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Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates

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Materials and Methods
SOM Text

Fig. S1

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Production of Liquid Alkanes by Aqueous-Phase Processing of Biomass-Derived Carbohydrates

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Liquid alkanes with the number of carbon atoms ranging from C_7 to C_{15} were selectively produced from biomass-derived carbohydrates by acid-catalyzed dehydration, which was followed by aldol condensation over solid base catalysts to form large organic compounds. These molecules were then converted into alkanes by dehydration/hydrogenation over bifunctional catalysts that contained acid and metal sites in a four-phase reactor, in which the aqueous organic reactant becomes more hydrophobic and a hexadecane alkane stream removes hydrophobic species from the catalyst before they go on further to form coke. These liquid alkanes are of the appropriate molecular weight to be used as transportation fuel components, and they contain 90% of the energy of the carbohydrate and H_2 feeds.

The production of liquid fuels from renewable biomass resources is particularly attractive because gasoline- and diesel-powered hybrid electric vehicles are being developed that have overall energy efficiencies comparable to those of vehicles powered by fuel cells based on current technologies (1). Approximately 75% of the dry weight of herbaceous and woody biomass is composed of carbohydrates (2). Several processes currently exist to convert carbohydrates to liquid fuels, including the formation of bio-oils by liquefaction or pyrolysis of biomass (3), the production of alkanes or methanol by Fischer-Tropsch synthesis from biomass-derived $CO:H_2$ gas mixtures (2), and the conversion of sugars and methanol to aromatic hydrocarbons over zeolite catalysts (4, 5).

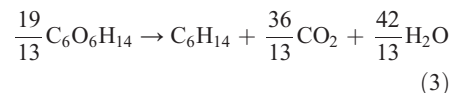
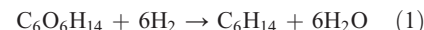
However, the conversion of glucose to ethanol is the most widely practiced process (6)

for producing liquid fuels from biomass, with an overall energy efficiency from corn (the heating value of ethanol divided by the energy required to produce ethanol from corn) equal to about 1.1 without coproduct energy credits (7). 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 (7, 8).

In comparison, the production of alkanes from aqueous carbohydrate solutions would involve the spontaneous separation of the alkanes from water. Accordingly, we estimate that the overall energy efficiency for alkane production from corn would be increased to approximately 2.2, if we assume that this process eliminates the energy-intensive distillation step but still requires all of the remaining energy inputs needed for the production of ethanol from corn (9).

We have recently shown how an aqueous solution of sorbitol (the sugar-alcohol of glucose) can be converted to hexane (Eq. 1) with a catalyst containing both acid (e.g., $SiO_2-Al_2O_3$) and metal (e.g., Pt or Pd) sites to

catalyze dehydration and hydrogenation reactions, respectively (10). Hydrogen for this reaction can be produced from the aqueous-phase reforming of sorbitol (Eq. 2) in the same reactor or in a separate reactor with a non-precious metal catalyst (11). The net reaction (Eq. 3) is an exothermic process in which approximately 1.5 mol of sorbitol produce 1 mol of hexane.



Alkanes produced in the aqueous-phase dehydration/hydrogenation (APD/H) of carbohydrates would provide a renewable source of transportation fuel to complement the rapidly growing production of biodiesel from vegetable oils and animal fats (12). Unfortunately, the high volatility of hexane makes this compound of low value as a fuel additive (13). Thus, the production of high-quality liquid fuels from carbohydrates requires the formation of larger alkanes, and this production can be accomplished by first linking carbohydrate-derived moieties through the formation of C-C bonds before APD/H processing. Here we present a catalytic process for the conversion of biomass-derived carbohydrates to liquid alkanes in the higher mass ranges (from C_7 to C_{15}) that can be used as sulfur-free fuel components. We note that C-O-C linkages (as found in disaccharides) are broken under APD/H reaction conditions. The formation of C-C bonds between carbohydrate-derived moieties can be carried out by a variety of chemical routes, and we have chosen a dehydration step (acid-catalyzed) followed by an aldol-condensation (base-catalyzed) step (Fig. 1).

Our current APD/H process cannot be used to produce alkanes from large water-soluble organic compounds because extensive amounts of coke form on the catalyst surface (between

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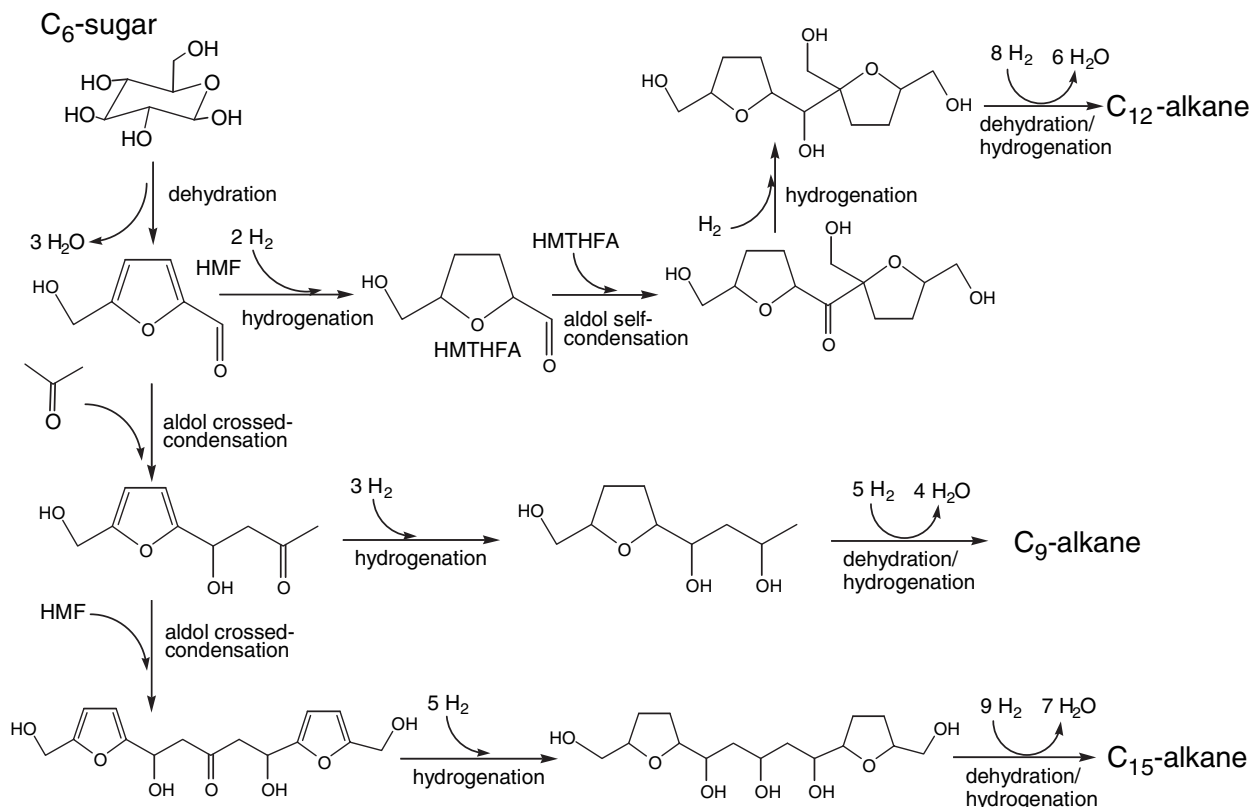


Fig. 1. Reaction pathways for the conversion of biomass-derived glucose into liquid alkanes.

20 and 50% of the reactant converts to coke). Accordingly, we have modified our reactor system to carry out dehydration/hydrogenation reactions in a four-phase reactor system consisting of (i) an aqueous inlet stream, which contains the large water-soluble organic reactant; (ii) a hexadecane alkane inlet stream; (iii) an H_2 inlet gas stream; and (iv) a solid catalyst ($Pt/SiO_2-Al_2O_3$). As dehydration/hydrogenation takes place, the aqueous organic reactant becomes more hydrophobic, and the hexadecane alkane stream removes hydrophobic species from the catalyst before they go on further to form coke. In an industrial setting, the alkanes produced from the reaction would be recycled to the reactor and used for the alkane feed. Reaction kinetics experiments conducted with pure water as the aqueous feed showed that only a small amount of hexadecane was converted to lighter alkanes in the four-phase dehydration/hydrogenation (4-PD/H) reactor system ($0.007 \mu\text{mol min}^{-1} \text{g}_{\text{catalyst}}^{-1}$), and this low reactivity was subtracted from all of our subsequent experimental data.

To benchmark the performance of our 4-PD/H reactor, we studied the conversion of a 5 weight percent (wt %) aqueous solution of sorbitol for different feed rates of the hexadecane alkane stream. Results for these measurements showed that increasing the hexadecane flow rate decreased the conversion of sorbitol (table S3, entries S1 to S3). No major differences were observed in the selectivity of the reaction

Table 1. Selected values for conversion and process conditions for 4-PD/H of biomass-derived molecules. The full table is available in (16). All 4-PD/H reactions were carried out at 523 to 538 K, 52 to 60 bars, and H_2 gas hourly space velocities (cm^3 of H_2/cm^3 of catalyst) of 1000 to 3000 hour^{-1} . A 4 wt % $Pt/SiO_2-Al_2O_3$ catalyst was used for these reactions. Each experimental point was collected after 20 hours on stream. Condensed feeds were prepared by aldol condensation at room temperature using Mg-Al-oxide and NaOH catalysts. SC, self-condensed; Fur, furfural; Ace, acetone; org, organic. Numbers listed in parentheses indicate the molar ratio of feeds. All feeds were hydrogenated in a Parr reactor with a Pd/Al_2O_3 catalyst before conversion in the 4-PD/H reactor. Entries 1 to 3 and 5 to 7 were hydrogenated in methanol or a methanol/water mixture, with all other feeds being hydrogenated in H_2O . wt (%) refers to wt % organics in aqueous feed solution. WHSV is weight hourly space velocity, which is the mass of aqueous feed solution per mass of catalyst per hour. Org/Aq is the organic (hexadecane)-to-aqueous volumetric feed ratio.

Entry	Feed	wt (%)	WHSV (hour^{-1})	Org/Aq	% Carbon in phase		
					Org	Gas	Aq
1	Furoin	2.0	0.26	3.0	69.2	18.5	2.3
2	Fur:Ace (1:1)-1	1.9	0.26	3.0	100.0	6.3	1.6
3	Fur:Ace (1:1) org*	5.0	0.51	∞	73.2	7.8	NA
4	Fur:Ace (1:1)-3	12.5	0.29	3.0	91.2	4.1	0.7
5	Fur:Ace (2:1)	1.0	0.29	3.0	79.0	2.4	0.8
6	HMF:Ace (1:1)-1	1.8	0.25	3.0	66.1	15.7	1.5
7	HMF:Ace (1:1)-2†	1.9	0.26	3.0	69.5	7.7	0.9
8	HMF:Ace (1:1)-3	1.8	0.29	3.0	53.3	31.1	2.3
9	HMF:Ace (1:10)	9.5	0.35	0.7	77.2	10.3	20.0
10	HMF:Fur:Ace (1:1:2)	1.9	0.29	3.0	48.5	27.8	3.1
11	SC THF3A	5.0	0.35	0.7	53.2	44.1	4.2
12	SC THF2A	3.9	0.35	0.7	47.9	20.8	13.0

*Fur:Ace (1:1) org was added to the hexadecane feed, and no aqueous flow was used for this feed. †This feed was condensed with twice the amount of Mg-Al-oxide than was the feed above it (entry 6).

when the hexadecane-to-water flow rate ratio was increased (table S4, entries S1 to S3). Here we report only data collected from the 4-PD/H reactor at high conversion ($>70\%$), so that alkanes are the primary product. At these high conversions and slow liquid flow rates, it

is probable that transport limitations occur that decrease the reaction rates (14).

Furoin [purchased from Aldrich, St. Louis, Missouri, and prepared from furfural by the Pinnacol coupling reaction (15)], furfural-acetone (1:1) (purchased from Aldrich and

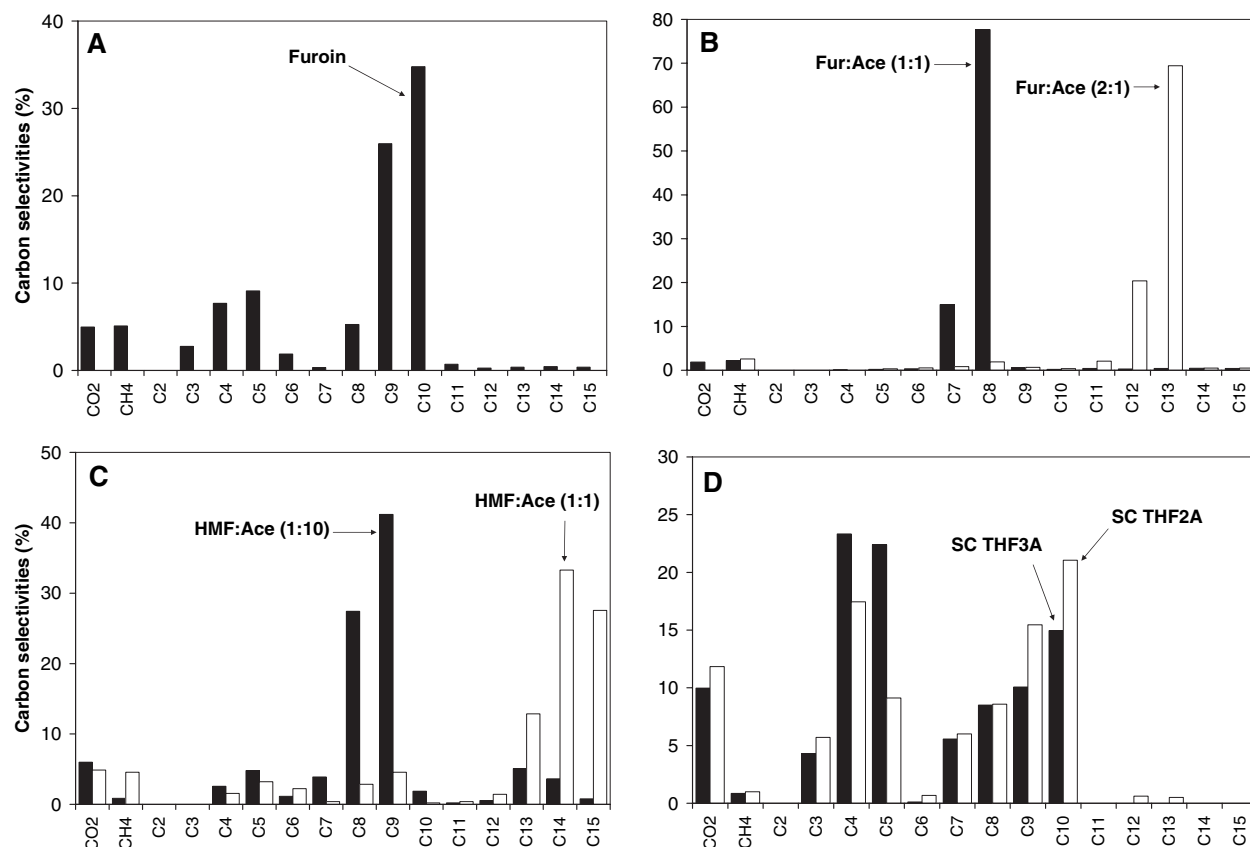


Fig. 2. Carbon selectivities from 4-PD/H processing of various condensed feeds. See Table 1 for the feed key. (A) Furoin (Table 1, entry 1). (B) Furfural (Fur):acetone (Ace) (1:1)-1 (entry 2), black; Fur:Ace (2:1) (entry 5),

white. (C) HMF:Ace (1:10) (entry 9), black; HMF:Ace (1:1)-2 (entry 7), white. (D) Self-condensed (SC) THF3A (entry 11), black; SC THF2A (entry 12), white.

prepared by aldol condensation of furfural and acetone), and furfural-acetone (2:1) [prepared by aldol condensation of furfural-acetone with furfural and NaOH (16)] were hydrogenated in methanol in a stainless-steel batch reactor (Parr Instruments, Moline, Illinois, at 55 bars of H_2 pressure and 393 K) with a Pd/ Al_2O_3 catalyst. This hydrogenation step was carried out to minimize possible coking reactions that may take place from unsaturated molecules on the Pt/ SiO_2 - Al_2O_3 catalyst in the 4-PD/H reactor and to increase the solubility of the condensed products in water. These hydrogenated compounds were then dissolved in water and converted to alkanes in the 4-PD/H reactor. The main products of the hydrogenated furoin were C_9 and C_{10} alkanes (Fig. 2A).

The hydrogenated furfural-acetone (1:1) was added to both water and hexadecane, and both feeds produced mainly C_7 and C_8 alkanes in the 4-PD/H process (Tables 1 and 2, entries 2 and 3). Hydrogenated furfural-acetone (2:1) produced primarily C_{11} to C_{13} alkanes from the 4-PD/H reactor (Fig. 2B).

Furfural-acetone (1:1) could also be hydrogenated in water without using methanol as a solvent (Tables 1 and 2, entry 4). In this step, we added the furfural-acetone (1:1) adduct, Pd/ Al_2O_3 , and water into a Parr reactor, which was subsequently pressurized with H_2 (at 55

bars) and heated to 393 K. As shown in entry 4 of Tables 1 and 2, we could prepare an aqueous solution of 12.5 wt % hydrogenated furfural-acetone (1:1), and this feed produced primarily C_7 and C_8 alkanes in the 4-PD/H reactor. The results from these experiments indicate that our process for producing liquid alkanes from biomass-derived resources does not require the use of alcohol solvents, and it is not limited to dilute aqueous feeds (17).

Aldol-condensation reactions are particularly relevant for the production of large organic compounds from biomass, because various species containing carbonyl groups can be formed from carbohydrates, including furfurals, dihydroxyacetone, and acetone. For example, glucose and xylose do not undergo aldol-condensation reactions because the carbonyl group undergoes intramolecular reactions to form ring structures (18), but dehydrating glucose and xylose yields 5-hydroxymethylfurfural (HMF) and furfural, respectively, with mineral or solid acid catalysts (Fig. 1) (2, 19–22). Both HMF and furfural have an aldehyde group, and although they do not have an α -H atom, they can condense with other molecules that can form carbanion species such as acetone, dihydroxyacetone, or glyceraldehyde (Fig. 1) (23). Acetone can be produced from the fermentation of glucose (2),

and dihydroxyacetone and glyceraldehyde can be produced from the retro-aldol condensation of glucose (18, 24).

Crossed aldol condensation of HMF with acetone was carried out with HMF:acetone molar ratios of 1:1 and 1:10 by using a mixed Mg-Al-oxide catalyst at room temperature (Tables 1 and 2, entries 6 to 9). The Mg-Al-oxide catalyst was prepared by coprecipitation (16) similar to the method reported elsewhere (25–27). The condensed molecules were then hydrogenated in a batch reactor in a methanol/ H_2O solvent for the HMF:acetone (1:1)-1 and (1:1)-2 feeds, followed by the conversion to alkanes in the 4-PD/H reactor. All other feeds discussed in this paper were batch hydrogenated in H_2O . As shown in Fig. 2C, the condensed HMF:acetone feeds produced mainly C_8 to C_{15} alkanes in the 4-PD/H reactor, depending on the HMF:acetone ratio used in the aldol-condensation step. When the HMF:acetone ratio decreases, the alkane distribution shifts to lighter alkanes (Fig. 2C). The selectivity can also be shifted to heavier alkanes by increasing the extent of conversion for the aldol condensation step of HMF:acetone (Table 2, entries 6 and 7).

To improve the potential practical utility of our process, we studied whether hydrogenation of the HMF:acetone adduct could be accomplished without using methanol as a

Table 2. Selected values for alkane and CO₂ selectivities from 4-PD/H of biomass-derived molecules. The full table is available in (76). Table 1 contains relevant process conditions, the feed key, and the conversion data. Selectivity is defined as (moles of product × number of carbon atoms in product)/(total moles of carbon

atoms in products) × 100. The selectivity takes into account only the products in the organic and gas phases. Alkane products are mostly straight chain in form, except for the SC THF3A and SC THF2A feeds. At lower conversions, small amounts of alcohols (<10% of total products) are also observed in the organic phase.

Entry	Feed	Alkane and CO ₂ selectivities (%)															
		CO ₂	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅
1	Furoin	5.2	5.2	0.0	2.8	8.0	9.2	1.8	0.3	5.4	26.2	34.0	0.7	0.3	0.3	0.4	0.2
2	Fur:Ac (1:1)-1	1.8	2.2	0.0	0.0	0.1	0.2	0.3	15.0	77.7	0.6	0.2	0.4	0.3	0.4	0.4	0.4
3	Fur:Ac (1:1) org	0.0	4.7	0.2	1.7	1.8	2.0	1.9	4.5	71.4	2.4	2.2	2.2	2.1	2.4	0.6	0.0
4	Fur:Ac (1:1) -3	1.7	0.4	0.0	0.1	0.1	0.1	0.2	17.1	64.4	7.4	5.8	2.5	0.1	0.1	0.1	0.0
5	Fur:Ac (2:1)	0.0	3.0	0.0	0.0	0.0	0.4	0.7	1.0	2.1	0.8	0.5	2.1	19.7	68.6	0.6	0.5
6	HMF:Ac (1:1)-1*	6.8	3.3	0.0	0.0	6.0	14.6	9.3	0.4	6.8	9.5	0.0	0.0	0.7	8.5	19.5	14.5
7	HMF:Ac (1:1)-2*	5.0	4.0	0.0	0.0	1.5	3.2	2.2	0.4	2.9	4.6	0.2	0.4	1.5	13.5	32.9	27.6
8	HMF:Ac (1:1)-3	5.7	3.5	0.0	23.5	3.8	10.0	7.0	0.7	5.9	6.9	0.1	0.3	1.0	6.2	14.5	10.9
9	HMF:Ac (1:10)†	6.0	0.9	0.0	0.0	2.6	4.8	1.1	3.9	27.4	41.2	1.9	0.2	0.5	5.1	3.6	0.8
10	HMF:Fur:Ac (1:1:2)	4.0	3.0	0.0	25.3	3.8	7.2	3.3	2.5	10.2	5.6	0.0	1.0	4.8	14.3	10.8	4.4
11	SC THF3A‡	9.4	0.7	0.0	4.2	23.4	25.1	0.1	3.4	6.7	11.6	14.3	0.1	0.9	0.0	0.0	0.0
12	SC THF2A§	11.4	1.3	0.0	5.1	15.1	9.9	0.5	5.2	13.0	17.7	19.4	0.3	0.9	0.3	0.0	0.0

*C₃ selectivity is zero because acetone was removed during the separation of hydrogenated products from methanol-water solution.

†Propane is not included in the alkane selectivity calculation for this feed.

‡Liquid alkanes produced in this feed were mostly branched. The C₁₀ alkane was 3-methyl-5-dimethyl-heptane.

§Liquid alkanes produced in this feed were mostly branched. The C₁₀ alkane was 4-methylnonane.

solvent. For this case, we first carried out the aldol condensation of HMF:acetone (1:1) in water over the Mg–Al–oxide catalyst, and we then added Pd/Al₂O₃ to the reaction slurry, followed by treatment with H₂ (at 55 bars) at 393 K in the Parr reactor. Similar to hydrogenation of furfural:acetone in water, we found that the hydrogenation of the HMF:acetone adduct increases its solubility in water, and the aqueous solution from this hydrogenation step produced significant amounts of C₁₄ and C₁₅ alkanes from the 4-PD/H reactor (Table 2, entry 8). The results in Tables 1 and 2 also show that mixtures of HMF and furfural (Tables 1 and 2, entry 10) can be condensed with acetone to form alkanes ranging from C₇ to C₁₅. Unlike the production of ethanol by fermentation, cellulose and hemicellulose need not be separated for the effective production of liquid alkanes by 4-PD/H processing.

Results for crossed aldol condensation of furfural and HMF with dihydroxyacetone and glyceraldehyde are summarized in entries S15 to S20 of tables S3 and S4. These condensation reactions over a Mg–Al–oxide catalyst showed a large disappearance of furfural and HMF based on high-performance liquid chromatography (table S1); however, as shown in table S4, fewer than 30% of the alkane products are heavier than the C₅ and C₆ reactants (for reactions of furfural and HMF, respectively). Condensing furfural with hydroxyacetone gave an alkane distribution similar to that produced from the condensation of furfural with dihydroxyacetone (table S4, entry S18). Thus, although it is possible to make heavier liquid alkanes by crossed aldol condensation of furfural and HMF with dihydroxyacetone, hydroxyacetone, or glyceraldehydes, the selectivities of these processes will need to be improved.

Another route to make large water-soluble organic compounds is to selectively hydrogenate the C=C double bonds of HMF and furfural,

producing 5-hydroxymethyl-tetrahydrofurfural (HMTHFA) and tetrahydrofuran-2 carboxyaldehyde (THF2A), respectively. These species can form carbanion species and undergo self-aldol-condensation reactions (Fig. 1). The results in Fig. 2D show that the self-aldol condensation of tetrahydrofuran-3 carboxyaldehyde (THF3A, purchased from Aldrich) and THF2A produced liquid hydrocarbons ranging from C₈ to C₁₀ from the 4-PD/H reactor. THF2A was produced by the dehydrogenation of tetrahydrofurfuryl alcohol in the gas phase over a Cu/SiO₂ catalyst (16).

The conversion of carbohydrates to liquid alkanes requires the storage of a considerable amount of hydrogen in the fuel (i.e., essentially one molecule of H₂ is used to convert each carbon atom in the carbohydrate reactant to an alkane moiety). The liquid alkanes retain 90% of the energy content of the carbohydrate and H₂ reactants. Thus, the carbon in the carbohydrates serves as an effective energy carrier for transportation vehicles, which is analogous to the role of carbohydrates as energy storage compounds for living organisms. We have demonstrated the feasibility of producing liquid alkanes from biomass-derived compounds, but future research is needed to determine how to minimize undesired coking reactions and to develop new catalysts that exhibit long-term stability under aqueous-phase reaction conditions [see (16) for a brief discussion of the stability of solid base catalysts under our reaction conditions].

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Supporting Online Material

www.sciencemag.org/cgi/content/full/308/5727/1446/DC1

Materials and Methods

Fig. S1
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Kinetic Evidence for Five-Coordination in $\text{AlOH}(\text{aq})^{2+}$ Ion

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 Brian L. Phillips,⁷ William H. Casey^{2,4,5*}

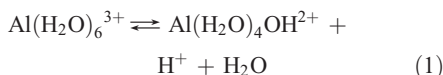
Trivalent aluminum ions are important in natural bodies of water, but the structure of their coordination shell is a complex unsolved problem. In strong acid ($\text{pH} < 3.0$), Al^{III} exists almost entirely as the octahedral $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion, whereas in basic conditions ($\text{pH} > 7$), a tetrahedral $\text{Al}(\text{OH})_4^-$ structure prevails. In the biochemically and geochemically critical pH range of 4.3 to 7.0, the ion structures are less clear. Other hydrolytic species, such as $\text{AlOH}(\text{aq})^{2+}$, exist and are traditionally assumed to be hexacoordinate. We show, however, that the kinetics of proton and water exchange on aqueous Al^{III} , coupled with Car-Parrinello simulations, support a five-coordinate $\text{Al}(\text{H}_2\text{O})_4\text{OH}^{2+}$ ion as the predominant form of $\text{AlOH}(\text{aq})^{2+}$ under ambient conditions. This result contrasts Al^{III} with other trivalent metal aqua ions, for which there is no evidence for stable pentacoordinate hydrolysis products.

Aluminum is the third most abundant element in Earth's crust, after oxygen and silicon, and its chemistry in water is central to geochemistry, environmental science, and medicine (1, 2). In particular, the speciation (3) and ligand substitution kinetics (4) of the Al^{III} ions in the pH range 3 to 7 govern its toxicity toward plants, fish, and humans, yet the hydrolytic chemistry of Al^{III} remains poorly understood. The structures of the octahedral ion $\text{Al}(\text{H}_2\text{O})_6^{3+}$, which dominates at $\text{pH} < 3.0$, and the tetrahedral aluminate ion $\text{Al}(\text{OH})_4^-$, which dominates at $\text{pH} > 7$, are well established (5). The first hydrolysis product, $\text{Al}(\text{H}_2\text{O})_{n-1}\text{OH}^{2+}$, where n is the coordination number, becomes important at $3.0 < \text{pH} < 4.3$. It coexists with $\text{Al}(\text{H}_2\text{O})_{n-2}(\text{OH})_2^+$ above $\text{pH} 4.3$ and with $\text{Al}(\text{OH})_4^-$ at $5.2 < \text{pH} < 6.7$ (3, 5–7). At high Al^{III} concentrations ($> 0.05 \text{ mol L}^{-1}$), oligomers such as $(\text{H}_2\text{O})_4\text{Al}(\text{OH})_2\text{Al}(\text{OH})_2^{4+}$ and the Keggin ion $\text{AlO}_4(\text{Al}(\text{OH})_2)_2(\text{H}_2\text{O})_{12}^{7+}$ (which contains one four-coordinate and twelve six-coordinate

Al^{III} atoms) appear around $\text{pH} 5$ (5, 6, 8, 9). Thus, not only is the speciation of $\text{Al}^{\text{III}}(\text{aq})$ complicated in the pH range 4.3 to 7.0, rendering quantitative studies difficult, but there is a shift from dominant six- to four-coordinate over this range.

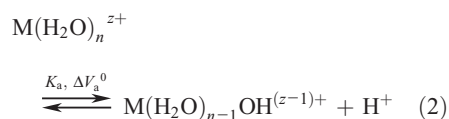
It is generally assumed (5, 6) by analogy with several other trivalent metals but without experimental justification that octahedral coordination is retained in $\text{Al}(\text{H}_2\text{O})_{n-1}\text{OH}^{2+}$ and most other hydrolytic species. Martin (3, 7) pointed out that the remarkable closeness of the acid dissociation constants K_a of $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{H}_2\text{O})_{n-1}\text{OH}^{2+}$, $\text{Al}(\text{H}_2\text{O})_{n-2}(\text{OH})_2^+$, and $\text{Al}(\text{H}_2\text{O})_{n-3}(\text{OH})_3$ ($\text{p}K_a = -\log K_a = 5.5, 5.8, 6.0$, and 6.2 , respectively, in dilute solution) could be explained by a progressive reduction of coordination number n from 6 toward 4 across this sequence: Decreasing n shortens Al-O bond lengths, increasing the polarization and hence the acidity of the remaining aqua ligands.

We report high-pressure ^{17}O -nuclear magnetic resonance (NMR) data that support Martin's basic hypothesis. We have studied the hydrogen-ion dependence of the rate of exchange of water ligands bound to the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ with free solvent, and our results are consistent with coupling of proton and water dissociation from $\text{Al}(\text{H}_2\text{O})_6^{3+}$ via a five-coordinate $\text{Al}(\text{H}_2\text{O})_4\text{OH}^{2+}$ ion.



The key data are volumes of activation $\Delta V_M^\ddagger [-RT(\partial \ln k_M/\partial P)_T]$, where k_M is the corresponding rate constant for water exchange on aqueous metal ions $\text{M}(\text{aq})^{z+}$, because they are considered to be diagnostic of the reaction mechanism (10). These ΔV_M^\ddagger parameters are extracted from the pressure dependence of the measured rate constants. Formation of an intermediate in which the coordination number n is reduced is termed a dissociative (D) mechanism, for which $0 \ll \Delta V_M^\ddagger \leq +14 \text{ cm}^3 \text{ mol}^{-1}$, whereas formation of an intermediate of expanded n is called an associative (A) mechanism and shows $0 \gg \Delta V_M^\ddagger \geq -14 \text{ cm}^3 \text{ mol}^{-1}$ (11). Cases in which the entry and departure of water molecules are coupled (no long-lived intermediates) are called interchange mechanisms: dissociative interchange (I_d) for which, operationally, ΔV_M^\ddagger is positive, and associative interchange (I_a) for which it is negative. For the acid-independent water-exchange pathway on $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (i.e., for the direct exchange of H_2O with $\text{Al}(\text{H}_2\text{O})_6^{3+}$), $\Delta V_{\text{Al}}^\ddagger$ is $+5.7 \text{ cm}^3 \text{ mol}^{-1}$ (12), indicating a dissociatively activated mechanism, in agreement with the results of ab initio calculations (13). The ΔV^\ddagger value and mechanism for the first hydrolyzed complex, $\text{AlOH}(\text{aq})^{2+}$, is reported here.

The standard model (10) for water exchange via conjugate-base species $[\text{MOH}(\text{aq})^{(z-1)+}]$ holds that proton exchange is much more rapid than oxygen exchange, and that a pre-equilibrium state is established with retention of the first coordination sphere, characterized by an equilibrium constant, K_a , and an equilibrium pressure dependence described by a volume of reaction, $\Delta V_a^0 = -RT(\partial \ln K_a/\partial P)_T$:



The rate-determining step is then water exchange on the $\text{M}(\text{H}_2\text{O})_{n-1}\text{OH}^{(z-1)+}$ ion (rate constant k_{MOH}). Experiments support this mechanism for a wide range of metal ions (5).

From ^{17}O -NMR data in aqueous AlCl_3 , we obtained rate constants k_{obs} for water exchange on aluminum species (Fig. 1A), and they vary inversely with $[\text{H}^+]$, as expected [e.g., (14)].

$$k_{\text{obs}} = (k_1 + k_2/[\text{H}^+]) \times X_1 \quad (3)$$

X_1 is the mole fraction of Al^{III} present as $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (the calculated pressure depen-

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