

Production of Liquid Hydrocarbons from Biomass

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*Dedicated to Professor Dieter Lenoir
on the occasion of his 70th birthday*

Research is being conducted worldwide to develop new technologies for the generation of liquid fuels from renewable resources. In this context, it was stated recently that “biomass is the only practical source of renewable liquid fuel”.^[1] This is of utmost importance for sustainable development.^[2] Currently, biodiesel is produced by transesterification of vegetable oils^[3] and ethanol by fermentation of glucose. Processes for the efficient gasification of biomass to produce CO and H₂ (synthesis gas) are being developed.^[4,5] The synthesis gas can be further processed to produce methanol or liquid alkanes by Fischer-Tropsch synthesis using well-established industrial processes.

In Agenda 21, Chapter 4.20, the United Nations call for “criteria and methodologies for the assessment of environmental impacts and resource requirements throughout the full life-cycle of products and processes”. A simple metric for biofuel production is the overall energy efficiency, that is, the heating value of the biofuel divided by the energy required to produce the biofuel from the respective biomass. Biodiesel production from rapeseed oil in Germany has an overall energy efficiency (not taking into account potential glycerol use) of about 1.9^[6] and from soybean oil in the USA of about 3.^[7]

The overall energy efficiency for the production of ethanol from corn in the USA equals about 1.1 without energy

credits for coproducts.^[8] However, Pimentel pointed out quite recently: “In the U.S. ethanol system, considerably more energy, including high-grade fossil fuel, is required to produce ethanol than is available in the energy ethanol output. Specifically about 29% more energy is used to produce a gallon of ethanol than the energy in a gallon of ethanol.”^[9] Approximately 67% of the energy required for ethanol production is consumed in the fermentation/distillation process, of which over half is used to distill ethanol from water.^[8] A process without the energy-consuming distillation step would be most important.

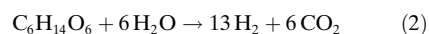
Huber et al. have recently demonstrated that it is possible to produce light alkanes by aqueous-phase reforming (APR) of biomass-derived oxygenates such as sorbitol, which can be obtained from glucose by hydrogenation.^[10,11] The production of alkanes from aqueous carbohydrate solutions would be advantageous because of the easy separation of the alkanes from water. Accordingly, it was estimated that the overall energy efficiency for alkane production from corn would be increased to approximately 2.2, assuming that this process eliminates the energy-intensive distillation step but still requires all of the remaining energy input needed for the production of ethanol from corn.^[8]

Much hydrogen is needed to reduce biomass-derived oxygenates to alkanes as shown in Equation (1). The main

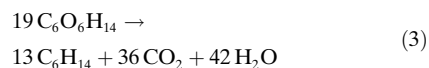


problem arises immediately, as with any hydrogen technology: currently, there is no energy- and cost-efficient method for making hydrogen, let alone burning it as a fuel. Importantly, it was shown in earlier work that hydrogen can be

produced in a catalytic process at 500 K in water from biomass-derived polyols having a C/O stoichiometry of 1:1 such as sorbitol [Eq. (2)].^[12,13] The equilibrium constant for reaction (2) per mole of CO₂ is of the order of 10⁸ at 500 K, indicating that the conversion of sorbitol in the presence of water to H₂ and CO₂ is highly favorable.



Equations (1) and (2) show that it should be feasible to generate from the molecules of the biomass in the presence of an appropriate catalyst the hydrogen needed to reduce them to alkanes, possibly in a one-pot reaction. The overall reaction (3) is an exothermic



process and converts approximately 1.5 mol of sorbitol into 1 mol of hexane. About 95% of the heating value but only 30% of the mass of the biomass-derived reactant is retained in the product. The remaining 70% of the biomass is found as CO₂ and water.

Production of alkanes by aqueous-phase reforming of sorbitol takes place in a one-pot reaction by a bifunctional reaction pathway that involves first the formation of hydrogen and CO₂ on the appropriate metal catalyst (such as Pt/Al₂O₃) and the dehydration of sorbitol on a solid acid catalyst (such as silica-alumina). These initial steps are followed by hydrogenation of the dehydrated reaction intermediates on the metal catalyst. When these steps are balanced properly, the hydrogen produced in the first step is fully consumed by hydrogenation of the dehydrated reaction intermediates, which leads to

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the overall conversion of sorbitol to alkanes plus CO₂ and water. A rationalization of the reaction pathway is given in Figure 1.

Figure 2 shows that not only hexane but also lighter alkanes from methane to pentane are formed from the C₆-polyol sorbitol. Up to 60% overall yield of alkanes was obtained. Interestingly, the moderate yield of alkanes seems to be limited mainly by the moderate yield of hydrogen. Thus, a maximum yield of 61% of hydrogen with respect to sorbitol was obtained over Pt/Al₂O₃ under optimized reaction conditions.^[12] In contrast, the yield of alkanes could be increased up to 98% when hydrogen was co-fed with the aqueous sorbitol stream. Under these reaction conditions sorbitol is converted to alkanes and water without the formation of CO₂ since hydrogen is supplied externally and not produced as an intermediate in the process. However, the weight hourly space velocity seems to be rather low. The mass of 10% sorbitol solution reacted per mass of catalyst per hour was 1.3.

Consequently, high-yielding processes are feasible to produce alkanes from biomass-derived polyols such as sorbitol. A disadvantage would be that sorbitol has to be produced in two reaction

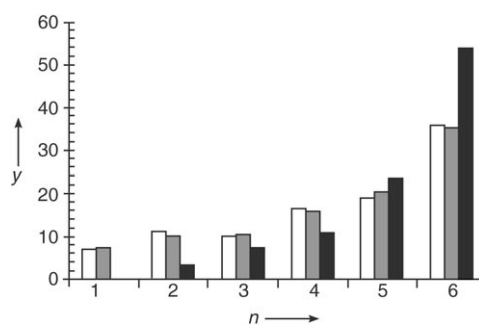


Figure 2. Selectivity γ for aqueous-phase reforming of 5 wt% sorbitol over Pt/SiO₂/Al₂O₃ versus the number of carbon atoms n in the alkane; white: 498 K and 34.8 bar; gray: 538 K and 60.7 bar; black: co-feeding H₂ at 498 K and 34.8 bar.^[10]

steps, for example, from the renewable feedstock starch via glucose, which has to be hydrogenated and already requires one equivalent of hydrogen. It has been demonstrated that glucose can be used as substrate for the APR process to generate hydrogen. The yield of 50% hydrogen is much lower than that with sorbitol.^[12] Starch has not been used as a substrate.

Another important problem is the fact that the highest alkane that can be formed by APR from sorbitol is hexane. Unfortunately, the high volatility of hexane makes this compound a poor fuel additive. Thus, the production of

high-quality liquid fuels from carbohydrates requires the formation of longer-chain alkanes, which cannot be obtained from biomass-derived carbohydrates consisting predominantly of pentoses and hexoses. Huber et al.^[8] proposed to solve this problem by first linking carbohydrate-derived moieties through the formation of C–C bonds before APR processing. They presented a catalytic process for the conversion of biomass-derived carbohydrates to liquid alkanes in the higher mass ranges (from C₇ to C₁₅). Furfural and hydroxymethylfurfural

(HMF), which are available from pentoses and hexoses, respectively, by dehydration are key intermediates. An efficient industrial process for the production of HMF must be developed because it is a key intermediate of a biobased chemical industry as well.^[14] Furfural and HMF were transformed in two to three reaction steps by well-known reactions, for example the aldol reaction, into molecules containing C₈ to C₁₅ chains. An example is given for the condensation of two equivalents of furfural with one equivalent of acetone in Figure 3. These molecules yielded higher alkanes predominantly with the chain length of the substrate by a modified process (four-phase reactor system). The normal APR process could not be used because extensive amounts of coke formed on the catalyst surface.

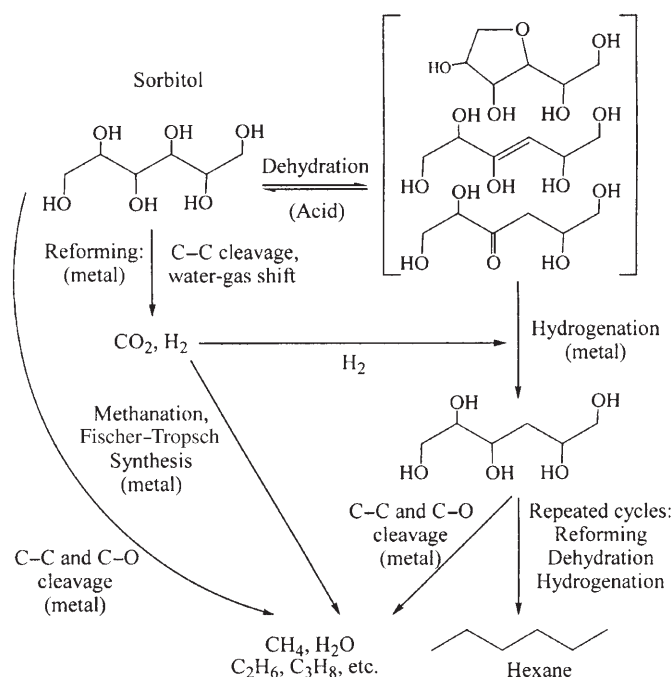


Figure 1. Reaction pathways for the production of alkanes from sorbitol in aqueous solution over a Pt/SiO₂/Al₂O₃ catalyst.^[10]

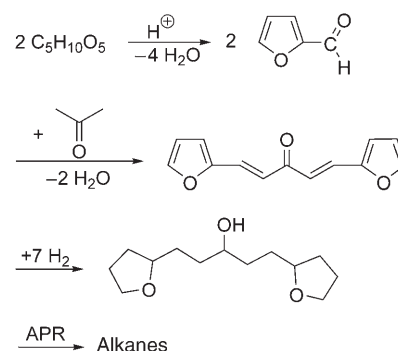


Figure 3. Synthesis of a C₁₃ substrate derived from pentoses via furfural followed by aldol condensation with acetone and hydrogenation. In the modified APR process at 523–538 K, a 1% solution of hexadecane with externally supplied hydrogen yielded 79% alkanes with a selectivity of 69% C₁₃ and 20% C₁₂.^[8]

The encouragement of environmentally sound and sustainable use of renewable natural resources is one aim of Agenda 21 (Chapter 4.18). The main problem of the APR process seems to be that the substrates are carbohydrates and compounds derived therefrom. It is obvious that most plant-derived biomass consists of carbohydrates. But the carbohydrates needed for the APR process can be obtained only from agricultural products such as sugar cane and corn. In contrast, feedstocks used for the production of liquid fuels and hydrogen should preferably be obtained from high-productivity biomass crops that do not require synthetic fertilizers and biocides.^[15] This is not the case with corn, sugar cane, and other agricultural crops. In addition, the area based energy yield per year is relatively low compared to that of the lignocellulosic biomass of wood, which can be cultivated largely without synthetic fertilizers and biocides. Unfortunately the APR process cannot be applied to lignocelluloses. Most importantly, lignocelluloses like other types of biomass can be completely gasified to synthesis gas, which can be further processed to produce methanol or liquid alkanes by the Fischer–Tropsch synthesis.^[4,5] In addition to the complete gasification, the fast pyrolysis of lignocelluloses has been investigated to give a “bio-oil”. This “bio-oil” can be gasified in a second reaction step to synthesis gas or can be separated to give a lignin-derived phenolic fraction. The latter can possibly be used for the production of phenolic resins, while the carbohydrate-derived fraction is catalytically steam-reformed to produce hydrogen (Biorefinery^[16]).^[17]

Remarkably, Olah proposed recently “Beyond Oil and Gas: The Methanol Economy”.^[18] In the suggested methanol economy, methanol would be used as a convenient energy-storage material, a fuel, and a feedstock for the synthesis of hydrocarbons and their products. A

sustainable approach to a methanol economy could be the reforestation of wasteland to supply the necessary quantities of lignocellulosic biomass^[19] and their efficient conversion to synthesis gas followed by conversion to methanol and liquid hydrocarbons.^[20]

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- [19] The current global energy consumption amounts to 400×10^{18} J. The average energy content of wood is 17×10^9 J per ton. Thirty billion tons of wood per year would be required for the global energy consumption if one assumes an energy conversion efficiency of 80%, which should be possible but is not yet realized. Fast-growing tree species in moderate latitudes produce up to twenty tons of round timber per hectare and year, and tropical dry forests produce even up to 30 tons. An area of one billion hectares of tropical dry forests and 1.5 billion hectares of forests in the moderate latitudes, respectively, would be necessary to provide the global energy demand. Agricultural areas are not available. They are required to produce food for the increasing global population of up to 9 billion. The existing forests can be used only partially. However, there are sufficient areas available globally suited for reforestation. Some billion hectares of formerly wooded areas have been denuded across all continents by human activities. Currently, the desertification is advancing most rapidly. The most important transdisciplinary challenge for science and technology is to stop and reverse the desertification, to reforest the billion hectares of wasteland, and to use the lignocellulose continuously to produce methanol and hydrocarbons, which would meet the global energy demand. The contributions of chemistry to cope with this task will be of utmost importance.
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