PERP Program – Butadiene/Butylenes
New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning program has published a new report, ***Butadiene/Butylenes (05/06-5)***. To view the table of contents or order this report, please click on the link below:
http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

C_4 STREAM COMPONENTS

Components of the C_4 stream are mainly consumed in the production of synthetic rubber (butadiene), polyethylene comonomer (butene-1), specialty chemicals, engineering plastics and solvents. The family tree of C_4 derivatives is given in Figure 1. C_4 molecules are consumed in contained C_4 steams or as pure components.

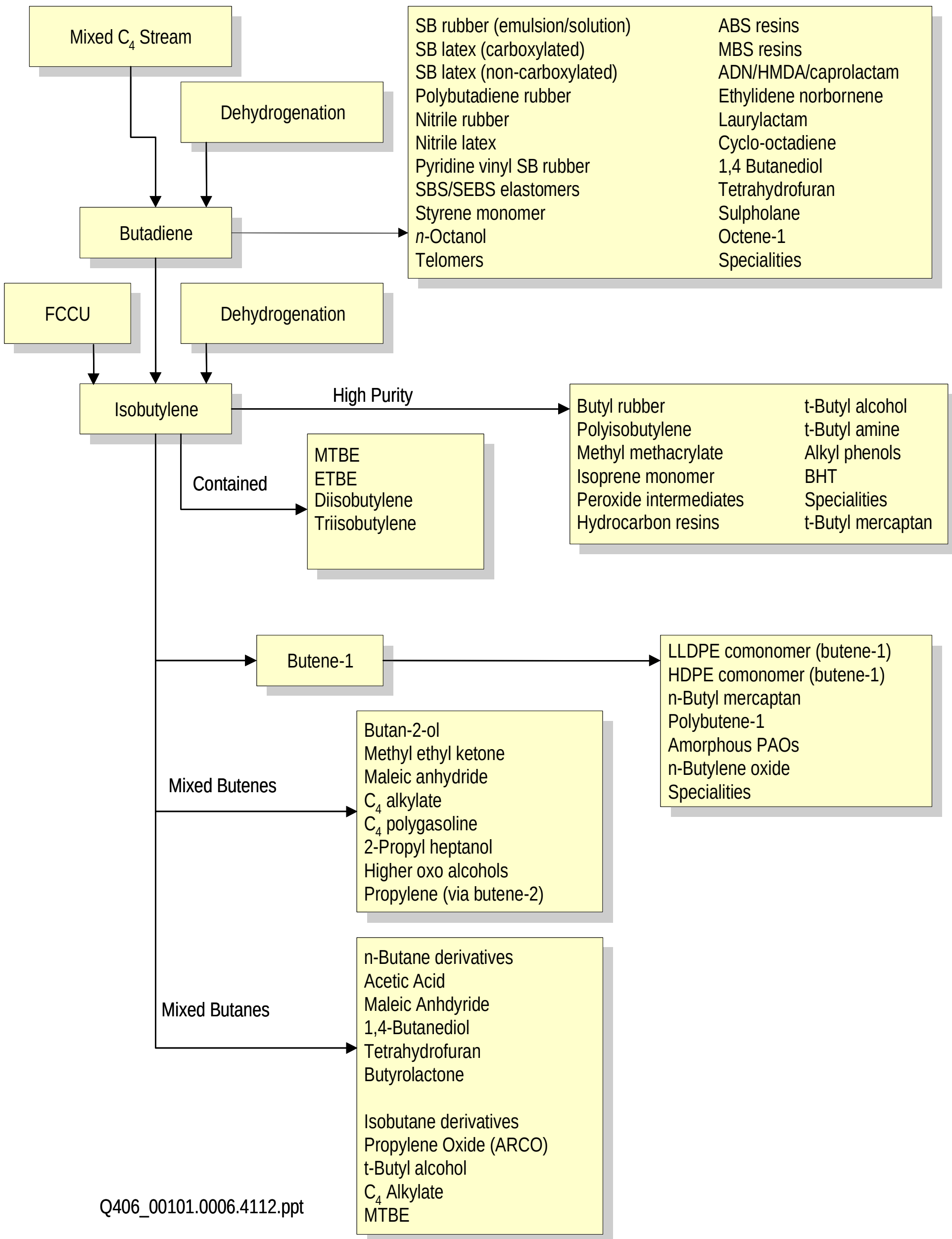
Butadiene

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 rubber, PBR), or copolymerized with a number of monomers, including styrene (SBR, SBS, etc.) and acrylonitrile (NBR). The properties of the elastomers vary greatly with formulation, polymerization conditions, etc.

Butadiene is also consumed in the production of engineering resins, notably ABS, and naphthalene dicarboxylic acid. Butadiene is used as a feedstock for HMDA, laurylactam and now caprolactam for the production of different nylons.

Butadiene has some use in specialties, e.g., the production of tetrahydrophthalic anhydride via reaction with maleic anhydride. However, butadiene is used in the production of ENB – a termonomer for EP rubber production. Butadiene is also used in the commercial production of 1,4-butanediol and tetrahydrofuran. 1,4-Butanediol is a feedstock for the production of specialty polymer resins, including PBT. Tetrahydrofuran finds some use as a solvent, but mostly provides feedstock for PTMEG for the production of Spandex fibers.

Figure 1
The C_4s Derivative Chain



Recently developments in butadiene-based chemistry have included conversion to octene-1 and n-octanol by telomerization synthesis, styrene monomer by cyclodimerization, and new routes to caprolactam.

Isobutylene (2-Methyl Propene)

Isobutylene is mainly consumed in the production of MTBE (or ETBE) which is used as an octane booster and supply of contained oxygen for unleaded gasoline. However, MTBE is being phased out in the U.S.

This versatile molecule can also be used as a pure stream for the manufacture of polymers and specialty chemicals, e.g., peroxides. One of the early uses for isobutylene was the production of butyl rubber during the Second World War in the absence of natural rubber. Other uses for isobutylene include synthetic lubricants in the form of functionalized medium molecular weight oligomers.

Butene-1

Butene-1 is well known as a co-monomer in the production of LLDPE and HDPE. Butene-1 is also consumed in the production of polybutene-1 and various specialties. One such example is butylene oxide which is used to produce polyols in the formulation of gasoline additives.

n-Butenes

n-Butenes can be reacted in the presence of butanes to produce such products as the solvents sec-butyl alcohol and subsequently MEK. Other chemical uses include feedstocks for dimerization and oligomerization in the production of higher oxo alcohols for the manufacture of plasticizers, etc. The bulk of normal butenes are, however, mainly consumed in alkylation units within the refinery. Butenes and isobutane can be reacted in the presence of strong acid catalysts (HF and H_2SO_4) to produce trimethylpentanes (TMP) known as C_4 alkylate. TMPs are highly branched and exhibit high RON and MON values.

n-Butene streams can be treated to maximize the concentration of butene-2 via isomerization. This can be fed to a refinery alkylation unit or be extracted and reacted with ethylene via metathesis chemistry to produce propylene. However, the C_4 stream must be essentially free of butadiene and low in isobutylene.

Mixed and Refined Butanes

Technologies for processing butanes usually involve selective oxidation or dehydrogenation. Butanes are also routinely co-cracked to produce ethylene and propylene.

Isobutane is used as chemical feedstock to produce propylene oxide. This process was developed by Halcon and involves the oxidation of isobutane to tertiary-butyl hydroperoxide. Isobutane dehydrogenation produces isobutylene. Dehydrogenation to isobutylene is usually performed as part of an MTBE complex based on butanes.

n-Butane can be selectively oxidized. Different processes produce very different products. Celanese practices butane oxidation to acetic acid in the United States. The preferred manner of making maleic anhydride is also via n-butane oxidation. Processes are now available to convert n-butane to 1,4-butanediol and tetrahydrofuran. The dehydrogenation of n-butane, whilst being very energy intensive, can be used as a source of butadiene.

ECONOMICS

The report presents economics for various scenarios of recycle co-cracking of C_4's, purification of the pure components, and various approaches for adding value.

The following Cost of Production analyses are provided in the report:

Recycle Co-Cracking

- Selective hydrogenation of mixed C_4 stream
- Full hydrogenation of mixed C_4 stream
- Ethylene via cracking of light naphtha with butadiene extraction and raffinate-1 as byproduct
- Ethylene via cracking of light naphtha with full hydrogenation and recycle of the C_4s
- Ethylene via cracking of light naphtha with metathesis (selective hydrogenation of the butadiene to butylenes)

Pure C_4 Components

- Butadiene via extractive distillation using acetonitrile
- Butadiene via oxidative dehydrogenation of raffinate-2
- Isobutylene via MTBE cracking
- Isobutylene via t-butyl alcohol cracking

- Isobutylene via isobutane dehydrogenation (large scale – Oleflex)
- Isobutylene via isobutane dehydrogenation (small scale – Krupp Uhde)
- Isobutylene via acid extraction
- Butene-1 via fractionation and hydrogenation
- Butene-1 via fractionation
- Butene-1 via fractionation plus double bond isomerization
- Butene-1 via extractive distillation (Nippon Zeon)
- Butene-1 via UOP Sorbutene process
- Butene-1 via ethylene dimerization (Alphabutol process)

Adding Value

- Psuedo-raffinate-1 via skeletal isomerization of raffinate-2 (Isofin Process)
- Mixed butenes via raffinate-2 (Butenex process)
- Butadiene via selective hydrogenation with isobutylene and butene-1 as by-products
- Butadiene via Oxo-D, isomerization, with isobutylene and butene-1 as by-products
- Butadiene via selective hydrogenation with isobutylene and butene-1 as by-products

Regional

Supply/demand forecasts for pure isobutylene, butene-1 and butadiene are also provided.

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