CHEMICALS FROM C_4 COMPOUNDS

BUTANE AND BUTENES

BUTADIENE

Properties

- *Description : Colorless gas*
- *Molecular formula* C_4H_6 (CH_2=CH.CH=CH_2)
- *Boiling point* *-4.4 °C*
- *Solubility Very slightly soluble in water (735 mg/L);* soluble in ethanol, ether, acetone, benzene and organic solvents.
- It is a hazardous chemical due to its flammability, reactivity, and toxicity.

Uses

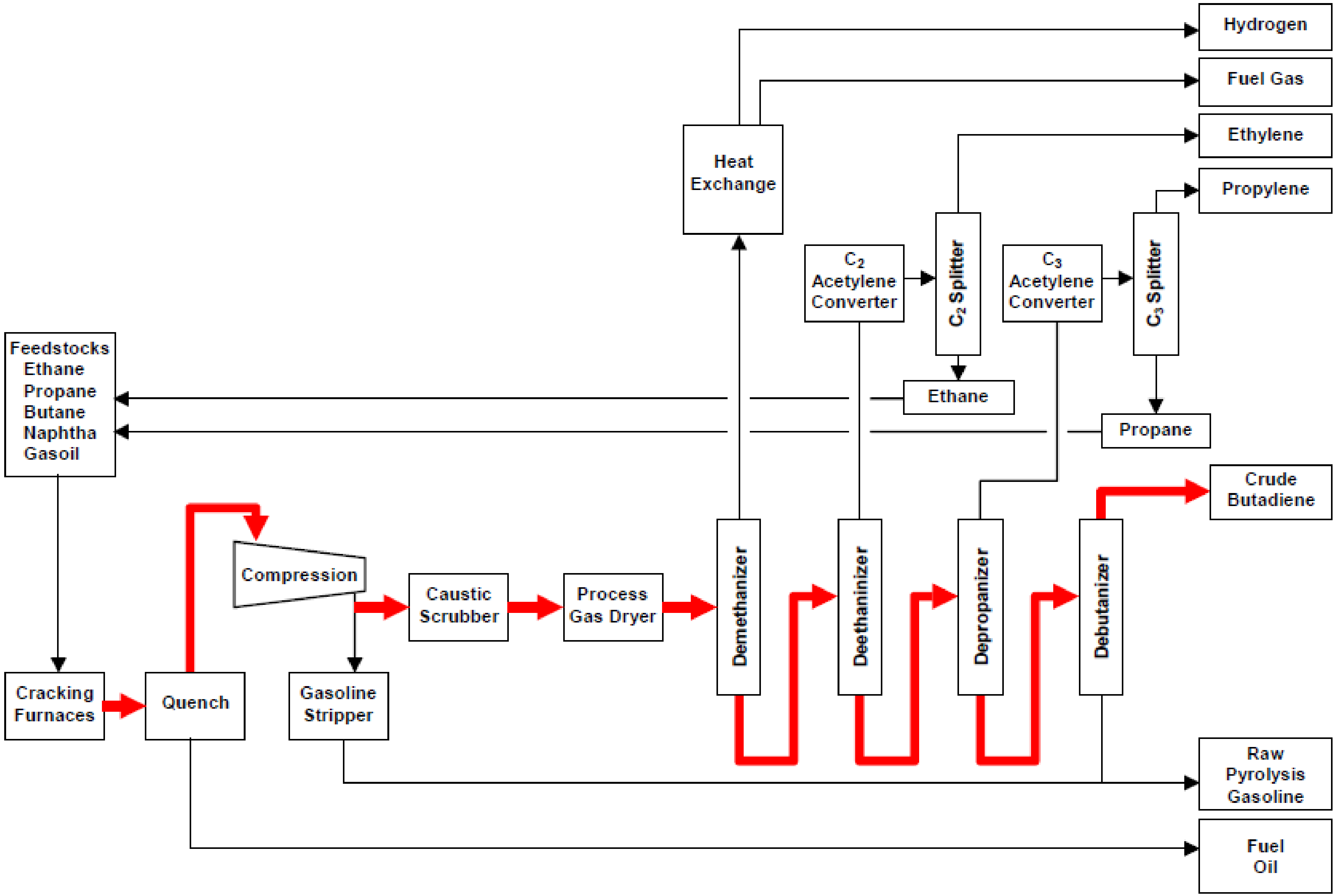
- Used primarily as a chemical intermediate
- As a monomer in the manufacture of polymers such as synthetic rubbers or elastomers : styrene-butadiene rubber (SBR), polybutadiene rubber (PBR), polychloroprene (Neoprene) and nitrile rubber (NR).
- Major use of butadiene is in the production of tires.
- Manufacture of polymers, latexes, and plastics.

Production Methods : Butadiene is produced commercially by three processes:

- Steam Cracking of Paraffinic Hydrocarbons: In this process, 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).

Each of these processes produces a stream commonly referred to as crude butadiene that is rich in 1,3-butadiene.

Steam Cracking of Paraffinic Hydrocarbons



Flow path for C_4 Components including butadiene

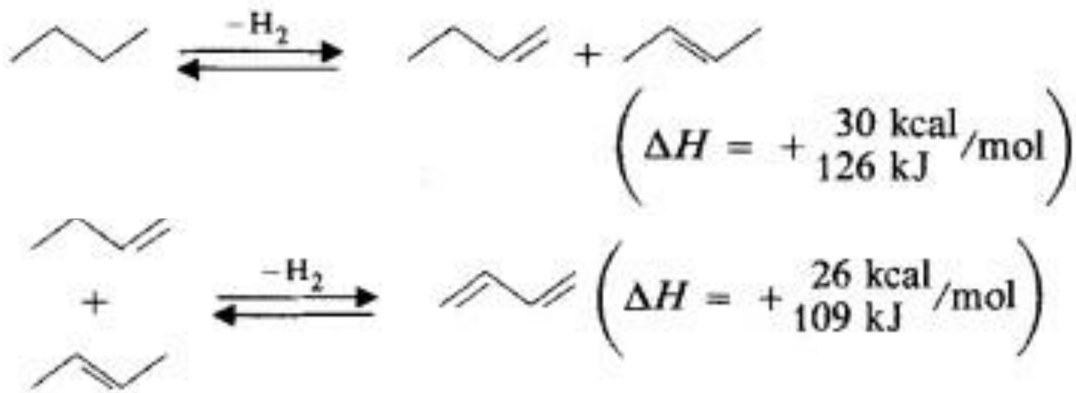
Quality of a crude C_4 stream via steam cracking process (Vary from source to source)

Table 1.1: Example of a Crude Butadiene Analysis

Component	Crude Butadiene Vol %	Example Range
C3 & Lighter	0.40	0.01-1.00
i-Butane	1.00	0.50-18.00
n-Butane	5.00	3.00-33.00
Butene-2 (Cis)	4.05	2.50-10.00
Butene-2 (Trans)	5.45	3.50-12.00
Butene-1	14.88	7.00-17.00
i-Butylene	22.50	12.00-27.00
1,2-Butadiene	0.16	0.10-2.00
1,3-Butadiene	44.00	10.00-75.00
C4 Acetylenes	1.41	0.05-3.50
M-Acetylene	0.06	0.01-0.50
E-Acetylene	0.20	0.01-1.00
V-Acetylene	1.15	0.01-2.50
C5+	0.90	0.10-4.00
Other	0.25	
	100.0	

Catalytic Dehydrogenation of n-Butane and n-Butene (the Houdry process).

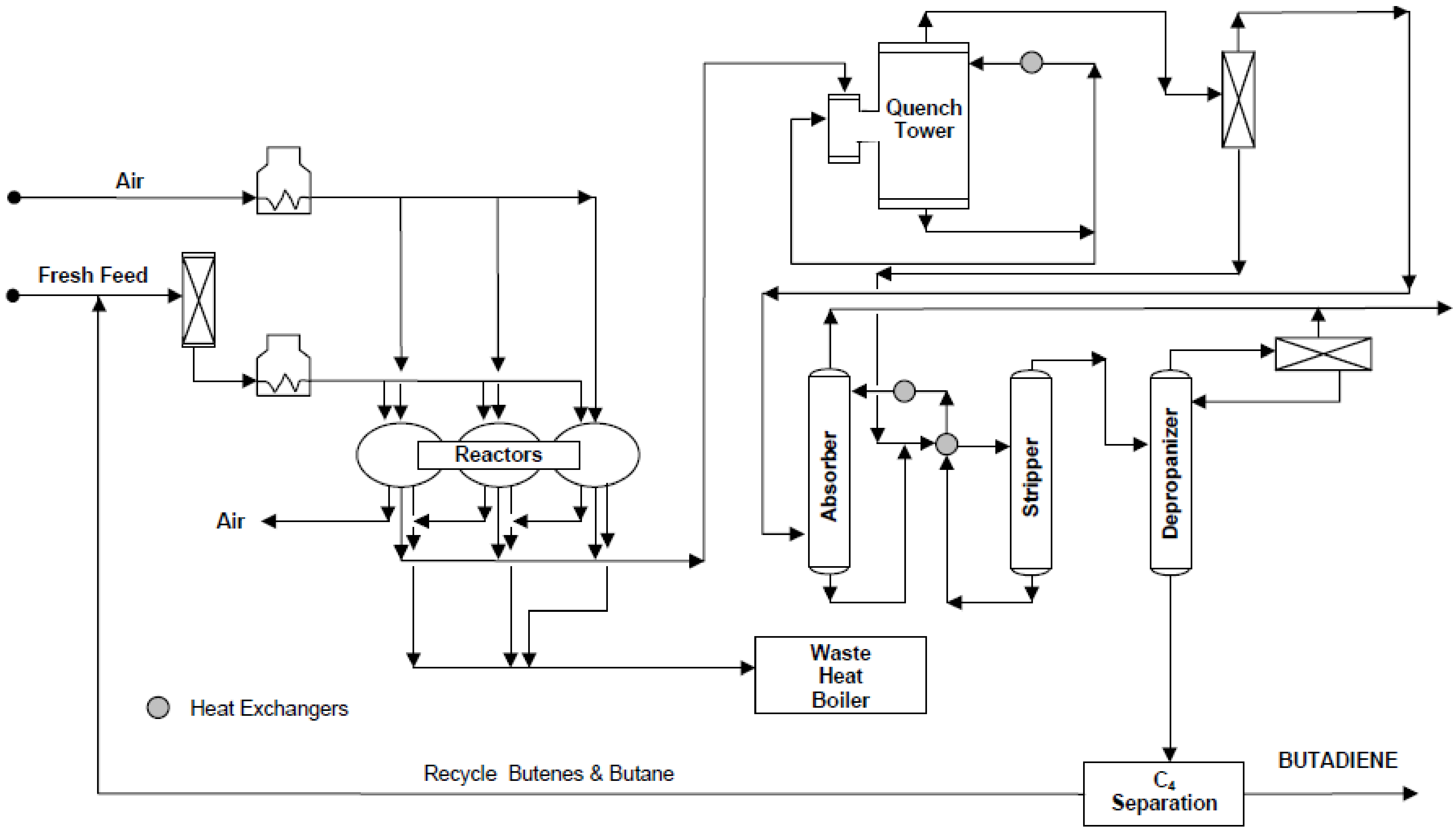
- The catalytic dehydrogenation of n-butane is a two-step process; initially going from n-butane to n-butenes and then to butadiene. Both steps are endothermic.



  - Relatively high temperatures (600-700 °C) are necessary to achieve economical conversions. At these temperatures, side reactions such as cracking and secondary reactions involving the unsaturated compounds become important. Therefore, a short residence time and a selective catalyst must be used.
  - In the Houdry process, n-butane is dehydrogenated over chromium-alumina oxide catalysts.

Process Flow Sheet

Figure 1.2: Catadiene Process*



Process Description

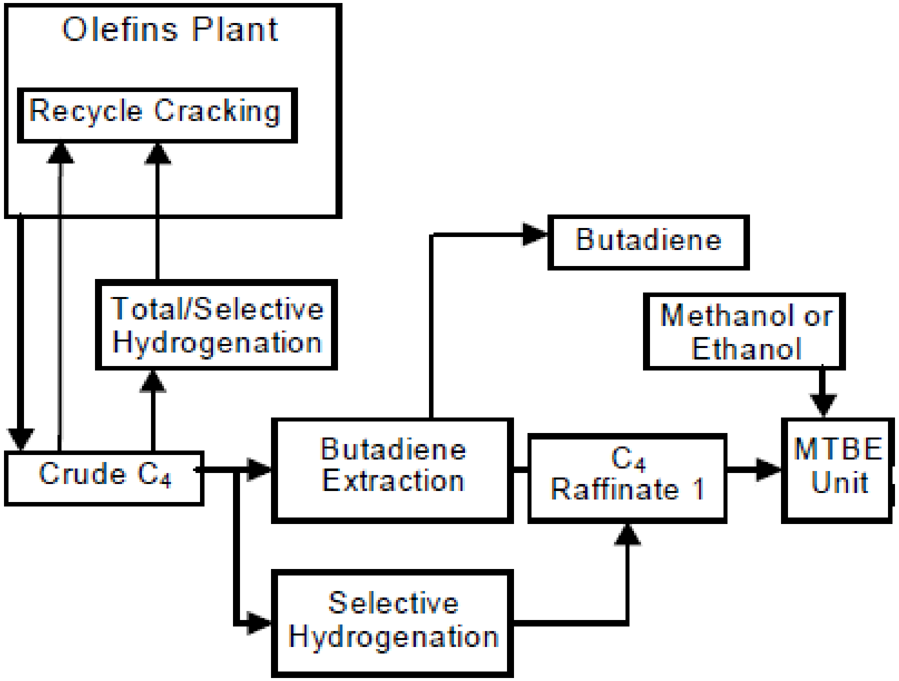
- The reactors normally operate at 0.2-0.4 bar absolute pressure and approximately 600-680 °C. Three or more reactors can be used to simulate continuous operation: while the first reactor is on-line, the second is being regenerated, and the third is being purged prior to regeneration.
- Residence time for feed in the reactor is approximately 5-15 minutes. As the endothermic reaction proceeds, the temperature of the catalyst bed decreases and a small amount of coke is deposited.
- In the regeneration cycle, this coke is burned with preheated air, which can supply essentially all of the heat required to bring the reactor up to the desired reaction temperature.
- The reactor effluent goes directly to a quench tower, where it is cooled. This stream is compressed before feeding an absorber/stripper system, where a C_4 concentrate is produced to be fed to a butadiene extraction system for the recovery of high purity butadiene.

Butadiene Production via Oxidative Dehydrogenation of n-Butenes (the Oxo-D or O-X-D process)

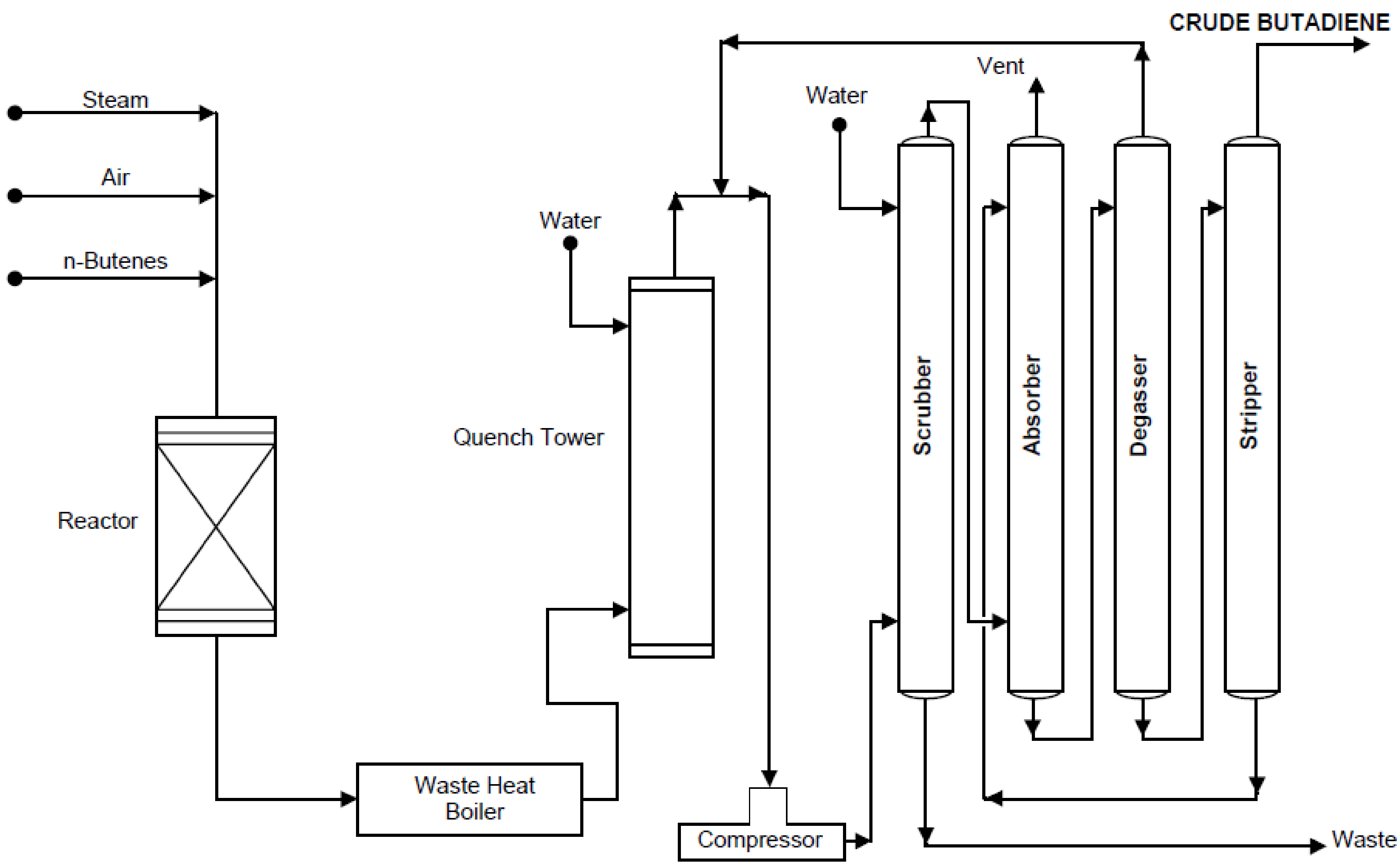
- Oxidative dehydrogenation of n-butenes has replaced many older processes for commercial (on-purpose) production of butadiene.
- In this process, the dehydrogenation equilibrium between butenes and butadiene is displaced by the addition of oxygen towards greater formation of butadiene.
- Butenes are much more reactive, however, and they require less severe operating conditions than that of n-butane to produce an equivalent amount of product. Therefore, the use of n-butane as a feedstock in this process may not be practical.
- In industrial operation, a sufficient quantity of oxygen (as air) is introduced so that the heat supplied by the exothermic water formation roughly equals the heat required for the endothermic dehydrogenation. In this way the butene conversion, the selectivity to butadiene, and the lifetime of the catalyst can be improved. By using an excess of air, the maximum temperature can be controlled by addition of steam. Mixed oxide catalysts based on Bi/Mo or Sn/Sb are most often used.
- In general, in an oxydehydrogenation process, a mixture of n-butenes, air and steam is passed over a catalyst bed generally at low pressure and at temperature approximately 500-600 °C.

- The heat from the exothermic reaction can be removed by circulating molten heat transfer salt, or by using the stream externally for steam generation. The air feed rate is such that an oxygen/butene molar ratio of approximately 0.55 is maintained, and the oxygen is totally consumed. A steam to butene ratio of 10:1 has been reported as necessary to absorb the heat of reaction and to limit the temperature rise
- The reactor effluent is cooled and the C_4 components are recovered in an absorber/ degasser/stripper column combination. The lean oil flows from the bottom of the stripper back to the absorber, with a small amount passing through a solvent purification area. Crude butadiene is stripped from the oil, recovered in the overhead of the stripper, then it is sent to a purification system to recover the butadiene product.

Processing of Crude Butadiene Streams



Process Description



Petrochemical from Aromatics

- Aromatics
  - Benzene
    - → Styrene → Polystyrene, Rubber
    - → Phenol → Resin, Polymer
    - → Dichlorobenzene → DDT
  - Toluene
    - → Benzoic Acid
    - → Solvent
  - Xylene → o-Xylene, m-Xylene, p-Xylene
  - Naphthalene
    - → Phthalic anhdride
    - → Dyes, Drug, Insect repellent