Overview -1,3-Butadiene Physical and Chemical Properties

Summary

This paper provides a high-level description and overview of 1,3-Butadiene manufacture and use as a reactant. 1,3-Butadiene is generally used in the manufacture of synthetic rubber, or to manufacture other chemicals. It is important to understand its physical and chemical properties, as they are unique compared to other chemicals that have undergone the TSCA Risk Evaluation Process.

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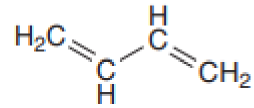
A. What is 1,3-Butadiene?

1,3-Butadiene (CAS No. 106-99-0) is a colorless gas with a mild aromatic or gasoline odor at ambient temperature and pressure. Its molecular formula is C_4H_6 and its chemical structure is represented in Figure 1 [1].

Figure 1
1,3-Butadiene



B. What are the physical and chemical properties of 1,3-butadiene?

A summary of physical and chemical properties is shown in Table 1, as compiled by the EPA in the "Final Scope of the Risk Evaluation for 1,3-Butadiene" [2].

1,3-butadiene is a gas at ambient temperature and pressure. It is highly flammable and susceptible to ignition due to its extremely low flash point. It is a liquid below 24° F. Contact with the liquid butadiene can cause frostbite. Its vapors are heavier than air and a flame can flash back to the source of a leak very easily. It can asphyxiate by the displacement of air. [3] It polymerizes readily, especially in the presence of oxygen. [1] With respect to water solubility, it is important to understand that although the experimental water solubility of 1,3-butadiene measured value at 20 °C was reported as 735 mg/L, the measurement was performed in a closed system. In the NIH *Report on Carcinogens*, it is described as insoluble in water [1].

Table 1 – Physical and Chemical Properties of 1,3-Butadiene

Property or Endpoint	**Value [a]**	**Reference**	**Data Quality Rating**
Molecular formula	C4H6	NA	NA
Molecular weight	54.09 g/mol	NA	NA
Physical state	Colorless gas	Rumble (2018a)	High
Physical properties	Colorless, mildly aromatic or gasoline- like odor	NLM (2003)	High
Melting point	-108.966°C	O'Neil (2013)	High
Boiling point	-4.5°C at 760 mm Hg	O'Neil (2013)	High
Density	0.6149 g/cm3 at 25°C and >1 atm	Rumble (2018a)	High
Vapor pressure	2110 mm Hg	U.S EPA (2019b)	High
Vapor density	1.87 (air = 1)	NLM (2003)	High
Water solubility	735 mg/L at 20°C	NLM (2003)	High
Octanol/water partition coefficient (log Kow)	1.99 at 25°C	Rumble (2018c)	High
Henry's Law constant	0.204 atm·m3 /mol at 25°C	Rumble (2018b)	High
Flash point	-76.111°C	RSC (2019)	High
Auto flammability	420°C	Rumble (2018a)	High
Viscosity	0.00754 cP at 20°C	NLM (2003)	High
Refractive Index	1.4292	Rumble (2018a)	High
Dielectric constant	2.050	Rumble (2018a)	High

[a] Measured unless otherwise noted. NA = Not applicable

C. How is 1,3-Butadiene Made?

1,3-Butadiene is produced commercially by three processes [4]:

- Steam Cracking of Paraffinic Hydrocarbons - Butadiene is a co-product in the manufacture of ethylene (the ethylene co-product process).
- Catalytic Dehydrogenation of n-Butane and n-Butene (the Houdry process*).
- Oxidative Dehydrogenation of n-Butene (the Oxo-D or O-X-D process*).

  ** The Houdry and Oxo-D process descriptions can be found in reference 4 or 5.*

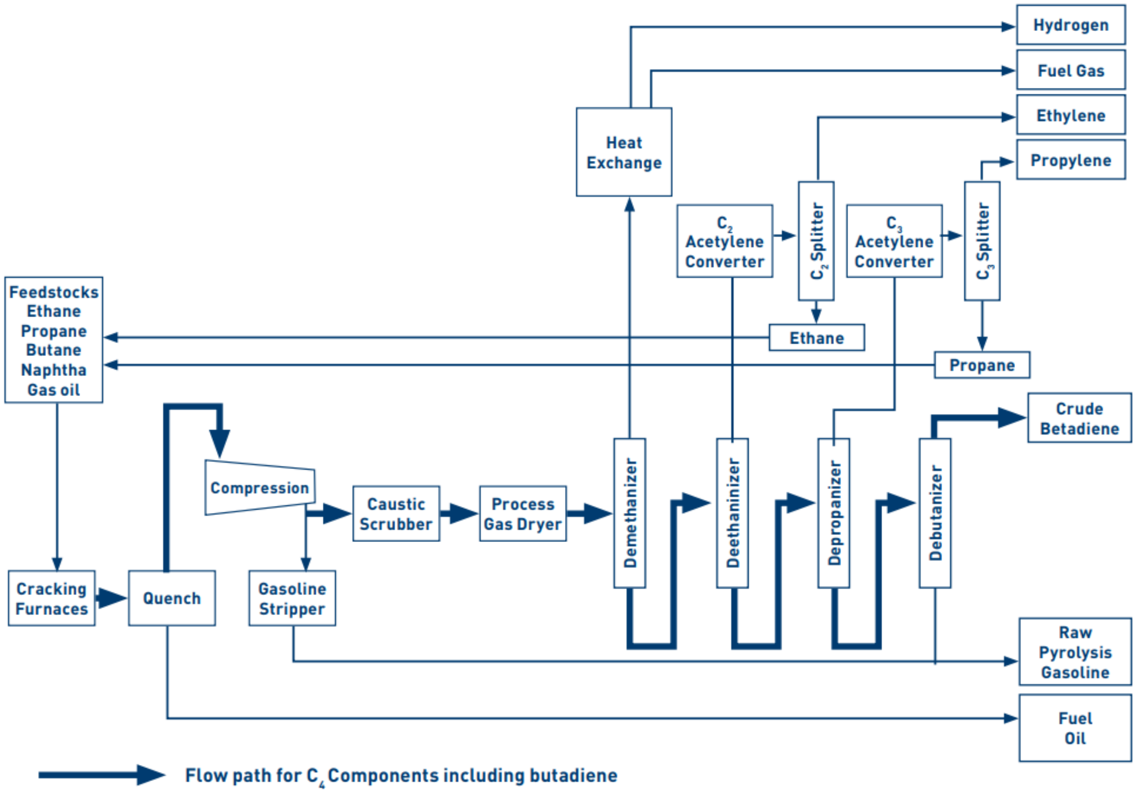
The predominant process is the steam cracking of paraffinic hydrocarbons, accounting for over 96% of global butadiene production in 2022, according to S&P Global Commodity Insights [5].

It is important to note that the processes described below are an enclosed system and any emissions from the system are controlled by pollution control equipment to minimize emissions, as required by EPA Clean Air Act operating permits and state regulations.

Feedstocks, such as ethane, propane, butane, naphtha, or gas oil, are fed in a pyrolysis furnace and combined with steam and heated to temperatures between 1450 and 1525 °F (790-830 °C) to “crack” the hydrocarbon feed molecules. The products made by this process include hydrogen, ethylene, propylene, butadiene, benzene, toluene, and other olefins co-products. After the pyrolysis reaction is quenched, the co-products are separated by distillation. Figure 2 depicts a typical Olefins Plant process flow [4]. Note that this figure does not represent any specific plant process but is provided to give a general overview. The 1,3-butadiene ends up in a stream commonly referred to as crude butadiene, which is a mixture of predominately C4 (hydrocarbons with 4 carbon atoms) that is rich in 1,3-butadiene.

The relative concentration of 1,3-butadiene in the crude butadiene stream is dependent on the initial feedstock that is cracked. Lighter feedstocks such as ethane or propane will yield less 1,3-butadiene than a heavy naphtha feedstock [4].

Figure 2: Typical Olefins Plant Process [5]



Other components present in the mixture vary depending on several factors such as feedstock used, operational conditions of the cracking process, and plant design. Examples of components found in the crude butadiene stream may include but are not limited to: i-butane, n-butane, isomers of butene, i-butylene, and C4 acetylenes among others [5].

D. Recovery of 1,3-butadiene

There are several processing options to further isolate 1,3- butadiene from the crude butadiene stream. This list is not all inclusive and many factors determine which process a butadiene manufacturer may use. The prevalent process options include [5]:

1) Recycle back to the olefins plant cracking furnaces;
2) Hydrogenation followed by recycle cracking;
3) Selective hydrogenation of the butadiene to produce an isobutylene/butene-1 rich stream;
4) Butadiene extractive distillation.

The boiling points of the various components are very close to each other. Extractive distillation using solvent is the most common method used to isolate 1,3-butadiene from other components in the crude butadiene stream. There are several solvent extraction processes in use by manufacturers including [6]:

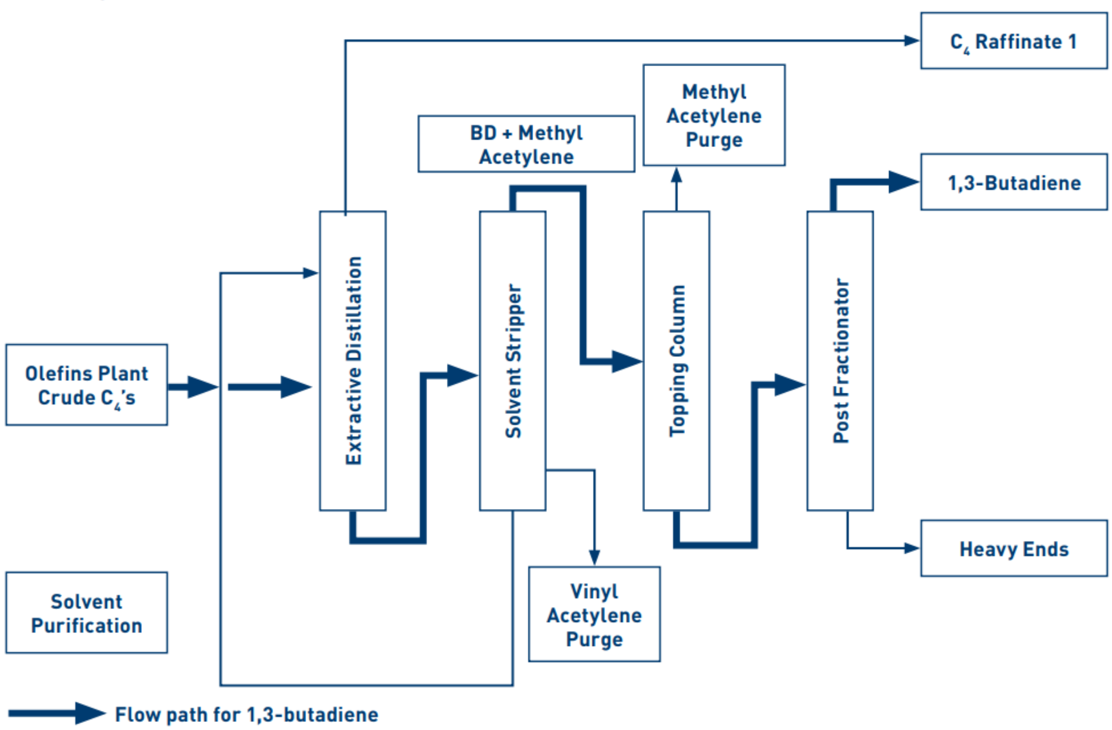
• Acetylene hydrogenation and extractive distillation using aqueous methoxyproprionitrile/furfural;

• extractive/conventional distillation using aqueous n-methyl-2-pyrrolidone;
• dimethylformamide solvent extractive process (nonaqueous); and
• aqueous separation and acetonitrile extraction.

Detailed descriptions of the solvent extraction processes listed above may be found in references [3][4].

Figure 3 shows an example process for extractive distillation process using aqueous separation and acetonitrile. The crude butadiene (C4s) stream is routed to the extractive distillation column. The overheads contain butanes/butylenes (C4 Raffinate 1) and the bottoms consist of 1,3-butadiene and acetylenes. Next, the stream moves to the solvent stripping column, where the solvent is stripped and returned to the initial column while the 1,3-butadiene and methyl acetylene are transported overhead. Vinyl or ethyl acetylene is purged from the stripper bottoms. The topping column is used to separate methyl acetylene while the bottoms from this column can be fed to a post fractionator. The 1,3-butadiene from the overheads is chilled and moved through a coalescer to remove any entrained water. The purity of 1,3-butadiene once this process is complete is typically >99.5% [7].

Figure 3: Example Extractive Distillation Process for 1,3-Butadiene [5]



E. How is 1,3-butadiene stored and transported?

Once the 1,3-butadiene is separated and isolated, it is stored as a liquified or compressed gas in a pressurized sphere, due to its high vapor pressure as required by OSHA standard 1910.110 Hazardous Materials: Storage and handling of liquified petroleum gases [12]. It is important to note that pressurized spheres do <u>not</u> have working losses. Tertiary-butyl catechol (TBC) is added as a stabilizer/inhibitor to prevent peroxide formation [4][5].

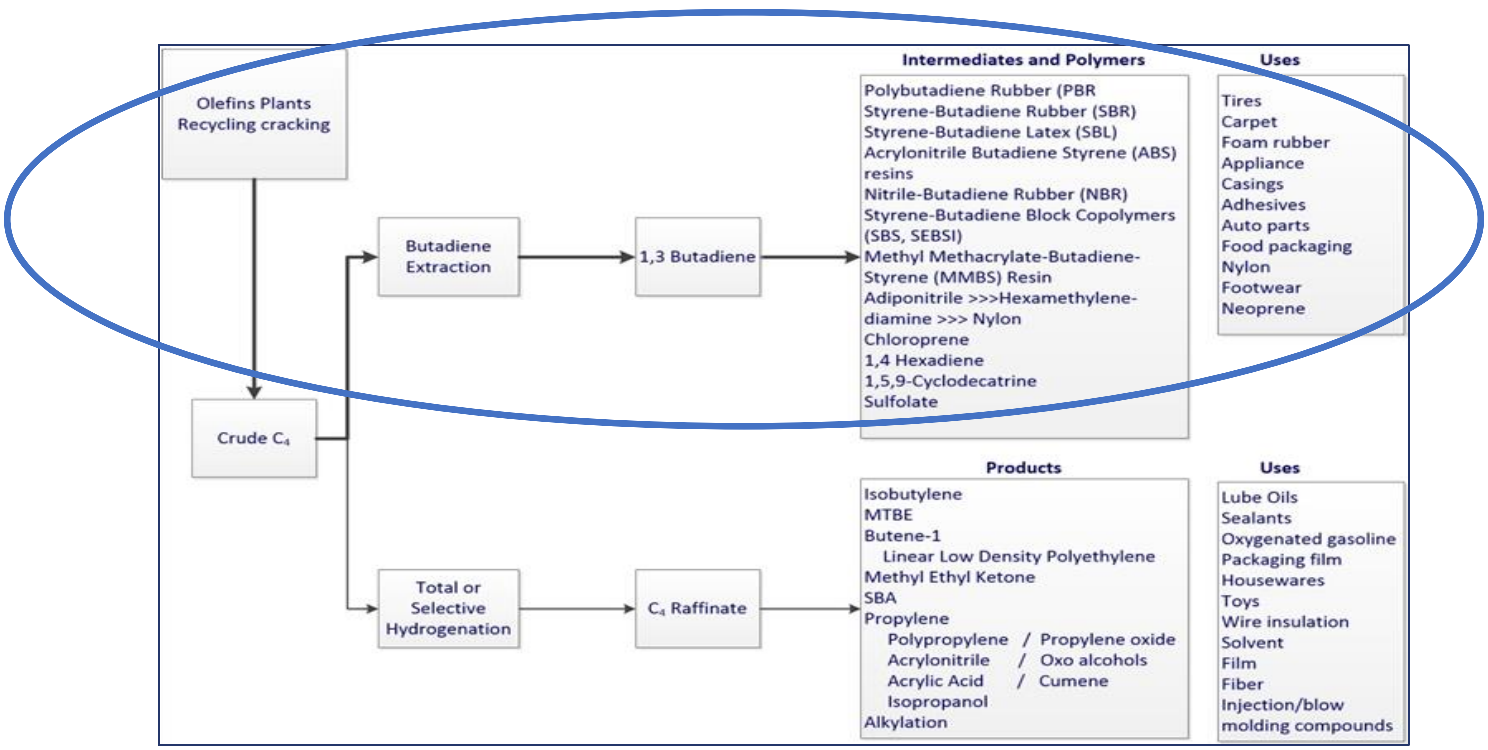
1,3-butadiene with TBC inhibitor is shipped as a liquified product by pipeline, ship, barge, rail tank car and bulk liquid container under pressurized conditions [7]. Transportation is regulated by PHMSA, IMDG and state or local transportation authorities.

F. How is 1,3-butadiene used?

1,3-butadiene is a building block chemical that is reacted or polymerized and may be further processed to create a range of materials that can be used to make downstream consumer goods.

Figure 4 shows an overview of the supply chain for 1,3-butadiene, as modified from the ACC 1,3-Butadiene Product Stewardship Guidance Manual [5]. The upper portion circled shows overall value chain from 1,3-butadiene manufacture to the intermediate chemicals and polymers. End-use products have one or more additional manufacturing steps beyond polymer or intermediate chemical usage before ending up as the consumer good.

Figure 4: Supply Chain Overview of 1,3-Butadiene [5]



G. Description of Chemical/ Polymer Manufacturing using 1,3-Butadiene

Polymerization is the process of chemically bonding monomer building blocks to form large molecules, like individual links attaching together to form a chain. The most basic component of plastic and elastomer materials is polymers [8].

Polybutadiene rubber (PBR) (CAS No. 9003-17-2) is the simplest polymer made from 1,3-butadiene. Other significant use polymers made from 1,3-butadiene include Styrene-Butadiene Rubber (SBR), Styrene-Butadiene Latex (SBL), Nitrile-Butadiene Rubber (NBR), Styrene-Butadiene Block Copolymers (SBS, SEBSI), Methyl Methacrylate-Butadiene Styrene (MMBS) resin and Acrylonitrile Butadiene Styrene resins (ABS). Three dimensional models of many of these polymers may be viewed at the Polymer Science Learning Center website [9].

Manufacture of these polymers is considered a primary condition of use of 1,3-butadiene monomer, as it is consumed in the reaction that creates the polymer. As an example, the general process for the manufacture of Styrene-Butadiene Rubber (SBR) is provided.

1. Styrene Butadiene Copolymer Manufacture Example

Styrene Butadiene Rubber (SBR) or Styrene-Butadiene (SB) latex is composed of the monomer units 1,3-butadiene and styrene. The feed composition and drying process dictates whether the material will be a solid or an emulsion. Generally, if the polymer contains more than 45% 1,3-butadiene (SBR), it will exhibit rubber-like properties. In contrast, the polymer becomes “plastic-like” when the styrene content is over 45% for SB latex [13].

Figure 5 shows the emulsion polymerization process for Styrene-Butadiene Rubber [14]. Monomers of 1,3-butadiene and styrene are fed to a reactor along with a soap solution and activator catalyst modifier. Polymerization is carried out in a series of reactors. The initial product formed in the emulsion phase of the reaction mixture is called latex and is milky white in appearance. Typically, the reaction is stopped when the conversion yield is approximately 60 %, due to decreases in reaction rate and degradation in product quality. This is the reason the “shortstop” is used to stop the reaction at the desired conversion.

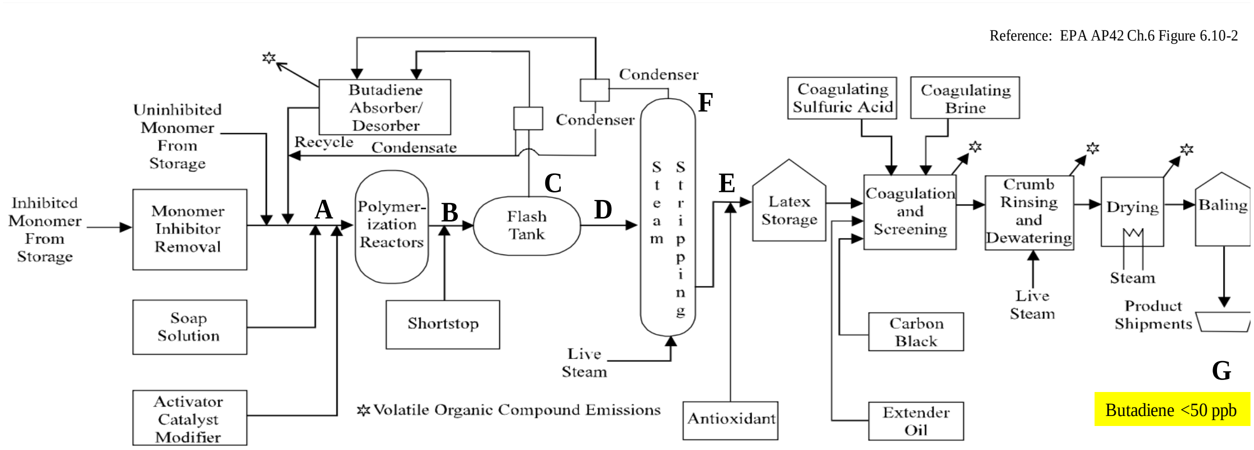
Unreacted 1,3-butadiene and styrene monomers in the latex emulsion are recovered and returned to storage for reuse. The latex emulsion is fed to the Flash Tank. Vacuum flashing removes the unreacted butadiene, where it is collected and passed through adsorber/desorber unit and returned to storage for reuse. Next, a steam stripping column is used to recover the styrene from the latex emulsion and returned to the styrene storage tank for reuse. From this point, the latex emulsion moves to storage tank(s).

The latex is pumped from the storage tanks to coagulation vessels and receives dilute sulfuric acid and sodium chloride. This brine mixture causes the emulsion to break up and releases the styrene-butadiene polymer as crumb rubber product, followed by rinsing, dewatering, and drying. The polymer crumb rubber is baled and shipped to downstream processors who use it as a material to manufacture their end products. According to information presented in the 1,3-butadiene TSCA risk evaluation docket by the International Institute of Synthetic Rubber Producers (IISRP) [15], the mass balance residual is less than 50 parts per billion 1,3-butadiene in the crumb SBR product.

Other common types of synthetic rubbers include [16]:

- Acrylonitrile Butadiene Rubbers (NBR)
- Acrylonitrile Butadiene Styrene (ABS)
- Butadiene Rubbers (BR)
- Styrene Isoprene Butadiene Rubbers (SIBR)
- Styrene Block Copolymers (SBC)

Figure 5 - Overview of Emulsion Polymerization process of SBR [14]



Another example of a polymer material made from three components is acetonitrile-butadiene-styrene resin (ABS). Manufacturers use either an aqueous phase reaction process similar to SBR or a continuous mass process, where polybutadiene rubber is dissolved in styrene and acrylonitrile with modifiers and other reaction initiators. The ABS polymer formed from the continuous mass process occurs through phase inversion, where the ABS falls out of solution. The ABS polymer is extruded, cooled in a water bath and chopped into pellets. Since this manufacturing technology begins with polybutadiene, 1,3-butadiene emissions are not expected when this process is used [13].

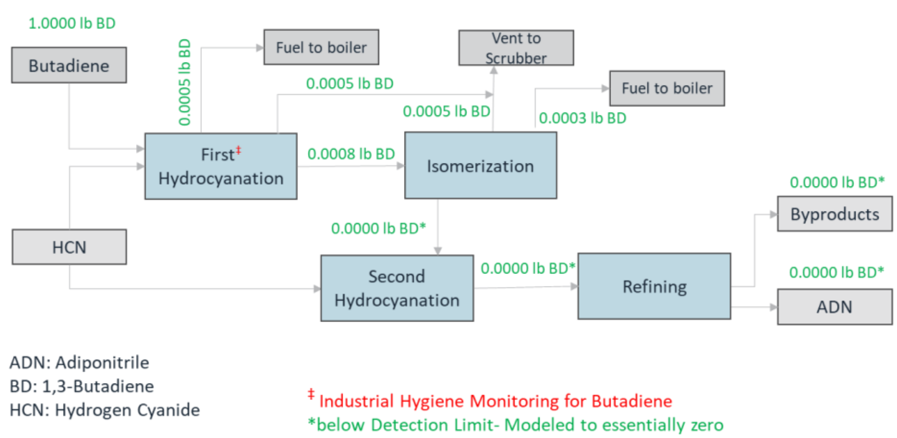
2. Chemical Intermediates Manufacturing Examples

Chemical intermediates starting from 1,3-butadiene include 1,4 Hexadiene, Sulfolane and 1,5,9-Cyclodecatriene [7]. Other industrial chemistries use 1,3-butadiene to make 1-Octene, 1-Octanol, and

Adiponitrile. Newer chemical approaches include those that use catalysts to transform 1,3-butadiene to chemicals such as adipates, adipic acid, and 3-ethyl-6-vinyltetrahydro-2H-pyran-2-one (EVP) [10].

An example of one such chemistry is adiponitrile. 1,3-butadiene is used as a building block chemical to make nylon 6,6 through the adiponitrile process, as shown in Figure 6 [15]. 1,3-butadiene is fed through a closed, tightly monitored system into a hydrocyanation process to form adiponitrile. Any residual 1,3-butadiene vapors during the hydrocyanation process are sent to destruction devices. By the end of the hydrocyanation process, at which point adiponitrile has been created, 1,3-butadiene has been completely consumed and is no longer detectable in the product stream. Adiponitrile is then converted to produce hexamethylene diamine, a nylon intermediate that is used to produce nylon 6,6 polymer.

Figure 6 – Overview of the Adiponitrile Manufacturing Process [15]



H. **What End Products are made from 1-3-Butadiene derived Synthetic Rubbers or Chemical Intermediates**?

Figure 4 in the upper right box lists the most common products that are derived from polymer or chemical intermediates uses. Generally, synthetic rubbers are the starting point for manufacture of articles or components for finished goods. Many chemical intermediates end up as other types of synthetic rubber or resins. Examples include 1,4-Hexadiene to make Ethylene Propylene Diene Rubber and 1,5,9-Cyclodecatriene to make nylon resins.

Products, such as tires, are one or more steps removed from the polymerization process. Final end use products made from polymers use vulcanization or other thermal injection molding processes. This makes it unlikely for unreacted 1,3-butadiene to remain in the final products.

Tires are manufactured using separate compounds for different parts of the tire. The various raw materials, such as PBR or SBR and pigments/other additives, are mixed into a homogenized batch of black material with the consistency of gum. The compounded materials are sent to machines to make sidewalls, treads or other tire parts. The parts are pressed together, making an uncured tire. The final step is to place the uncured tire in a mold and heat to more than 300°F for 12-15 minutes. This vulcanization step bonds the components together and cures the rubber to its final form. (The US Tire Manufacturers Association's website has a video depicting the process) [11].

See references [5], [7], [16] for more detailed listings of downstream uses or end products derived from 1,3-butadiene.

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