PRODUCTION OF MONOFUNCTIONAL HYDROCARBONS FROM BIOMASS DERIVED CARBOHYDRATES VIA CATALYTIC CONVERSION ON CARBON SUPPORTED PLATINUM-RHENIUM

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Introduction

The cost of transportation fuels produced from ligno-cellulosic biomass is currently not competitive with the cost of petroleum, due primarily to the high costs associated with the processing of biomass to produce the fuel. New processes for the conversion of biomass to liquid fuels must therefore be developed with a limited number of processing steps.[1] In previous studies, we developed a process to produce liquid alkanes via integrated glycerol conversion to synthesis gas with Fischer-Tropsch synthesis.[2] Recently, we have developed a novel catalytic approach which converts carbohydrates (sorbitol and glucose) derived from cellulose, to mono-functional chemical intermediates[3], which are currently derived exclusively from fossil fuels, and which can be converted to higher molecular weight alkanes (e.g., C_5-C_{12} for gasoline, C_9-C_{16} for jet fuel, and C_{10}-C_{20} for diesel applications).[4] Figure 1 illustrates these approachs. While glycerol is converted primarily to H_2/CO gas mixtures[2,5], sorbitol and glucose are converted to monofunctional hydrocarbon intermediates such as alcohols, ketones, carboxylic acids, and heterocyclic compounds with 4-6 carbon atoms on the same Pt-Re/C catalyst at similar reaction conditions (483-523 K, 18-27 bar).[3] Subsequent aromatization, isomerization, aldol-condensation, and/or ketonization processes convert these functional molecules to alkanes suitable for use as fuel components.[3]

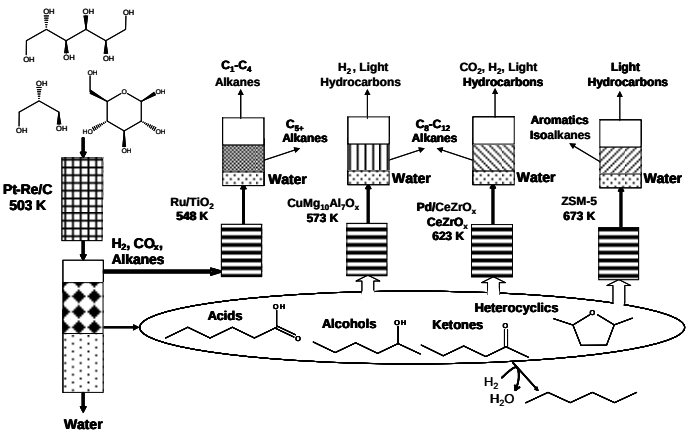

Figure 1. Catalytic reactor sequence for conversion of glycerol, sorbitol, or glucose to liquid fuel components via conversion to monofunctional platform molecules on Pt-Re/C followed by liquid hydrocarbon formation. Adapted from Kunkes, et al.[3]

This approach represents an advance toward the economic conversion of biomass to liquid alkane fuels in that a limited number of catalytic reactors or beds (e.g., 2) are employed, and in that the liquid alkane products can be both processed and distributed by existing petrochemical technologies and infrastructure with immediate use in existing transportation vehicles. An additional benefit of this approach is that the mono-functional compounds produced as intermediates have use in chemical applications[6], forming a platform for the production of liquid fuels for the high-volume transportation market, and/or the production of intermediates for the lower-volume, but higher value, chemicals and polymers markets.

Experimental

A carbon-supported Pt-Re catalyst was prepared by incipient wetness impregnation of carbon black (Norit-SX1 G) with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ and $HReO_4$ (Strem Chemicals) to yield a catalyst with loadings of 5.1 wt% Pt and 4.9 wt% Re (atomic Pt:Re ratio of 1:1). The support was dried in air for 12 h at 373 K prior to impregnation, and 1.7 g of solution were used for every gram of support. The catalyst was dried at 403 K for 12 h in air after impregnation. Prior to reaction kinetics measurements, the catalysts were reduced in H_2 (180 cm^3(STP) min^{-1} for 2 h at 723 K (0.5 K min^{-1})). The adsorption uptakes of carbon monoxide and H_2 at 300 K were measured on a gas adsorption apparatus, and the number of catalytic sites was taken to be equal to the irreversible CO uptake.[5]

The catalytic conversion of glycerol, sorbitol, and glucose on Pt-Re/C was carried out on an apparatus described elsewhere.[5] Sorbitol and glycerol conversion studies were carried out at pressures of 6.5 bar (for glycerol only), 18 bar, and 27 bar, temperatures of 483 K, 503 K, and 523 K, and with a aqueous solutions of 60 wt% sorbitol or 80 wt% glycerol.[3, 5] Space velocity studies for sorbitol conversion were carried out at 27 bar and 503 K at flow rates of 0.04 cm^3 min^{-1}, 0.08 cm^3 min^{-1}, and 0.16 cm^3 min^{-1} with 3 grams of Pt-Re/C.[3] Glucose conversion was carried out at 483 K and 18 bar with a 40 wt% glucose in water solution.[3]

Details of hydrogenation, acid removal, and subsequent aromatization, isomerization, aldol-condensation, and ketonization of monofunctional hydrocarbons derived from sorbitol and glucose are described elsewhere.[3] Briefly, aromatization/isomerization reactions were carried out on H-ZSM-5 at 673 K, aldol-condensation was carried out on $CuMg_{10}Al_7O_x$ at 573 K, and ketonization was carried out on $CeZrO_x$ at 623 K (Figure 1).[3]

Results and Discussion

Catalytic Conversion of Sorbitol and Glycerol.

The initial step of the process described in Figure 1 involves partial deoxygenation of the carbohydrate/polyol feed using H_2 derived from reforming a portion of the feed on Pt-Re. Figure 2 shows a schematic of the surface chemistry associated with this initial step.[3] The reforming reactions involve adsorption and dehydrogenation of the feed molecule,

followed by C-C cleavage to give adsorbed CO species, which react with water to form H_2 and CO_2.

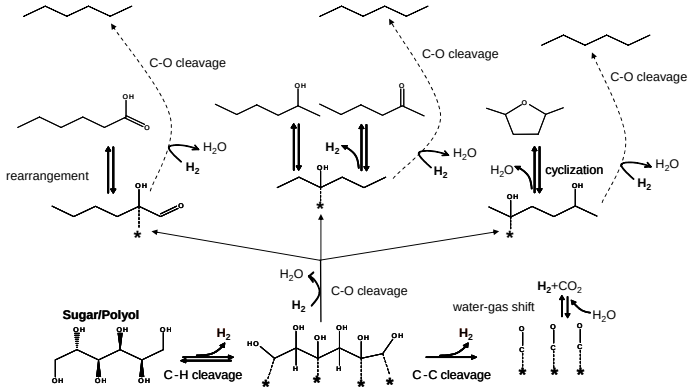

Figure 2. Surface reactions involved in the conversion of carbohydrates on Pt-Re/C. The H_2 for C-O cleavage is generated by C-H and C-C cleavage reactions and water-gas shift. Adapted from Kunkes, et al.[3]

Thus, the formation of CO_2 is necessary, and balancing these reforming reactions that produce H_2 with deoxygenation reactions requires that a minimum amount of the carbon in the feed be converted to CO_2. (This minimum value is 25% in the case of conversion of a 60 wt% sorbitol solution at 503 K and 18 bar on Pt-Re/C.[3]) Alternatively, these adsorbed polyol species can undergo successive C-O bond scissions leading to surface intermediates that either desorb as monofunctional hydrocarbons or alkanes.[3] These reaction pathways on Pt-Re/C involving C-C and C-O bond scission lead to the formation of CO, CO_2, and H_2 when C-C cleavage rates are high, whereas alkanes and mono-oxygenated species are produced when rates of C-O cleavage are high.[7]

Table 1 shows the effects of temperature, pressure, and space velocity on the carbon selectivities for conversion of a 60 wt% sorbitol solution and 80 wt% glycerol solution on Pt-Re/C.[3,5] Carbon in the glycerol feed is converted either to gaseous CO_x and C_1-C_3 alkanes or to light alcohols, diols, acetone, or hydroxyacetone in the liquid phase. At constant temperature, an increase in pressure from 6.5 bar to 18 bar results in an increase in alkane production at the expense of CO_x species, alcohols/diols, and acetone (Table 1A). However, at 27 bar, the production of oxygenated hydrocarbons in the aqueous phase increases while the production of gaseous species decreases. The increase in oxygenated hydrocarbons indicates a shift in selectivity from C-C bond breaking to C-O bond breaking at elevated pressures. As pressure increases, the rate of C-O bond cleavage slows, and the production of more oxygenated species (alcohols) becomes favored over the formation of alkanes. The conversion of sorbitol exhibits similar effects of process conditions as glycerol conversion. However, the larger carbon backbone of sorbitol can lead to the production of alkanes and high molecular weight oxygenates with between 4-6 carbon atoms and 0-1 monofunctional oxygen groups. These organic molecules spontaneously separate from the aqueous effluent which contains more highly oxygenated species (e.g., diols and isosorbide).[3]

Table 1. Carbon Selectivities (%) for the Conversion of A.) Glycerol at 483-523 K and 6.5-27 bar on Pt-Re/C and B.) Sorbitol at 483-523 K and 18-27 bar and C.) at 503 K and 27 bar with space velocities of 0.6-2.4 h^{-1} on Pt-Re/C. Data adapted from Kunkes, et al.[3, 5]

A.)	523 K			503 K			483 K		
	6.5 bar	18 bar	27 bar	6.5 bar	18 bar	27 bar	6.5 bar	18 bar	27 bar
CO_x	58	50	41	41	39	36	25	31	20
Alkanes	13	27	22	7	22	14	5	13	6
Acetone	5	4	4	10	5	3	10	3	1
Alcohols	19	19	33	42	34	47	55	50	44
Glycerol	4	0	0	0	0	0	6	3	29

B.)	523 K		503 K		483 K	
	18 bar	27 bar	18 bar	27 bar	18 bar	27 bar
CO_x	29	28	26	26	20	20
Alkanes	44	71	19	52	15	25
Ketones	16	0	23	17	19	19
Alcohols	8	0	14	2	17	17
Acids	0	0	5	0	7	2
Aqueous	2	1	13	3	22	17

C.)	503 K, 27 bar 0.6 h^{-1}	503 K, 27 bar 1.2 h^{-1}	503 K, 27 bar 2.4 h^{-1}
CO_x	26	30	33
Alkanes	52	21	9
Ketones	17	22	8
Alcohols	2	18	11
Acids	0	3	4
Aqueous	3	7	35

The gaseous effluent contains CO_x species and light alkanes. Changing the temperature, pressure, and/or space velocity causes the carbon distribution amongst the three product phases to shift.[3] Increasing the pressure results in a shift of the effluent carbon from aqueous phase species to organic phase species at 483 K and from aqueous phase species to gaseous species at 503 K. Pressure has a negligible effect at 523 K on the carbon distribution. The production of alkanes increases at the expense of oxygenated species as pressure increases from 18 bar to 27 bar at constant temperature (Table 1B). Increasing temperature from 483 K to 523 K at constant pressure leads to an increase in the production of alkanes and a decrease in high molecular weight oxygenates (Table 1B). In addition, the amount of water-soluble, oxygenated hydrocarbons decreases with increasing pressures and/or temperatures. An increase in the space velocity from 0.60 to 1.2 h^{-1} at constant temperature and pressure causes increased production of organic phase species at the expense of gaseous products (Table 1C). Furthermore, the amount of ketones, alcohols, and acids increases while the concentration of alkanes decreases. However, a further increase of space velocity to 2.4 h^{-1} shifts the carbon distribution toward aqueous phase oxygenates. Of the CO_2 produced during sorbitol conversion, 70-80% was associated with the stoichiometric value discussed previously while the remainder results from excess water-gas shift reaction. All

reaction conditions were tested for at least 24 hours time-on-stream, and the carbon balances closed to within 10%. At 503 K and 18 bar, Pt-Re/C showed excellent stability during 7 weeks time-on-stream.[8] This organic liquid (Sorb_18_503) contains 54-49% of the carbon in the sorbitol feed (70% of the theoretical maximum) and was used for subsequent catalytic processing.[3,8]

Conversion of Monofunctional Hydrocarbons to Transportation Fuels.

The second step in our approach involves reactions that form C-C bonds amongst the monofunctional intermediates from carbohydrate conversion and the removal of the remaining oxygen to give high molecular weight alkanes suitable for transportation applications.[3] The C_4-C_6 ketones and secondary alcohols in the organic liquid derived from the conversion of sorbitol on Pt-Re/C can undergo C-C coupling by aldol-condensation on basic catalysts to produce $C_8 - C_{12}$ compounds which can undergo subsequent hydrodeoxygenation (e.g., over Pt/Nb2O5 at 548 K) to produce $C_8 - C_{12}$ alkanes.[9] The aldol-condensation step can be carried out at 573 K in the presence of H_2 on a bi-functional $CuMg_{10}Al_7O_x$ catalyst, where the $Mg_{10}Al_7O_x$ component provides sites for aldol-condensation, and Cu sites provide for both hydrogenation of C=C double bonds in dehydrated aldol-adducts and dehydrogenation of secondary alcohols to ketones, a process that is thermodynamically favored at these reaction conditions.[10] The small amounts of organic acids and esters in the organic liquid derived from sorbitol must be removed prior to aldol condensation because these compounds cause deactivation of the $CuMg_{10}Al_7O_x$ catalyst, probably by adsorbing strongly on basic sites.[11] To this end, Sorb_503_18 was refluxed with a 20 wt% NaOH solution at 343 K and atmospheric pressure to hydrolyze esters and neutralize organic acids. Subsequently, this treated organic liquid was passed over a $CuMg_{10}Al_7O_x$ catalyst at 573 K and 5 bar pressure with 20 cm^3min^{-1}(STP) H_2 co-feed (weight hourly space velocity of feed equal to 0.4 h^{-1}). Table 2A shows the resulting product distribution. At these reaction conditions, 2-ketones undergo self aldol condensation or crossed aldol condensation with 3-ketones, whereas self-aldol condensation of 3-ketones is less likely due to steric and electronic effects. The primary alcohols present in the liquid organic phase undergo crossed aldol condensation with ketones (taking place via the intermediate formation of aldehydes). Light species containing between 4 and 6 carbon atoms and 0 and 1 oxygen atoms (C_4-C_6) comprise 55% of the carbon in the products, caused primarily by the low reactivity for condensation of 3-ketones. These light species contain C_4 alcohols (3% of total carbon) and heterocyclic hydrocarbon compounds (substituted tetrahydrofurans and tetrahydropyrans; 9% of total carbon) which will form C_4-C_6 alkanes upon hydrodeoxygenation. C_5-C_6 ketones and secondary-alcohols contribute 32% of the carbon in the products while hexane and pentane contribute 10% of the carbon. The remaining carbon (45%) is associated with condensation products containing between 8 and 12 carbon atoms and 0 and 1 oxygen atoms (C_8-C_{12}). The condensation products can be converted by hydrodeoxygenation to the corresponding alkane products, leading to a distribution similar to that shown in Table 2A. Alternatively, the C_8-C_{12} fraction can be separated from the C_4-C_6 fraction and converted to heavy alkane products, while the C_4-C_6 fraction (consisting primarily of 3-hexanone, 3-pentanone, tetrahydrofurans, and tetrahydropyrans) can be used as fuel additives, solvents or chemical intermediates.

Table 2. Carbon Selectivities (%) for the Conversion of Monofunctional Hydrocarbons Derived from Sorbitol Conversion on Pt-Re/C via A.) Aldol-Condensation, B.) Aromatization, C.) Ketonization, and D.) Combined Ketonization and Aldol-Condensation. Data adapted from Kunkes, et al.[3]

A.)	C%
C_{4-5}	26
C_6	29
C_8	6
C_9	8
C_{10}	13
C_{11}	10
C_{12}	8

B.)	C%
C_{1-3}	26
C_4	29
C_{5-6}	7
Benzene	5
Toluene	14
C_2 Benzene	11
C_{3-6} Benzene	8

C.)	C%
C_{4-5}	36
C_6	31
C_7	8
C_8	11
C_9	10
C_{10}	4
C_{11}	1.5

D.)	C%
C_{4-5}	24
C_6	19
C_7	10
C_8	13
C_9	9
C_{10}	10
C_{11}	8
C_{12}	5
C_{12+}	3

Liquid fuel components can also be produced by reacting oxygenated hydrocarbons over H-ZSM-5 to produced aromatics, olefins and paraffins.[12] Accordingly, we have found that Sorb_503_18 can be converted to liquid fuel components by first hydrogenating the ketones to alcohols (at 433 K and 55 bar H_2 pressure over 5 wt% Ru/C)[8], followed by dehydration/alkylation at 673 K and atmospheric pressure over H-ZSM-5.[3] As shown in Table 2B, 25% and 29% of the carbon in the sorbitol-derived organic phase is converted to paraffins and olefins containing 3 and 4 carbon atoms, respectively, while 38% of the carbon is converted to aromatic species. Of this aromatic fraction, 12%, (5% of total) and 37% (14% of the total) is converted to benzene and toluene, respectively, while 29% (11% of the total) is converted to a C_2 benzene (a benzene with two additional carbon atoms such as xylenes, or ethyl benzene). The remaining 22% of the aromatic fraction (8% of the total) is split between C_3–C_6 substituted benzene.

An additional process to form C-C bonds involves ketonization reactions between two carboxylic acid molecules to form a ketone, CO_2, and H_2O.[13] This reaction can be performed instead of the hydrolysis step, eliminating the use of non-renewable agents such as NaOH, and is effective for feeds with high concentrations of organic acids such as those produced from glucose conversion over Pt-Re/C.[3] Table 2C

shows the carbon selectivity for the ketonization on $CeZrO_x$ at 573 K and 20 bar of the monofunctional hydrocarbons derived from conversion of a 40 wt% glucose feed on Pt-Re/C at 483 K and 18 bar.[3] This ketonization process yielded 85% conversion of the monofunctional oxygenates to a liquid organic product stream and achieved greater than 98% conversion of the carboxylic acids in the feed to C_7-C_{11} ketones.[3]

This ketonization step can be combined with aldol-condensation on $Pd/CeZrO_x$ at 623 K.[3] Table 2D shows the carbon selectivity for aldol-condensation of the product from ketonization of monofunctional hydrocarbons from glucose conversion. Of the carbon in the organic product from this combined ketonization-aldol condensation, 57% is in the form of C_{7+} ketones with 34% resulting from ketonization and 23% resulting from aldol-condensation. Products with carbon-chain length greater than C_{12} were also observed, likely resulting from aldol condensation of methyl ketones with C_{7+} ketones formed during ketonization. The combined ketonization and aldol-condensation process completely converted the carboxylic acids into C_{7+} ketones.[3]

Conclusions

The processing of lingo-cellulosic biomass requires the removal of oxygen atoms in tandem with C-C bond formation such that the chemical intermediates formed have the proper functionality for chemical applications or conversion to molecules having the proper molecular weights, energy content, and combustion properties for fuel applications.[14] The catalytic approach shown in Figure 1 represents an advance in the production of fuels and chemicals from biomass because it employs a limited number of flow reactors, thus achieving low capital costs but is sufficiently flexible that it can be employed to produce a variety of liquid-fuel components.[3,8]

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