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Completing the Puzzle: 100% Plant-Derived PET



Paraxylene is converted into Terephthalic Acid [Graph: Simon, KR] he interest in bio-based plastics falls into two main areas – sustainability and economics, and there is significant overlap between these areas. Many companies including Coca-Cola, Pepsi, Danone, WalMart, Heinz, Nike and others, have initiated sustainability goals including recycled PET (rPET), lightweighting and the most recent introduction of partially bio-based PET. These sustainability goals and programs have been driven by companies' desires to reduce their environmental footprint and to respond to a growing consumer demand for sustainable and renewable packaging. Non-Government Organizations, such as the World Wildlife Fund (WWF), have also played a large part in raising concerns over traditional petroleum based packaging materials. The sustainability of packaging is no longer just a 'nice to have' or exclusively part of a company's corporate social responsibility, but is seen as a business necessity to attract consumers and protect market share in certain regions.

The other main driver for interest in bio-based plastics is the need to find an alternative to crude oil as a basic feedstock. In the long run, crude oil will increase in price as demand continues to grow and new oil resources become ever more expensive to locate and develop. Therefore, companies using PET packaging are seeking alternatives that will help them to reduce costs and minimize volatility. While switching to other materials such as glass, metal and paper composites is an option in certain cases, PET has replaced these materials in many uses



because of a variety of benefits it offers (light-weight, clarity, resilience, etc). Users will not give up these benefits easily. In addition to the long run cost increases that will result from using oil, the recent volatility of crude oil prices has also caused problems for end users of PET. Since January 2008, PET prices have fluctuated between \$1,400 (€ 985) and \$2,400 (€ 1,700) per tonne with recent prices in April 2011 hitting all-time highs (source: CMAI Chemical Market Ass. Inc.). These price fluctuations put pressure on the end users of PET and wreak havoc with business planning, profit margins and supply contracts. The risk that such volatility introduces into the PET supply chain has a real economic cost.

Meeting sustainable packaging goals requires an efficient and economical manner for producing renewable chemicals that are identical to existing petroleum-derived counterparts. Molecules that can be 'dropped-in' to existing supply chains and recycling infrastructure take advantage of the extensive capital infrastructure and production know-how already in place today. Virent's technology allows for leveraging of the existing infrastructure for the production of biobased chemicals and polymers.

PET Overview

PET (Polyethylene Terephthalate) was developed in the 1940s as a synthetic fiber polymer. Demand for the polymer grew exponentially in the 1960s and 1970s as knit fabrics gained popularity in fashion apparel. Today, it is a major part of the polyester family of polymers. According to CMAI, global demand for PET will be ~54 million metric tons in 2011.

Fibers are the dominant application of PET, accounting for 62% (CMAI) of total PET demand. PET is a high performing synthetic fiber, as the polymer keeps its shape, color and is extremely stain resistant. The second largest use (31%, CMAI) of total PET demand is found in PET bottle resin. This application started commercially in the 1970s as the soft drink industry was attempting to source a lighter-weight

bottle to replace glass, while still maintaining the clarity and appeal of a glass bottle. The industry found PET resin was ideal for its needs, and the stretch blow molding process was born. The remaining demand for PET is in films (4%) and other small niche market applications (3%).

There are two streams of raw materials which comprise PET: Mono-Ethylene Glycol (MEG), and Purified Terephthalic Acid (PTA). PTA is made from paraxylene, and historically, all of these raw materials have been sourced from fossil resources (crude oil and natural gas).

The MEG portion of PET can be produced from traditional petrochemical routes via ethylene or can be produced from natural plant sources (via fermentation to ethanol and dehydration to ethylene). The PTA/paraxylene portion, representing approximately 70% (by wt. or even 80% if we just look at the carbon atoms) of the PET molecule has remained a fossil-fuel component derived from petroleum refinery streams, due to the difficulty of producing the aromatic paraxylene molecule from bio-based sources. That has been the difficulty for companies seeking a 100% bio-based PET polymer. Now Virent has demonstrated a route to make bio-based paraxylene that opens up the potential for 100% bio-based PET.

BioFormPX[™] Production Enabling a 100% Biobased PET bottle

Virent is making paraxylene as well as other chemicals and biofuels through its patented technology. Coupled with biobased MEG, Virent's BioFormPX allows bottlers and other packaging companies to offer their consumers 100% renewable and recyclable PET bottles as well as fibers and films.

Virent's BioForming® Platform

Virent's process, trademarked BioForming[®], is based on a novel combination of Aqueous Phase Reforming (APR)







Figure 2. Virent's BioForming process utilizes the patented APR process coupled with conventional catalytic conversion technologies and petrochemical operations to produce BioFormPX.

Bottles



Figure 3. Virent uses catalysts to reduce the oxygen content of the feedstock. Once formed, the mono-oxygenated species are converted to non-oxygenated hydrocarbons in a continuous process using conventional catalytic condensation and hydrotreating techniques.

Virent Energy Systems, Inc.

Virent was founded in 2002 and is headquartered in Madison, WI, USA. The company produces the chemicals and fuels the world demands from a wide range of naturally occurring, renewable resources. Using patented catalytic chemistry, Virent converts soluble biomass-derived sugars into products molecularly-identical to those made with petroleum, including gasoline, diesel, jet fuel, and chemicals used for plastics and fibers. Virent's technology has the potential to replace over 90% of the products derived from a barrel of crude oil.

technology with modified conventional catalytic processing technologies. The APR technology was discovered at the University of Wisconsin in 2001 by Virent's founder and Chief Technology Officer, Dr. Randy Cortright. The BioForming platform expands the utility of the APR process by combining APR with catalysts and reactor systems similar to those found in standard petroleum oil refineries and petrochemical complexes. The process converts aqueous carbohydrate solutions into a mix of hydrocarbons. The BioForming process has been demonstrated with conventional sugars as well as a wide variety of cellulosic biomass from non-food sources.

Virent's aqueous phase reforming methods utilize heterogeneous catalysts at moderate temperatures (450 to 575 K) and pressure (10 to 90 bar) in a number of series and parallel reactions to reduce the oxygen content of the feedstock. The reactions include: (1) reforming to generate hydrogen, (2) dehydrogenation of alcohols/hydrogenation of carbonyls; (3) deoxygenation reactions; (4) hydrogenolysis; and (5) cyclization. Once formed, Virent has found that these 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.

The production of Virent's bio-paraxylene, branded BioFormPX involves the APR process followed by a modified acid condensation catalyst (ZSM-5) which produces a stream similar to a petroleum derived reformate, branded BioFormate[™]. In the acid condensation step, the APR products are converted into a mixture of hydrocarbons, including paraffins, aromatics and olefins. The similarity between Virent's BioFormate stream and a typical petroleum reformate stream is shown in Fig 4.

The resultant BioFormate stream has been blended into the gasoline pool and can be subsequently processed into high value chemical intermediates, such as paraxylene using commercially proven and practiced technologies. Virent's BioFormate stream has been blended by Royal Dutch Shell into a gasoline fuel used by the Scuderia Ferrari Formula 1 racing team.

Virent has produced sufficient quantities of its BioFormate through operation of its 37,800 Liter (10,000 gallon) per year demonstration plant to generate volumes for further processing to paraxylene. Virent completed in house purification through the use of commercial crystallization techniques to produce a purified bio-paraxylene product. The use of crystallization technology is used to meet the industry required specification of 99.7+% purity.

Bottles





Road to Commercialization

Virent is currently in discussions with a number of major end users of PET fiber, bottle resin and film, to commercialize the BioForming platform for the production of BioFormPX. Manufacturers involved in the traditional petrochemical PET supply chain have also expressed interest in contributing to building out the biobased PET supply chain. The ability of Virent to use existing petrochemical assets and technologies accelerates the time to commercial deployment. Virent is targeting commercial production of its BioFormPX by 2015 or earlier and believes that the demand pull from the major end users of PET is crucial to the initial commercialization and success of bio-based PET.

Virent's BioForming platform for BioFormPX produces other bio-based aromatic intermediates, including benzene, toluene and other xylenes, as well as biofuels. These other aromatic intermediates can be used to produce biobased polystyrene, polycarbonate, and polyurethane. This diversified product slate allows for de-risking of commercial deployments as the profitability is not dependent on one molecule or market. Virent has produced material that would be suitable using today's aromatics processing infrastructure from its 37,800 Liter per year demonstration plant. While that is sufficient volume to provide samples to prospective partners, the current demand for plant-based paraxylene is even more significant and is poised to grow at high rates in the future. Virent envisions the BioForming platform as being an industry wide solution enabling 100% bio-based PET while complementing petroleum based PET.

The ability of Virent to use existing petrochemical assets and technologies accelerates the time to commercial deployment. The scale of this plant is yet to be finalized and will depend on a number of factors including feedstock source, logistics, and customer demand. Potential plant sizes range from 30,000 tonnes/yr to 225,000 tonnes/yr of BioFormPX production. The large scale plant could produce 30 Billion 0.295 Liter (10 oz) bio PET water bottles or 17 Billion 0.590 Liter (20 oz) bio PET soft drink bottles. The introduction of this first plant can have a large impact on the PET bottle industry and the implementation of future plants will increase the impact.



Figure 5. Virent's 10,000 gallon/yr BioFormate demonstration plant (top) and Virent's BioFormPX (bottom) in its crystalline form during in house purification.



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