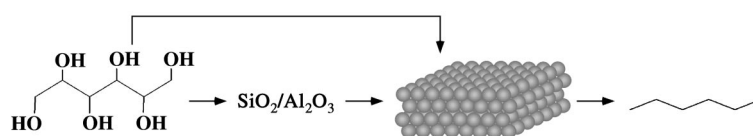**Alkane Production**

Renewable Alkanes by Aqueous-Phase Reforming of Biomass-Derived Oxygenates

A clean stream of alkanes from renewable biomass resources is obtained through aqueous-phase reforming in a single reactor. Alkanes are produced from biomass-derived sorbitol through a bifunctional pathway (see scheme) that involves the dehydration of sorbitol on acid sites (SiO_2/Al_2O_3) and hydrogenation of intermediates on a metal catalyst under a H_2 atmosphere. Hydrogen is produced from sorbitol and water on the metal catalyst in the same reactor.

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Alkane Production

Renewable Alkanes by Aqueous-Phase Reforming of Biomass-Derived Oxygenates**

*George W. Huber, Randy D. Cortright, and James A. Dumesic**

Research is being conducted world-wide to develop new technologies for the generation of energy from renewable resources. In this respect, it has recently been stated that "biomass is the only practical source of renewable liquid fuel".[1] Current technologies to produce liquid fuels from biomass are typically multistep and energy-intensive processes, including the production of ethanol by fermentation of biomass derived glucose,[2] bio-oils by pyrolysis or high pressure liquefaction of biomass,[3, 4] polyols from hydrogenolysis of biomass derived sorbitol,[5] and biodiesel from vegetable oils.[6] Biomass can also be gasified to produce CO and H_2 (synthesis gas), which can be further processed to produce methanol or liquid alkanes by Fischer–Tropsch synthesis.[3] In addition, liquid hydrocarbons can be formed from biomass-derived carbohydrates over zeolite catalysts at temperatures from 570 to 920 K, accompanied by formation of carbonaceous residues on the catalyst.[7]

We have recently demonstrated that it is possible to produce hydrogen and light alkanes (primarily methane) by aqueous-phase reforming (APR) of biomass-derived oxygenates, including glucose, sorbitol, and glycerol.[8, 9] The APR process offers a simple route for the production of renewable fuels from biomass, since this process takes place in a single reaction vessel. Herein, we show how aqueous-phase reforming of sorbitol (the sugar alcohol obtained by hydrogenation of glucose) can be tailored to selectively produce a clean stream of heavier alkanes consisting primarily of butane, pentane, and hexane. The conversion of sorbitol to alkanes plus CO_2 and water is an exothermic process that retains approximately 95% of the heating value and only 30% of the mass of the biomass-derived reactant.

Production of alkanes by aqueous-phase reforming of sorbitol takes place by a bifunctional reaction pathway that involves first the formation of hydrogen and CO_2 on the appropriate metal catalyst (such as Pt) and the dehydration of sorbitol on a solid acid catalyst (such as silica-alumina[10]).

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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 the overall conversion of sorbitol to alkanes plus CO_2 and water.

Figure 1 shows the essential features of the bifunctional reaction pathway for the production of alkanes from sorbitol. Hydrogen is produced on the metal by cleavage of C−C bonds
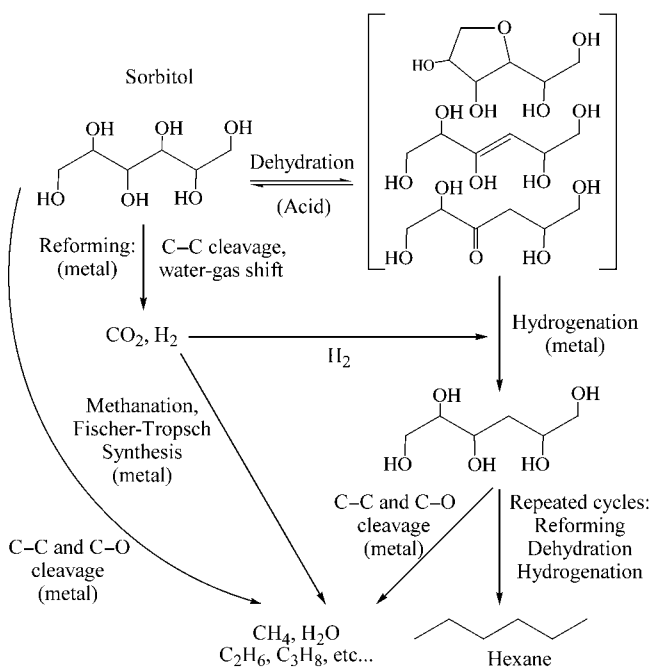
Figure 1. Reaction pathways for the production of alkanes from sorbitol over catalysts with metal and acidic components.

followed by the water–gas shift reaction. Dehydrated species such as ring compounds like isosorbide or enolic species are formed on acid sites,[11] which migrate to metal sites where they undergo hydrogenation reactions. Repeated cycling of dehydration and hydrogenation reactions in the presence of hydrogen leads to heavier alkanes (such as hexane) from sorbitol. Formation of lighter alkanes takes place by more rapid cleavage of C−C bonds compared to hydrogenation of dehydrated reaction intermediates. Lighter alkanes can also be formed by hydrogenation of CO and/or CO_2 on metals such as Ni and Ru.[12] Accordingly, the selectivities for production of various alkanes by aqueous-phase reforming depend on the relative rates of C−C bond cleavage, dehydration and hydrogenation reactions. The selectivities for the production of alkanes can be varied by changing the catalyst composition, the reaction conditions, and by modifying the reactor design. In addition, these selectivities can be modified by co-feeding hydrogen with the aqueous sorbitol feed, leading to a process in which sorbitol can be converted to alkanes and water without the formation of CO_2 (since hydrogen is supplied externally and need not be produced as an intermediate in the process). As another variation, the production of alkanes can be accomplished by replacing the

solid acid with a mineral acid (such as HCl) that is co-fed with the aqueous sorbitol reactant.

Table 1 summarizes the experimental results for aqueous-phase reforming of sorbitol at various reaction conditions. These data were collected over catalysts consisting of 4 wt % $Pt/SiO_2-Al_2O_3$ (Pt–SiAl), 3 wt % $Pd/SiO_2-Al_2O_3$ (Pd–SiAl), 3 wt % Pt/Al_2O_3 (Pt–Al) and physical mixtures of Pt–Al with $SiO_2-Al_2O_3$ (SiAl). The Al_2O_3 content of the $SiO_2-Al_2O_3$ support was 25 wt %. All data were collected after 20 h on-stream. Experimental details are given in the Supporting Information.

The Pt–SiAl catalyst showed no deactivation after 6 days on-stream at a conversion of 92 % and 498 K. As shown in Table 1, the carbon selectivity for production of butane, pentane and hexane over Pt–SiAl varies from 58 to 89 %, depending on the reaction conditions. The selectivity to hexane increases for the Pt–SiAl catalyst at 498 K as the pressure increases from 25.8 to 39.6 bar, and slightly decreases as the pressure is increased further to 52.7 bar. The alkanes are formed by a combination of metal and acidic components, since they are formed in only small amounts on the Pt–Al catalyst. The alkanes formed are straight-chain compounds with only minor amounts of branched isomers (less than 5 %). Alkanes heavier than hexane were not formed under the reaction conditions of this study.

As shown in Figure 2, the selectivity for production of hexane increases when hydrogen is co-fed with the aqueous sorbitol stream. Thus, increasing the hydrogen partial pressure in the reactor increases the rate of hydrogenation compared to C−C bond cleavage on the metal catalyst surface. No major difference is observed in the alkane
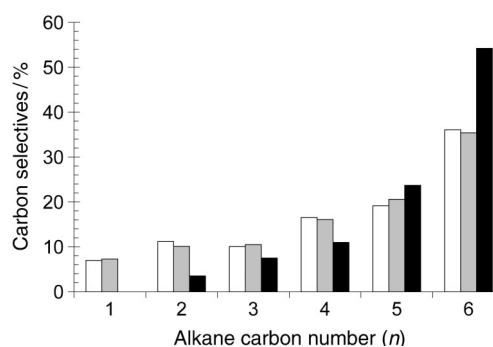

Figure 2. Carbon selectivities for aqueous-phase reforming of 5 wt % sorbitol over Pt–SiAl: white, 498 K and 34.8 bar; gray, 538 K and 60.7 bar; black, co-feeding H_2 at 498 K and 34.8 bar.

distribution as the temperature is increased from 498 to 538 K (Figure 2).

Figure 3 a shows that the selectivities to heavier alkanes increase as more solid acid sites are added to a non-acidic Pt–Al catalyst by making physical mixtures of Pt–Al and SiAl. The alkane selectivities for an acidic Pt–SiAl catalyst and for a mixture of Pt–Al and SiAl components are similar, both having the same ratio of Pt to acid sites. The alkane distribution also shifts to heavier alkanes for the non-acidic Pt–Al catalyst when the pH of the aqueous sorbitol feed is lowered by the addition of HCl, as shown in Figure 3 b.

By changing the nature of the metal component in the catalyst, one can vary the relative rates of C−C bond cleavage versus hydrogenation, thereby controlling the selectivities for the production of different alkanes. Reaction-kinetics studies

Table 1: Experimental data for aqueous phase reforming of 5 wt % sorbitol

Catalysts and additives to feed	Pt–SiAl							Pt–SiAl H_2[b]	Pt–SiAl H_2[b]	Pd–SiAl H_2[b]	Mix 1[c]	Mix 2[c]	Pt–Al	Pt-Al HCl pH 3	Pt-Al HCl pH 2	Pt-Al Void[d]
WHSV [h^{-1}][a]	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	0.29	1.4	0.46	0.75	0.75	0.75	2.4
Temperature [K]	498	498	498	498	498	538	538	498	498	538	538	538	538	538	538	538
Pressure [bar]	25.8	33.1	34.8	39.6	52.7	55.5	60.7	29.3	34.8	58.2	57.5	57.5	57.5	57.5	57.5	57.5
Carbon in liquid phase effluent [%]	16	13	10	10	27	8	8	12	11	28[e]	10	5	10	8	11	16
Carbon in gas phase effluent [%]	81	89	93	92	76	95	95	84	85	67	91	94	86	88	89	80
Carbon selectivity [%][f]																
CH_4	15	11	7	6	10	11	7	0	0	2	7	35	42	24	9	17
C_2H_6	13	9	11	8	10	9	10	3	4	2	9	20	25	19	7	9
C_3H_8	14	10	10	8	9	11	11	6	7	4	13	16	17	21	14	12
C_4H_{10}	20	18	17	17	15	17	16	11	11	8	18	12	8	15	22	17
C_5H_{12}	17	19	19	21	19	21	21	25	24	28	23	10	5	12	25	20
C_6H_{14}	21	33	36	40	37	31	35	55	54	56	30	7	3	9	23	25
Alkane to total gas phase carbon [%][g]	46	58	63	64	53	58	60	91	91	98	53	31	27	29	47	53
H_2 selectivity [%][h]	21	2	2	1	1	7	4	–	–	–	11	46	43	31	6	16

[a] WHSV = weight hourly space velocity; mass of sorbitol solution per mass of catalyst per hour. [b] H_2 co-fed at a gas-hourly space velocity of 120–900 h^{-1}. Densities of SiO_2-Al_2O_3 catalysts are 0.54 g cm^{-3}. [c] Mix 1 contains Pt-Al (1.45 g) and SiAl (1.11 g). Mix 2 contains Pt-Al (3.30 g) and SiAl (0.83 g). [d] Empty void space representing 70 % of the total reactor volume located upstream from the catalyst bed. [e] Approximately 25 % of the carbon was in a volatile organic liquid phase product and 3 % of the carbon was in the aqueous phase product. The carbon selectivities are based on gas phase products. [f] Carbon selectivity = (moles alkane × number of carbon atoms in alkane)/(total moles of carbon atoms in alkane products) × 100. [g] The gas phase carbon consisted of alkanes and carbon dioxide. [h] % H_2 selectivity = (molecules H_2 produced/C atoms in gas phase) × (6/13) × 100.
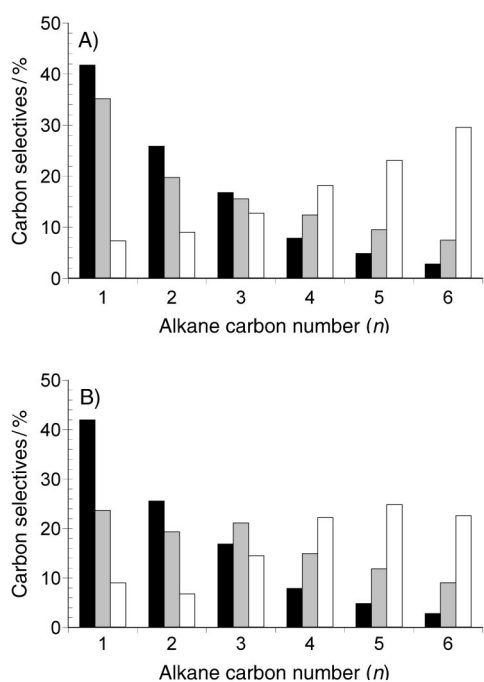
Figure 3. Carbon selectivities for aqueous-phase reforming of 5 wt% sorbitol at 538 K and 57.6 bar. A) Addition of solid acid to Pt–Al: black, Pt–Al; gray, mixture 2: Pt–Al (3.30 g) and SiAl (0.83 g); white, mixture 1: Pt–Al (1.45 g) and SiAl (1.11 g). B) Addition of mineral acid (HCl) in feed over Pt–Al: black, $pH_{feed} = 7$; gray, $pH_{feed} = 3$; white, $pH_{feed} = 2$.

for aqueous-phase reforming of ethylene glycol over silica-supported Pd and Pt catalysts indicate that the rate of C–C bond cleavage is approximately one order of magnitude lower for Pd than for Pt,[12] whereas Pd catalysts are used as hydrogenation catalysts for various reactions.[13] As shown in Table 1, a Pd–SiAl catalyst exhibits very high selectivity for the production of alkanes versus CO_2 when hydrogen is co-fed with aqueous sorbitol into the reactor, as the rate of C–C bond cleavage on Pd is slower than the rates of dehydration on acid sites and hydrogenation reactions on Pd sites. Furthermore, this catalyst system shows very high selectivity for the production of hexane. This example shows that effective bifunctional catalysts can be formulated by using metals that, by themselves on non-acidic supports, show low activities for hydrogen production by aqueous-phase reforming reactions. The hydrogen used for this process can be obtained by APR of sorbitol in a separate reactor over nonprecious metal catalysts.[8]

Another factor that affects the selectivities for the production of alkanes is the presence of void space in the reactor, in which sorbitol can undergo homogenous liquid-phase reactions. Products such as isosorbide and organic acids ($\approx$ 100–500 ppm) were observed in the liquid products from an empty reactor with a feed of 5 wt% sorbitol heated at 538 K and 57.5 bar, whereas negligible amounts of liquid products were observed at 498 K and 36.5 bar (both experiments conducted with similar liquid residence times as used for studies of supported Pt catalysts). As seen in Table 1, the presence of void space in the reactor at 538 K leads to higher

selectivities for the production VCH of alkanes over Pt–Al, since the intermediates formed by homogeneous reactions in the liquid phase are hydrogenated to alkanes over Pt.

The general conclusion from this work is that a clean stream of alkanes can be formed by aqueous-phase reforming of sorbitol over bifunctional catalyst systems in which sorbitol is repeatedly dehydrated by an acid catalyst (e.g., a solid acid or an aqueous mineral acid) and then hydrogenated on a metal catalyst (e.g., Pt or Pd). Hydrogen, which is needed for the hydrogenation reaction, can be produced in situ by aqueous-phase reforming of sorbitol over a catalyst (such as Pt) that facilitates C–C bond cleavage and water–gas shift reactions, or it can be co-fed to the reactor with the aqueous sorbitol reactant. The selectivities for production of heavier alkanes can be controlled by the choice of reaction conditions and by co-feeding hydrogen to the reactor. It is likely that advances in the understanding of new types of solid-acid catalysts[14] as well as new metal alloy catalysts[8] will lead to further process improvements.

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