Production of Conventional Liquid Fuels from Sugars

Paul G. Blommel

and

Randy D. Cortright

Virent Energy Systems, Inc.

Madison, WI 53704, USA

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A white paper describing the conversion of biomass-derived sugars to conventional liquid fuels through a multistep catalytic process.

Abstract

Virent Energy Systems, Inc. has discovered and is now developing innovative and novel catalytic methods to convert plant sugars into high-energy hydrocarbons mixtures that can be used directly or blended seamlessly to make conventional liquid fuels. The methods utilize Virent's patented Bio-Forming® technology to produce renewable gasoline, diesel, and jet fuel from a wide range of biomass feedstocks, including non-food varieties. The BioForming platform expands the utility of the aqueous phase reforming (APR) process by combining APR with catalysts and reactor systems similar to those found in standard petroleum oil refineries to convert sugar-based compounds into non-oxygenated hydrocarbons mixtures. The hydrocarbon mixtures have significantly higher volumetric energy content than ethanol, do not require the energy intensive dewatering steps associated with ethanol production, and can be brought to market using the current petroleum infrastructure and pipelines, which are not available to the ethanol industry. Preliminary economic analysis suggests that converting sugars to conventional liquid fuels using Virent's BioForming process can economically compete with petroleum fuels at crude oil prices greater than $60/bbl.

Background

Conventional liquid transportation fuels, such as gasoline, jet fuel and diesel fuel, are essential for modern economies. Over the last 100 years, increasing demand for transportation fuels has resulted in significant advancements in the development and optimization of crude oil refining technologies for the economic production of liquid fuels. Conventional liquid fuels are produced by first fractionating crude oil into different boiling point fractions including light ends, straight run gasoline, naphtha, middle distillates and resid. The fractions are then collected and/or upgraded by proven catalytic processes such as hydrotreating, olefin formation, condensation (including alkylation) of

light hydrocarbons to form heavier hydrocarbons, and reforming of low octane hydrocarbons to hydrogen, aromatics and branched hydrocarbons. The resulting product streams are often blended to generate a mixture of hydrocarbons appropriate for gasoline, jet fuel or diesel fuel. Such fuels contain mixtures of compounds made up of only carbon and hydrogen (hydrocarbons), thus providing the highest volumetric energy density, high storage stability, and vapor pressure and/or freezing point characteristics required for the particular fuel application.

Renewable replacements for gasoline, diesel and jet fuel are needed to maintain global economic activity while addressing environmental and energy supply concerns. Plants exploit carbohydrates, i.e., sugars and starches, for either energy storage or as building blocks for structural materials, such as cellulose and hemicellulose. As a consequence, carbohydrates are the most widely distributed, naturally occurring organic compounds on Earth, and hold considerable potential to serve as a primary energy source. They are highly reactive and readily oxidized by living organisms to generate energy, carbon dioxide and water. Commercial biofuel generation technologies attempt to utilize the naturally occurring biocatalytic capabilities of various living organisms, optimized through natural selection and genetic engineering, to maximize the conversion of sugars into ethanol. In these biocatalytic applications, the presence of oxygen in the molecular structure of the carbohydrate contributes to the reactivity of the sugar. Ethanol fermentation processes take advantage of this highly reactive nature to produce ethanol. Through fermentation, the highly reactive sugars are essentially de-functionalized to generate the partially oxidized hydrocarbon–ethanol.

Ethanol produced via fermentation of carbohydrates is a well established renewable transportation fuel, although, ethanol has some drawbacks. The fuel provides a low net energy return on energy invested [1], has a lower volumetric energy content than hydrocarbon-based gasoline, and cannot be readily integrated into the existing fuel infrastructure. Other biofuel alternatives are needed that can more effectively capture the energy contained in biomass and that can use today's infrastructure to deliver cost-effective, environmentally-friendly fuels to market.

Virent's BioForming® Platform

Virent discovered in early 2006 that it is possible to integrate aqueous phase reforming (APR) with proven catalytic processing technologies to generate hydrocarbons for direct use as a biofuel or as blending components for conventional liquid fuels (gasoline, jet fuel, and diesel) [2-5]. Virent has previously reported methods for the renewable production of alkanes and hydrogen from biomass derived carbohydrates [6, 7], and recently reported methods for the renewable production of oxygenated components, such as alcohols, ketones, aldehydes, furans and other polyols [8].

Virent's aqueous-phase reforming methods utilize heterogeneous catalysts at moderate temperatures (450 to 575 K) and pressures (10 to 90 bar) in a number of series and parallel reactions to reduce the oxygen content of the carbohydrate feedstock. The reactions include: (1) reforming to generate hydrogen; (2) dehydrogenation of alcohols/ hydrogenation of carbonyls; (3) deoxygenation reactions; (4) hydrogenolysis; and (5) cyclization. A key feature of this

method is the use of *in-situ* generated hydrogen [6] for the de-functionalization of the highly re-active carbohydrate to a less reactive mono-oxygenated species. Virent has found that the mono-oxygenated species (e.g., alcohols, ketones, and aldehydes) can be converted to non-oxygenated hydrocarbons in a continuous process using conventional catalytic condensation and hydrotreating techniques. Virent has now advanced the integration of APR with these conventional catalytic processes to provide Virent's BioForming® platform for converting water soluble carbohydrates to renewable liquid fuels having the same volumetric energy value as fossil fuel derived liquid fuels. Virent currently holds over 50 pending or issued patents in the U.S. and abroad covering all aspects of this technology.

The BioForming process, as depicted in Figure 1, is based on the novel combination of Virent's core APR technology with conventional catalytic processing technologies such as cata-lytic hydrotreating and catalytic condensation processes, including ZSM-5 acid condensation, base catalyzed condensation, acid catalyzed dehydration, and alkylation. Like a conventional petroleum refinery, each of these process steps in the BioForming platform can be optimized and modified to produce a particular slate of desired hydrocarbon products. For example, a gasoline product can be produced using a zeolite (ZSM-5) based process, jet fuel and diesel can be produced using a base catalyzed condensation route, and a high octane fuel can be produced using a dehydration/oligomerization route.

The key enabling step in the BioForming process is the APR step, which converts water soluble carbohydrates into hydrogen, lower alkanes, and high yields of condensable chemical intermediates. Once formed, the chemical intermediates undergo further catalytic processing to generate the hydrocarbons for gasoline, jet fuel, or diesel, or chemicals for use in other industrial applications. The hydrogen is used in the pro-
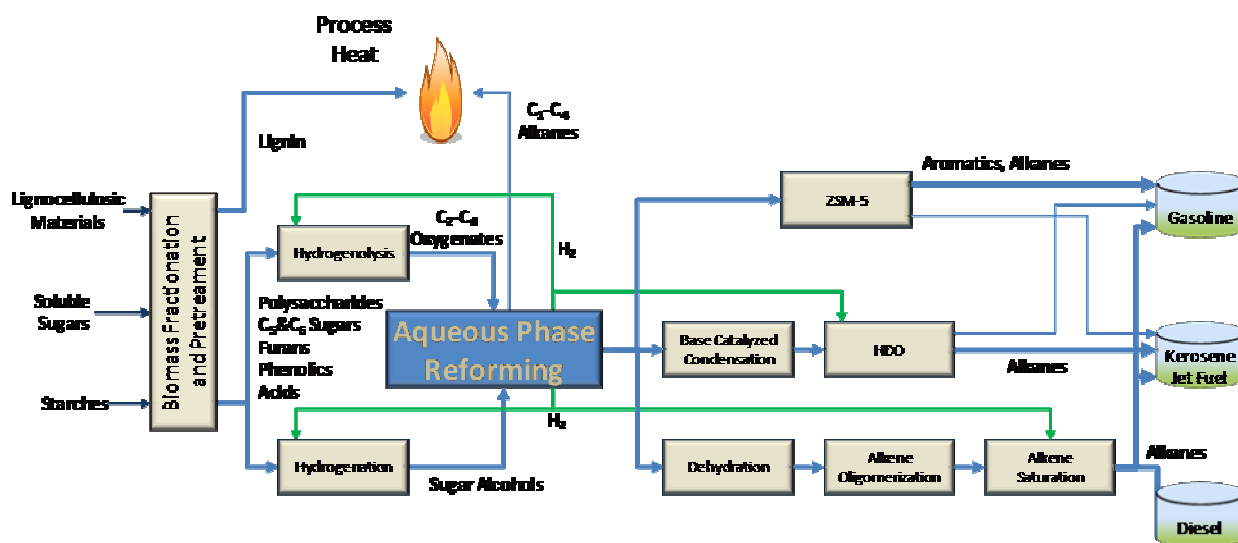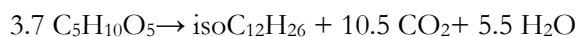

Figure 1. **Virent's BioForming® process to produce conventional liquid transportation fuels from biomass feedstocks. APR enables the process to partially defunctionalize carbohydrate feedstocks for further catalytic upgrading.**

duction of the condensable chemical intermediates, with any excess recycled for use in upgrading aqueous solutions of complex sugars (C_5 and C_6 sugar mixtures) or biomass hydrolysate prior to processing in the APR reactor, or downstream in later process applications. The lighter alkanes, such C_1-C_4 fuel gases, are useful for providing process heat so as to minimize the need for external fuel resources. Figure 1 illustrates the BioForming platform, including the integration of potential biomass pretreatment technologies, catalytic hydrotreating, APR, and various catalytic condensation processes.

Unlike traditional biocatalytical processes, which are limited to working with only one specific sugar type, the BioForming process is able to convert a broad range of carbohydrates into conventional liquid fuels. The BioForming process is not plant or carbohydrate restrictive, but able to process any type of plant sugar once reduced to its water soluble form. Potential carbohydrates include sucrose (from sugar cane or sugar beets), corn sugar (glucose from conversion of corn starch), sugars derived from hydrolysis of hemicellulose and cellulose (including polysaccharides, organic acids, and furfural byproducts), and water soluble oxygenated compounds such as diols, glycerol and sugar alcohols.

The energy conversion benefits of the BioForming process can be understood by evaluating the stoichiometry of the overall process. For illustration purposes, the stoichiometries for two reactions (non-food xylose ($C_5H_{10}O_5$) to a branched hydrocarbon with 12 carbons (iso $C_{12}H_{26}$) for jet fuel blending and sucrose ($C_{12}H_{22}O_{11}$) to a high octane xylene (C_8H_{10}) for gasoline blending):

$$3.7\ C_5H_{10}O_5 \rightarrow isoC_{12}H_{26} + 10.5\ CO_2 + 5.5\ H_2O$$

$$0.875\ C_{12}H_{22}O_{11} \rightarrow C_8H_{10} + 2.5\ CO_2 + 4.6\ H_2O$$

Based on the above stoichiometry it can be seen that it is theoretically possible for the resulting hydrocarbons to capture 64% of the carbon from the carbohydrates and over 94% of the sugar lower heating value.

Biomass Pretreatment

The BioForming process can convert a broad range of carbohydrates, including carbohydrates derived from non-food biomass, into conventional liquid fuels. The feedstock is a solution of water and water soluble oxygenated hydrocarbons (e.g., sugars, sugar alcohols, saccharides and other polyhydric alcohols). The oxygenated hydrocarbons can originate from a variety of sources, such as sugar crops, grain crops, agricultural wastes (corn stalks, straw, seed hulls, sugarcane leavings, bagasse, nutshells, and manure from cattle, poultry, and hogs), wood materials (wood or bark, sawdust, timber slash, and mill scrap), municipal waste (waste paper and yard clippings), and energy crops, such as poplars, willows, alfalfa, switch grass, prairie bluestem, corn, soybean, and the like.

Prior to being fed into the BioForming process the biomass is generally first processed to extract the sugars or starches contained within the plant matter. For instance, lignocellulosic biomass will typically undergo fractionation and pretreatment to separate the cellulose, hemicellulose, and lignin. The fractionated cellulose and hemicellulose is then further processed to generate 5 and 6 carbon sugars using any one or more of the various enzymatic or acid hydrolysis techniques currently available. In most cases, the lignin is combusted to provide energy for the biorefinery or to produce electricity.

Hydrotreating

Depending on the particular application, the water soluble carbohydrates may undergo an initial hydrotreating step to convert the sugars and organic acids into polyhydric alcohols. This step consists of either hydrogenation [9, 10] to form polyhydric alcohols or hydrogenolysis [11, 12] to form shorter-chain oxygenated compounds, such as glycerol, propylene glycol, ethylene glycol, etc. The hydrotreating step can use hydrogen from an external source, hydrogen generated in situ using APR, or excess hydrogen recycled from the system.

Aqueous Phase Reforming

Aqueous Phase Reforming (APR) is the key step in the BioForming process. The aqueous product stream from the hydrotreating step above is fed to the APR reactor where the oxygenated hydrocarbons react with water over a proprietary heterogeneous catalyst to form hydrogen, carbon dioxide, alcohols, ketones, aldehydes, and byproduct alkanes, organic acids, and furans [8]. The aqueous-phase reforming process operates at moderate temperatures (450 to 575 K) and pressures (10 to 90 bar), thereby providing significant process efficiencies and beneficial operating conditions. At these conditions, a number of thermodynamically favorable series and parallel reactions occur that reduce the oxygen content of the oxygenated hydrocarbon to a more favorable intermediate product for the downstream condensation reactions. Without being held to a single theory, it is believed that the reactions include: (1) reforming to generate hydrogen; (2) dehydrogenation of alcohols/ hydrogenation of carbonyls; (3) deoxygenation reactions; (4) hydrogenolysis; and (5) cyclization. One key feature of this process is that the hydrogen is generated *in-situ* [6] and used to further de-functionalize the highly reactive carbohydrate to the less reactive monooxygenated species–alcohol, ketones, and alde-
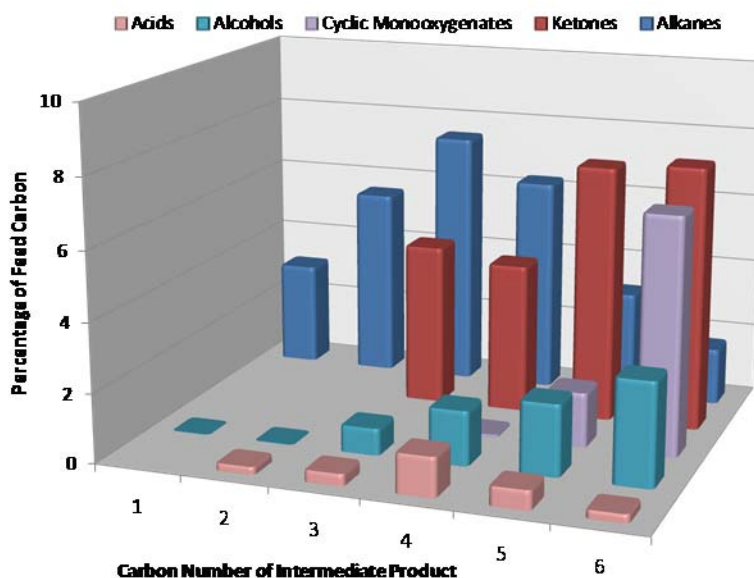

Figure 2. Carbon number and classification of intermediate products of sucrose conversion through hydrogenation and APR.

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hydes.

The generation of hydrogen and condensable intermediates by APR is the critical step in the overall BioForming process. Figure 2 shows the range of oxygenates generated from a sucrose solution through consecutive deoxygenation and APR processing. In this study, an aqueous solution of sucrose was hydrogenated over a Ru/C catalyst into a sorbitol/mannitol mixture. The mixture was reacted across a zirconia supported Pt/Re catalyst. Approximately 35% of the feed carbon was converted to CO_2, resulting in the production of the compounds shown in Figure 2 and 0.76 moles of hydrogen per mole of sugar monomer. The data shows that besides the C_1 through C_6 alkanes, the APR catalyst system generated an oxygenated intermediate stream containing alcohols, ketones, acids, and cyclized components suitable for condensation to longer-chain hydrocarbons.

Hydrogen produced by APR may exit the system as molecular H_2 or be consumed by hydrogenation reactions. The total amount of reforming that has occurred within the reaction system (and thus the hydrogen generated *in situ*) can be determined through overall reaction stoichiometry. For sorbitol the stoichiometry is as follows:

$$C_6H_{14}O_6 + 6\ H_2O \rightarrow 13\ H_2 + 6\ CO_2$$
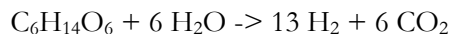
For each mole of CO_2 generated, the overall stoichiometry of sorbitol reforming dictates that 13/6 mole of hydrogen was produced. Note that under these conditions, the water gas shift equilibrium heavily favors CO_2 and H_2. For this reason, carbon monoxide is only present at trace levels and may be excluded from the analysis. Incomplete reforming, i.e. sorbitol to xylitol, $C_6H_{14}O_6 + H_2O \rightarrow CO_2 + 2\ H_2 + C_5H_{12}O_5$

results in a slightly lower estimate of hydrogen produced to CO_2 generated, 2/1.

Condensation Pathways to Liquid Fuels

While oxygenates generated by APR are generally limited to six or fewer carbon atoms, their chemistries support the formation of carbon-carbon bonds and the production of hydrocarbons appropriate for liquid fuels. One benefit of the BioForming process is that the system and operating conditions can be readily modified to produce different intermediate compounds appropriate for use in downstream condensation reactions structured to produce the desired final liquid fuel product or chemical. Depending upon the particular condensation technologies employed, the BioForming process can generate hydrocarbons for gasoline, jet fuel, diesel fuel, or other industrial applications.

Acid Condensation (ZSM-5)

The BioForming process can convert alcohols, ketones, aldehydes, and organic acids to gasoline-range hydrocarbons, including aromatics and isoalkanes, via direct catalytic condensation over acid catalysts, such as solid acids and zeolites [13-17]. In the case of a zeolite ZSM-5 catalyst, a series of reactions occurs, including: (a) the dehydration of oxygenates to alkenes; (b) oligomerization of the alkenes; (c) cracking; (d) cyclization and dehydrogenation of larger alkenes to form aromatics; (e) alkane isomerization; and (f) hydrogen-transfer to form alkanes [18, 17]. While most of the product hydrocarbons have gasoline-range boiling points, the heavier compounds can be separated by distillation and blended into jet fuel.

Virent has demonstrated the integration of APR with a condensation step in a continuous process for the conversion of sucrose and

xylose into gasoline-range hydrocarbons using a proprietary APR catalyst and ZSM-5. A reactor system containing four different catalyst beds operating at the same pressure and with no intermediate separations (Figure 3A) was used to demonstrate the integrated process.

Each catalyst bed operated at different temperatures and promoted different reactions. External hydrogen was used to hydrogenate the sucrose/xylose mixture to corresponding sugar alcohols over a Ru/carbon hydrogenation catalyst. The combined water, sugar alcohol, and hydrogen stream was immediately passed over a Pt/Re/Carbon APR catalyst at 523 K, where the sugar alcohols reacted with water to generate hydrogen, light alkanes, and condensable oxygenates. The resulting effluent was heated to 648 K and passed over two acid catalysts, tungstated zirconia and ZSM-5, where the oxygenates were dehydrated and underwent a series of acid-catalyzed reactions to form the hydrocarbon products shown in Figure 3B. Importantly, 93% of the lower heating value of the sugar and hydrogen feed was recovered in the products,
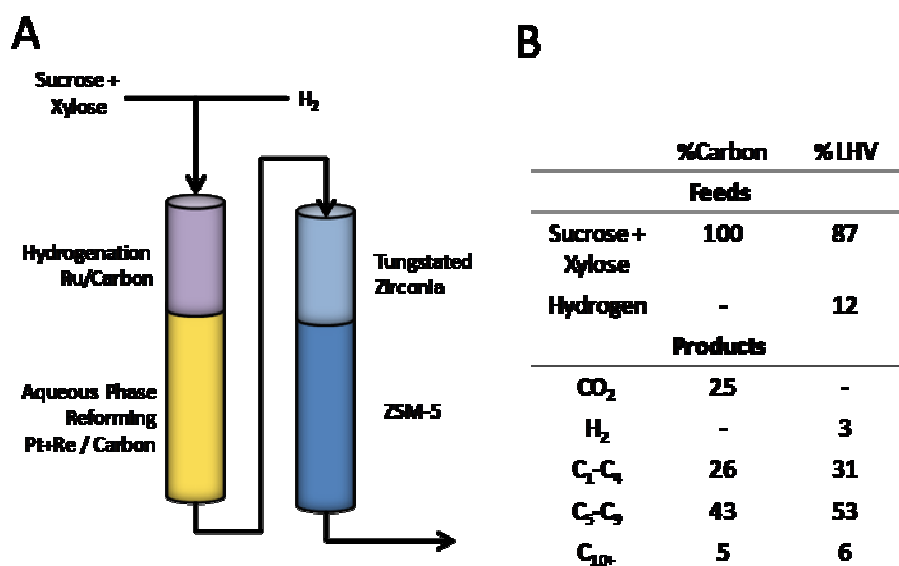

	%Carbon	%LHV
Feeds		
Sucrose + Xylose	100	87
Hydrogen	-	12
Products		
CO_2	25	-
H_2	-	3
C_1-C_4	26	31
C_5-C_9	43	53
C_{10+}	5	6

Figure 3. Panel A illustrates the catalytic steps used to convert sucrose and xylose to gasoline-range hydrocarbons. Panel B summarizes the molar carbon and heating value yields of the resulting products.

with 59% of this heating value contained in hydrocarbons having greater than 5 carbons.

Figure 4 shows the breakdown by carbon number of hydrocarbon species generated, with the majority being alkanes or aromatics. In addition, low levels of alkenes, oxygenates and cyclic alkanes were observed in the product stream. Although hydrogen was fed into the system prior to hydrogenation, 60% of the hydrogen required for deoxygenation was produced *in situ* by APR.

Base Condensation

The BioForming process is also able to convert alcohols, ketones, and aldehydes into jet fuel range hydrocarbons via direct catalytic condensation over a base catalyst. In this application, oxygenates are passed over multifunctional solid-base catalysts to promote condensation reactions to occur, including: (1) aldol condensation to form a β-hydroxyketone or β-

hydroxyaldehyde; (2) β-hydroxyketone or β-hydroxyaldehyde dehydration to form a conjugated enone; (3) hydrogenation of the conjugated enone to form a ketone or aldehyde, which may be further condensed or hydrogenated to an alcohol; and (4) the removal of hydroxyls by dehydration/hydrogenation or hydrogenolysis to form alkanes. This multi-functional process enables the generation of longer branched-chain hydrocarbons from shorter-chain oxygenated compounds[20-23]. The resulting hydrocarbon mixture is primarily in the jet fuel-range, but the product can be distilled to provide gasoline and diesel fuel fractions as well.

Carbon-carbon bonds are formed in base condensation reactions by the catalytic processing of oxygen-containing precursors through aldol and decarboxylative condensation. Many oxygenates generated by APR, including alcohols, carbonyls, and acids, can be condensed through these reactions [23-25]. In general,
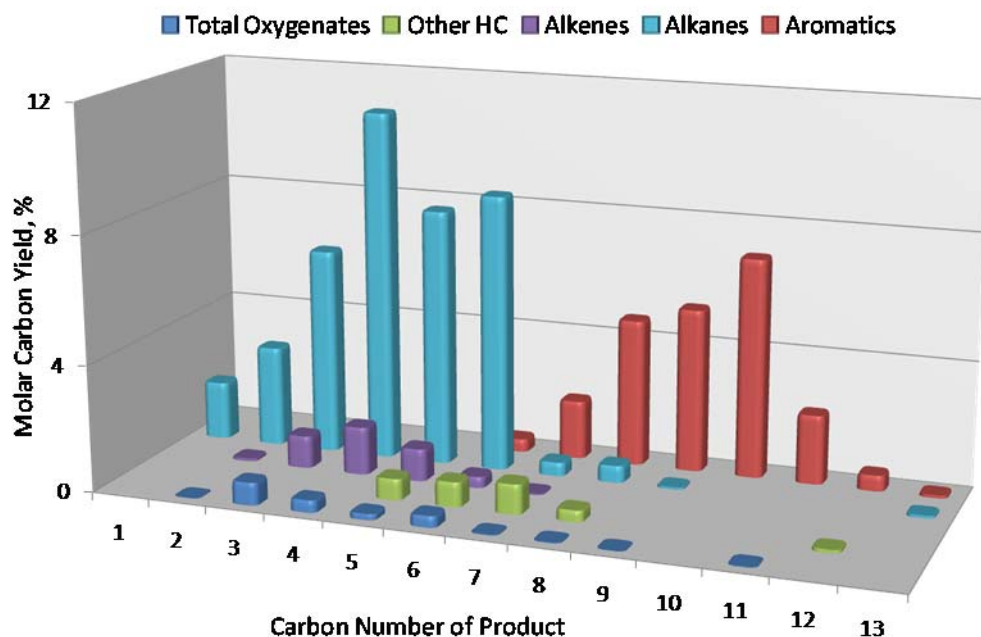

Figure 4. Carbon number distribution and classification of products from sucrose and xylose conversion to hydrocarbons using a four step, continuous catalytic process.

aldol condensation is equilibrium limited and more favorable at lower temperatures. However, by coupling the condensation with hydrogenation of the resulting condensed product, high yields of hydrocarbons appropriate for gasoline and jet fuel can be obtained at higher temperatures. Figure 5 shows equilibrium conversions for aldol condensation and coupled aldol condensation and hydrodeoxygenation. The aldol condensation of acetone becomes less favorable as temperatures are increased (solid line). When coupled with dehydration and hydrodeoxygenation, the overall reaction is more favorable as shown by the dash-dot series for acetone and the dotted line series for 2-pentanone.

The potential of base catalyzed condensation coupled with hydrogenation to produce longer-chain alkanes was demonstrated using model feeds containing 3 and 5 carbon oxygenates generated by APR. The overall alkane forming reaction starting from 2-pentanone would be: $2C_5H_{10}O + 3\ H_2 \rightarrow C_{10}H_{22} + 2\ H_2O$. This reaction is very favorable at moderate temperatures, with free energy changes ranging from -146 KJ/mole at 300K to -45 KJ/mole at 700K. Two zinc aluminate catalysts were developed to complete this process, operated at 573K to 648K and at 42 bar pressure. The first catalyst possessed basic and metal functions to accomplish condensation, dehydration, and enone hydrogenation. A second catalyst, placed downstream from the first and possessing basic, acidic, and metal functions, hydrogenated the condensed ketones from the first step to alkanes. Mixed acid-base functionality was achieved by lowering the ratio of zinc oxide to alumina. Deoxygenation reactions were also promoted through substitution of palladium with platinum. The multiple functionalities designed into the second catalyst worked together
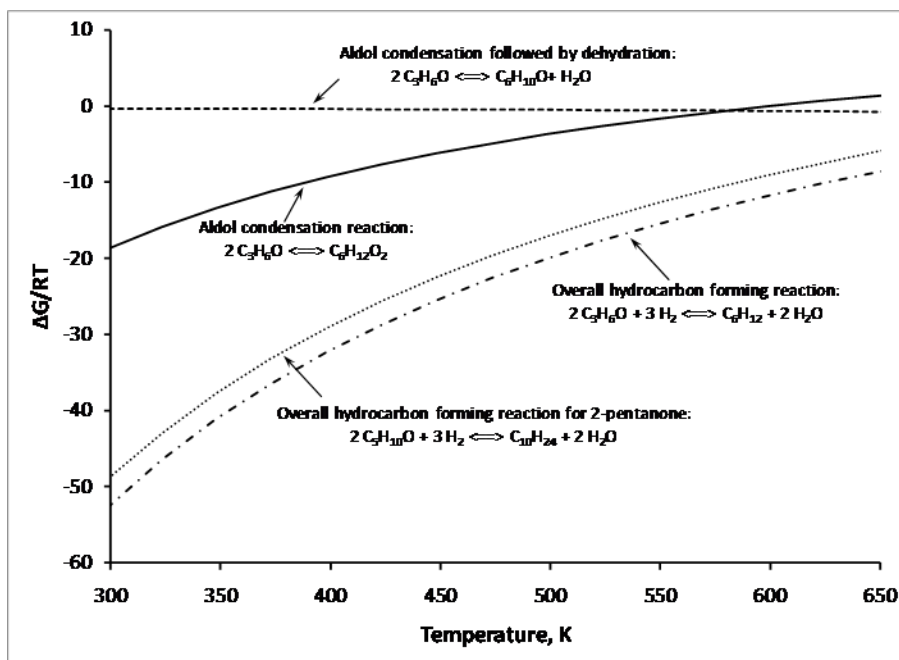

Figure 5. Equilibrium conversions for aldol condensation, coupled aldol condensation, and hydrodeoxygenation.

as follows: the basic sites supported further condensation and reacted carbonyls with hydrogen to form alcohols; and the acidic sites promoted the dehydration of alcohols formed on basic and metal sites to form alkenes; the metal sites saturated alkenes to alkanes and may have participated in the hydrogenation of carbonyls to alcohols, both reactions requiring hydrogen.

Hydrogen was combined with the feed at a ratio of 2 moles of hydrogen per mole of feed. With 100% 2-propanol feed delivered at WHSV=1, the reaction system yielded 78% condensation products (those containing 4 or more carbon atoms) on a molar carbon basis, with 90% of the conversion products being alkanes. Likewise, a pure 2-pentanone feed re-

Table 1. **Results from characterization of coupled condensation/hydrodeoxygenation product produced from 3-, and 5- carbon oxygenates.**

Property	Limit	Result
Appearance		Pass
Composition		
Acidity mg KOH/g	0.1 max	0.006
Aromatics, vol%	25 max	1.1
Sulfur, wt%	0.3 max	<0.001
Sulfur, Mercaptan, wt%	0.003 max	<0.0001
Volatility		
Initial Boiling pt (C)		138.6
10% vol at C	205 max	153.1
50% vol at C		173.1
90% vol at C		211.7
Final Boiling pt (C)	300 max	240.7
Fuel Recovered, vol%		98.7
Residue, vol%	1.5 max	1
Loss, vol%	1.5 max	0.3
Flash Point, C	38 min	33
Density at 15C, kg/m3	775min, 840max	739.8
Fluidity		
Freezing Pt, C	-40 max	<-70
Viscosity at -20C, cSt	8 max	2.74
Combustion		
Specific Energy, MJ/kg	42.8 min	44.21
Smoke Point, mm	25 min	>25
Corrosion		
Copper corrosion		Pass
Stability (at 260C)		
Filter Pressure Differential, mmHg	25 max	1
Tube Deposit Rating	3 max	<2
Contaminants		
Existant Gum, mg/100ml	7 max	<1
Microseparometer	85 min	100

sulted in 58% yield of condensed products (those containing 6 or more carbons), with >95% of these being alkanes. Mixed feeds containing 2-propanol, acetone, and 2-pentanone showed similar results. In all cases, a second pass through the system of the first pass product resulted in essentially complete deoxygenation to yield >99.5% hydrocarbons.

The products from these experiments were combined and fractionated in a batch laboratory still, reserving the material with boiling points between 423K and 523 K. The material was submitted for ASTM D1655 aviation turbine fuel analysis. Detailed results of that analysis are shown in Table 1. All specifications were met except for the flash point, due to inadequate removal of light components in the laboratory still and the density, due to low aromatic content. Note that the fuel's freeze point was <-70° C, the testing method's limit. Some unconventionally produced jet fuels (primarily those produced by Fischer-Tropsch chemistry) have difficulty meeting this important characteristic due to high normal alkane content. The majority of alkanes produced through aldol condensation contain a single branch, significantly reducing their freeze points. The C_{9+} aromatics from the ZSM-5 condensation process and the moderately branched alkanes from the base condensation route can be combined to produce a complete biomass-derived aviation turbine fuel that meets current fuel specifications.

Dehydration/Oligimerization

Dehydration of alcohols produced by APR can also generate alkenes as feedstocks for alkylation or condensation. Alkenes may also be dimerized to produce gasoline-range product or oligomerized for kerosene or diesel fuel using solid phosphoric acid or zeolite catalysts [26]. In this case, the oxygenates derived from the APR process are converted into paraffins and olefins through dehydration reactions and/or successive hydrogenation-dehydration reactions. In dehydration cases, alcohols are further defunctionalized to olefins by the removal of the –OH group through the interaction between the hydroxyl group and acid sites on the dehydration catalyst. If ketones, acids and aldehydes are present, they too can be defunctionalized by first reducing the carbonyl compound in the ketone, acid or aldehyde to a primary or secondary alcohol by a hydrogenation reaction involving the introduction of H_2 over a hydrogenation catalyst, followed by a subsequent dehydration reaction as described above to provide olefins and, in some instances, paraffins.

Summary

In summary, APR integrated with conventional catalytic processing can convert biomass-derived sugars to hydrocarbons for use as conventional gasoline, jet fuel, and diesel fuel. With crude oil prices currently over $100/bbl, these integrated processes provide a cost-effective method for generating conventional liquid fuels from non-food biomass, resulting in increased energy efficiencies and lower CO_2 footprints. By altering conditions and catalysts, the BioForming® process can be easily tailored to produce the specific desired liquid fuel. The BioForming process uses a wide variety of food and non-food sugars, broadening the range of cost-effective feedstocks available for conversion to fuels. Unlike ethanol, the process uses minimal energy to generate fuels compatible at high blends with today's engines, fuel pumps, and pipelines. The biofuel product separates naturally from water, thereby eliminating the

energy-intensive distillation step required in ethanol processes and providing more net energy, and match petroleum fuels in composition, functionality, and performance. These advantages position the BioForming process to provide a cost effective renewable fuel with minimal impact on global food and water resources.

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