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http://www.git-labor.de/forschung/umwelt/xylochemie-ein-beitrag-zur-nachhaltigen-chemischen-synthese .

Xylochemistry – A Contribution to Sustainable Chemical Synthesis

Wood instead of Petroleum as Carbon Source

Till Opatz and Anthony J. Arduengo, III

Abstract: Xylochemistry - the use of wood as a source of raw materials for chemical synthesis - provides a climate-neutral alternative to the conventional use of fossil carbon sources such as natural gas or oil. Illustratively, we reported the utilization of wood constituents as the sole carbon source for the production of complex chemical compounds and thus one of four main challenges to a sustainable chemical industry is addressed.

Introduction

In the early days of organic chemistry, natural substances such as ethanol or bitter almond oil (benzaldehyde) were examples of the very few organic chemical substances available in relative purity. In the 19th century an initially worthless waste product, coal tar, became an important source of important basic chemicals such as aniline or naphthalene. This development formed the basis of tar-chemistry that soon provided light-fast dyes and synthetic pharmaceuticals. Only in the course of the 20th century was coal tar replaced by today's dominant raw material, crude oil. Presently, most chemical value chains originate from this latter source. However, only a small portion of the world's crude oil production is refined into complex chemical products, nonetheless this still represents a staple entry point for high value modern chemical synthesis. The use of fossil carbon sources, connected with the required recovery from underground deposits, however, leads to the steady increase in the carbon inventory in the atmosphere, which contributes to global warming.

Petroleum is formed over geological time from biomass under extreme temperatures and pressures, through which the heteroatoms (non-carbon or non-hydrogen atoms) and most chirality (in carbohydrates, proteins, and lipids) are lost through successive defunctionalization, so-called *kerogenesis*, leaving finally simple hydrocarbons. The use of petroleum as a raw material for industrial chemicals requires that such useful functionalities and heteroatoms be reintroduced at considerable expense through often complex procedures. The direct use of biomass as a raw material for chemical production or alternative energy sources would circumvent the functionality loss through kerogenisis, but such potentially economical processes are currently almost completely without commercial significance.

Xylochemistry

The concept that we designate as *Xylochemistry* (Figure 1) is an approach to a sustainable chemical economy based on the use of wood as an alternative, and more practical carbon source. Presently, the global annual production of timber and oil are comparable. The yearly world-wide wood production is about 5 × 10^9 m^3, while the global oil production currently amounts to 4 × 10^9 m^3 per year [1,2]. Xylochemistry is CO_2-neutral and could, depending on the life of the products produced therefrom even lead to a decrease in the atmospheric carbon inventory. Wood contains, as opposed to fossil resources, additional important functionalities such as hydroxyl or carboxyl groups, which can be used for the production of high-value products.

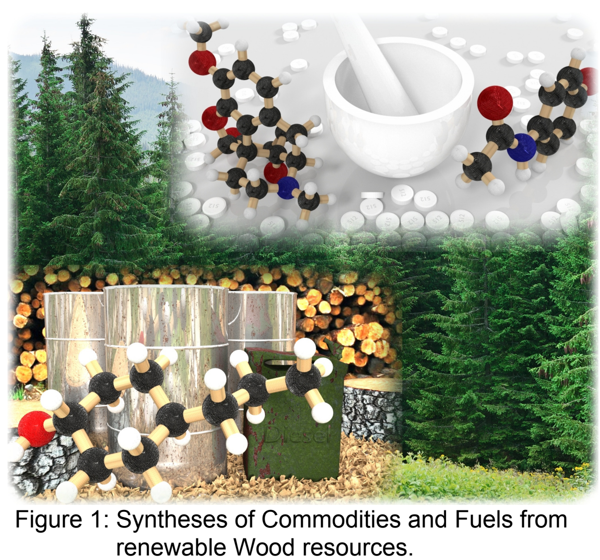

Figure 1: Syntheses of Commodities and Fuels from renewable Wood resources.

Implementation of a xylochemical approach to a sustainable chemical industry will only succeed if it is economically competitive. This viability requires that four key challenges be addressed[3]:

- Renewable wood resources must be utilized as sources of chemical building blocks and reagents.
- Wood's naturally occurring functionality (chirality, heteroatoms) should be retained to as large an extent as possible.
- Catalysts must be developed that can competitively cope with the attainable purity of the biomass and maximally exploit its structure and chemical potential.
- Xylochemical syntheses should be designed to run as continuous rather than batch processes.

About 50% of the dry weight of wood is carbon with oxygen and hydrogen (about 44% and 6% resp.) comprising the remainder[4]. About half of its mass is Celluose which is particularly important for the pulp industry. However, today's digital revolution is reducing this demand and the resource is increasingly becoming available for new applications. Cellulose can be converted by hydrolysis into glucose, which may also be regarded as a formaldehyde oligomer via Butlerov's Formose reaction. The other half of the dry weight of the wood is approximately equal amounts of lignin and hemicellulose. The latter are, like cellulose, polysaccharidic in nature and from these, pentoses such as xylose or arabinose as well as hexoses like glucose, mannose and galactose may be prepared by hydrolysis.

From a chemical point of view, lignin is a particularly attractive raw material that consists of a structurally diverse network multiple oxygenated phenylpropyl units which are connected by different types of covalent cross links. In addition to this biopolymer, the corresponding phenolic monomers, such as ferulic acid, sinapinic acid or gallic acid are present in wood. These latter substances can be isolated by extraction or by distillation as their methyl esters[5]. In general, the depolymerization of lignin to soluble monomers offers a rich source of small aromatic blocks with six to nine carbon atoms. For example, Waldvogel *et al*. generated vanillin in high yield by electrochemical oxidation of *black liquor*, a by-product of pulp production[6]. Such chemical building blocks are conventionally prepared from unsustainable fossil resources (petrochemicals) through the selective (and expensive) introduction of oxygen and other functionality.

Synthesis with Wood-based Chemicals

To demonstrate the potential of wood constituents, Xylochemicals, in preparative organic chemistry, we recently introduced the synthesis of a complex natural product, the dimeric Berberin-alkaloids Ilicifoline B from the shrub *Berberis ilicifolia* (Figure 2) [7,8]. The carbon skeleton and the vast number of heteroatoms were derived from three Xylochemicals: ferulic acid, veratrole and methanol. The latter is also known under the name wood spirit or wood alcohol and can – like acetone and other well-known basic chemicals – be obtained by dry distillation of wood. This first synthesis of the natural substance, ilicifoline B, lacks an alternative petrochemical route for comparison of efficiency. However, our earlier asymmetric synthesis of (-)-dihydrocodine (related to the morphine analgesic) demonstrates that the avoidance of petrochemical

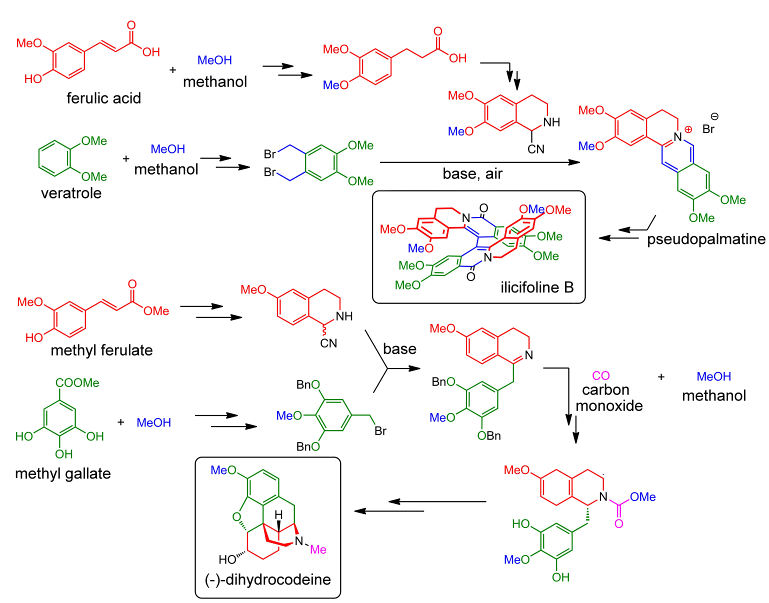

Figure 2: Syntheses of Illicifoline B and Dihydrocodine from Wood-based Chemicals. The color of the molecular fragments indicate their source.

feedstocks need not be associated with a reduced efficiency[8,9]. From the Xylochemicals, methyl ferulate and methyl gallate, we produced a key intermediate in the dihydrocodine synthesis that can be subsequently and conveniently elaborated into the final product. The overall yield of 11.2% in a total of 15 linear synthesis steps starting from methyl ferulate and two additional Xylochemicals, methanol and carbon monoxide is achieved. By way of comparison, the most efficient previously known (petrochemical) asymmetric synthesis of morphinans has a total yield of 4.8% [10].

Wood is also well-suited as a source of valuable basic chemicals and commodities utilized for the production of polymers or plastics, dyes, adhesives, fuels and a host of other consumer goods (Figure 3). The four challenges to the implementation of Xylochemistry mentioned above can be addressed through the development and use of modern and efficient chemical methods targeted for this renewable resource. The historical view of resource utilization presented at the beginning of this article combined with the growth in the chemical sciences can provide a sustainable and economical Xylochemical alternative to conventional petrochemistry.

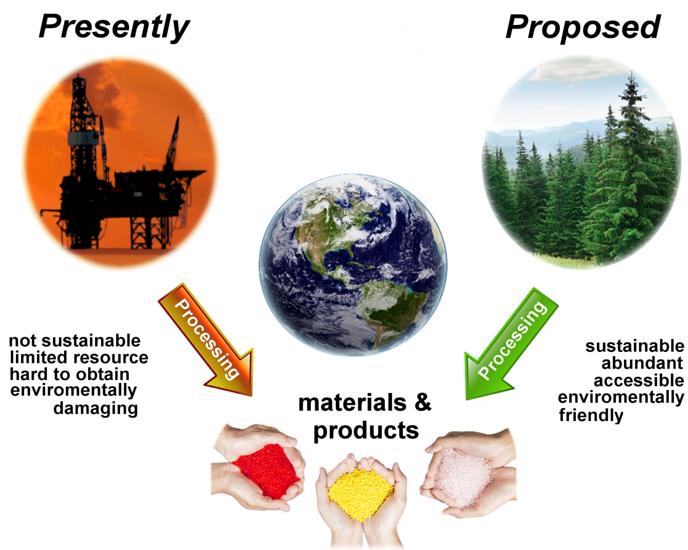

Figure 3: Xylochemistry as a sustainable alternative to petrochemistry.

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