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On-Purpose Butadiene

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Report Abstract
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INTRODUCTION

Butadiene is predominantly sourced by extraction from the mixed C_4 stream produced in steam crackers. The yield of C_4s from a cracker and the composition of the C_4 stream vary considerably dependent on feedstock and severity of operation. Cracking naphtha yields a large amount of valuable co-products including propylene, mixed C_4s and aromatics, in addition to the primary ethylene product. Although butadiene (and other mixed C_4s) is only a small fraction of the steam cracker output, extractive distillation of the mixed C_4 stream is the source of 95 percent of global butadiene supply. Historically the revenue from these valuable co-products maintained margins for cracking naphtha at a premium to cracking lighter natural gas liquids (NGLs - ethane, propane and butane). This situation, however, is changing quickly.

Due to growing supplies of unconventional sources, U.S. natural gas prices have fallen well below crude oil equivalent. At the same time, ethylene feedstock in the United States has quickly shifted to lighter feeds. The use of ethane as a steam cracker feedstock has risen from 46 percent in 2005 to 65 percent in 2011.

Cracking naphtha yields a large amount of valuable co-products in addition to the primary ethylene product. As crude oil prices surged to new highs in 2008, the cost of naphtha feedstock became considerably less competitive than ethane and other NGLs. With around 3.2 tons of naphtha required per ton of ethylene, the high cost burden of acquiring naphtha pushed margins towards the floor of alternative feedstocks in 2007. Meanwhile, the global ethylene market is expected to continue to shift towards lighter steam cracker feedstock.

Long term decisions around cracker feedstock selection are a key driver on availability of mixed C_4 streams for butadiene extraction. In recent years, a number of underlying factors have combined to drive a modest shift towards the use of lighter feedstocks at steam crackers. The ratio of C_4s to ethylene is dropping as gas-based expansion in the United States and the Middle East outpaces liquids-based developments in other regions. In the United States a number of steam cracking projects employing ethane feed have been announced. In addition there are numerous other cracker expansions being planned for the USGC.

A possible remedy for this shortage of butadiene is butane or butene dehydrogenation particularly in the United States, China and Russia. However, so far only TPC Group and two Chinese firms have announced alternative butadiene capacity additions. This report reviews the current commercial technologies and developing technologies for on-purpose production of butadiene including routes from renewable sources. The outline of this report is as follows:

- An overview of the licensing technology status is given
- Current production technology is discussed
- Specific licensor processes are also described in detail (e.g., OXO-D, Catadiene)
- A patent review has been carried out and developing technologies and improvements are discussed

- Generic cost of production economics are provided
- Commercial end-use applications, global and regional market overview analysis is given

TECHNOLOGY

In the Former Soviet Union (FSU), before the political and economic transition at the start of the 1990s, there was limited access to natural rubber and synthetic rubber feedstocks through imports, and therefore local resources had to be used, (i.e., the plentiful supplies of natural gas liquids). Dehydrogenation was the preferred technology to produce synthetic rubber feedstocks (butadiene and isoprene) from these streams. Butadiene and isoprene are therefore manufactured by the dehydrogenation of paraffins. The processes which have been used for these reactions are versions of Catadiene® (Lummus) and the Yarsintez fluid bed process.

The dehydrogenation of butene has been improved over time through the development of oxidative dehydrogenation, developed by Petro-Tex Chemical (now TPC Group) in the early 1960s.

The process to convert ethanol into butadiene is not new, but rather inefficient. The conversion of ethanol into butadiene was practiced in Germany in the 1930s. Ethanol was converted into acetaldehyde after which an aldolization was performed followed by dehydration. Acetaldehyde could also be manufactured from acetylene. Butadiene and styrene were, in effect, almost completely coal-derived and from this feedstock Buna-S® rubber was developed to support the German war effort. The post war inspection teams visiting German chemical industry installation revealed a tremendous level of innovation including, for example, the production of ethanol from cellulose.

In the post-war asset acquisition strategy of the FSU, the technology for ethanol to butadiene was removed from Germany. Facilities were established in the FSU in places like Togliatti supporting rubber production. However, the FSU in time moved its industry to a platform based on dehydrogenation rather than ethanol. However, the technology has operated outside the FSU, namely in India.

As in many cases feedstock cost is the major driver for the process and that in turn depends on the upstream ethanol process. Exploiting the Brazilian sugarcane base provides the lowest cost ethanol. However, over time a biomass or cellulosic-based ethanol process in Europe or the United States may well surpass such techno-economic performance.

An alternate route to on-purpose butadiene is to convert syngas to mixed alcohols with a fair amount of linear butanols. Then the butanols can be dehydrated to butenes and then dehydrogenated to butadiene.

Another route is to produce n-purpose butadiene from propylene. This route would produce methanol from either coal or natural gas, followed by a methanol to propylene unit or propane dehydrogenation unit, metathesis of propylene to ethylene and normal butenes, and oxidative dehydrogenation of the normal butenes to butadiene. The metathesis of propylene to ethylene and butene was originally patented by Phillips. Historically this route would not have made much sense, as the difference in price between the two was small. However, since the beginning of 2010 the market prices for these two chemicals has diverged and in the last 5 quarters the difference in price has been greater than $1 000 per ton.

Other technology developments by Asahi Kasei, BASF, Braskem, Fina, Genomatica, Gevo, Global Bioenergies, Invista, LanzaaTech, Lummus, Mitsubishi, Mitsui, SK and Uhde are discussed.

PROCESS ECONOMICS

Detailed cost of production estimates are presented for:

- Extractive distillation (ED)
- OXO-D/ED
- BDH (nonoxidative catalytic dehydrogenation)/ODH (oxidative catalytic dehydrogenation)/ED
- Catadiene/ED
- Dimerization/OXO-D/ED (petroleum-based and bio-based)
- PDH (propane dehydrogenation)/metathesis/OXO-D/ED
- MTP (methanol-to-propylene)/metathesis/OXO-D/ED
- Global Bioenergies route
- Gevo route

The current price scenario shows some unexpected results that are discussed in the report. Sensitivity analyses (feedstock price, capex scale) have been carried out.

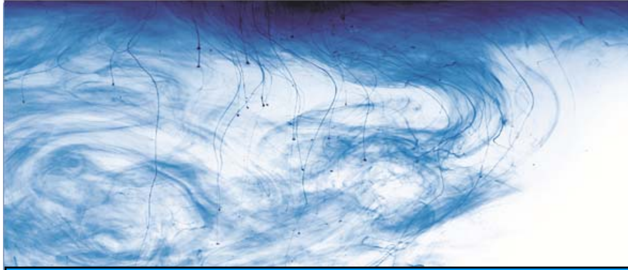
A comparison has been developed for the cost of production of butadiene in various regions including the USGC, Russia, Middle East, and China for 2017.

Detailed cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities consumed (electrical energy, cooling water, fuel etc.), direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate. Capital costs are broken down according to inside battery limits (ISBL), outside battery limits (OSBL), other project costs, and working capital. Major equipment items used in ISBL and OSBL is listed.

COMMERCIAL MARKET REVIEW

Butadiene is a feedstock for the production of a wide variety of synthetic rubbers and polymer resins. In the case of synthetic rubbers, butadiene can be homopolymerized (polybutadiene or butadiene rubber), or copolymerized with a number of monomers, including styrene (SBR, SBS, etc.) and acrylonitrile to produce nitrile rubber (NBR). The properties of the elastomers vary greatly with a number of factors including formulation and polymerization conditions, etc. Butadiene is also consumed in the production of engineering resins, notably acrylonitrile butadiene styrene (ABS), and naphthalene dicarboxylic acid. Butadiene is used as a feedstock for HMDA, lauryl lactam and now caprolactam for the production of different nylons.

- Global supply, demand and trade data is given and discussed
- In addition, supply, demand and trade data is given and discussed according to key regions (i.e., United States, Western European, and Asia Pacific)
- A list of production plants in each of the key regions above is given showing specific plant capacities, owning company, location and annual tonnage produced



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