KLM Technology Group Practical Engineering Guidelines for Processing Plant Solutions	KLM Technology Group Engineering Solutions www.klmtechgroup.com	Page : 1 of 74 Rev: 01 September 2013
KLM Technology Group P. O. Box 281 Bandar Johor Bahru, 80000 Johor Bahru, Johor, West Malaysia	**Kolmetz Handbook of Process Equipment Design** **BUTADIENE PROCESSING UNIT SELECTION, SIZING AND TROUBLESHOOTING** **(ENGINEERING DESIGN GUIDELINES)**	Co Author: Rev 01 Mochamad Adha Firdaus Author / Editor Karl Kolmetz

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INTRODUCTION

Scope

This guideline provides the details of the processes for the production of 1,3 – Butadiene and its derivatives. This guidelines discuses butadiene extraction or extractive distillation plants, which produce high purity 1,3-butadiene from raw C_4 (steam cracker) feeds. There are more than 100 such plants in the world. Process layouts considered are: (i) two extractive distillations, whereby in the first stage raffinate-1 is the distillate and in the second stage acetylenic components are removed, (ii) single extractive distillation with superfractionation, (iii) single extractive distillation with selective hydrogenation of acetylenic components. The benchmark also includes butane or butene dehydrogenation plants, which have a different feedstock.

Extractive Distillation is an important tool for the separation of isomers and close boiling species. An extractive distillation solvent is added to the column increasing the relative volatility of the close boiling species allowing distillation to be utilized. Several applications of extractive distillation have been successfully commissioned

General Design Considerations

1,3 Butadiene is a conjungated diene with the formula C_4H_6. It is an important industrial chemical used as a monomer in the production of synthetic rubber. In the United States, Western Europe, and Japan, butadiene is produced as a byproduct of the steam cracking process used to produce ethylene and other olefins.

When mixed with steam and briefly heated to very high temperatures (often over 900^oC), aliphatic hydrocarbons give up hydrogen to produce a complex mixture of unsaturated hydrocarbons, including butadiene. The quantity of butadiene produced depends on the hydrocarbons used as feed. Light feeds, such as ethane, give primarily ethylene when cracked, but heavier feeds favor the formation of heavier olefins, butadiene, and aromatic hydrocarbons.

Butadiene is typically isolated from the other four-carbon hydrcarbons produced in steam cracking by extractive distillation using a polar solvent such as acetonitrile, N-methylpyrrolidone, furfural, or dimethylformamide, from which it is the stripped by distillation.

Most butadiene is polymerized to produce synthetic rubber. While polybutadiene itself a very soft, almost liquid material, copolymers prepared from mixtures of butadiene with styrene and/or acrylonitrile, such as acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene (NBR) and styrene-butadiene (SBR) are tough and/or elastic. SBR is the material most commonly used for the production of automobile tires.

Smaller amounts of butadiene are used to make the nylon intermediate adiponitrile, by the addition of a molecule of hydrogen cyanide to each of the double bonds in a process called hydrocyanation. Other synthetic rubber materials such as chloroprene, and the solvent sulfolane are also manufactured from butadiene. Butadiene is used in the industrial production of 4-vinylcyclohexane via a Diels Alder dimerization reaction.

Storage of butadiene as a compressed, liquified gas carries a specific and unusual hazard. Overtime, polymerization can begin, creating a crust of solidified material (popcorn polymer) inside the vapor space of cylinder. If the cylinder is then disturbed, the crust can contact the liquid and iniatiate an auto-catalytic polymerization. The heat released accelerates the recaction, possibly leading to cylinder rupture.

Inhibitors are typically added to reduce this hazard, but butadiene cylinders should still be considered short-shelf life times. The hazard presented by popcorn polymer is also present in bulk commercial storage tanks. It is important to keep the oxygen concentration in the tanks and any process wash water low in order to reduce the rate of polymerization.

As with other light hydrocarbons, butadiene leaks can be detected bu the formation of ice balls (from the evaporative freezing of water out of the atmosphere) even when the temperature is well above 0^{o}C.

Manufacturing

The pattern of commercial production of 1,3-butadiene parallels the overall development of the petrochemical industry. Since its discovery via pyrolysis of various organic materials, butadiene has been manufactured from acetylene. On a global basis, the importance of these processes has decreased substantially because of the increasing production of butadiene from petroleum sources.

China and India still convert ethanol to butadiene using the two-step process while Poland and the former USSR use a one-step process. In the past butadiene also was produced by the dehydrogenation of *n*-butane and oxydehydrogenation of *n*-butenes. However, butadiene is now primarily produced as a by-product in the steam cracking discolation situations, butadiene is almost exclusively manufactured by this process in United States, Western Europe, and Japan.

A series of articles was pblished in 1942 describing all the methods used to produce butadiene. Historically butadiene was industrially produced from acetylene by two processes as shown in Figure 25.

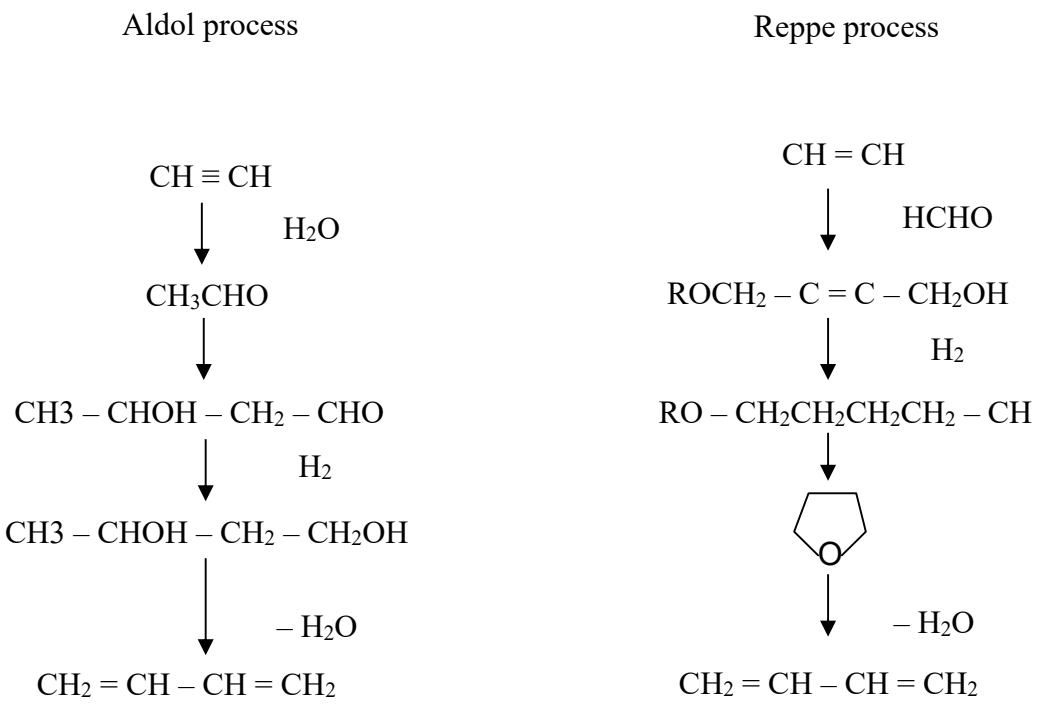


Figure 25. Producing of butadiene from acetylene

These methods are no longer used as the production of acetylene requires much energy and is expensive. Only the first steps of Reppe process leading to 1,4-butanediol and tetrahydrofuran are commercially employed today.

The production from ethanol was frist developed by IPATJEW and OSTROMISLENSKY and was midified by LEBEDEW into commercial process followed by reaction :

$$2\ CH_3CH_2OH \rightarrow CH_2{=}CHCH{=}CH_2 + 2\ H_2O + H_2$$

This process, which operates at 370 – 390°C on $MgO–SiO_2$ or $SiO_2–Al_2O_3$ catalysts with a selectivity of up to 70% can be interest for contries with chel ethanol or a large surplus of agricultural alcohol. Nowadays, butadiene is prefentially isolated from C_4 fractions obtained by cracking naphtha and gas oil to ethylene. The dehydrogenation of *n*-butane or *n*-butenes plays a minor role is only operated on a campaign basis when there is a large enough differential between feedstock and butadiene prices.
Steam Cracking

Steam cracking is acomplex, highly endothermic pyrolysis reaction. During the reaction a hydrocarbon feedstock is heated to approximately 800°C and 34 kPa (5 psi) for less than a second during which carbon – carbon and carbon – hydrogen bonds are broken. As a result, a mixture of olefins, aromatics, tar and gases are formed. These products are cooled and separated into spesific boiling range cuts of C_1, C_2, C_3, C_4, etc. The C_4 fraction contains butadiene isobutylene, 1-butene, 2-butene, and some other minor hydrocarbons.

The overall yields of butadiene depend on both process parameters and the composition of feedstocks (Table 4). Generally, heavier steam cracking feedstocks produce greater amounts of butadiene as a by-product. Thus, with heavier feedstocks like light haptha or virgin gas oil, up to about 5.4 wt% of the total product is butadiene.

Table 4. Product distribution from steam cracking

Feedstock	Product yield, wt %					
	Ethylene	Propylene	Butadiene	Butenes	BTX	Fuel Products
Ethane	77.5	2.8	1.9	0.8		17.0
Propane	42.0	16.8	3.0	1.3	3.0	33.9
Light Naphtha	33.7	15.6	4.5	4.2	9.1	32.9
Light VGO	20.4	14.1	5.4	6.3	8.5	45.3

Dehydrogenation of *n*-Butane and *n*-Butenes

The dehydrogenation reactions are endothermic, the following values being valid at 430^{o}C :

Butane → 1 – Butene + H_2, ΔH = 131 kJ/mol
Butane → *cis*-Butene + H_2, ΔH = 118 kJ/mol
Cis-2-Butene → Butadiene + H_2, ΔH = 126 kJ/mol

According to the Le' Chatelier's principle, the yield is increased by decreasing the partial pressure of the reaction products. Practically, the dehydrogenation can be improved by conducting the reaction under vacuum or by addition of steam. The latter has the following advantages :

- Reduces coking of the dehydrogenation catalyst.
- Provides the heat required for the endothermic dehydrogenation process.
- Steam can be easily separated from the reaction products by condensation.

A further increase in yield is achieved by raising the reaction temperature. Undesirable side reaction are cracking, isomerization, and polymerization. Compounds which tend to undergo these reactions are removed before the dehydrogenation process. As the dehydrogenation process does not proceed to completion, the reaction products must be

separated, and the starting materials must be recovered and recycled into the dehydrogenation process.

The best known one-step dehydrogenation is the Houdry Catadiene process (Figure 26), which has been in operation on commercial scale since 1943. In this adiabatic process, several packed-bed reactos, arranged parallel to each other, are operated alternatingly. Aluminum oxide mixed with approximately 20% chromium oxide is the catalyst.

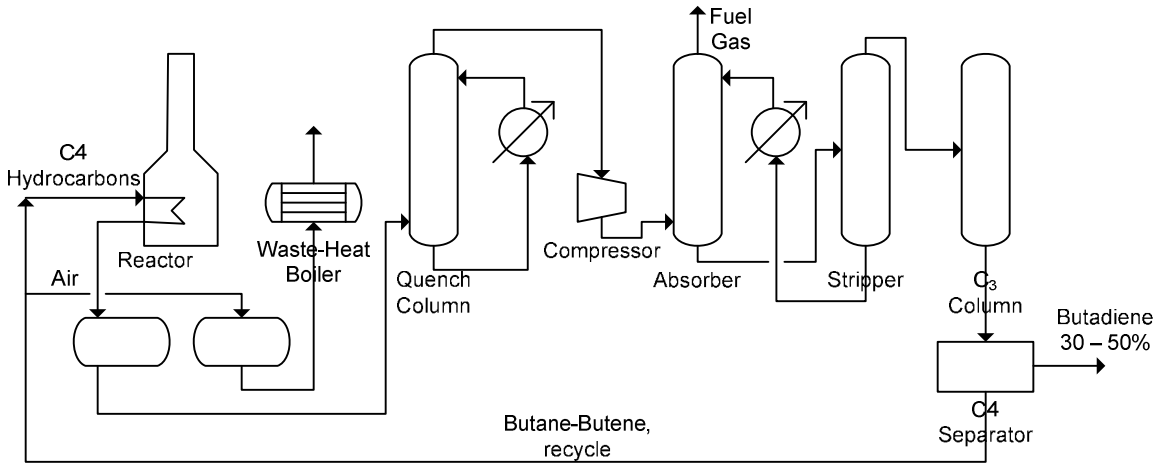


Figure 26. The Houdry Catadiene Process

n-Butane is subjected to dehydrogenation as such or in a mixture of *n*-butenes at 600 – 700°C and 10 – 25 kPa. The use of high temperatures results in byproducts like C1 – C3 hydrocarbons, hydrogen, and carbon deposits on the catalyst. After 5 – 15 minutes of running time, the reactor is switched to regeneration. The heat generated by burning the coke residue during the regeneration phase is stored in the catalyst and in the added inert material and is then reused in the next reaction phase.

The concentration of butadiene at the outlet of the reactor is 15 – 18 %. During the recovery process, which includes absorption of the C_3 and C_4 hydrocarbons, compression, stripping, and separation from unconverted *n*-butane and *n*-butenes, the

concentration to butadiene is increased to 30 – 50%. Approximately 550 tons of butadiene is obtained from 1000 tons of *n*-butane.

Extractive Distillation

The method of choice for the isolation of butadiene from C_4 fractions is extractive distillation with selective organic solvents. The affinity of hydrocarbons to polar solvent depends directly upon their degree of unsaturation. A highly unsaturated hydrocarbon is not only more soluble in a polar solvent, but the solvent is a lots more effective in decreasing the volatility of the hydrocarbon as listed in Table 8.

Table 8. Comparison of relative volatility

	Without solvent	NMP*	DMF*	Acetonitrile	DMAC*	Furfural
Butane	1.17	3.66	3.43	3.13	3.13	2.89
1-Butene	1.08	2.38	2.17	1.92	2.07	1.78
Trans-2-Butene	1.23	1.90	1.76	1.59	1.71	1.20
Cis-2-Butene	1.37	1.63	1.56	1.45	1.52	1.26
1,3-Butadiene	1.00	1.00	1.00	1.00	1.00	1.00
1,2-Butadiene	1.79	0.74	0.72	0.73	0.71	0.65
Methylacetylene	2.16	0.81	0.72	1.00	0.73	1.04
Ethylacetylene	1.62	0.42	0.42	0.48	0.44	0.52
Vinylacetylene	1.44	0.21	0.23	0.39	0.23	0.41

*NMP, *N*-Methylpyrrolidone; DMF, Dimethylformamide; DMAC Dimethylacetamide

Process Overview

A typical butadiene extraction plant consists of four basic process sections : Extractive Distillation, Conventional Distillation, Solvent Degassing, and Solvent Regeneration (Figure 27). The C_4 feed is sent to extractive distillation is required due to small difference in relative volatility between n-butane and n-butenes (Figure 28).

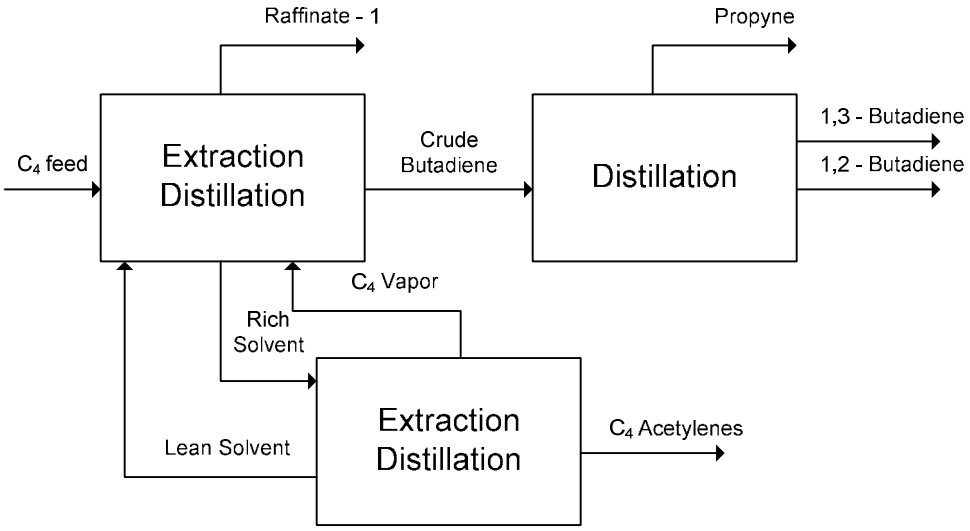


Figure 27. Butadiene Extraction Overview.

DEFINITIONS

Bottoms – The stream of liquid product collected from the reboiler at the bottom of a distillation tower.

Bubble point – The temperature at constant pressure (or the pressure at constant temperature) at which the first vapor bubble forms when a liquid is heated (or decompressed).

Dew point – The temperature at constant pressure (or the pressure at constant temperature) at which the first liquid droplet forms when a gas (vapor) is cooled (or compressed).

Distillate – The vapor from the top of a distillation column is usually condensed by a total or partial condenser. Part of the condensed fluid is recycled into the column (reflux) while the remaining fluid collected for further separation or as final product is known as distillate or overhead product

Downcomer - a vertical channel that connects a tray with the next tray below which carries froth and creates residence time which helps the vapor disengage from the froth.

Downcomer Area - is the area available for the transport of liquid from one tray to the next tray below.

Endothermic - A process or reaction that absorbs heat, i.e. a process or reaction for which the change in enthalpy, ΔH, is positive at constant pressure and temperature

Entrainment – liquid carried by vapor up to tray above and caused by high vapor flow rates

Exothermic - A process or reaction that absorbs heat, i.e. a process or reaction for which the change in enthalpy, ΔH, is negative at constant pressure and temperature

Flooding – brought about by excessive vapor flow, causing liquid to be entrained in the vapor up the column.

Popcorn – butadiene polymerizes to polybutadiene.

Reboiler –Is a heat exchanger typically used to provide heat to the bottom of industrial distillation columns. They boil the liquid from the bottom of a distillation column to generate vapors which are returned to the column to drive the distillation separation.

Reflux ratio – The ratio of the reflux stream to the distillate. The operating reflux ratio could affect the number of theoretical stages and the duties of reboiler and condenser.

Relative volatility –Defined as the ratio of the concentration of one component in the vapor over the concentration of that component in the liquid divided by the ratio of the concentration of a second component in the vapor over the concentration of that second component in the liquid. For an ideal system, relative volatility is the ratio of vapor pressures i.e. $\alpha = P2/P1$

Steam cracking - High-temperature cracking of petroleum hydrocarbons in the presence of steam.

Splitter - A name applied to fractionators, particularly those separating isomers

NOMENCLATURE

atm	Standard atmosphere, 101325 Pascal
ABS	Acrylonitrile Butadiene Styrene
CR	Chloroprene Rubber
DM	Deutsche Mark, Official currency of Germany
bp	Boiling Point
mp	Melting Point
kJ	Kilo Joule
K	Quality characterization factor
NBR	Nitrile Butadiene Rubber
Pa	Pascal
P_c	Critical Pressure
ppm	Part per million
SBR	Styrene Butadiene Rubber
SG	Spesific Gravity
T_c	Critical Temperature
T_k	Molal average boiling point, Kelvin
t/a	Tons/Annual
t/yr	Tons/Year
USITC	The United States Internation Trade Commission
US$	The United States Dollar, Official currency of US
Vol %	Percent volume
wt %	Percent weight

THEORY

Properties

Butadiene is a colorless gas undernormal conditions. Some physical properties are summarized in the following :

mp at 101.3 kPa	-108.9°C
bp at 101.3 kPa	-4.4°C
Critical Temperature, T_c	425 K
Critical Pressure, P_c	4.32 MPa
Critical molar volume	221 cm^3/mol
Density	
At 0°C	0.646 g/cm^3
At 25°C	0.616 g/cm^3
At 50°C	0.582 g/cm^3
Gas Density (air = 1)	1.87
Viscosity of liquid	
At 0°C	0.25 mPa.s
At 50°C	0.20 mPa.s
Vapor Pressure	
At -4.4°C	101.3 kPa
At 0°C	120 kPa
At 25°C	273.6 kPa
At 50°C	537.9 kPa
At 75°C	986.7 kPa
At 100°C	1733 kPa
Enthalphy of vaporization	
At -4.4°C	22.47 kJ/mol
At 25°C	20.86 kJ/mol
Enthalphy of formation	110.0 kJ/mol (gaseous, at 298 K, 101.3 kPa)
Enthalphy of combustion	2541.5 kJ/mol (gaseous, at 298 K, 101.3 kPa)
Enthalphy of formation	199.0 J/mol.K (liquid, at 298 K, 101.3 kPa)
Enthalpy of melting	7.988 kJ/mol (at 164.2 K, 101.3 kPa)

The technical data important for reasons of safety are, above all, the flash point, –85°C, the ignition temperature, 415°C, and the explosion limits when mixed with air and oxygen (Table 1). Unstabilized or insufficiently stabilized butadiene forms explosive peroxides with atmospheric oxygen. Table 2. lists azeotropic mixtures relevant to distillation of butadiene-containing hydrocarbons.

Table 1. Explosion limits of butadiene in air

Limit	At 101.3 kPa, 20°C		At 490.4 kPa, 30°C	
	Vol %	g/cm^3	Vol %	g/cm^3
Lower Limit	1.4	31	1.4	150
Upper Limit	16.3	365	ca. 22	ca. 2400

Table 2. Binary azeotropic mixtures of 1,3 butadiene

Mixture	*bp*, °C (at 101.3 kPa)	Composition
Butane/Butadiene ***trans*-2-Butene/1-butyne**	Min.	25.5 wt % 1 butyne
***cis*-2-Butene/vinylacetylene**	Min.	
Butadiene/2-butene	-5.53	24.5 wt % 2-butene
Methylamine/vinylacetylene	-6.8	2.5 wt % vinylacetylene
Ammonia/butadiene	-37	45 wt% butadiene
Ammonia/1-butene	-37.5	55 wt% 1-butene
Ammonia/isobutene	-38.5	55 wt% isobutene
Ammonia/n-butane	-37.1	55 wt% n-butane
Ammonia/isobutane	-38.4	65 wt% isobutane
Methylamine/butadiene	-9.5	58.6 wt% butadiene
Acetaldehyde/butadiene	5.0	94.8 wt% butadiene

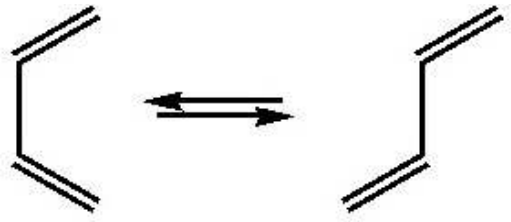
Butadiene is sparingly soluble in water, see Table 3, soluble in methanol and ethanol, and very soluble in higher-boiling polar solvents, e.g., methylpyrrolidone.

Table 3. Solubility α of butadiene in water at 101.3 kPa, and solubility *L* of water in liquid butadiene

t,°C	α, m3/m3	*L*, g H2O/kg butadiene
10	0.29	0.53
20	0.23	0.66
30	0.19	0.82
40	0.16	

1,3 Butadiene, the simplest conjungated diene, has been the subjected of intensive theoretical and experimental studies to understand its physical and chemical properties. The conjungation of double bonds makes it 15 kJ/mole (3.6 kcal/mol) more thermodynamically stable than a molecule with two isolated single bonds. Butadiene has two conjugated double bonds and therefore can take part in numerous reactions, which include 1,2- and 1,4-additions with itself (polymerization) and other reagents, linear dimerization and trimerization, and ring formation.

The *s*-trans isomer, often called the trans form, is more stable than the *s*-cis form at room temperature. Although there is a 20 kJ/mole (4.8 kcal/mol) rotational barrier, rapid equilibrium allows reactions to take place with either the *s*-cis or the *s*-trans form (Figure 1)



(a) (b)

Figure 1.(a) the *s*-cis form, (b) the *s*-trans form