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| <b>KLM Technology Group</b><br><br>Practical Engineering Guidelines for Processing Plant Solutions                             | <br><br><b>Engineering Solutions</b><br><br><a href="http://www.klmtechgroup.com">www.klmtechgroup.com</a> | Page : 1 of 69                                       |
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| KLM Technology Group<br><br>Malaysia<br>#03-12 Block Aronia,<br>Jalan Sri Perkasa 2<br>Taman Tampoi Utama<br>81200 Johor Bahru | <b>Kolmetz Handbook<br/>         of Process Equipment Design</b><br><br><b>BUTADIENE PROCESSING UNIT<br/>         (ENGINEERING DESIGN GUIDELINE)</b>   | Co Author:<br><br>Rev 01<br>Mochamad Adha<br>Firdaus |
|  |  | Author / Editor<br><br>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<sub>4</sub> (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

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## General Design Considerations

1,3 Butadiene is a conjugated 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  $900^\circ C$ ), 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 hydrocarbons produced in steam cracking by extractive distillation using a polar solvent such as acetonitrile, N-methylpyrrolidone, furfural, or dimethylformamide, from which it is 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.

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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 initiate an auto-catalytic polymerization. The heat released accelerates the reaction, 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 by the formation of ice balls (from the evaporative freezing of water out of the atmosphere) even when the temperature is well above 0°C.

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## 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,  $\Delta H$ , 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,  $\Delta H$ , 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.

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**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.  $\alpha = P_2/P_1$

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

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

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## NOMENCLATURE

|           |   |
|-----------|---|
| atm       | Standard atmosphere, 101325 Pascal                |
| ABS       | Acrylonitrile Butadiene Styrene                   |
| CR        | Chloroprene Rubber                                |
| DM        | Deutsche Mark, Official currency of Germany       |
| <i>bp</i> | Boiling Point                                     |
| <i>mp</i> | 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        | Specific Gravity                                  |
| $T_c$     | Critical Temperature                              |
| $T_k$     | Molal average boiling point, Kelvin               |
| t/a       | Tons/Annual                                       |
| t/yr      | Tons/Year   |
| USITC     | The United States International Trade Commission  |
| US\$      | The United States Dollar, Official currency of US |
| Vol %     | Percent volume                                    |
| wt %      | Percent weight                                    |

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## THEORY

### Properties

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

|                             |  |
|-----------------------------|--|
| <i>mp</i> at 101.3 kPa      | -108.9°C                                     |
| <i>bp</i> 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 <sup>3</sup> /mol                     |
| Density                     |  |
| At 0°C                      | 0.646 g/cm <sup>3</sup>                      |
| At 25°C                     | 0.616 g/cm <sup>3</sup>                      |
| At 50°C                     | 0.582 g/cm <sup>3</sup>                      |
| 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                                     |
| Enthalpy of vaporization    |  |
| At -4.4°C                   | 22.47 kJ/mol                                 |
| At 25°C                     | 20.86 kJ/mol                                 |
| Enthalpy of formation       | 110.0 kJ/mol (gaseous, at 298 K, 101.3 kPa)  |
| Enthalpy of combustion      | 2541.5 kJ/mol (gaseous, at 298 K, 101.3 kPa) |
| Enthalpy 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)         |

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The technical data important for reasons of safety are, above all, the flash point,  $-85^{\circ}\text{C}$ , the ignition temperature,  $415^{\circ}\text{C}$ , 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 <sup>3</sup> | Vol %              | g/cm <sup>3</sup> |
| 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                    | Min.                  | 25.5 wt % 1 butyne      |
| <i>trans</i> -2-Butene/1-butyne     |                       |                         |
| <i>cis</i> -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      |

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| <b>KLM Technology Group</b><br><br>Practical Engineering Guidelines for Processing Plant Solutions | <b>Kolmetz Handbook of Process Equipment Design</b><br><br><b>BUTADIENE PROCESSING UNIT (ENGINEERING DESIGN GUIDELINES)</b> | Page 15 of 69  |
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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  $\alpha$  of butadiene in water at 101.3 kPa, and solubility  $L$  of water in liquid butadiene

| t, °C | $\alpha$ , m <sup>3</sup> /m <sup>3</sup> | $L$ , g H <sub>2</sub> O/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 conjugated diene, has been the subjected of intensive theoretical and experimental studies to understand its physical and chemical properties. The conjugation 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)

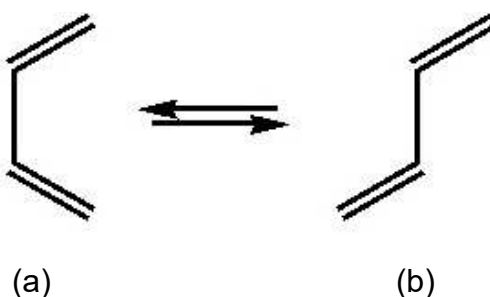


Figure 1.(a) the s-cis form, (b) the s-trans form

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