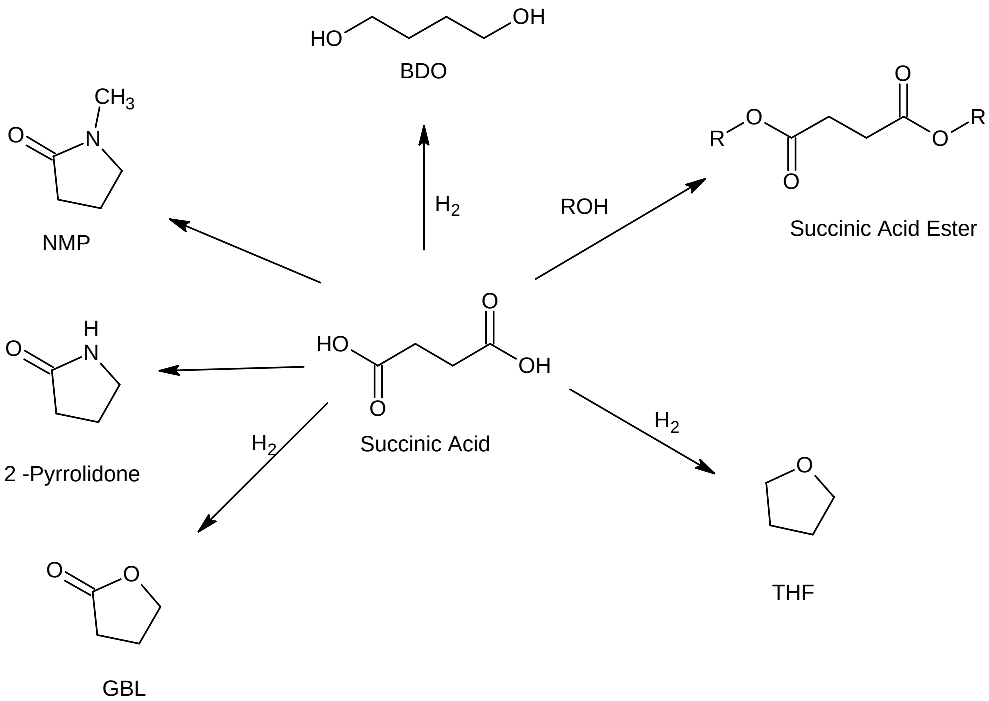
(2,5-FDCA) were identified early as very promising chemical intermediates obtained by the catalytic conversion of carbohydrates based on C6 units.[28-30]5-HMF was obtained by dehydration of fructose in the presence of soluble or solid acid catalysts from glucose or even polysaccharides by more complex catalytic systems and reaction media.[The key issue was to prepare 5-HMF with economically acceptable processes that could be scaled up at the industrial level.There are currently numbers of catalysts that are active in the dehydration of sugars to form HMF. However, most of them also promote side reactions that for undesired byproducts, and rehydrate HMF to form levulinic acid and formic acid. Thus, these catalysts are often limited to simple sugar feedstocks, such as fructose.[31]



5-HMF and its various derivatives

3.1.3. Succinic acid platform

Recent advances in fermentation from carbohydrates and purification technologies succeeded in making bio-based succinic acid economically attractive.The economic and environmental analysis of a biorefinery producing succinic acid showed that biosuccinic acid may become a promising intermediate provided that its production cost could be lowered.[32] Succinic acid, anhydride, and esters are primary product from maleate hydrogenation. While succinic acid is currentl produced from butane through maleic anhydride. Most fermentation micro-organisms are not tolerant to the acidic media, and the fermentation must be neutralized, producing salts of succinic acid. Conventional methodologies for separation and recovery of succinic acid involve filtration and acidification of the succinates to form the succinic acid, where as the salts is precipitated. There has been consider-able research to develop improved fermentation micro-organisms and separation technology to reduce the overall cost of bio-based succinic acid.[33] In order for fermenta-tion-derived succinates to compete with butane-derived maleic anhydride, the production cost for succinic acid must approach the production cost for maleic anhydride.Various chemicals that have a well established market can be produced from the SA platform, such as 1, 4-butanediol (BDO), g-butyrolactone (GBL), tetrahydrofuran (THF), 2-pyrrolidone, N-methyl-2-pyrrolidone, and SA esters . Abundant patent literature was published on the hydrogenation of maleic or succinic anhydride to the three industrial hydro genation products. Investigations were conducted to under- stand how catalysts can modify the selectivity towards one of the three hydrogention products. Deshpande and coworkers222 showed that GBL, BDO and THF were formed successively.



Succinic acid and its derivatives

4. Biomass conversion and process economy

The development of bioproducts at a large industrial scale requires that their quality and cost meet consumer demand. The final cost of bioproducts includes the price of the starting feedstock, but it also depends heavily upon the processing cost. The latter may be decreased by reducing the number of synthesis steps and improving their yields, but a judicious choice of biomass conversion strategy could be essential to achieve a cost-effective development of biomass utilization towards bioproducts.In the future the platform molecule value chain could become more and more successful to produce high tonnages of bioproducts, but in the meantime most of the high tonnage ndustrial bioproducts are produced by a different strategy which does not aim at producing pure isolated chemicals competing with those derived from petroleum. This strategy consists of converting biomass in minimum steps to functional products such as surfactants, lubricants, plasticisers, polymers, paper additives, binders, paints, food additives, and cosmetics .[34,35]

5. Biomass conversion and green chemistry

The use of renewable carbon fulfills one of the green chemistry principles, but not necessarily the others. The present literature survey indicates that the benefits for green chemistry are very contrasting depending upon feedstocks, processes and products. Processes requiring too many conversion and separation steps affect the overall atom economy, energy demand and waste emissions.[36] The proportion of renewable carbon in final pro- ducts is also liable to decrease with the number of synthesis steps. Because of the inhomogeneous composition of renew- ables and because other impurities are potentially added during fermentation steps, clean and energy efficient separation and purification technologies are of primary importance. Biomass conversion processes achieved in one or few steps without separation of intermediates as described in Sections 4 and 5 of this review are certainly more performing in terms of biomass utilisation and waste minimisation than the more traditional approach via platform molecules. There are a number of examples in the literature of biomass conversion fulfilling nicely all green chemistry principles. Thus, the conversion of starch to isosorbide via glucose and sorbitol or the aerobic oxidation of glucose could be achieved with 100% atom economy in aqueous solutions over hetero- geneous catalysts that can be recycled many times. On the other hand the green character of some biomass conversion processes is impaired by the use of toxic reagents and solvents, generates a lot of waste and has a modest atom economy.[37]

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