

# The future of butadiene

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The chemical process industries (CPI) have experienced many benefits from the so-called shale-gas boom — recent years have seen an unprecedented rise in construction and expansion activity in the petrochemicals sector. Shown in Figure 1 is construction at the Freeport, Tex. facility of The Dow Chemical Company (Dow; Midland, Mich.; [www.dow.com](http://www.dow.com)). Dow is just one of many companies to initiate large petrochemical projects on the U.S. Gulf Coast in the wake of increased shale-gas availability.

"We are in the midst of unprecedented growth due to the abundance of natural gas liquids," explains Bob Maughon, Dow's global R&D director for performance plastics and feedstocks. "The use of natural-gas liquids took hold in 2009. In 2011 and 2012, the abundance of ethane compelled the industry to flex strongly toward natural-gas feedstocks and away from petroleum-derived naphtha."

## **The Dow Chemical Company**

Since this shift, though, the changing feedstock landscape in petroleum refineries has led to shortages for many co-products, including 1,3-butadiene (butadiene; Figure 2), an important building block for synthetic rubber and nylon. Says Maughon: "As naphtha cracking has waned and ethane cracking increases, cracker co-product production drops. The slate of products that have been affected include propylene, butadiene, isoprene, benzene and others. It isn't that the industry doesn't want to produce these chemicals. The economics of ethane-only cracking have become so compelling that naphtha cracking has been squeezed. Production is driven to the lighter feedstocks and co-product production is lost."

Figure 3 shows the variation in production from naphtha-cracking operations versus the cracking of lighter feedstocks. The shale-gas-imposed scarcity for chemicals like butadiene presents opportunities for new technologies to arise. This article covers some actions that companies are taking in response to butadiene shortages, including the development of on-purpose production methods and the use of bio-based feedstocks.

## **Oxidative dehydrogenation**

TPC Group Inc. (Houston; [www.tpcgrp.com](http://www.tpcgrp.com)), has been commercially operating its OXO-D butadiene process technology for over 40 years. TPC's OXO-D technology converts butylenes into butadiene through oxidative dehydrogenation. In June 2014, TPC announced a partnership with Honeywell's UOP LLC (Des Plaines, Ill.; [www.uop.com](http://www.uop.com)) to further develop and globally license this technology in the wake of increased demand for on-purpose butadiene. There will be research and development teams and pilot plants at both companies' facilities to jointly develop process advancements. Also, through this agreement, UOP acquires the worldwide exclusive licensing rights of the TPC OXO-D process.

Jim Rekoske, petrochemicals global business director for UOP, describes what attracted UOP to this partnership, saying "A key distinguishing feature of the OXO-D process is the more than 40 years of operating experience. This operating experience allows TPC and UOP to understand and position on-purpose butadiene technology for our licensing customers." Rekoske goes on to emphasize that timing is key for this collaboration, stating that "This is not a technology that needs a long development period or a long market incubation period — the opportunities are now."

## **The Dow Chemical Company**

Both companies stress the importance of on-purpose butadiene production going forward — demand for butadiene-based products, such as tires, is rising, as traditional feedstocks are becoming less readily available. "Lighter feedstock slate means, on average, fewer kilograms of butadiene produced per metric ton of ethylene produced. On-purpose butadiene technologies will be needed to fill this gap," explains Rekoske.

With the ongoing flurry of activities in the shale-gas sector, TPC Group sees global potential for the licensing of the OXO-D process. Miguel Desdin, senior vice president and chief financial officer of TPC Group states that "The global market will need on-purpose butadiene to meet future demand, and in order to satisfy that demand, multiple on-purpose butadiene plants in various regions of the world will be required." Desdin goes on to say, "Since the announcement, there has been a significant amount of interest in the technology. UOP is currently in the process of creating a licensing package for the OXO-D technology, which will be available to prospective licensees in the fourth quarter of 2014."

In the earlier stages of development is another technology partnership focused on butadiene, also announced in June 2014, by The Linde Group (Pullach, Germany; [www.linde.com](http://www.linde.com)) and BASF SE (Ludwigshafen, Germany; [www.basf.com](http://www.basf.com)). The two companies are collaborating on the development and licensing of an on-purpose route from butane to butadiene via butenes. For butene synthesis from butane, BASF is contributing a high-yield monolithic catalyst. In the presence of a metal-oxide catalyst, those butenes are then subsequently converted via an oxydehydrogenation step into butadiene. Although the process is still quite new, progress to commercialization is moving ahead, with developments occurring at both kilogram-scale and pilot-plant-scale operations in Ludwigshafen (Chem. Eng., July 2014, p. 14).

Last year, Wison Engineering Ltd. (Shanghai; [www.wison.com](http://www.wison.com)) introduced its own on-purpose butadiene technique, also based on oxidative dehydrogenation principles (Chem. Eng., June 2013, p. 15). With a proprietary high-yield catalyst in its arsenal and a process-design package completed, Wison expects to announce a license agreement for commercial deployment of the technology in the coming months.

Another on-purpose technology developed in response to the prevalence of lighter cracking feedstocks and the associated reduction in butadiene supply is the butene-to-crude-butadiene process (abbreviated BTcB), which was introduced by Mitsubishi Chemical Corp. (MCC; Tokyo, Japan; [www.m-kagaku.co.jp](http://www.m-kagaku.co.jp)) at the 2014 American Institute of Chemical Engineers (AIChE) Spring Meeting. The BTcB process (Figure 4) involves the oxidative dehydrogenation of a C4 mixture to produce 1,3-butadiene in the presence of air, steam and a very selective catalyst. Yields are estimated to be 10–25% higher than past butadiene-production technologies, per MCC's evaluations. Also, the catalyst achieves a very long operational life without the need for regeneration, says the company. The reaction runs at ambient pressure, and operating temperatures are typically between 300 and 400°C. MCC also estimates that this process involves up to 80% less wastewater than past butadiene technologies, decreasing the environmental impact of operations.

The process is flexible enough that all industrial C4 mixtures, including n-butenes and C4 streams from naphtha cracking and fluid-catalytic-cracking (FCC) operations can be processed to produce butadiene. The feedstock versatility of this process makes it feasible to retrofit into an existing facility or construct new-build plants. Testing at a demonstration plant with a capacity of 200 metric tons per year (m.t./yr) and development of a process design package were both completed in 2013, and technology licensing activity commenced in 2014. Currently, feasibility studies for commercial plants are being executed with potential customers.

## **Mitsubishi Chemical**

### **Bio-based butadiene**

While many groups are investigating on-purpose butadiene solutions that utilize existing chemical streams (like butene or butane) as feedstock, others are investing in bio-based routes to alleviate concerns associated with butadiene availability. Last fall, a bio-based butanediol process technology from Genomatica (San Diego, Calif.; [www.genomatica.com](http://www.genomatica.com)) was awarded the Kirkpatrick Chemical Engineering Achievement Award (Chem. Eng., November 2013, pp. 15–19). In the months since winning the Kirkpatrick Award, Genomatica has announced multiple milestones in developing its next bio-based process technology focused on the production of bio-based butadiene. They have announced two high-profile partnerships with Braskem S.A. (São Paulo, Brazil; [www.braskem.com.br](http://www.braskem.com.br)) and Eni S.p.A.'s (Rome; [www.eni.com](http://www.eni.com)) chemical subsidiary Versalis.

The combination of these strategic collaborations gives Genomatica global reach for the licensing of its bio-butadiene technology. Under a December 2013 agreement, Genomatica and Braskem will together develop and commercialize a process to make butadiene from renewable raw materials. With this agreement, Braskem gains exclusive licensing rights to use the technology in the Americas. The Versalis partnership is targeted on licensing activities for bio-butadiene production in Europe, Asia and Africa, and will specifically focus on using non-food lignocellulosic biomass as a raw material.

Genomatica sees global viability for bio-butadiene, citing shifting refinery feeds and an increased awareness of product sustainability. The company says that the butadiene development program is off to a fast start, with \$100 million in industry investment and strategic partners with commercialization intent.

Genomatica's butadiene platform employs proprietary microorganisms that convert biological feedstocks into butadiene directly or via an intermediate. All of the steps in these metabolic pathways have demonstrated functional expression. A patent was granted in November 2013 covering a method for the direct production of butadiene. According to the company, the process involves all aspects of separation and purification to deliver a chemical product that will work in existing applications without requiring changes by downstream users. This versatility, along with the use of renewable feedstocks, are the main aspects that have drawn commercial interest in the process.

Another company seeking a renewable pathway to butadiene is Cobalt Technologies (Mountain View, Calif; [www.cobalttech.com](http://www.cobalttech.com)), which has developed a fermentation platform that takes sugars sourced from cellulosic biomass and converts them into n-butanol, which can subsequently be reacted to form many other chemicals, including butadiene. The ability to leverage the flexibility of n-butanol as a chemical starting point is a huge benefit, says Andy Meyer, president of Cobalt Technologies. "N-butanol is an incredible building block into other renewable chemicals and fuels. Given our cost position in the production of n-butanol, and given the impact of shale gas on C4 molecules, it became a natural fit to pursue butadiene as a product platform."

According to the company, Cobalt is finalizing a joint-development agreement with strategic partners in Asia, which will complete the work required to scale the remaining elements of the technology. "Upon successful completion, we plan to move forward with commercialization with our Asia partners and further monetize the technology globally through other licensing and partnership arrangements," says Meyer. Cobalt is also in the preliminary stages of pursuing various opportunities in the U.S.

Cobalt and Genomatica are just two of the many companies at the forefront of bio-based butadiene technology. Several other notable developments have been announced in the past year, including the BioButterfly project, a research partnership between Axens (Rueil-Malmaison, France; [www.axens.net](http://www.axens.net)), IFP Energies Nouvelles (Rueil-Malmaison, France; [www.ifpenergiesnouvelles.com](http://www.ifpenergiesnouvelles.com)) and Michelin (Clermont-Ferrand, France; [www.michelin.com](http://www.michelin.com)) to create and market a process for producing bio-sourced butadiene. Scoped for eight years, the project is focused on the need for alternative raw-material sources for the synthetic rubbers industry, and, with €52 million in backing, the partners hope that it will be a major step toward a more environmentally friendly rubber industry.

Additionally, Global Bioenergies (Evry, France; [www.global-bioenergies.com](http://www.global-bioenergies.com)) was granted a patent in April 2014 for production of bio-butadiene via enzymatic dehydration. Further development of this process is the scope of a partnership with Synthos Group S.A. (Oswiecim, Poland; [www.synthosgroup.com](http://www.synthosgroup.com)). Also investigating enzymatic technology for butadiene production is Arzeda Corp. (Seattle, Wash.; [www.arzeda.com](http://www.arzeda.com)), which has designed specific enzymatic pathways to convert biomass into butadiene. For the process development of this technology, Arzeda has collaborated with Invista (Wichita, Kan.; [www.invista.com](http://www.invista.com)), citing butadiene price volatility as one of the main drivers behind this partnership.

## **LanzaTech**

### **Utilizing waste gas**

A novel technology developed by LanzaTech (Skokie, Ill.; [www.lanzatech.com](http://www.lanzatech.com)) aims to create a platform for butadiene synthesis from waste-gas feedstocks. The feed gases for LanzaTech's process can come from a variety of sources, both industrial and biological, including offgases from steel mills and CPI plants, and syngas generated from municipal solid waste or agricultural waste.

Together with SK Innovation, (SKI; Seoul, South Korea; [www.sk.com](http://www.sk.com)) in a partnership announced in late 2013, LanzaTech plans to commercialize a two-step platform to create butadiene from waste gases that contain carbon monoxide (CO). First, through a patented fermentation process, an acetogenic microbe converts the CO from the feed gas into 2,3-butanediol and ethanol. Via downstream catalytic technology provided by SKI, the 2,3-butanediol fermentation intermediate undergoes double dehydration to form 1,3-butadiene.

The biochemical pathway used in LanzaTech's process (called the Wood-Ljungdahl pathway) for fermentation to 2,3-butanediol is shown in Figure 5. A hallmark of this process technology is its ability to run continuously rather than in batches. "Syngas can be constantly processed and butanediol can continuously pass to the catalysis step," says Alice Havill, senior process engineer and separations lead at LanzaTech. With advanced lab-scale testing underway at both companies, a pilot demonstration of this technology is planned for the first quarter of 2015 at SKI's research facility in Daejeon, Korea, with an eventual goal of making the platform available for licensing.

Another benefit of this process is its versatility. As seen in Figure 5, either CO or CO<sub>2</sub> can be used as a raw material to synthesize butadiene. LanzaTech has partnered with Invista on further development of processes utilizing a CO<sub>2</sub>/H<sub>2</sub> feedstock, targeting the nylon 6 and 6,6 product chain as a potential application for the butadiene product. Commercialization for this project is expected in 2018.

Commercial interest has been piqued, especially in the areas of polymers, synthetic rubbers and industrial solvents, with companies requesting samples of fermentation-based butadiene as a "drop-in" replacement for butadiene produced via traditional methods. LanzaTech touts the technology's unique feedstock as a driver for commercial success, citing price fluctuations as a crucial factor in the development of new butadiene-production techniques, not only in the case of crude oil, but also in the sugar-based feedstocks that are used for many bio-based routes, which can experience similar price volatility. According to Havill, "LanzaTech has developed an innovative platform that recycles carbon-rich waste gases and residues and converts these local, highly abundant waste and low-cost resources into sustainable, valuable commodities." She continues, saying "The need for new butadiene sources will only be exacerbated by the rising global demand for butadiene-based products. This will especially be evident in the growing consumption of rubber in emerging markets — the commercial reach is global."

### **Eliminating butadiene**

The use of alternative raw materials can also allow companies to decrease their reliance on butadiene. At the 2013 PCI American Nylon Symposium, Rennovia, Inc. (Menlo Park, Calif.; [www.rennovia.com](http://www.rennovia.com)) announced the demonstration of a continuous bio-based pathway to hexamethylenediamine (HMD) that utilizes widely available, renewable feedstocks. Traditionally, HMD, an important component in the production of nylons and polyurethanes, is produced from a butadiene hydrocyanation reaction forming adiponitrile, which is then hydrogenated to HMD. Rennovia's new process uses glucose as a raw material for a two-step catalytic conversion to HMD — no butadiene is required. The process has been demonstrated to run continuously, and the construction of a mini-plant is planned for 2015. In February 2014, Archer Daniels Midland Co. (ADM; Decatur, Ill.; [www.adm.com](http://www.adm.com)) invested \$25 million for the advancement of Rennovia's renewable technologies. Subsequently, Genomatica announced in August 2014 that they would begin developing bio-based routes to various nylon intermediates, including HMD, caprolactum and adipic acid.

Others are searching for alternative products altogether. In addition to their butadiene partnership with Genomatica, Versalis has joined forces with agricultural biomaterials company Yulex Corp. (Phoenix, Ariz.; [www.yulex.com](http://www.yulex.com)) for the manufacture of biorubber materials using guayule, a renewable, non-food crop, as a raw material. Plans for an industrial production facility in Europe are underway, where the biorubber will be a supplementary product to Versalis' traditional butadiene-based synthetic rubber. Once again, forecasted scarcity and price volatility of butadiene are among the factors driving this partnership.

### ***On-purpose chemistry's future***

In the case of butadiene, it is clear that on-purpose and bio-based technologies are not merely a fad. Companies are investing and showing confidence in the commercial potential of these processes. On the future of on-purpose technologies in the CPI, Dow's Bob Maughon remains optimistic about the industry's willingness to adapt, saying, "In general, we were forced into the co-product ecosystem and we learned to love it. I am convinced that we will learn to love the on-purpose world even more." He also emphasizes one major positive aspect of an on-purpose economy: companies can apply capital to make precisely the product they want. There are obviously great opportunities in the field of on-demand production technologies for byproducts of crude-refining processes. Beyond butadiene, speaking about the next on-purpose trend on the horizon, Maughon explains that cyclopentadiene, like butadiene, is a cracker co-product with many uses. However, there are no on-demand routes to it currently. Also among the chemicals affected by the move toward ethane-only cracking are isoprene and piperylene, as well as aromatics like benzene, toluene and xylene. It seems likely that companies will continue investigating advanced butadiene process technologies, and perhaps they will follow suit for cyclopentadiene and other chemicals.

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