KLM Technology Group Malaysia #03-12 Block Aronia, Jalan Sri Perkasa 2 Taman Tampoi Utama 81200 Johor Bahru USA PO Box 1814 Livingston Texas 77351	BUTADIENE PROCESSING UNIT (ENGINEERING DESIGN GUIDELINE)	Author: Rev 01 Mochamad Adha Firdaus Karl Kolmetz

TABLE OF CONTENT

INTRODUCTION 5

Scope 5

General Design Consideration 6

DEFINITION 8

NOMENCLATURE 10

THEORY 11

Properties 11

Manufacturing 28

Extractive Distillation 35

Advantages of Extractive Distillation 44

Spesifications 45

Stabilization, Storage, and Transportation 46

Uses and Economic Importance 47

APPLICATION 50

Application Case : Problems in Extractive Distillation 50

REFEREENCE 60

LIST OF TABLE

Table 1: Explosion limits of butadiene in air 12

Table 2: Binary azeotropic mixtures of 1,3 butadiene 12

Table 3: Solubility α of butadiene in water at 101.3 kPa 12

Table 4: Product Distirbution from steam cracking 30

Table 5: Catalytic dehydrogenation of butenes 33

Table 6: Feedstocks and steam cracking yields (in wt%) 33

Table 7: Typical analysis of C_4 fractions (in vol%) 34

Table 8: Comparison of relative volatility 35

Table 9: Comparison of Solvent swap 40

Table 10 : Typical spesifications of butadiene 45

Table 11 : Butadiene production, capacities, and consumption in 1998 47

Table 12 : Butadiene usage in 1998 48

LIST OF FIGURE

Figure 1.(a): The *s*-cis form **13**

Figure 1.(b): The *s*-trans form **13**

Figure 2: 1,2 – addition product **14**

Figure 3: 1,4 – addition product **14**

Figure 4: The intermediate of addition product **14**

Figure 5: The addition of HI **15**

Figure 6: The addition of HCN **16**

Figure 7: 1,2-cyclic intermediate **17**

Figure 8: Chloroprene production **17**

Figure 9: Addition of SO_2 **18**

Figure 10: 1,4-butadienol production **18**

Figure 11 : *Trans*-2-butene-d_2 **19**

Figure 12: Oxidized products of butadiene **20**

Figure 13: Direct oxidation butadiene with air or oxygen **21**

Figure 14: The Diels-Alder reaction **22**

Figure 15: 1,4 Addition with sulfur dioxide to butadiene **22**

Figure 16.(a) : 1,6-octadiene **24**

Figure 16.(b) : 1,7-octadiene **24**

Figure 17: Dimerization in the presence of reducing agents **24**

Figure 18.(a) : COD **24**

Figure 18.(b) : CTT 24

Figure 18.(c) : TTT 24

Figure 19: Telomerization of butadiene with a carboxylic acid 25

Figure 20: Process 26

Figure 21: Telomerization butadiene with ammonia 26

Figure 22: Telomerization of butadiene with carbon dioxide 27

Figure 23: Tricarbonyl complex 27

Figure 24: *O*-xylene reacts with butadiene 28

Figure 25: Producing butadiene from acetylene 29

Figure 26: The Houdry Catadiene Process 31

Figure 27: Butadiene Extraction Overview 36

Figure 28: Extractive Distillation between n-Butane and n-Butene 36

Figure 29: Extractive distillation process with NMP 37

Figure 30: Butadiene Extraction Plant 39

Figure 31: Eco-Efficiency Analysis for NMP Solvent 40

Figure 32: Classic Design of Extraction Distillation Section 42

Figure 33: Divided Wall Design 42

Figure 34: Classic Design of Degassing Section 43

Figure 35: New Compressorless Degassing System 44

Figure 36: Butadiene's price in Western Europe, 49

Figure 37: Causes of column malfunctions 52

Figure 38: Typical Plant for Butadiene Extraction **53**

Figure 39: Evolutionof Structured Packing **54**

Figure 40: Liquid Hold Up Profile **55**

Figure 41: Popcorn Polymer **56**

Figure 42: Deck Opening Size Efficiency **57**

Figure 43: Stagnant Zones **58**

Figure 44: Baffle bar on the tray **58**

Figure 45: Elimination Stagnant zone **59**

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^{o}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 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 $0^{o}C$.

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

NOMENCLATURES

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

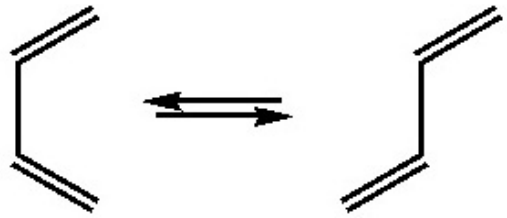
Butadiene is sparingly soluble in water, see Table 3, soluble in methanol and ethanol, and very soluble in higher-boiling polar solvents, e.g., methylpyrrolidone.

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

The double-bond length in 1,3-butadiene is 0.134 nm, and the single-bond, 0.148 nm. Since normal carbon-carbon single bonds are 0.154 nm, this indicates the extent of double-bond character in the middle single-bond. Upon complexing with metal carbonyl

moieties like $Fe(CO)_3$, the two terminal bonds lengthen to 0.141 nm, and the middle bond shortens even more to 0.145 nm.

Reactions

Since the discovery of 1,3-butadiene in the 19th century, it has grown into extremely versatile and important industrial chemical. Its conjungated double bonds allow a large number of unique reactions at both the 1,2- and 1,4-positions. Many of these reactions produce large volumes of important industrial materials.

Addition

1,3-Butadiene reacts readily via 1,2- and 1,4-free radical or electrophilic addition reactions to produce 1-butene or 2-butene substituted products, resperctively. The reactions shows in Figure 2 & Figure 3 The natures of these polymers depends greatly on the way in which they are prepared and on the catalyst system employed.

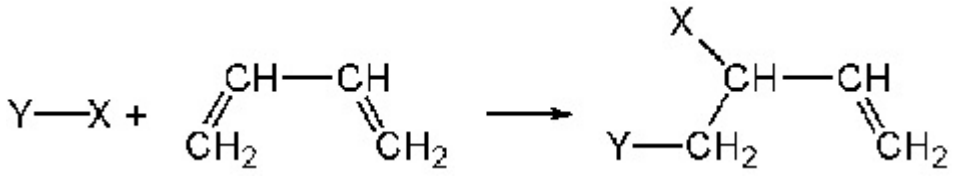


Figure 2. 1,2-addition product

Figure 3. 1,4-addition product

The intermediate in these reactions in the case of the addition of XY is consistent with the addition of Y to the 1-position to form an allylic intermediate to which X adds to produce either the 1,2 – or 1,4-product as follows in Figure 4.

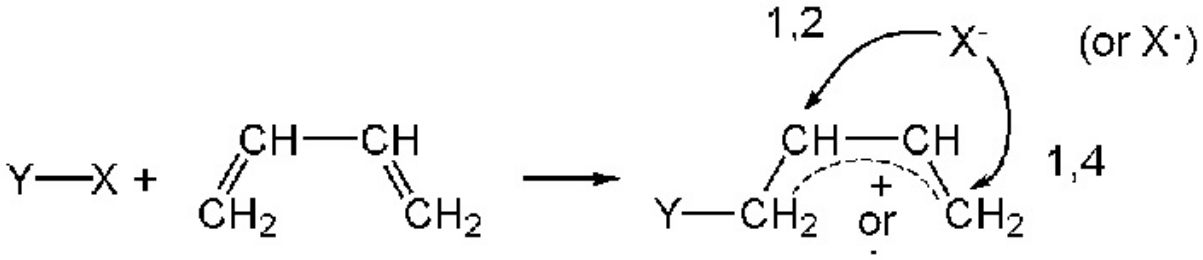


Figure 4. The intermediate of addition product.

The addition of HX, where X is halogen compounds, has been thoroughly investigated. Wether 1,2- or 1,4-product dominates depends on reaction conditions. For instance, although HCl adds to butadiene at low temperature to produce 75 – 80% of the 1,2 – addition product, the thermodynamically more stable 1,4-isomer is favored at higher temperatures. On the other hand, HI has been shown to add to butadiene in the vapor phase by a pericyclic mechanism to produce the 1,4-product.

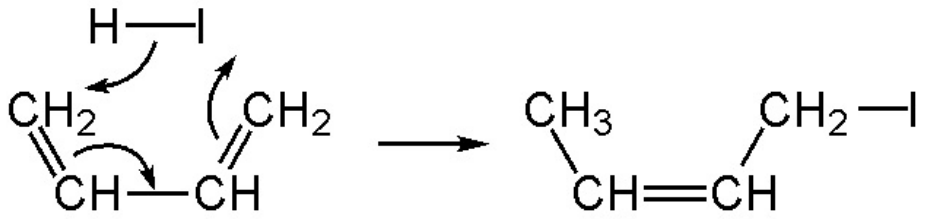


Figure 5. The addition of HI.

Addition of water or alcohols directly to butadiene at 40 – 100^{o}C produces the corresponding unsaturated alcohols of ethers. Acidic ion exchangers have been used to catalyze these reactions. The yields for these latter reactions are generally very low because of unfavorable thermodynamics.

At 50^{o}C addition of acidic acid to butadiene produces the expected butenyl acetate with 60 – 100% selectivity at butadiene conversions of 50%. The catalysts are ion-exchange resins modified with quaternary ammonium, quaternary phosphonium, and ammonium substituted ferrocenyl ions.

Addition of amines yields unsaturated alkyl amines. The reaction can be catalyzed by homogenous catalysts such as $Rh[P(C_6H_5)_3]_3Cl$ of heterogeneous catalyst such as MgO and other solid bases.

The manufacture of hexamethylenediamine[2], a key comonomer in nylon-6,6 production proceeds by a two step HCN addition reaction to produce adiponitrile[3] (Figure 6), $NCCH_2CH_2CH_2CH_2CN$. The adiponitrile is then hydrogenated to produce the desired diamine. The other half of nylon-6,6, adipic acid, can also be produced from butadiene by means of either of two similar routes involving the addition of CO. Reaction between the diamine and adipic acid produces nylon-6,6.

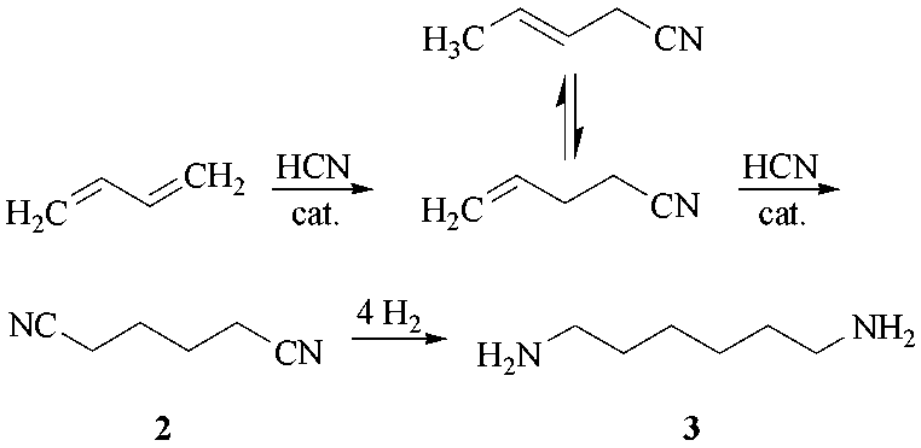


Figure 6. The addition of HCN

In the production of adiponitrile and hexamethylenediamine, hydrogen cynide reacts with butadiene in two steps, and the adiponitrile thus obtained is hydrogenated to give the diamine. Typical catalysts are Ni^0 phospoine and phospite complexes with Al/Zn promotors. Typical reaction conditions are 90 – 150^oC and ambient pressure in THF.

The first CO route to make adipic acid is a BASF process employing CO and methanol in a two-step process producing dimethyl adipate which is then hydrolyzed to the acid. Cobalt carbonyl catalysts such as $Co_2(CO)_8$ are used. Palladium catalysts can be used to effect the same reactions at lower pressures.

The other CO route for adipic acid manufacture involves 1,4 addition of CO and O_2 to butadiene to produce an intermediate, which is subsequently hydrogenated and hydrolyzed to adipic acid. This is called the oxycarbonylation process. Both the BASF and the oxycarbonylation processes have been intensively investigated.

Halogenation of butadiene has also attracted a lot of interest. Both 1,2- and 1,4-isomers are formed. Since the *trans*-1,4-isomer was observed from the 1,4 addition product, researchers postulate that the electrophilic X^+ forms a 1,2-cyclic intermediate (Figure 7) and not a 1,4-cyclic intermediate that would form the *cis*-1,4-addition product.

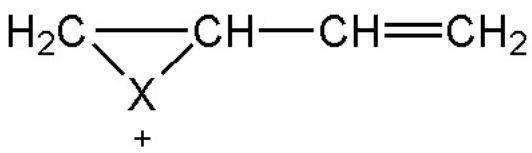


Figure 7. 1,2-cyclic intermediate

Fluorination with XeF_2 or $C_6H_5IF_2$ gives both the 1,2- and 1,4-difluoro products. This reaction proceeds via initial electrophilic addition of F^+ to the diene.

Chloroprene, 2-chloro-1,3-butadiene (Figure 8), is produced commercially from butadiene in a three-step process. Butadiene is first chlorinated at 300°C to 60:40 mixtures of the 1,2- and 1,4-dichlorobutene isomers. This mixture is isomerized to the 3,4-dichloro-1-butene with the aid of a Cu-Cu_2Cl_2 catalysts followed by dehydrochlorination with base such as NaOH.

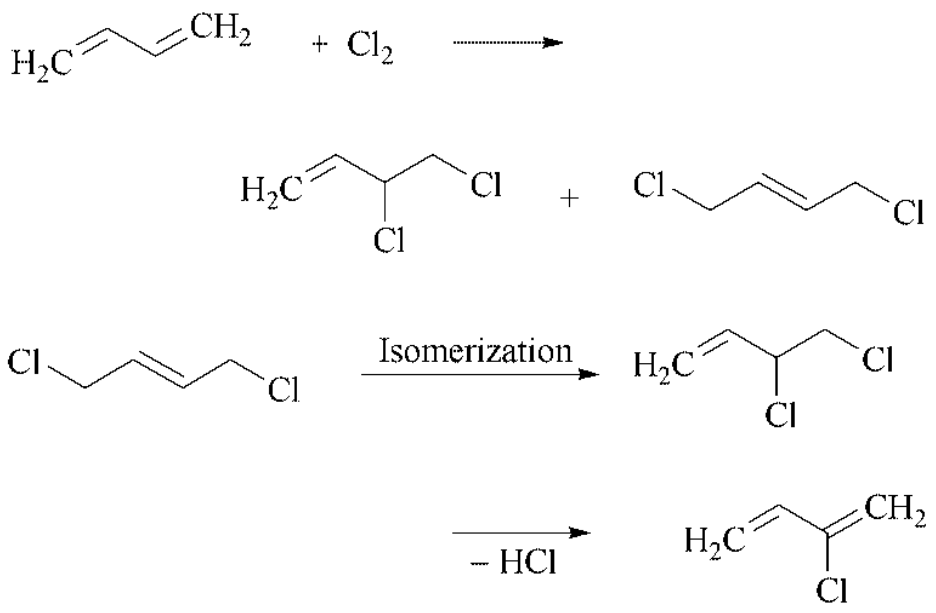


Figure 8. Chloroprene production.

Butadiene also undergoes a 1,4-addition reaction with SO_2 to give sulfolene. This reaction followed by hydrogenation is commercially used to manufacture sulfolane (Figure 9).

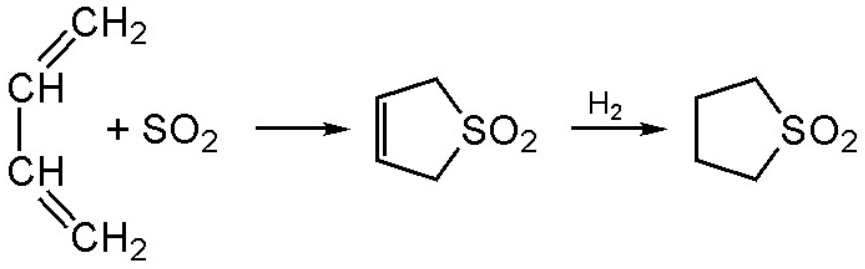


Figure 9. Addition of SO_2

Formaldehyde also reacts with butadiene via the Prins reaction to produce pentenediols or their derivatives. This reaction is catalyzed by a copper-containing catalyst in a

carboxylic acid solution or $RuCl_3$. The addition of hydrogen also proceeds via 1,2- and 1,4-addition.

Several processes have been developed for the production of 1,4-butanediol from butadiene. In the three-step Mitsubishi process, butadiene catalytically reacts with acetic acid to give 1,4-diacetoxy-2-butene, which in turn is hydrogenated to 1,4-butanediol. A similar process was reported by BASF.

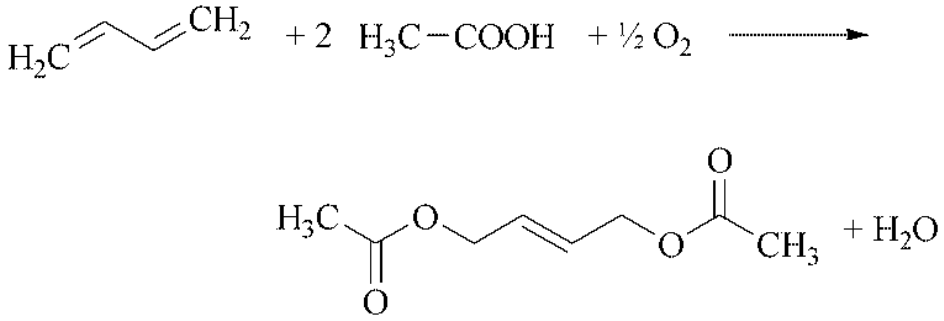


Figure 10. 1,4-butanediol production (Mitsubishi process)

The Toyo Soda process for the preparation of 1,4-butanediol involves the reaction of the butadience chlorine addition products 1,4-dichloro-2-butene and 1,2-dichloro-3-butene with sodium acetate or formate to give 1,4-diacetoxy-2-butene or 1,4-diromyl-2-butene, which are then hydrolyzed and hydrogenated to 1,4-butanediol.

Hydrogenation Reactions

Butadiene can be hydrogenated to *n*-butanes and *n*-butane using a large number of heterogenous and homogenous catalysts. Palladium-containing membranes have also been used to allow the use of permeated hydrogen to effect hydrogenation. Many catalysts have been developed and used commercially to remove small quantities (≥ 3%) of butadiene from 1-butene streams.

Since 2-butene is more stable thermodynamically than 1-butene under mild conditions, catalysts that promote 1,2-addition and do not isomerize 1-butene are essential for getting high 1-butene selectivity. Many of the palladium catalysts require the use of CO to improve 1-butene selecitvity.

Selectivities to various isomers are more difficult to predict when metal oxides are used as catalysts. ZnO prefentially produced 79% 1-butene and several percent of *cis*-2-butene. CdO catalyst produced 55% 1-butene and 45% *cis*-2-butene. It was also reported that while interconversion between 1-butene and *cis*-2-butene was quite facile on CdO, cis-trans isomerization was slow. This was attributed to the presence of a π-allyl anion intermediate. High *cis*-2-butene selectivities were obtained with molybdenum carbonyl encapsulated in zeolites. On the other hand, deuteration using ThO_2 catalyst produced predominantly the 1,4-addition product, *trans*-2-butene-d_2 with no isotope scrambling.

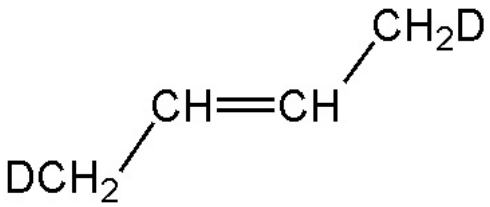


Figure 11. *Trans*-2-butene-d_2

Although supported Pd catalysts have been the most extensively studied for butadiene hydrogenation, a number of other catalysts have also been the object of research studies. Some examples are Pd film catalysts, molybdenum sulfide, metal catalysts containing Fe, Co, Ni, Ru, Rh, Os, Ir, Pt, Cu, MgO, $HCo(CN)^{3-}_5$ on supports, and $LaCoC_3$ Perovstrike. There are many others. Studies on the well-characterized Mo(II) monomer and Mo(II) dimer on silica carrier catalysts have shown wide variations not only in catalyst performance, but also of activation energies.

Another method to hydrogenate butadiene occurs during an oxidation-reduction reaction in which n alcohol is oxidized and butadiene is reduced. Thus copper-chromia or copper-zinc oxide catalyzes the transfer of hydrogen from 2-butanol or 2-propanol to butadiene at 90 – 130^{o}C.

Oxidation Reactions

Like all reactions between oxygen and hydrocarbons, complete oxidation of butadiene is controlled by lmiting the oxygen and operating at spesific temperature ranges. Other ways to control selectivity to spesific products involve the use of catalysts and /or conducting the reaction in the presence of other reagents. Some of the many oxidized products are depicted in Figure 12.

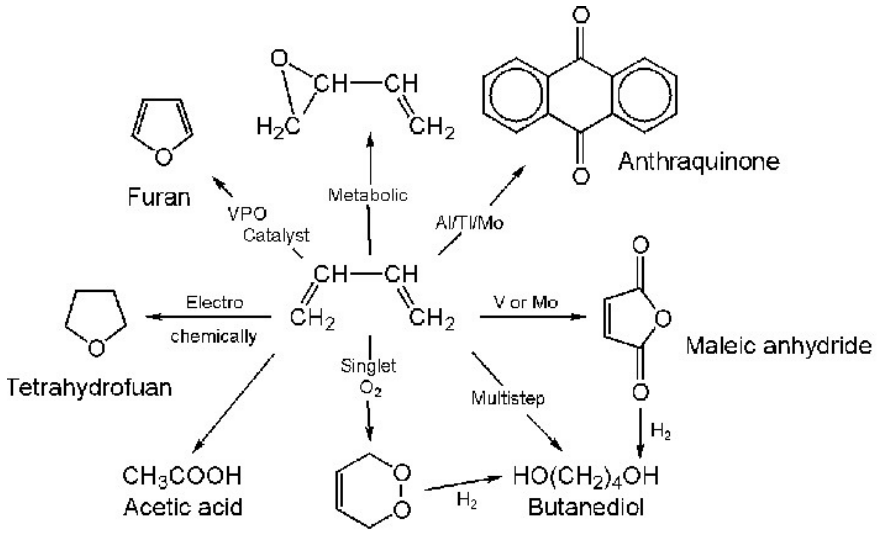


Figure 12. Oxidized products of butadiene.

The direct oxidation butadiene with air or oxygen, a method introduced by Eastman Chemical, is an economic process for production of several C_4 derivatives. In the oxidation 3,4-epoxy-1-butene is formed with high selectivity. Thermal rearrangement of 3,4-epoxy-1-butene followed by hydrogenation affords tetrahydrofuran, which can be hydrolytically ring opened to give 1,4-butanediol. Hydrogenation of 3,4-epoxy-1-butene affords ethyloxirane (Figure 13).