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Butadiene/Butylenes

PERP 09/10-5

Report Abstract
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INTRODUCTION

This report focuses on the processes for producing pure butadiene and butylenes (isobutylene and 1-butene) as well as co-cracking the mixed C_4 stream from a steam cracker.

CURRENT TECHNOLOGY

In this section, commercial technologies are discussed including:

- An overview of the C_4 integration within an ethylene plant and the options to upgrade the C_4 stream
- The processing of the mixed C_4 steam is considered. The topics of recycle co-cracking, with and without selective or full hydrogenation are discussed and the potential to improve C_4 value
- Selective and full hydrogenation processes and technologies for the mixed C_4 stream that are commercially readily available are discussed. Some of the leading licensors are Axens, UOP (Huels SHP-CB process) and Lummus (BASF Selop® process)
- The processes and technologies for the production of butadiene, are discussed. Over 95 percent of butadiene is produced as a byproduct of ethylene production from steam crackers and recovered via extractive distillation. In certain parts of the world there are still some production units based on on-purpose routes to butadiene (i.e., dehydrogenation technology). The majority of dehydrogenation capacity is found in the Former Soviet Union. These processes tend to be either 2 stage processes based on butane dehydrogenation, or single step processes based on butenes. In the United States, TPC Group Inc. runs its oxidative dehydrogenation plant Oxo-D™ on a campaign basis. In the past ethanol has also been used as a feedstock for on-purpose butadiene (similar to the adol condensation of acetaldehyde)
- Processes and technologies for the production of pure isobutylene are discussed. Isobutylene is produced via four major routes, namely:
    - MTBE Decomposition
    - TBA Decomposition (co-product from Halcon/Arco PO process)
    - Isobutane Dehydrogenation
    - Cold Acid Extraction (CFR)
- The processes and technologies for the production of 1-butene are discussed. There are currently four processes available for license to produce 1-butene, other than as part of an alpha olefins mixture from ethylene oligomerization which is reviewed at the end of this sub section. These processes include:
    - Hydrogenation (Huels SHP)/Fractionation
    - Extractive Distillation (Zeon – Dimethyl formamide solvent)
    - orbutene® (UOP)
    - Alphabutol® (Axens/SABIC developed ethylene dimerization)

In addition butenes can be produced from bio sources, such as corn.

  - Biobutene process technology is discussed

- The interconversion of C4 olefins streams with respect to the main strategic issue of adding maximum value is analyzed. This section is primarily concerned with the inter-conversion of C4 olefin streams in order to add value. Options for converting the mixed C4 stream are covered in detail in a previous section. This has included an examination of hydrogenation technology, extractive distillation for butadiene production and the production of other C4 components. The discussion in this subsection focuses on the integration of technologies which are in use today to inter-convert C4s as part of upgrading chains. The combinations of the following technologies are analyzed in the economic analysis section:
  - Skeletal isomerization
  - Dehydrogenation (specifically Oxo-D®)
  - Olefin paraffin separation via Butenex® (Uhde)
  - Chains with Butadiene extraction; MTBE production; 1-butene extraction

DEVELOPING TECHNOLOGIES

This section discusses the notable patents and inventions that have been awarded concerned with the production of butadiene, isobutylene, 1-butene and 2-butene in the past four years since the last PERP report on this subject. Developments by the following companies are covered:

- BASF
- Fina Technology Inc.
- Mitsubishi Chemical Corp (MCC)
- Saudi Basic Industries Corporation (SABIC)
- Shell Oil Company
- Snamprogetti S.p.A.
- Süd-Chemie
- UOP

ECONOMICS

In this section tables giving cost of production estimates for various technologies are given. The tables include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a full cost estimate (a simple nominal return on capital is also included).

Cost estimates for the following recycle co-cracking processes are evaluated:

- Production of C_4 Olefins via Selective Hydrogenation of Mixed C_4 Stream (Axens)
- Production of Mixed Butanes via Full Hydrogenation of Mixed C_4 Stream (Lummus)
- Production of Ethylene via Steam Cracking of Light Naphtha 2/Butadiene Extraction and Raffinate-1 as a Byproduct
- Production of Ethylene via Steam Cracking of Light Naphtha w/Full Hydrogenation and Recycle of the C_4s
- Production of Ethylene via Steam Cracking of Light Naphtha w/Metathesis (Selectivity hydrogenate the butadiene to butylenes)

The production of mixed C_4 streams is strongly dependent on steam cracker severity and feedstock, as is the butadiene content of the mixed C_4 stream. There are butadiene units which pool C_4 streams from a variety of sources, (e.g., TPC Group in the United States, and Oxeno at Marl in Germany). Given changes in C_4 and contained butadiene make, the production economics of butadiene extraction are likely to vary significantly. A table showing the variation in mixed C_4 and butadiene as a function of cracker feedstock and severity is given.

Cost estimates for the following butadiene production processes are evaluated:

- Production of Butadiene via Extractive Distillation using NMP (BASF Process)
- Production of Butadiene via Oxidative Dehydrogenation (Oxo-D™ Plus Extractive Distillation)
- Production of Butadiene via the Catadiene Process

Cost estimates for the following isobutylene production processes are evaluated:

- Production of Isobutylene via: MTBE Cracking (DD/B Process)
- Production of Isobutylene via TBA Cracking
- Production of Isobutylene via Isobutane Dehydrogenation
- Production of Isobutane via the Butamer Process
- Production of Isobutylene via Acid Extraction

Cost estimates for the following 1-butene production processes are evaluated:

- Recovery of 1-Butene from Raffinate-2 via Fractionation/Hydrogenation
- Recovery of 1-Butene via Super Fractionation alone
- Production of 1-Butene via Fractionation plus Double-Bond Isomerization
- Production of 1-Butene via Extractive Distillation (Zeon)
- Production of 1-Butene via Sorbutene (UOP)
- Production of 1-Butene via Alphabutol

As an example, economics of the full range LAO has been evaluated:

- Production of Alpha Olefins (LAO) via the ChevronPhillips Process

Cost estimates for bio routes to butenes and butadiene have been developed:

- Production of Bio-Butanol via the Blaschek et al, Advanced Continuous ABE (C. biejerinckii with Gas stripping) Process
- Production of Bio-Butanol via Thermochemical Biomass Gasification
- Production of Bio-Butenes via Butanol Dehydration – Fixed Bed
- Production of Bio-Butadiene via the Oxo-D™ Plus Extractive Distillation Process

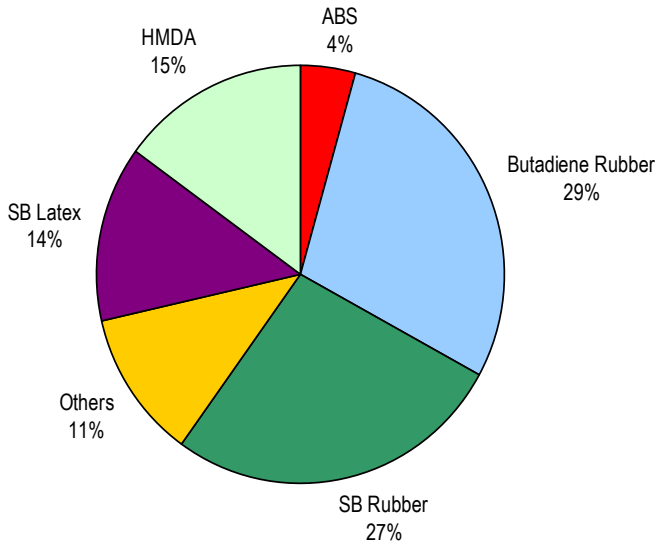
Cost estimates for possible "added value" C_4 routes have been evaluated:

- Production of Pseudo raffinate-2 via the ISOFIN™ (BP ExxonMobil/Kellogg) Process
- Production of Mixed Butenes via the Butenex® (Uhde) Process
- Production of Butadiene via Upgrading Chain w/Selective Hydrogenation (Isobutylene, 1-Butene coproducts)
- Production of Butadiene via Upgrading Chain w/ Selective Hydrogenation (MTBE, 1-butene coproducts)
- Production of Butadiene via Upgrading Chain w/Oxo-D™, Isom, (Isobutylene, 1-Butene coproducts), Butenex®(Base Case: Oxo-D™, Isom, Butenex® Not Operating)
- Production of Butadiene via Upgrading Chain w/Selective Hydrogenation, I(sobutylene, 1-Butene coproducts) (Oxo-D™ Operating; Isom, Butenex® not Operating)
- Production of Butadiene via Upgrading Chain w/Selective Hydrogenation, (Isobutylene, 1-Butene coproducts) (Isom, Butenex® Operating; Oxo-D™ not Operating)

COMMERCIAL ANALYSIS

Components of the C_4 stream are mainly consumed in the production of synthetic rubber (butadiene), polyethylene comonomer (1-butene), specialty chemicals, engineering plastics and solvents. This is illustrated in the figure below which shows the end-use pattern for butadiene consumption in the United States. The family tree of C_4 derivatives is given in the report. C_4 molecules are consumed in contained C_4 steams or as pure components.

U.S. Butadiene End-Use Pattern



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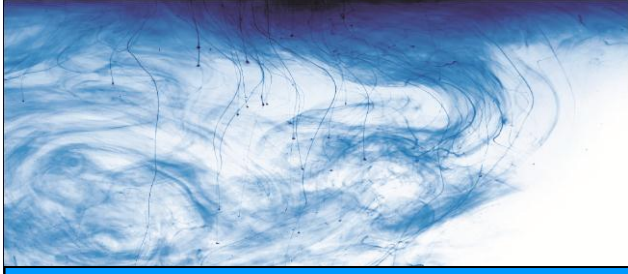
- Butadiene supply, demand and trade data are given and discussed for the United States, Western Europe and Asia Pacific.

- Butadiene capacity listings are given for plants located in the various regions given above, detailing their location, nameplate capacity, process operation and ownership.



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