Mastering the challenges of the energy and raw materials markets

The global energy and raw materials markets are in a state of flux. The supply of raw materials is changing, and new systems and processes are replacing old ones. However, Evonik’s Catalysts Business Line is ready for the changes. Their customers will be able to count on their exceptional flexibility, innovative strength, and practical mindset for years to come.

A major part of the world’s hunger for energy will still be met by coal, oil, and natural gas even in the year 2040. This was the conclusion drawn by the International Energy Agency in the most recent version of its World Energy Outlook published in November of last year. The report states that crude oil, coal, and fossil fuel gases will continue to be our most important sources of electricity, heat, and chemical raw materials for the foreseeable future. Does that mean everything is just business as usual?

Not by a long shot: energy markets have seen more drastic change over the past several years than they have in quite a long time. The practice of fracking has opened up unconventional sources of oil and gas lying deep within the rock (tight oil and tight gas),...
Dear Reader,

It is amazing how many things have changed within the last year which have a significant impact on our customers’ markets and therefore our markets: The continued success story of shale gas and tight oil in the US (other countries may follow), the dramatic drop of crude oil prices going along with breaking the power of the OPEC cartel, the “new normal” of only 7% GDP growth in China, the devaluation of the EURO against the US$ and other currencies, and hopefully the potential comeback of Iran as a growth market for petrochemical and chemical industry in the Middle East, just to name a few. These market fundamentals change the competitive position of products and processes. For instance bio based chemical building blocks, which were quite competitive at crude oil prices above 100 US$ / bbl, are no longer an economical alternative, hampering new process and catalysts development in case the low oil prices persist. You can read more about this on the following pages.

The review article in this Catalysts Insight issue on BDO processes is also a good example how raw material costs, catalysts, process technology, and geographical factors impact the preferred route. It is intriguing to see how many commercially established processes, all with sophisticated catalyst technologies, exist to make a “simple” molecule such as 1,4-Butanediol.

Is India coming back again with the new government being more business friendly? We shall see, because coincidently the Evonik Catalysts Business Line has completed the acquisition of Monarch Catalyst Pvt. Ltd. in India, located near Mumbai. Monarch is active in oils & fats hydrogenation catalysts, activated base metal catalysts and precious metal catalysts – an excellent strategic complement to our existing business with a production site in an attractive growth region. Closing took place on June 5, 2015 and you will certainly read more about this acquisition in the next issue of our magazine.

As always: please let us know at www.evonik.com/catalysts your opinion and suggestions of what you would like to read here in future issues.

Happy Reading

Dr Wilfried Eul
Senior Vice President
Head of Business Line Catalysts
wilfried.eul@evonik.com
It makes no fundamental difference whether a base chemical is derived from traditional or unconventional sources of oil or gas. Changes in the energy market, however, mean that supply structures, process requirements, and the prices and availability of raw materials can change as well – parameters that determine whether (petro)chemical processes will be profitable and how well the catalysts used will perform. This transformation of the global energy market is also ushering in changes in demand and new challenges for Evonik’s catalyst developers.

A prime example of this is propylene, one of the most important starting materials in petrochemical applications. Roughly two-thirds of global production is earmarked for manufacturing polypropylene (a bulk plastic made from propylene) and important chemical intermediates such as propylene oxide, butyraldehyde (and oxo alcohols), cumene, acrylonitrile, acrolein, and acrylic acid.

For a long time, propylene was obtained almost exclusively as an ethylene by-product either in steam crackers or in catalytic cracking processes at refineries. In a steam cracker, a mix of hydrocarbons from petroleum is split into shorter molecules. In recent years, the propylene-to-ethylene ratio in the mix of cracker products has been thrown off balance due to rising demand for propylene. The recent change to lightweight blends of reactants produces less propylene. Therefore important players in the US, China, and the Middle East are increasingly looking to new plants and processes capable of selectively generating propylene from low-cost, short-chained hydrocarbons such as propane or methane.

What is known as “shale oil” (tight oil) and “shale gas” (tight gas) now allow refineries to obtain significantly larger quantities of the starting material (propane) at much lower prices than was the case just a few years ago. As a result, thermocatalytic conversion of propane has become an increasingly
important alternative route to propylene. Over the past five years, roughly 15 new plants have been constructed around the world to accommodate the propane dehydrogenation process, and more than 10 additional plants are in the project development or planning stages. This has increased the demand for new specialty catalysts to drive reactions such as selective hydrogenation, which breaks down the undesirable multiple bonds arising as by-products of the propane dehydrogenation core process. Evonik makes catalysts that selectively hydrogenates these by-products. Not only does this prevent coking within the reactor system, but it also increases propylene yields while keeping by-products to a minimum, resulting in an increased cost efficiency of the overall process.

Changes in the energy market are reinforcing two major trends in catalyst development. On the one hand, modern methods are expected to generate as few by-products as possible and consume as little energy as possible. That requires catalyst systems to be highly selective and active. Also, certain impurities in the reactor feed have an impact on product life, and manufacturers are increasingly looking for catalysts that are not sensitive to these substances such as sulfur. This is where Evonik’s expertise with tailor-made catalysts comes into play. The benefits of customized catalysts are twofold: they increase the yield and efficiency of processes and methods, plus they can facilitate a new breakthrough synthesis route to counter changing raw materials supplies.

Renewable resources have to be part of any discussion of energy markets, as roughly ten percent of all chemical products are already made from bio-based raw materials. One of the blockbusters in this market is bioethanol obtained by fermenting sugars derived from plant material, and leading the way over the past ten years are the United States and Brazil, which have built up enormous bioethanol production capacities. Today’s global output from bioethanol plants is roughly the same as the amount of propylene produced throughout the world. While the lion’s share of this alcohol is burned as a gasoline additive, bioethanol is also becoming increasingly important as a chemical raw material.

Evonik’s catalyst experts have various projects underway to explore the potential for using bioethanol in new catalytic processes. Currently, a number of projects of the Catalysts Business Line (within the Industrial & Petrochemicals market segment) is focused on bio-based developments. Working alongside customers, researchers are investigating conditions for manufacturing high-quality chemicals, such as solvents or monomers, from reactants like ethanol. The company uses its many years of experience with tailor-made catalyst systems to find new solutions for new questions: Which new or modified catalyst is most suitable? How well does it perform in a large-scale plant? What basic process engineering operations are needed for the scale-up process to yield the ideal catalyst?

It is an open secret that the predominant price of oil always defines the search for biological alternatives: high oil prices make investing in new bioprocesses worthwhile; when prices are low, however, interest in bio-based processes vanishes fairly quickly. That, however, is very short-sighted. Over the long term, processes based on renewables will continue to gain importance, as renewable resources often have better energy and emissions profiles, foster innovation, and, last but not least, can ease our dependence on fossil fuels – the key reasons why renewable raw materials receive political support.

The world is clearly going to continue needing more energy. But because no one is currently in a position to say how production structures, suppliers, and markets will look like in ten or twenty years. Most public debates revolve around short-term shifts in supply and demand. While fracking, for instance, is generating considerable discussion and headlines, in the greater scheme of things it only accounts for a relatively small portion of the world’s supply of energy and raw materials. Plus, the profitability of unconventional deposits grows and shrinks as crude oil prices rise and fall. The same applies to the boom in biomaterials. The rate at which bio-based raw materials grow in importance on a global scale depends on a number of factors, not least of which are the political environment and the willingness of industry to make the corresponding investments.

One thing is certain: the variety and quantity of raw materials are changing all over the world. Another certainty is that the only players that will rise to these new challenges are those that are flexible, reliable, and practical in their constant efforts to find the best solutions for their customers in a changing market. The Catalysts Business Line has long embraced this attitude. The catalysts that the business line develops in collaboration with customers and partners are competitive – in business, technological, and ecological terms – and will outlast the rapid ups and downs in the media and popular opinion. They will also help ensure that highly efficient processes will be available for the future.

Contact persons:
Tim Busse
Dr Hans Lansink Rotgerink
3 questions for ...

... Dr Claus Rettig,
chairman of the Management Board of the Resource Efficiency Segment

1: The Catalysts Business Line now belongs to the Resource Efficiency Segment. Sounds logical, right?

Our segment is in fact the right home for Evonik’s catalysts business – we are, after all, the specialty chemicals segment at Evonik. We focus on solutions for industrial customers and applications, so the catalysts business fits in perfectly. What’s more, our catalysts enable the efficient use of resources such as raw materials and energy.

2: The new segments manage the operational business of Evonik. What advantage does that offer for (catalyst) customers?

The new Evonik structure is less centralized, which means it is more flexible and above all quicker at making major decisions. The business systems and the strategy of our Resource Efficiency Segment are aligned with our specific customer groups and markets. Our segment is made up of 9 different business lines, some of which serve the same customers. In the future, our customers should perceive better coordination between the individual units. Furthermore, we hope to become significantly more innovative, which is why we have bundled our research and development together in the segment.

3: How does the Segment Management Board plan to further develop the catalysts business?

The catalysts business is one of our business areas in which we want to see substantial growth – on a global level. To help achieve this, we will be more active in looking into suitable acquisition options. A first example of this is the takeover of the Indian catalyst specialists, Monarch. The acquisition of Monarch has not only expanded our technology basis, but also our global presence.
Success in difficult conditions

In 2014 Evonik performed well in difficult market conditions and achieved its forecast targets. Speaking at the Evonik Financial Press Conference in Essen, Germany, Evonik Industries AG Chairman Klaus Engel stated, “We invested in demonstrating a good deal of ‘Power to create.’”

“We did our homework and are now poised for a new phase of profitable growth.” In the past year, he explained, Evonik had made worldwide investments in new production capacities, in innovation, and in its employees, had continued optimizing its administrative and cost structures, and had solidified its sound financial profile. “Our new Group structure allows far more differentiated management of the various business and more targeted development,” he pointed out.

The stage has been set for fiscal 2015 sales and operating profit figures to be slightly higher than those of the previous year, Engel said, outlining the company’s expectations. Given the strong start to the year he is optimistic that Evonik will achieve its targets.

Evonik intends to continue its disciplined growth strategy based on its strong performance and solid financial profile. “We will mobilize the company’s resources and funds for further growth,” said Engel. He also said that innovations are the driving force of Evonik’s growth strategy. The aim is to strengthen Evonik’s leading market positions and to benefit from megatrends such as health, nutrition, resource efficiency and globalization.

“Our goal is to address the ongoing change in our sector and play a part in shaping it from a position of strength,” Engel continued. In 2014, Evonik invested €1.1 billion in new production facilities, including around €420 million at its German sites. The largest single investment in the company’s history prior to this had been the methionine complex in Singapore, which came on stream last year.
Innovative packaging for a great product

Evonik now offers Raney-type nickel catalysts in combi drums, which offer major advantages over standard steel drums.

Raney-type nickel catalysts from Evonik have long proven their value in the pharma, agro chemicals and food ingredients industry. They are used for manufacturing sorbitol (a low-calorie sugar), by hydrogenation of glucose, and for synthesizing active pharmaceutical ingredients and intermediates. Such applications require high-quality materials according to the regulatory standards for these industries. The catalysts are metallic nickel skeleton materials with a very large internal surface. Due to their pyrophoric properties they are classified as dangerous goods that generally require the catalyst to be shipped as an aqueous suspension. Exemptions are so called pellets, where the catalyst is imbedded in fats or waxes for use in non-aqueous system. Up to now, the catalyst suspension has been stored and shipped to the customer in steel drums that are coated on the inside and outside and filled to just under the brim. The drum lids have a pressure relief valve to release small quantities of hydrogen to the atmosphere. The hydrogen is permanently liberated from the catalysts.

Occasionally the steel drum corrodes at the interface between the liquid and gas phases. This phenomenon is due in part to hydrogen gas, which is constantly being released. Under unfavorable storage or transportation conditions (higher temperatures or long storage times) it diffuses through the coating layer. This causes the coating to peel away from the steel, allowing local areas of corrosion to develop. While such local corrosion generally does not impair the catalyst performance, concerns and complaints customers in particular from the pharma and food ingredients industries were reason enough to take action.

Evonik experts first tried testing new coating systems on standard steel. When that did not work, they decided to introduce an innovative packing known as a combi drum. A combi drum is a steel drum coated with a special black finish; then a highly stable internal drum made of durable plastic is pressed into this outer drum like a liner, fitting just over the edge of the drum. The self-contained inner container is so robust that the drum will not leak, even if the outer wall is damaged, thus preventing unwanted release of the hazardous material.

Customers who obtain Raney-type catalysts in standard drums do not need to make any changes to their handling and emptying equipment, because the dimensions of the combi drums correspond to those of common drums. The internal liner is stable enough that the catalyst can be stirred in the drum itself. The previous standard drums will remain in our portfolio along with the new combi drums.

Contact: martin.bauer@evonik.com

Four advantages of combi drums

- Internal plastic container prevents direct contact between the product and the wall of the drum
- No modifications to existing handling and emptying equipment are required
- The catalyst can be stirred within the stable internal drum using suitable stirrers
- Outer wall of the drum treated with a special, durable finish
Twice as many reasons to celebrate

Evonik catalyst production in Tsukuba, Japan, celebrated its 25th anniversary in October 2014. The occasion also provided an opportunity to honor employees for accident-free operation from day one.

“After a difficult start, the breakthrough for our catalysts business in Japan came in the middle of the last decade when we successfully implemented a project for a key Japanese customer,” said Ulrich Sieler, president of Evonik Japan, speaking at the awards presentation. After this milestone, production volumes and the number of customers rose steadily. Picking up where Sieler left off, Tsutomu Nishio, the site manager and production manager for catalysts in Tsukuba, added, “Catalyst production conditions are very complex, and involve hazardous materials, extremely valuable precious metals, and a variety of constantly changing processes that require a great deal of manual labor – an environment that underscores the value of this achievement. Over the past three years, we have implemented several investment projects without interrupting operations or compromising production. Doing so has created additional challenges, but our employees have met these with flying colors,” Nishio went on to say.

The site employees were also recognized for their achievement in occupational safety: ever since it started up on September 27, 1989, the site has operated accident-free and without a single workday lost due to an accident. That is such an outstanding and rare achievement for a chemical production site that it has by far surpassed Evonik’s highest safety award – platinum for 20 accident-free years. Dr Wilfried Eul, Head of the Catalysts Business Line, congratulated the employees: “You can all be very proud of your accomplishments in occupational safety, in health and environmental protection, and in your business performance. All of our workers and supervisors in every area of the business line have always made on-the-job safety and environmental protection their top priority, agreeing upon clear goals and rules, and consistently monitoring for compliance. We encourage you to never stop giving it 100%.”

The team in Tsukuba produces chemical catalysts and specialty preparations containing precious metals, and operate Applied Technology laboratories for products containing precious metals. Evonik produces precious metal powder catalysts at six sites around the world: Tsukuba (Japan), Hanau (Germany), Calvert City (Kentucky, US), Shanghai (China), and Udaipur (Rajasthan, India). Precious metal powder catalysts are used in the pharmaceuticals, agrochemicals, fine chemicals, and industrial chemicals industries to provide economical, selective synthesis routes for a wide range of products.

Located roughly 60 km northeast of Tokyo on Japan’s main island of Honshu, Tsukuba was planned in the 1960s as a “science city” and is home to universities, public and private research institutes, and countless high-tech companies. Besides the catalyst production Evonik’s Tsukuba site provides services for pharmaceutical products and the Evonik Japan Coatings Lab, which the company operates to provide tailor-made solutions for customers in the paints and coatings industry.

Contact: hideo.funabashi@evonik.com

Evonik has been producing precious metal powder catalysts at its site in Tsukuba, Japan, for 25 years.

Evonik Tsukuba Site

1989 Start of Production
1989 – 2005 Customer base developed
2006 – 2007 Growth project launched aimed at strengthening marketing activities and technical support
2009 Capacity expanded with new plants
2011 Production interrupted for two weeks due to earthquake
2012 Research and development laboratories modernized and expanded
2014 25th anniversary
BDO: “Catalyst Technologies and Raw Materials; which technology will prevail?”

1,4-Butanediol (BDO) is a linear alpha, omega-diol with many industrial applications and an annual growth rate of 1.5 to 2 times that of GDP\(^1\). The main applications are for the production of tetrahydrofuran (THF, 50%), polybutylene terephthalate (PBT, 21%), gamma-butyrolactone (GBL, 13%) and polyurethanes (PU, 12%) as shown in Figure 1 below\(^1\). THF is by far the largest application and approximately 81% of it is converted to polytetramethylene ether glycol (PTMEG) which is a component of cast and thermoplastic urethane elastomers, spandex and high-performance co-polyester-polyether elastomers\(^2\). The second largest use of BDO is the production of PBT performance thermoplastics for the electronics industry. The conversion of BDO to GBL is the third largest application and even though GBL has its own uses in the agrochemicals, pharmaceutical and resin industries; it is also used to produce N-methyl-pyrrolidone and N-vinyl pyrrolidone. A considerable amount of BDO is used as a component in polyurethanes and it has smaller specialty applications as well. Although the applications of BDO are very diverse, approximately ~40% of it is used to make PTMEG and this is the major driver for growth.

---

**Figure 1. The applications of BDO\(^1\).**
Figure 2 displays the history and future of BDO as well as the price to % utilization correlation. This BDO market data came from available reports (1, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12) and data for beyond 2017 were supplemented with information from the database of ICIS Plants and Projects (13) as well as producer (14, 15) and licensor (16) internet sites. One can see that there was a normal relationship between BDO price, plant utilization, BDO capacity and BDO consumption up to 2006. From 2009 to 2012 there was surprisingly an increase in price even though the degree of utilization was falling due to the construction of new BDO capacity. Even though the current BDO price (1620 USD/t) is much lower than that of 2012, there are still plans to build more capacity. Almost all of the new capacity will be in China and Taiwan (1, 12, 13, 15, 16). The only exceptions will be the Bio-BDO plants to be built by BioAmber in North America and by Genomatica in Italy (1, 13). Figure 3 displays the commercial production processes for BDO (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30) and it shows how complex this market has become. BDO is commercially produced with possibly six different feedstocks via different technologies and the market share of each will be determined by its competitiveness.

Commercial quantities of BDO were first produced by the ethynylation of formaldehyde with acetylene over a CuBi catalyst to produce butynediol (BYD) that is then hydrogenated to BDO. Walter Reppe and his co-workers developed this ethynylation process (31, 32, 33, 34, 35, 36) where the Cu acetylide catalyst is doped with bismuth to inhibit the formation water insoluble polymeric cuprenes that can clog up the system (31, 33). The initial ethynylation process used high pressure acetylene over a fixed bed CuBi catalyst (35, 36) and it was difficult to control because acetylene is explosive at partial pressures above 1.4 bar (36). The extra costs and safety concerns of this process limited its use to only BASF, Dupont and GAF (currently Ashland) until the late 1970s (4). This high pressure process has since been replaced with various low pressure safer fluidized bed processes with improved heat transfer properties that use powder CuBi catalysts that may (37, 38, 39, 40) or may not utilize a support (41, 42, 43, 44, 45). These improvements in ethynylation safety and efficiency have made the BDO Reppe process more competitive and accessible.

BDO is commercially produced with possibly six different feedstocks via different technologies and the market share of each will be determined by its competitiveness.
There are 3 main BDO processes based on Reppe chemistry being used today. The most widely licensed and used process was initially developed by Dupont (23, 41, 42, 43, 44, 45) and it now belongs to Invista. The Invista process starts with a low pressure ethynylation that utilizes a fluidized bed of a Bi doped copper carbonate powder catalyst (41, 42, 43, 44, 45) followed by the subsequent hydrogenation of the resulting BYD to BDO over an in-situ activated NiAl alloy catalyst (23). The hydrogenation catalyst is in the form of 6 – 8 or 4 – 8 mesh 42 % Ni / 58 % Al alloy granules that are loaded in the reactor and activated in-situ with a dilute caustic solution that leaches away approximately 8 to 25 % of the aluminum to generate the active catalyst (23). Since beginning licensing activities, Invista will be expected to have sold 15 licenses to Asian customers (~96 % of these are in China) for the production capacity of 1175 kt of BDO by the end of 2015 (14).

Another widely used version of Reppe technology was developed by the GAF Corporation that then became ISP before it was taken over by Ashland. The Ashland Reppe process utilizes a CuBi catalyst supported on a magnesia silicate powder for the low pressure ethynylation of formaldehyde with acetylene and the hydrogenation of BYD is performed in two distinct stages. The BYD is initially hydrogenated in a stirred tank reactor with a powder activated Ni catalyst at the pressure of 13.8 to 20.7 bars and that is followed by a continuous high pressure hydrogenation over a Cu and Mn doped Ni on silica fixed bed catalyst in a polishing reactor (46). Ashland has licensed this technology to Shanxi Sanwei and a Shanxi Sanwei version of this process has been licensed to other companies in China. It is estimated that this technology accounts for 345 kt of the current BDO capacity in the world.

The original Reppe technology was developed at BASF and constant improvements have been made to keep it competitive. The current BASF process utilizes a Bi doped Cu on silica catalyst for the low pressure ethynylation of formaldehyde with acetylene (37) and the BYD hydrogenation is potentially carried out with a version of their NiO/ CuO/MoO4/ZrO2 catalyst that needs to be activated at 250 °C and 150 bar before use (47). It is estimated that at least 350 kt of BDO is produced with this technology and BASF will expand its BDO capacity in the USA by 10 % (14, 48). BASF has also used other BDO technologies and has even formed BDO joint ventures with others. BASF and its joint ventures have a world leading capacity of 670 kt BDO, however, if we do not count the joint ventures, BASF would have the second largest BDO capacity.

Acetylene was previously thought to be too expensive for BDO production (4), however acetylene only provides 29 % of BDO’s weight and the other 71 % comes from cheaper formaldehyde and hydrogen. Furthermore, acetylene produced by the partial oxidation of natural gas is far less expensive than that made from coal via the calcium carbide process (49). In spite of this, 98 % of the acetylene in China is made from coal via the calcium carbide process because China prefers to be self-sufficient by using their large coal reserves instead of imported gas and oil. This Coal-to-Chemicals program in China has led to the resurgence of acetylene based chemical production (50, 51) such as the Reppe process for BDO. The BDO yield for a typical Reppe process is 93 mole % based on acetylene and 90 mole % based on formaldehyde (4) and in some reports it can be calculated to be higher (3). The Reppe technologies have the fewest process steps and the highest yields which make them very competitive.
The Reppe technologies have the fewest process steps and the highest yields which make them very competitive.

Butadiene (BD) was the second feedstock used for the production of BDO. The Toyo Soda Company of Japan was the first to do so on a 4 kt BDO scale. The sequence of this process was BD chlorination to 1,4-dichloro-2-butene (DCB), DCB hydrolysis with sodium formate followed by NaOH neutralization to generate NaCl and 2-butene-1,4-diol (BED) and hydrogenation of BED to BDO over a Ni catalyst (5). This process was only used from the early 1970s to the early 1980s due to uncompetitive high raw material costs. Mitsubishi was the second to use BD and their process acetoxylates BD with acetic acid (HOAc) over a PdTe/C powder catalyst to yield 1,4-diacetoxyl-2-butene that is hydrogenated with a Pd/C catalyst to 1,4-diacectoxybutane and hydrolyzed to BDO with HOAc to recycle to the acetoxylation process (3, 4, 20). Mitsubishi not only uses this process, but they have also licensed it to Nau Ya (1). This process has the BDO yield of 80 to 85% based on BD (1) and its profitability is heavily dependent on the historically broad price swings of BD (3). In 2011 the price of BD was around 3 USD per kg in Asia (52) and Mitsubishi responded by keeping their 30 kt BD line closed for 2 years (53). BD currently costs ~0.81 to 0.90 USD/kg due to its surplus and a drop in demand. However the closing of naphtha crackers and the use of shale gas for ethylene production will drive the availability of BD down and result in higher prices (54), thereby making the future of this technology less certain.

Propylene is another BDO feedstock that has increased its market share since its introduction in 1990 by Arco (now LyondellBasell) (4). The LyondellBasell process starts with the epoxidation of propylene to propylene oxide (PO) with either ethylbenzene hydroperoxide (EBHP) or tertiary-butyl hydroperoxide (TBHP) over a homogeneous Mo catalyst. In the case of EBHP, methyl phenyl carbinol is the coproduct that is dehydrated to styrene for sale in the marketplace. If TBHP is used, terepyr-butylalcohol is the coproduct that can be dehydrated to isobutylene and converted to methyl tertiary-isobutyl ether with methanol. The PO yield with EBHP is 87 – 91% and with TBHP it is 94% (55, 56, 57). PO is then opened up with a Li2PO4 catalyst to allyl alcohol in 94% yield and the side products are propanal, acetone and propanol. The allyl alcohol is subjected to hydroformylation with a rhodium homogeneous catalyst to give a mixture of 4-hydroxybutan-1 (79.1%), 2-methyl-3-hydroxypropan1 (11.3%), propanal (6.4%) and propanol (3.2%). This mixture is then hydrogenated with a powder Raney-type Ni catalyst to BDO, 2-methyl-1,3-propanediol (MPO) and propanol (3, 4). The BDO-to-MPO ratio is controlled by the homogeneous Rh catalyst ligand system and both diols are sold in the market place (58). This BDO process has been successful, however it does have a lot of steps and its profitability depends on the value of its coproducts (53, 54, 57).

The Dairen Chemical Company also produces BDO from propylene (59) and they are currently the world’s largest single BDO producer with a capacity of 630 kt (53). This process starts by the acetoxylation of propylene with HOAc over a Pd+Cu on silica catalyst to yield allyl acetate that is hydrolyzed to allyl alcohol and HOAc (60, 61). The allyl alcohol then undergoes hydroformylation and hydrogenation in a similar fashion to that of the LyondellBasell process (62, 63). Dairen also sells both BDO and MPO (64).

There are two existing BDO processes that use butane. One of these processes was developed by BP, it was later sold to ISP and ISP was taken over by Ashland. Hence Ashland is now producing BDO by both Reppe chemistry and a butane process called Geminox™ (4, 21). This process starts with the oxidation of butane at 93.5% conversion per pass to a mixture of maleic anhydride (MAH) (52% yield), CO and CO2 (21). The maleic acid can be directly reduced with a PdReAg/C catalyst to a 94% BDO, 2% GBL, 1% THF and 3% butanol mixture (21). It was found that maleic acid is very corrosive under the acid to alcohol hydrogenation conditions and if maleic acid is first reduced with a Pd on titania catalyst to succinic acid, there is considerably less reactor corrosion (24, 25, 26). Hence this is now a two-step reduction. One 65 kt BDO plant based on this technology was built in Ohio and there have not been any announced plans to build another.

The other butane technology has been offered by Johnson Matthey Davy Technologies and it also starts with the oxidation of butane to MAH via a process initially developed by Huntsman (4, 21). The MAH yield from butane is also around 50% (21) and butane oxidation over vanadium phosphorous mixed oxide catalysts is typically assumed to yield around 50 to 60% MAH on a molar basis with at least 80% butane conversion (56, 65). The Davy process then converts MAH stepwise to the mono-methyl maleate ester with methanol and then to dimethyl maleate (DMM) with methanol and a macroporous acidic ion exchange resin. The DMM is then hydrogenated to BDO with a copper chromite catalyst (22). Converting MAH to DMM avoids the corrosion problems associated with maleic acid hydrogenation, but it comes with a higher capital investment and extra steps for BDO production. The Davy process is the most successful butane based BDO route and they have sold many licenses totaling more than 700 kt in BDO capacity.

Benzene can also be oxidized to MAH and further reduced to BDO. The oxidation of benzene to MAH is carried out with the V2O5 catalyst in oxygen at...
98% conversion and 70 – 73% yield (29). Although benzene oxidation to MAH is more effective than butane oxidation, benzene is considerably more expensive (66, 67). In the USA and Europe, most of the MAH plants use butane as a raw material due to improved economics and environmental reasons (28, 29). Approximately 81% of all MAH produced in China is from the oxidation of benzene and the remaining 19% is produced from butane (27). The Davy BDO technology has utilized butane oxidation for its MAH source (3, 4) and its current website lists MAH from either butane or benzene oxidation as a viable raw material (30).

The latest raw material for BDO is dextrose that is fermented with gene modified Escherichia coli bacteria to either BDO or succinic acid (SA) that can be further hydrogenated to BDO (17). Genomatica, BioAmber and Myriant have all worked on Bio-BDO and the potential advantages are fewer unit operations, greater selectivity, gentler operating conditions, commodity differentiation with the “bio” label and raw material diversification (68). Genomatica has a direct fermentation route to BDO that does not require a hydrogenation step and BASF has licensed this technology since 2013 (69). Both BioAmber and Myriant produce bio-SA that can be reduced to BDO (17). The future looks promising for Bio-BDO, however this technology has a somewhat lower throughput and it generates a lot of process water. The development of more robust bacteria that could function in concentrated BDO streams could solve these problems.

The upcoming BDO over capacity in Asia will put a lot of pressure on this market and only the best technologies will survive. Figure 4 shows which feedstocks have been used and will be used for the production of BDO. The use of acetylene based Reppe technology has dominated BDO production in the past and it will also dominate it in the future. The largest growth in BDO capacity will be expected to come from Invista Performance Technology licenses to Chinese BDO producers (16). It was thought in the 1990s that the improved economics of the newer butane/MAH based BDO plants would shut down most of the Reppe BDO plants (4), but this never happened due to low MAH yields and the costs of mitigating maleic acid corrosion. Recent information from the database of ICIS Plant and Projects, indicated that three plants known to use MAH as a BDO intermediate are being idled (13, 70, 71). These temporary closures suggest that the predicted growth of BDO based on MAH from either butane or benzene will probably not occur. It was also thought that Bio-BDO would be more competitive than Reppe BDO (17), however the currently low oil prices will probably postpone its rollout and could lead to its reassessment. Another BDO feedstock that may see a downturn is BD due to its anticipated shortages and higher prices that will follow the shift from naphtha to shale gas for ethylene production (54). The only BDO feedstock other than acetylene that is growing would be propylene and this is due mostly to its combination of raw materials costs and acceptable high yields in the corresponding processes. Hence the winning BDO technologies appear to be based on either Reppe chemistry or propylene and not on C4 or bio-feedstocks.

In any case, Evonik is well positioned to work with BDO producers to provide the best catalyst solutions to keep them competitive.

Dr Daniel Ostgard
Evonik successfully completes the acquisition of Monarch Catalyst in India

Evonik Industries AG, Essen (Germany) announces the successful completion of the acquisition of Monarch Catalyst Pvt. Ltd., Dombivli (India) on June 5th, 2015. An agreement to acquire Monarch Catalyst had been announced in March 2015, subject to certain closing conditions. The company employs approximately 300 employees and will be renamed to Evonik Catalysts India Pvt. Ltd. All of Evonik’s future catalyst activities in India will be operated through the newly acquired company. The parties have agreed to keep the purchase price confidential.

Evonik with its Business Line Catalysts is a global leader in producing specialty catalysts, custom catalysts and catalysts components for the Life Sciences & Fine Chemicals, Industrial & Petrochemical and Polyolefins market segments. Monarch’s global activities in oils & fats hydrogenation catalysts range is a broadening of the Evonik catalysts portfolio. The activated base metal catalysts and precious metal catalysts portfolio strengthens Evonik’s positions in India and the Asia region. Monarch’s existing customer base will continue to be served through the established sales channels.

Patrik Wohlhauser, Chief Operating Officer and member of Evonik’s Executive Board sees this acquisition as an excellent opportunity to strengthen the catalysts business in the growth region Asia. “The Catalysts Business Line belongs to the core businesses in Evonik’s Resource Efficiency Segment. With this acquisition we complement our competencies in innovation for products and technologies to make our customers’ processes and products more efficient,” comments Wohlhauser. “The timing of the acquisition fits also well with the changes in India, where the political leaders have put economic growth again on the top of the agenda to leverage the great growth potential the sub-continent of India has,” says Wohlhauser.

“With Monarch’s business in oils & fats hydrogenation catalysts we are one of the globally leading suppliers in this growing market segment,” says Dr Wilfried Eul. Head of Evonik’s Catalysts Business Line. “With the new production site in the vicinity of Mumbai we will be in an even better position to serve our customers in the Life Sciences & Fine Chemicals Market Segment in India and the growth region Asia”, explains Eul.

New HPPO catalyst operating successfully in China

In Jilin (China), the newly opened plant for hydrogen peroxide is operating at full stretch. It is part of an integrated project of Evonik and Chinese company Jishen Chemical Industry, which produces propylene oxide using the hydrogen peroxide to propylene oxide (HPPO) process. Evonik not only supplies hydrogen peroxide to Jishen, it also produces the catalyst required for the process. The raw material for the catalyst – a pyrogenic mixed oxide – is produced at the Evonik site in Rheinfelden (Germany). Scientists from Evonik developed the catalyst, which is based on the zeolite titanium silicalite 1 (TS-1), several years ago especially for the HPPO process. It was first used in the HPPO plant in Ulsan (Korea), where the specialty chemicals company has produced hydrogen peroxide since 2008 – also within the scope of an integrated system.

The catalyst was further developed in a cross-unit project in order to supply Jishen’s HPPO plant with an improved product. Continuous further development like this does more than just contribute towards expanding Evonik’s market position, it also forms the foundation for the success of the HPPO technology by continuously tuning the combination of the process and the catalyst. A completely new generation of catalyst is to be developed as part of a follow-up project aimed at enhancing the catalyst further.
Trade show appearances, conferences and events

<table>
<thead>
<tr>
<th>Trade show appearance, conference, name of event</th>
<th>Date</th>
<th>Where</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEPP 2015: 23rd Annual Polyethylene-Polypropylene Chain Global Technology and Business Forum</td>
<td>June 2 – 4</td>
<td>Zurich, Switzerland</td>
</tr>
<tr>
<td>12th annual Global Petrochemicals Conference</td>
<td>June 9 – 11</td>
<td>Dusseldorf, Germany</td>
</tr>
<tr>
<td>North American Meeting (NAM) 2015</td>
<td>June 14 – 19</td>
<td>Pittsburgh, Pennsylvania, USA</td>
</tr>
<tr>
<td>Chemspec Europe</td>
<td>June 24 – 25</td>
<td>Cologne, Germany</td>
</tr>
<tr>
<td>CPhI China</td>
<td>June 24 – 26</td>
<td>Shanghai, China</td>
</tr>
<tr>
<td>The 3rd International Symposium on Process Chemistry</td>
<td>July 13 – 15</td>
<td>Kyoto, Japan</td>
</tr>
<tr>
<td>EuropaCAT 12</td>
<td>August 30 – September 4</td>
<td>Kazan, Russia</td>
</tr>
<tr>
<td>The 4th Annual Event for Agro, Specialty, and Custom Chemicals</td>
<td>September 9 – 11</td>
<td>Charleston, South Carolina, USA</td>
</tr>
<tr>
<td>ChemOutsourcing 2015 Conference &amp; Exhibition</td>
<td>September 14 – 17</td>
<td>Long Branch, New Jersey, USA</td>
</tr>
<tr>
<td>Advances in Polyolefins 2015</td>
<td>September 21 – 24</td>
<td>Santa Rosa, California, USA</td>
</tr>
<tr>
<td>DGMK International Conference</td>
<td>October 7 – 9</td>
<td>Dresden, Germany</td>
</tr>
<tr>
<td>CPhI Worldwide 2015</td>
<td>October 13 – 15</td>
<td>Madrid, Spain</td>
</tr>
<tr>
<td>CPhI India</td>
<td>December 1 – 3</td>
<td>Mumbai, India</td>
</tr>
</tbody>
</table>

We would be happy to send Catalysts Insight to anyone you know.

Please send us the postcard or contact us directly:

**Evonik Industries AG**

Dr Andreas Freund  
Head of Marketing and Business Development  
Postcode 97-317  
Rodenbacher Chaussee 4  
63457 Hanau-Wolfgang  
**TELEPHONE** +49 6181 59-8735  
andreas.freund@evonik.com

**Imprint**

**Publisher**  
Evonik Industries AG  
Business Line Catalysts  
63457 Hanau-Wolfgang  
www.evonic.com/catalysts

**Editorial team**  
Frank Gmach (responsible)  
Franziska Freudenreich

**Layout/Design**  
Liebchen+Liebchen GmbH  
www.LplusL.de  
Frankfurt am Main, Germany

**Print**  
Druck- und Verlagshaus Zarbock GmbH & Co. KG  
www.zarbock.de  
Germany

**Pictures**  
all pictures © Evonik

Source: R. Ramachandran, B. Glasser, Rutgers the State University of New Jersey  
Source: Axel Mescher (Process Engineering, Drying Technology) and Peter Walzel (Technical University of Dortmund, Germany)

© Liebchen+Liebchen GmbH

The information provided here is, to the best of our knowledge, correct and up to date. They are, however, not binding. They are subject to changes within the scope of technological progress and operational advancement. Our information only describes the characteristics of our products and services and do not constitute any guarantee. The customer is not released from their responsibility to have the functions and/or possible applications of the products thoroughly checked by qualified personnel. This also applies to the protection of third party property rights. The inclusion of trade names of other companies does not constitute a recommendation and does not exclude the use of other similar products.