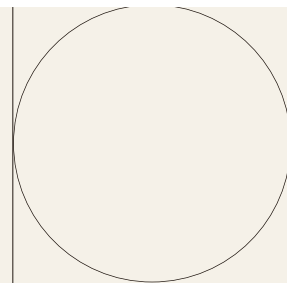


PROJECT DOCUMENTATION



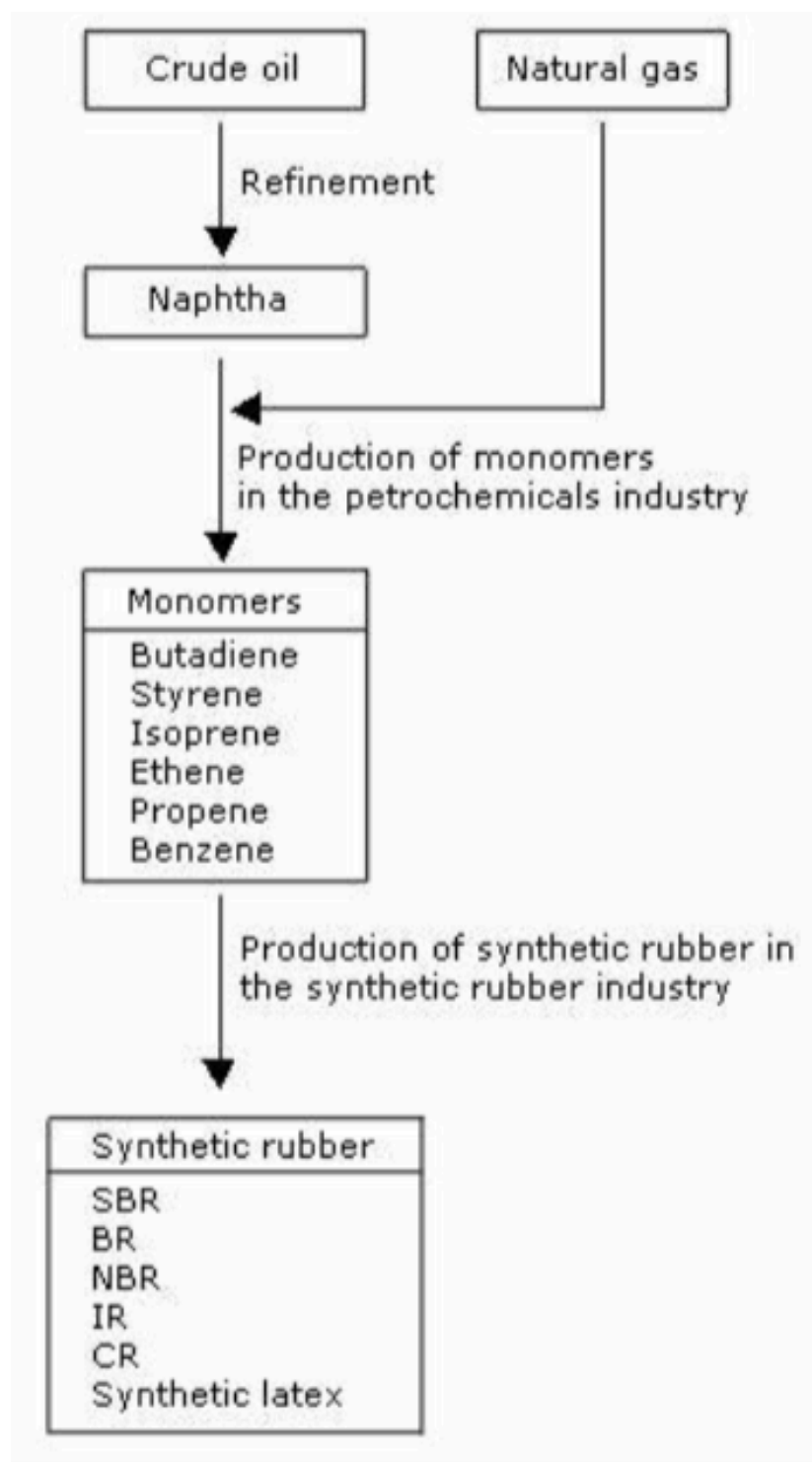
OVERVIEW

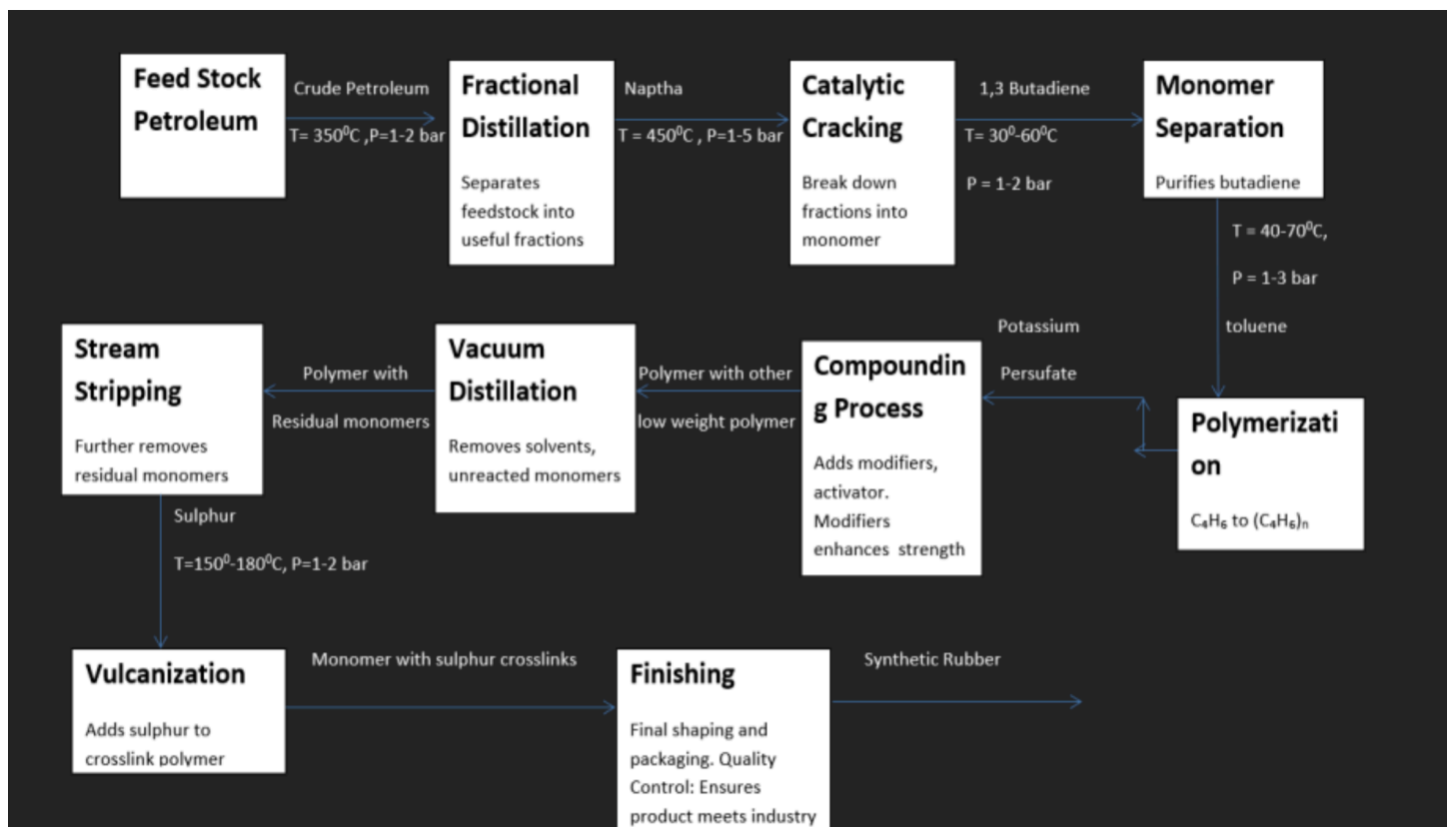
<i>Project Name</i>	PRODUCTION OF SYNTHETIC RUBBER FROM PETROLEUM
<i>Project Manager</i>	Neeraj Kajala-230691 Aditya Patil-230074 Navdeep- 230683 Kaushey- 230547 Nithin T M -230709 Aarnav Gupta 230014
<i>Background</i>	The production of synthetic rubber from petroleum involves several key steps, including fractional distillation, catalytic cracking, polymerization, compounding, processing, vulcanization, and finishing. The process starts with petroleum feedstock, which is separated into various fractions through distillation. The relevant fractions undergo cracking to produce monomer 1,3 butadiene.
<i>Objectives</i>	<ul style="list-style-type: none">● To simulate production of monomer 1,3 butadiene from crude oil● to explore uses and further modification of polymer butadiene rubber

PROJECT SPECIFICS

<i>Project Constraints</i>	<p>Many of the key information his unknown and a lot composition is used to through estimation , apart from that crude oil composition has been estimated and its major composition has been shown by representative compounds,</p> <p>Apart from that a major chunk of cracking products has been estimated</p>
<i>Deliverables</i>	<p>Report consisting of explanation , and simulation files used.</p>

FLOWSHEET OF PROJECT





Feedstock Petroleum

Composition: Crude Oil doesn't have a fixed composition, The primary component of crude oil, hydrocarbons are chemicals made up of hydrogen and carbon. The most common hydrocarbons in crude oil are paraffins, naphthenes, and aromatic. On basis of slit of fractional distillation the crude oil is divided into :LPG , Naphtha,kerosene,diesel,Residue .For the purpose of Simulation from each category a representative compound was chosen and then further process was done

LPG: LPG stands for liquefied petroleum gas. Like all fossil fuels, it is a non-renewable source of energy. It is extracted from crude oil and natural gas. LPG is composed hydrocarbons containing three or four carbon atoms. The normal components of LPG thus, are propane (C_3H_8) and butane (C_4H_{10}). Small concentrations of other hydrocarbons may also be present.

Representative Compound: Propane

mole fraction in simulation: 0.08

Naphtha: Less volatile fraction separated from coal tar by distillation. Contains naphthalene, acenaphthene, methylnaphthalenes, fluorene, phenol, cresols, pyridine, picolines, among other substances. Flash point greater than 100 °F. Toxic by inhalation and skin absorption. Less dense than water and insoluble in water. Vapors heavier than air.

Representative Compound: Cyclohexane

mole fraction in simulation:0.35

Kerosene: Chemically, kerosene is a mixture of hydrocarbons. The chemical composition depends on its source, but it usually consists of about 10 different hydrocarbons, each containing 10 to 16 carbon atoms per molecule. The main constituents are saturated straight-chain and branched-chain paraffins, as well as ring-shaped cycloparaffins (also known as naphthenes). Kerosene is less volatile than gasoline. Its flash point (the temperature at which it will generate a flammable vapour near its surface) is 38 °C (100 °F) or higher, whereas that of gasoline is as low as -40 °C (-40 °F). This property makes kerosene a relatively safe fuel to store and handle.

Representative Compound: N-Decane

mole fraction in simulation: 0.33

Diesel: Diesel, or fuel oil, is the standard liquid fuel for stationary gas turbines, due to the good storage and combustion properties. It is a product from crude oil in the distillation window between 200 °C and 350 °C. It consists of approximately 75% aliphatic hydrocarbons (C₁₀H₂₀–C₁₅H₂₈) and about 25% aromatic hydrocarbons (e.g. benzene, styrene). The typical atomic mass concentrations are about 86% C, 14% H and a minor fraction of sulfur depending on crude oil source and cleaning quality.

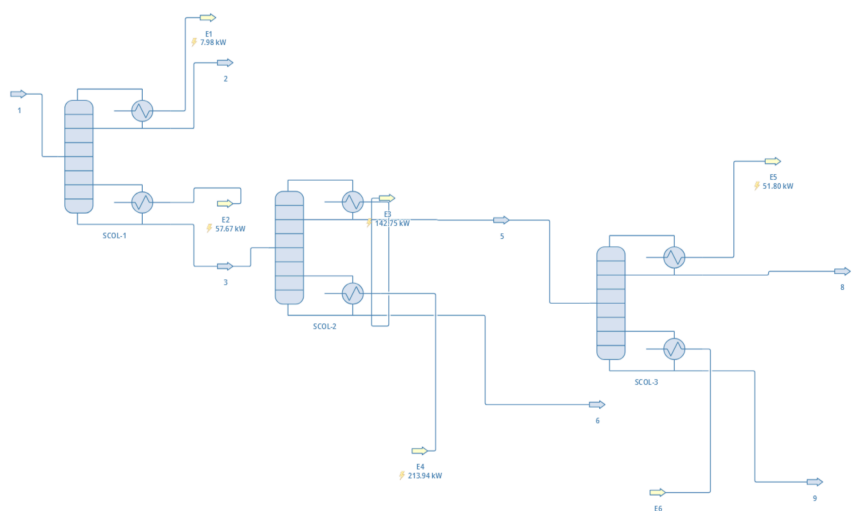
Representative Compound: N -HeptaDecane

mole fraction in simulation: 0.24

Residue: This primary consist of non volatile components which do not participate in distillation .For the purpose of simulation this was not included and mole fraction of other composition was normalised

Representative Compound: None

mole fraction in simulation:0%

***Fractional***

- Normally, the vapour composition of any liquid mixture does not remain equal to the liquid composition. When the

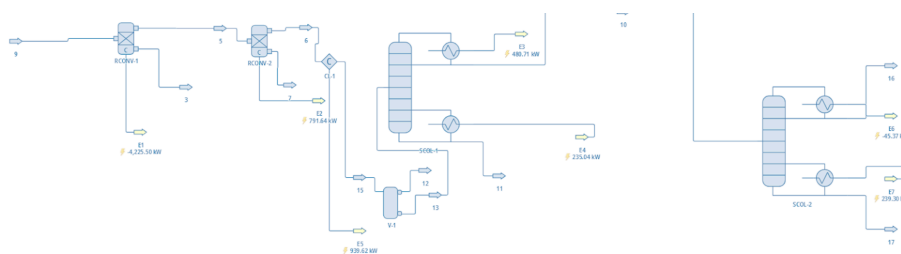
distillation

mixture is heated, the liquid with the lower boiling point boils and converts to vapours.

- The more volatile component remains in a vapour state longer than the liquid component. Repeated distillations and condensations are used in the process, and the mixture is usually separated into component parts.
- The more volatile components increase in a vapour state after heating, and when this vapour is liquefied, the more volatile components increase in a liquid state.

We obtain 201.58 kg/hr of Cyclohexane(naphtha) with a mole fraction of 0.978 in stream no 8 for a 1000 kg/hr input basis of crude oil

Flowsheet



Catalytic Cracking

Cracking of cyclohexane has been performed over a HZSM-5 catalyst with Si/Al ratios 28, 85 and 200, in the temperature region 400–650 °C and with partial pressures of cyclohexane up to 2 bar. The cracking kinetics for Si/Al = 200 can be adequately modelled by simple first order kinetics. Olefins and benzene appear to be the primary products from the cracking reaction, while alkanes and higher aromatics behave as secondary products. Combined selectivities of ethene + propene increase with increasing temperature, and more than 60% selectivity can be reached. Under the reaction conditions very rapid equilibration of olefins heavier than ethene is obtained.

During the ideal process the naphtha's are cracked to obtain butadiene or ethynes e, for the purpose of process simplification we chose cracking of cyclohexane and we assume input without impurities and only include major cracking products

The reactions are as follows

$-(CH_2)_6- \rightarrow 2CH_2CHCH_3$ Conversion rate of 20%
 $-(CH_2)_6- \rightarrow 3CH_2CH_2$ Conversion rate of 40%
 $-(CH_2)_6- \rightarrow CH_2CHCHCH_2 + CH_2CH_2 + H_2$ Conversion rate of 20%

We obtain

0.128 kg/hr of butadiene

0.466 kg/hr of ethylene

from 1 kg stream of cyclohexane

After this we perform another reaction for formation of butadiene from ethyne with conversion rate of 95%

Monomer Separation

For separation after reaction we first cool and pressurise the mixture to condense butadiene only and then remove vapour part to eliminate volatile part of mixture, then the remaining mixture is filtered through fractional distillation to obtain a stream of butadiene

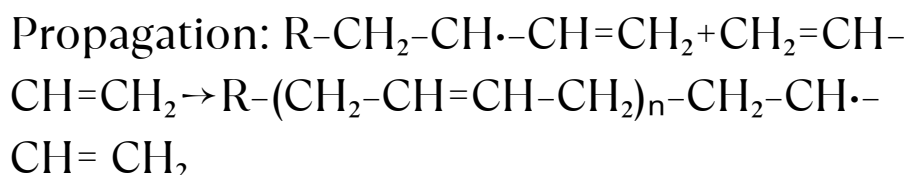
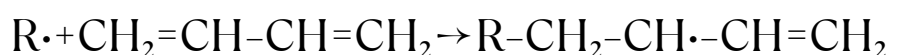
we obtain

0.477 kg/hr of butadiene

with mole fraction of 0.97 with an input of 1kg/hr of cyclohexane

Polymerization

Polymerization is the key chemical process used to create synthetic rubber from monomers derived from crude oil. Delving deeper into the polymerization process, we explore the chemistry, types, reaction mechanisms, catalysts, and the efficiencies of each process.



Termination: $R-(CH_2-CH=CH-CH_2)_n\cdot + R'-(CH_2-CH=CH-CH_2)_m\cdot \rightarrow R-(CH_2-CH=CH-CH_2)_n-R'$

1. Polymerization Overview

Polymerization is the process where small molecules known as **monomers** chemically bond together to form long chains or networks called **polymers**. For synthetic rubber, typical monomers include butadiene, styrene, and isoprene.

The polymerization process can be broadly categorized into:

- **Addition Polymerization (Chain-Growth Polymerization)**
- **Condensation Polymerization (Step-Growth Polymerization)**

For synthetic rubber production, **addition polymerization** is primarily used. The key sub-types of polymerization methods involved in synthetic rubber manufacturing are:

- **Emulsion Polymerization**
- **Solution Polymerization**

Solution Polymerization (Common for butadiene Rubber)

Solution polymerization is typically used to produce **butadiene rubber (BR)**. It involves dissolving the monomers in a hydrocarbon solvent and using catalysts like Ziegler-Natta or anionic initiators.

Process Overview:

- **Ingredients:** Monomers (butadiene, isoprene), hydrocarbon solvents (e.g., hexane, cyclohexane), and catalysts (e.g., Ziegler-Natta or anionic catalysts).
- **Reaction:** The monomers dissolve in the solvent, and polymerization occurs in the solution phase. This method yields linear polymers with controlled molecular weights.

Key Reactions:

- **Initiation:** Anionic initiators (like n-butyllithium) or coordination catalysts initiate the polymerization, creating

active chain ends.

- **Propagation:** Monomers add to the growing chain, one unit at a time.
- **Termination:** The chain stops growing either by reaction with a terminating agent or by running out of available monomers.

Reactor Types:

- **Continuous Stirred Tank Reactor (CSTR) or Tubular Reactor** is often used, especially for large-scale production.

Efficiencies and Control Parameters:

- **Monomer Conversion:** Typically around 80-95%, depending on factors like the type of solvent, temperature (often between -10°C and 60°C), and the choice of catalyst.
- **Temperature Control:** Lower temperatures (~0°C) are sometimes used to control the reaction rate and molecular weight distribution, as exothermic polymerization reactions can lead to runaway reactions.
- **Molecular Weight Control:** Chain transfer agents (like hydrogen or alkyl halides) are used to regulate molecular weight, ensuring the desired rubber properties.
- **Advantages:** Solution polymerization allows for better control over the molecular structure, resulting in polymers with specific mechanical properties (like elasticity and resilience).

Challenges:

- **Solvent Recovery:** One of the significant inefficiencies in solution polymerization is the need to recover and recycle the solvent, which adds to energy costs.
- **Heat Management:** Since the reaction is exothermic, efficient removal of heat is essential to maintain control over polymerization and avoid degrading the polymer.

Compounding

Compounding is the critical step following polymerization where raw synthetic rubber is mixed with various additives to enhance its properties for specific applications. The goal of compounding is to create a rubber material with desired mechanical, chemical, and thermal properties that meet the requirements for products like tires, seals, hoses, and industrial components.

1. Raw Polymer Handling

After polymerization, the raw synthetic rubber (e.g., **BR**, **PBR**, **IR**) is in a crude, unprocessed state. It has high elasticity but lacks strength, durability, and other functional properties. The polymer is typically received as bales or sheets and is fed into mixers for processing.

2. Key Additives in Compounding

To tailor the properties of the rubber for specific uses, a variety of additives are incorporated. These include:

- **Fillers:**
 - **Carbon Black:** Enhances tensile strength, abrasion resistance, and UV stability, making it ideal for tire manufacturing.
 - **Silica:** Used to improve tear strength and reduce rolling resistance in tires.
- **Plasticizers/Oils:** These reduce viscosity and improve flexibility, making the rubber easier to process and mold.
- **Vulcanizing Agents:**
 - **Sulfur:** The most common vulcanizing agent used to cross-link rubber molecules, increasing elasticity and durability.
 - **Accelerators:** Chemicals that speed up the vulcanization process (e.g., **zinc oxide**, **stearic acid**).
- **Antioxidants and Antiozonants:** Protect the rubber from degradation caused by oxygen and ozone exposure during its service life.
- **Processing Aids:** These additives improve the mixing and processing behavior of the rubber (e.g., **waxes** and **fatty acids**).

3. Mixing Process

Rubber and additives are combined in **industrial mixers** such as Banbury mixers or **two-roll mills**. The mixing process is carefully controlled to ensure uniform distribution of all components.

- **Step 1:** Raw rubber is softened by mechanical shearing and heat in the mixer.
- **Step 2:** Fillers, plasticizers, and processing aids are added to the softened rubber and thoroughly mixed.
- **Step 3:** Vulcanizing agents and accelerators are added last, ensuring they do not pre-react before the vulcanization stage.

Mixing Temperature and Time: Controlled to avoid premature vulcanization (scorching) and ensure proper dispersion of all additives. Typical temperatures range from **80°C to 120°C**, depending on the rubber type and additives used.

Processing

After the compounding stage, the compounded rubber undergoes several processing steps to transform it into finished products like tires, hoses, seals, and various industrial components. The key processes involved in rubber processing are shaping, preheating, vulcanization, and finishing. These processes are critical for achieving the desired physical and chemical properties in the final rubber product.

1. Shaping (Forming)

Once the rubber is compounded, it is shaped into the desired form before vulcanization. Various methods are used to shape rubber, depending on the product being manufactured.

Key Shaping Methods:

- **Extrusion:**
 - Rubber is fed into an extruder, where it is forced through a die to create continuous lengths of specific shapes (e.g., profiles, tubes, hoses).
 - The rubber is heated in the extruder, which helps soften and shape it.
 - This process is commonly used for making products like tires, seals, and gaskets.
- **Calendaring:**
 - In this process, rubber sheets or films are formed by passing the compound through a series of heated rollers (calendriers).
 - Calendaring is used for making large flat sheets or coating fabrics with rubber for products like conveyor belts or inflatable structures.
- **Molding:**
 - Rubber is placed into a mold where heat and pressure are applied to shape the rubber into the final form.
 - Injection Molding: Pre-heated rubber is injected into a mold cavity where it takes the shape of the mold.
 - Compression Molding: The rubber compound is placed in a mold, and the mold is closed under pressure, forcing the rubber into the shape of the cavity.
 - Molding is commonly used for making complex shapes like seals, gaskets, and certain automotive parts.

Vulcanization

Vulcanization is the chemical process that transforms raw, pliable rubber into a durable, elastic material with significantly improved mechanical properties. It is the most critical step in rubber processing, giving synthetic rubber its desired strength, flexibility, resilience, and resistance to various environmental factors. During vulcanization, cross-links are formed between the long polymer chains of the rubber, transforming it from a sticky, malleable substance into a robust, flexible material suitable for a wide range of applications.

1. Importance of Vulcanization

Raw rubber, whether natural or synthetic, lacks the strength and resilience needed for industrial and consumer products.

Without vulcanization, rubber tends to be:

- **Sticky:** It adheres to surfaces, making it difficult to handle and use.
- **Deformable:** It retains any shape it's molded into without returning to its original form.
- **Weak:** It lacks the tensile strength to withstand mechanical stress.
- **Poorly resistant:** It degrades quickly under heat, light, or exposure to chemicals like oils and ozone.

Through vulcanization, rubber is given the properties that make it practical for applications like tires, hoses, seals, and other industrial components.

2. The Vulcanization Process

Vulcanization involves the following key steps:

1. **Addition of Vulcanizing Agents:**
 - The most common vulcanizing agent is sulfur, but other agents like peroxides, metal oxides, and urethane cross-linkers can also be used depending on the desired properties.
 - The vulcanizing agent is mixed into the rubber compound during the compounding phase, ensuring even distribution.
2. **Application of Heat and Pressure:**
 - The rubber is shaped into its final form before the vulcanization process. This can be done through molding, extrusion, or calendering.
 - Heat and pressure are applied to the rubber either in a mold, an autoclave, or by using other methods like

continuous vulcanization systems.

- The temperature typically ranges from 140°C to 160°C, depending on the rubber type and the application. The pressure can vary but is often between 2 to 4 MPa in compression molding systems.

3. Cross-Linking Reaction:

- As the rubber is heated, the sulfur atoms (or other cross-linking agents) form bridges between the polymer chains of the rubber. These bridges (cross-links) bond the molecules together, creating a more interconnected, durable network.
- The degree of cross-linking determines the hardness, elasticity, and tensile strength of the vulcanized rubber. More cross-links typically result in harder, less elastic rubber, while fewer cross-links give a softer, more flexible material.

3. Types of Vulcanization

Depending on the product and the type of rubber used, several methods of vulcanization may be employed:

- Conventional Sulfur Vulcanization:
 - This is the most common method, especially for synthetic rubbers like SBR (Styrene-Butadiene Rubber) and PBR (Polybutadiene Rubber).
 - Sulfur, along with accelerators like zinc oxide and stearic acid, is mixed into the rubber. The accelerators reduce the time required for the vulcanization reaction.
 - Typical cure times range from 5 to 15 minutes, depending on the temperature and the type of rubber.
- Peroxide Vulcanization:
 - Used for rubbers that need to be resistant to high temperatures or aggressive chemicals. Peroxides (like dicumyl peroxide) create carbon-carbon cross-links, which provide better heat and chemical resistance than sulfur cross-links.
 - Commonly used for elastomers like EPDM (Ethylene Propylene Diene Monomer) or silicone rubber.
- Autoclave Vulcanization:
 - In this method, rubber products (e.g., large hoses, tires) are placed in an autoclave where they are exposed to steam heat and pressure. This method is used for products with large, complex shapes that cannot be easily cured in molds.
 - The autoclave maintains high-pressure steam (around 170°C to 180°C at 1.5 to 2 MPa) to ensure uniform curing.
- Continuous Vulcanization:

- For products like wire and cable insulation, extrusion is followed by continuous vulcanization, where the extruded rubber passes through a heated tunnel or tube filled with hot air, steam, or liquid.
- This process is highly efficient for long-length products and reduces cycle times compared to batch vulcanization.

4. Vulcanization Efficiency and Optimization

Vulcanization efficiency is critical for both the performance of the final product and the overall cost of the manufacturing process. Optimization of the vulcanization process involves:

- **Cure Time:** Determining the optimal cure time is crucial. Over-curing can lead to brittle rubber, while under-curing results in weak, underdeveloped material. Cure times are controlled through accelerators and precise temperature management.
- **Energy Efficiency:** Using advanced heating methods like microwave or infrared vulcanization reduces the energy consumption of traditional steam or hot-air curing processes, cutting down curing times by as much as 50%.
- **Cross-Link Density:** Managing the cross-link density is essential for achieving the desired balance between elasticity and strength. More cross-links result in harder, less elastic rubber, while fewer cross-links lead to more flexible but weaker rubber.

5. Testing and Quality Control in Vulcanization

After vulcanization, the rubber is tested for key performance metrics:

- **Hardness:** Measured on the Shore A or D scale, depending on the application. Harder rubbers are needed for applications like tires, while softer rubbers are used in seals and gaskets.
- **Tensile Strength:** The ability of the rubber to withstand stretching forces. Vulcanization increases the tensile strength significantly compared to unvulcanized rubber.
- **Elongation:** A measure of how much the rubber can stretch before breaking. Elasticity is a key property for many rubber products, especially in applications requiring flexibility.
- **Heat and Chemical Resistance:** The ability to withstand harsh environments is critical for many industrial applications. Properly vulcanized rubber resists degradation from heat, ozone, oils, and other chemicals.

6. Applications of Vulcanized Rubber

Vulcanized rubber has a wide range of applications due to its enhanced properties:

- **Tires:** Vulcanized rubber is used extensively in the tire industry due to its toughness, durability, and ability to withstand mechanical stresses and environmental conditions.
- **Seals and Gaskets:** Vulcanized rubber seals are used in various automotive and industrial applications where flexibility, chemical resistance, and durability are required.
- **Hoses and Belts:** In automotive and industrial sectors, rubber hoses and belts are vulcanized to provide the necessary elasticity, abrasion resistance, and tensile strength.

CONCLUSION

The synthesis of rubber from crude petroleum has revolutionized the production and accessibility of rubber, providing a reliable alternative to natural rubber. This process involves the conversion of crude oil into monomers like butadiene which are then polymerized to create synthetic rubber with consistent properties and enhanced durability. Synthetic rubber's versatility and resilience have made it indispensable in industries ranging from automotive to aerospace.

The synthesis techniques continue to evolve, reducing environmental impact and improving efficiency. However, challenges remain in minimizing energy usage and emissions. Ongoing research and development in this field aim to address these concerns, potentially creating even more sustainable production methods. In summary, the synthesis of rubber from petroleum not only meets global demand but also provides a foundation for future advancements in materials science and environmental responsibility.

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