

# Converting sugars to conventional liquid fuels

An aqueous-phase catalytic reforming pathway processes sugars from a variety of feedstocks into fuels that are interchangeable with conventional transportation

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Virent Energy Systems has discovered and is developing processing technologies that generate high-energy hydrocarbon mixtures from food and non-food plant sugars. Virent's BioForming process uses catalytic processing technologies similar to those used in today's petroleum refineries to generate liquid fuels from crude oil. However, instead of using crude oil as a feedstock, this process uses biomass-derived sugars to generate hydrocarbon mixtures that can be either directly used or seamlessly blended to make conventional liquid fuels and chemicals.

The BioForming process applies Virent's patented aqueous phase reforming (APR) technology, which converts sugars into hydrogen and chemical intermediates. The resulting chemical intermediates are then processed into gasoline, diesel or jet fuel components using one of several available catalytic routes. Unlike ethanol production, which requires a specific type of sugar feedstock and significant processing energy, and generates a single molecule with limited utility, BioForming technology can process a large variety of biomass feedstocks utilising low-energy separation technologies, and can generate an array of products for use in different transportation fuels and chemicals. Preliminary analysis suggests that converting sugars to conventional liquid fuels using the BioForming process can economically compete with petroleum fuels at crude oil prices greater than \$60 per barrel. In summary, this process broadens the



One of Virent's liquid fuel laboratories

range of viable feedstocks, provides significant net energy benefits, and produces fuels compatible with today's engines and pipeline infrastructures.

Conventional liquid transportation fuels refined from crude oil, such as gasoline, jet fuel and diesel fuel, are essential for modern economies. These oil-derived fuels are ideal for transportation applications because they consist of mixtures of hydrocarbons (compounds containing only carbon and hydrogen), which have high volumetric energy density and are easily transported and stored. While crude oil is currently the major source of hydrocarbons for conventional liquid fuels, its properties do not allow its use directly as a transportation fuel. Over the last century, refining technologies have been created and optimised to effectively convert crude oil into the different hydrocarbon mixtures that are

blended to make gasoline, jet fuel and diesel. These petroleum refining technologies have evolved from the production of kerosene by simple fractionation, to increasing product yields by simple thermal cracking, to cleaning up and functionalising different crude oil fractions by catalytic processing. Current oil refineries fractionate crude oil, process these fractions in different catalytic processing technologies, then blend products from these different processes to generate mixtures with the composition and properties appropriate for gasoline, jet fuel or diesel fuel.

Growing concern over environmental impact and energy supply are highlighting the need for renewable replacements for crude oil as a feedstock for the production of fuels required for transportation. Carbohydrates derived from biomass

hold considerable potential as a feedstock source for transportation applications. Carbohydrates are simply oxygenated hydrocarbons, containing carbon, hydrogen and oxygen, and are the most widely distributed naturally occurring organic compounds. Similar to crude oil, carbohydrates' properties do not allow for their direct use as transportation fuels. Carbohydrates must be refined to remove oxygen to form compounds that can be used as liquid transportation fuels.

The fermentation of carbohydrate-derived sugars to produce ethanol has been scaled up and is currently commercialised using either corn starch or cane sugar as a feedstock. While these fermentation processes remove some of the oxygen from the product, ethanol is still a partially oxidised compound. Accordingly, ethanol has a relatively low volumetric energy content and is miscible with water. This limits its use in existing fuel infrastructures and results in a low net energy return on energy invested due to the need for distillation.

In similar fashion to the refining of crude oil to generate liquid fuels, it is possible to catalytically process

## BioForming can process any type of water-soluble plant sugar, including mixed sugar streams and polysaccharides

carbohydrates to remove oxygen and so generate alternative, biomass-derived transportation fuels that have the same properties as oil-derived fuels. These new biofuel alternatives would more effectively capture the energy contained in biomass and could use today's infrastructure to deliver cost-effective, carbon-neutral fuels to market.

### BioForming

Virent discovered in 2006 that it is possible to apply established catalytic petroleum processing technologies to convert biomass into hydrocarbon fuels.<sup>1</sup> It did this by integrating its core APR technology with proven catalytic technologies, such as base and acid

condensation, to generate hydrocarbons for direct use as biofuels or as blending components for conventional gasoline, jet fuel and diesel.<sup>2</sup> Virent has previously reported methods for the renewable production of alkanes and hydrogen from biomass-derived carbohydrates,<sup>3,4</sup> and recently reported methods for the renewable production of oxygenated components, such as alcohols, ketones, aldehydes, furans and polyols.<sup>2</sup>

Virent's BioForming process, which encompasses the integration of APR with conventional catalytic processes, is characterised by the conversion of water-soluble carbohydrates into chemical intermediates for further catalytic processing into renewable liquid fuels. Figure 1 illustrates the BioForming platform, including the integration of potential biomass pretreatment technologies, catalytic hydrotreating, APR and various catalytic condensation processes. Virent currently holds over 50 pending or issued patents in the US and elsewhere covering all aspects of this technology.

### Biomass pretreatment

The BioForming process can accept a broad range of food and non-food

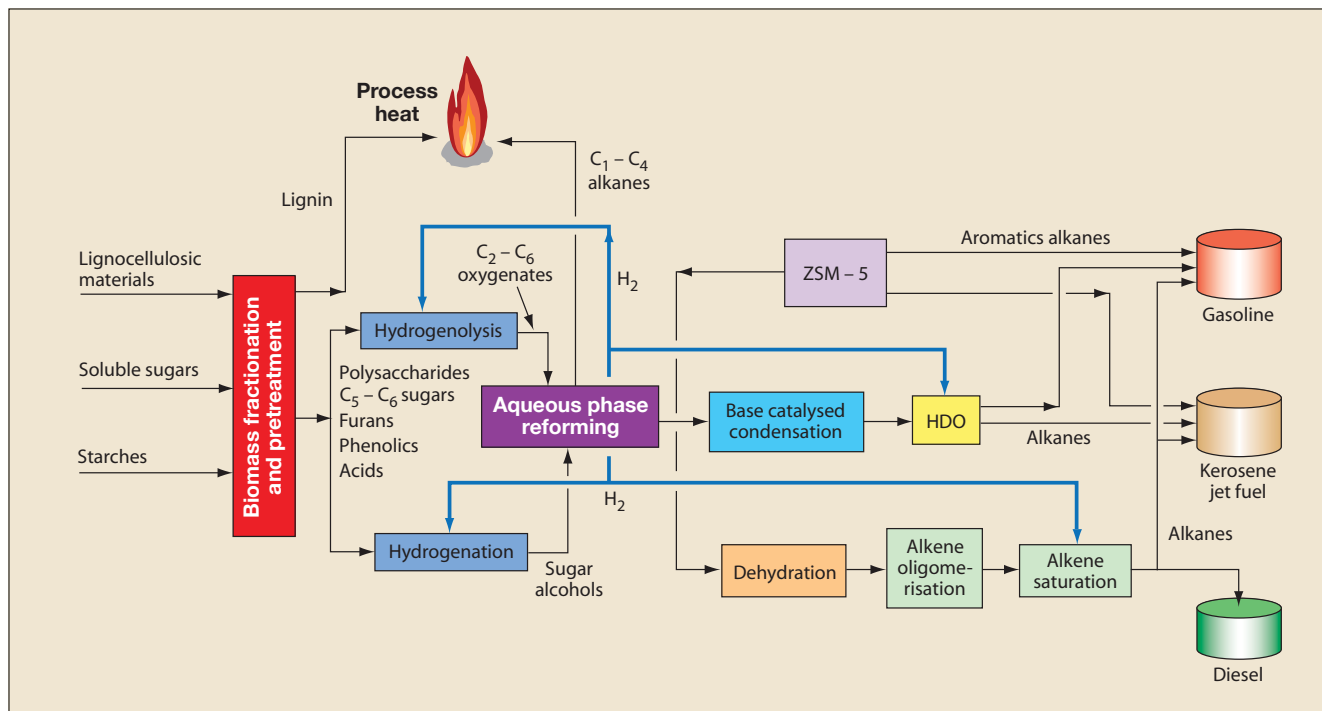


Figure 1 The BioForming process to produce conventional liquid transportation fuels from biomass feedstocks. APR enables the process to partially defunctionalise carbohydrate feedstocks for further catalytic upgrading

carbohydrates. Unlike fermentation processes, which can typically convert only one specific sugar type, BioForming can process any type of water-soluble plant sugar, including mixed sugar streams and polysaccharides or complex sugars. Potential carbohydrate feedstocks include sucrose (from sugar cane or sugar beets), corn sugar (glucose from the conversion of corn starch), sugars derived from hydrolysis of hemicellulose and cellulose (including polysaccharides, organic acids and furfural by-products), and water-soluble oxygenated compounds such as diols, glycerol and sugar alcohols. Feedstocks sources include sugar crops, grain crops, agricultural wastes, woody materials, municipal waste and energy crops, such as poplar, willow, sorghum, switchgrass and the like.

### Hydrotreating

Depending on the particular feedstock, 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 to form polyhydric alcohols, or of hydrogenolysis to form shorter-chain oxygenated compounds, such as glycerol, propylene glycol and ethylene glycol. The hydrotreating step can use hydrogen from an external source, hydrogen generated in situ using APR, or excess hydrogen recycled from the system. The hydrogen acts to reduce the functionality of the mixed sugar stream, enabling higher temperature processing in the subsequent APR step.

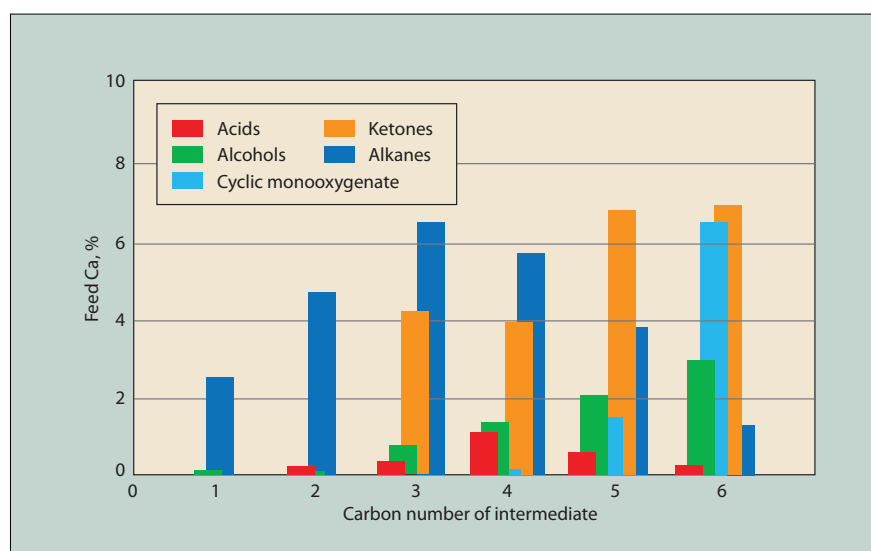
APR is the key technology of the BioForming process. The aqueous product stream from the hydrotreating step is fed to the APR reactor. In the reactor, oxygenated hydrocarbons react with water over a proprietary heterogeneous catalyst to form hydrogen, carbon dioxide, alcohols, ketones, aldehydes and by-product alkanes, organic acids and furans.<sup>2</sup> APR's in situ generation of hydrogen<sup>3</sup> defunctionalises (or removes oxygen from) highly reactive carbohydrates to form less reactive mono-oxygenates (for instance, alcohols, ketones and

aldehydes). The hydrogen is also used in the production of condensable chemical intermediates, with any excess hydrogen recycled for use in the hydrotreatment of aqueous solutions of complex sugars (C<sub>5</sub> and C<sub>6</sub> sugar mixtures) or biomass hydrolysate prior to processing in the APR reactor, or downstream in later process applications. The lighter alkanes, such as C<sub>1</sub>-C<sub>4</sub> fuel gases, provide process heat and so reduce the need for external fuel sources.

APR operates at moderate temperatures and pressures, thereby providing significant process efficiencies

### Condensation pathways to liquid fuels

While oxygenates or chemical intermediates 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 for use in downstream condensation reactions. These intermediates are structured to produce the desired final liquid fuel product or chemical.



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

and beneficial operating conditions. Under these conditions, a number of thermodynamically favourable series and parallel reactions occur that reduce the oxygen content of the oxygenated hydrocarbon to produce a more valuable intermediate product for downstream condensation reactions. Figure 2 shows the range of oxygenates generated from a sucrose solution through consecutive deoxygenation and APR processing. Data show that, besides the C<sub>1</sub> through C<sub>6</sub> alkanes, the APR catalyst system generates an oxygenated intermediate stream containing alcohols, ketones, acids and cyclised components suitable for condensation to longer-chain hydrocarbons.

Intermediate compounds generated by the APR process can be converted to non-oxygenated hydrocarbons in a continuous process using catalytic hydrotreating and catalytic condensation processes, including ZSM-5 acid condensation, base catalysed condensation, acid catalysed dehydration and alkylation. Catalytic processing steps generate alkenes, branched alkanes and/or aromatics that can be fractionated and blended into gasoline, jet fuel or diesel fuel. As in a conventional petroleum refinery, each BioForming process step can be optimised and modified to produce a slate of desired hydrocarbon products. For example, a gasoline product can be produced using a zeolite (ZSM-5)-

**Results from the characterisation 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
Sulphur, wt%	0.3 max	<0.001
Sulphur, mercaptan, wt%	0.003 max	<0.0001
Volatility		
Initial boiling point, °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 point, °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 15°C, kg/m <sup>3</sup>	775 min, 840 max	739.8
Fluidity		
Freezing point, °C	-40 max	<-70
Viscosity at -20°C, 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 260°C		
Filter pressure differential, mmHg	25 max	1
Tube deposit rating	3 max	<2
Contaminants		
Existant gum, mg/100ml	7 max	<1
Microseparator	85 min	100

**Table 1**

based process; jet fuel and diesel can be produced using a base catalysed condensation route; and a high octane fuel can be produced using a dehydration/oligomerisation route.

**Acid condensation (ZSM-5)**

The BioForming process can convert the appropriate chemical intermediates, or 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. While most of the hydrocarbons produced using this route have gasoline-range boiling points, the heavier compounds can be separated by distillation and blended into jet fuel. Importantly, in one example, 93% of the lower heating value of the sugar and hydrogen feed was recovered in the products, with 59% of this heating value contained in hydrocarbons with more than five carbon atoms.

**Base condensation**

The BioForming process can also produce jet fuel-range hydrocarbons through condensation reactions using multifunctional solid-base catalysts. This process generates longer branched-chain hydrocarbons from shorter-chain oxygenated compounds. 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 these 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. In general, aldol condensation is equilibrium limited. However, by coupling the condensation with hydrogenation of the resulting condensed product, the equilibrium

limitations can be overcome and high yields of hydrocarbons appropriate for gasoline and jet fuel can be obtained.

Products of these experiments were combined and fractionated in a batch laboratory still to reserve material with boiling points between 423°K and 523°K. The material was submitted for ASTM D1655 aviation turbine fuel analysis. Detailed results of this analysis are shown in Table 1. All specifications were met except for: flash point, due to inadequate removal of light components in the laboratory still; and density, due to low aromatic content. Note that the fuel's freezing 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 their high normal alkane content. The majority of alkanes produced through aldol condensation contain a single branch, significantly reducing their freezing points. C<sub>9</sub>+ aromatics from the ZSM-5 condensation process and 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/oligomerisation**

Dehydration of alcohols produced by APR can also generate alkenes as feedstocks for alkylation or condensation. Alkenes may also be dimerised to produce gasoline-range product, or oligomerised for kerosene or diesel fuel using solid phosphoric acid or zeolite catalysts. In this case, oxygenates from the APR process are converted into paraffins and olefins through dehydration reactions and/or successive hydrogenation-dehydration reactions. Alcohols can be dehydrated to olefins by the removal of the hydroxyl group through the interaction between the hydroxyl group and acid sites on the dehydration catalyst. If ketones, acids and aldehydes are present, they can also be defunctionalised 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<sub>2</sub> over a hydrogenation catalyst, followed by a subsequent dehydration reaction as described above to provide olefins and, in some cases, paraffins.

#### A fourth pathway

Virent's BioForming process is a new pathway to biofuels that cost-effectively and efficiently produces conventional gasoline, diesel, jet fuel and chemicals from plant sugars. Three other pathways to biofuels and bioproducts have been commercially developed: fermentation, gasification and pyrolysis. The BioForming process is a novel, fourth pathway which produces biofuels that are fungible with petroleum fuels, matching them in composition, functionality and performance. Virent's technology represents a practical alternative to other biofuel production routes with advantages in feedstock flexibility, energy efficiency and end products.

Virent has adapted all types of food and non-food sugars, expanding the range of cost-effective feedstocks available for conversion to fuels. Unlike fermentation, the BioForming process can generate fuels from mixed sugar streams, polysaccharides and fermentation inhibitors such as furans, which are formed during biomass deconstruction. This greatly increases Virent's ability to use cellulosic biomass as a viable feedstock. The process is scalable to match feedstock supply, while gasification technologies must be very large to be economical.

Unlike gasification and pyrolysis technologies, the BioForming process uses little energy, resulting in a much more positive net energy benefit. The technology is completely renewable, operating without traditional petroleum-based resources such as natural gas or natural gas-derived hydrogen. Both pyrolysis and gasification require external energy, especially hydrogen, to further process their intermediate products into hydrocarbon fuels. In the BioForming process, hydrogen, propane and hydrocarbon chemicals can be generated. Water is also produced,

providing a potential resource for agricultural and industrial applications.

The process renewably produces hydrocarbon biofuels that separate naturally from water, thereby eliminating the energy-intensive distillation step required in ethanol processes and providing more net energy. Its product fuels have a 20–30% per BTU cost advantage over corn ethanol. Moreover, because these renewable fuels and chemicals are the same as their petroleum counterparts, they can be used immediately in the marketplace, with no new investment in infrastructure. They are compatible at high blending levels with today's engines, fuel pumps and pipelines.



Preparing liquid fuel samples for analysis

They have the energy density and performance characteristics suitable for fuel applications that currently lack feasible biofuel solutions.

#### Summary

APR integrated with conventional catalytic processing can convert biomass-derived sugars to hydrocarbons for use as conventional gasoline, jet fuel and diesel fuels. This technology applies established petroleum processing methods to the generation of renewable fuels. With crude oil prices at high levels, 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<sub>2</sub>

footprints. By altering conditions and catalysts, the BioForming process can be tailored to produce specific liquid fuel properties. The biofuels separate naturally from water, thereby eliminating the energy-intensive distillation step required in ethanol processes and providing more net energy. They also match petroleum fuels in composition, functionality and performance.

BioForming is a mark of Virent Energy Systems.

#### References

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