

Petrochemical Technology

Production of Aromatics

Aromatics by Naphtha Reforming

Almost every refinery in the world has a reformer

Purpose is to enhance aromatic content of naphtha

Improve the octane rating for gasoline

Feed stocks to aromatic complex

Hydrogen rich gas

Due to the nature of the reactions, reforming process also produces:

Fuel gas,

LPG,

600 psig steam with the WHB

RON/MON is increased by chemical transformation

❖ Light Naphtha (C₅-80°C): Isomerization process

n-Paraffins \longrightarrow *i*-Paraffins

Example: *n*-Hexane (RON: 24.8) \longrightarrow 2,2-Dimethyl butane (RON: 91.8)

❖ Heavy Naphtha (80-180°C): Catalytic Reforming process

n-Paraffins, Naphthenes \longrightarrow Aromatics

Example: *n*-Hexane (RON: 24.8) \longrightarrow Cyclohexane (RON: 83)
 \longrightarrow Benzene (RON:108)

Primary reactions:

Paraffins \longrightarrow Naphthenes

Olefins \longrightarrow Paraffins \longrightarrow Naphthenes

Naphthenes \longrightarrow Aromatics

Other reactions: Dealkylation, Hydrocracking



Reformer Feed and Product Properties

Hydrocarbons	Composition (Vol%) of		Composition (Vol%) of	
	Paraffinic naphtha	Reformate	Naphthenic naphtha	Reformate
Paraffins	67	30	29	20
Naphthenes	22	15	62	10
Aromatics	11	55	9	70
RON	50	94	66	98

Process Variables

Pressure: 420-460 psig

Temperature: 495-525 °C

Space-velocity (LHSV): 1.4 – 2.0 h⁻¹

Hydrogen partial pressure (H₂/HC): 3-5

The yield of aromatics is increased by:

- (1) High temperature** (increases reaction rate but adversely affects chemical equilibrium)
- (2) Low pressure** (shifts chemical equilibrium to the right)
- (3) Low space-velocity** (promotes approach to equilibrium)
- (4) Low hydrogen to hydrocarbon mole ratios** (shifts chemical equilibrium to the right; however, a sufficient hydrogen pressure must be maintained to avoid excessive coke formation)

Catalyst

Pt on Silica or Silica-Alumina base

Bimetallic catalysts are now-a-days used with second metal as either **Ir** (0.02-0.2wt%), **Sn** (0.05-0.5wt%) and **Re** (0.02-0.2 wt%)

Second metal improves stability of dispersion over time, coke resistance, selectivity and activity.

Cylindrical catalyst for fixed bed reactors

(Dia: 0.8-1.6mm; Length: 5mm)

Spherical catalyst for continuous units (Dia: 0.8-1.6mm)

Platinum serves as the catalytic site for hydrogenation and dehydrogenation reactions and chlorinated alumina provides acid sites for isomerization, cyclization and hydrocracking reactions.

Feed Preparation

Certain metals, hydrogen sulfide, ammonia, and organic nitrogen and sulfur compounds deactivate Pt catalyst. Feed pretreating, in the form of hydrotreating, is usually employed to remove these materials.

Reforming Catalyst Poisons

Name of the poison	Type	Allowable limit in feed	Effect
Sulfur	Temporary	< 0.5 ppm wt.	➤ Deactivates dehydrogenation/hydrogenation function
Nitrogen	Temporary	< 0.5 ppm wt.	➤ Primarily inhibits acid sites
Chloride	Temporary	< 0.5 ppm wt.	➤ Too much chloride increases acid function beyond the optimum required for balanced catalyst performance, which leads to excessive cracking
Moisture	Temporary	2-4 ppm wt.	➤ Throws the acid function out of balance by stripping chloride from the catalyst ➤ Moisture-chloride balance is very crucial for optimum catalyst performance
As, Pb	Permanent	1-2 ppb wt. 10-20 ppb wt.	➤ Deactivates metal function permanently

Catalytic Reforming Processes

Catalytic Reforming Processes Based on Catalyst Regeneration

1. Semi-regenerative (1949) – unit taken off-stream anywhere from every 3 to 24 months
2. Cyclic (1960) – involves swing reactor. Basically, operate 3 out of 4 and use extra reactor to take one offline.
3. Continuous (1971) – catalyst is removed and replaced during the operation. Maintains high activity. Expensive.

Commercial Catalytic Reforming Processes

Rheniforming – Chevron (SR)

Platforming – UOP (SR)

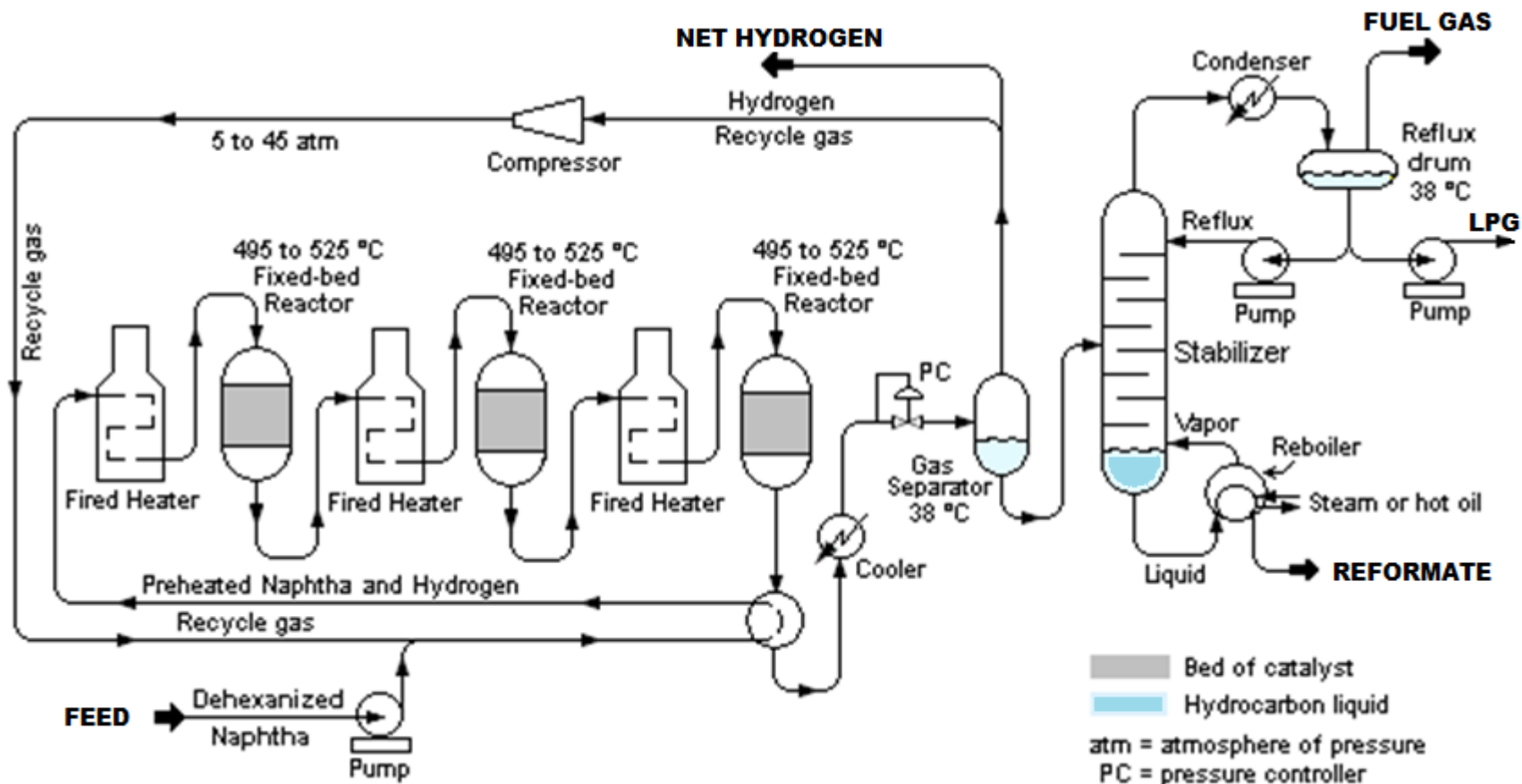
Powerforming – ExxonMobil (Cyclic)

Ultraforming – British Petroleum (CCR)

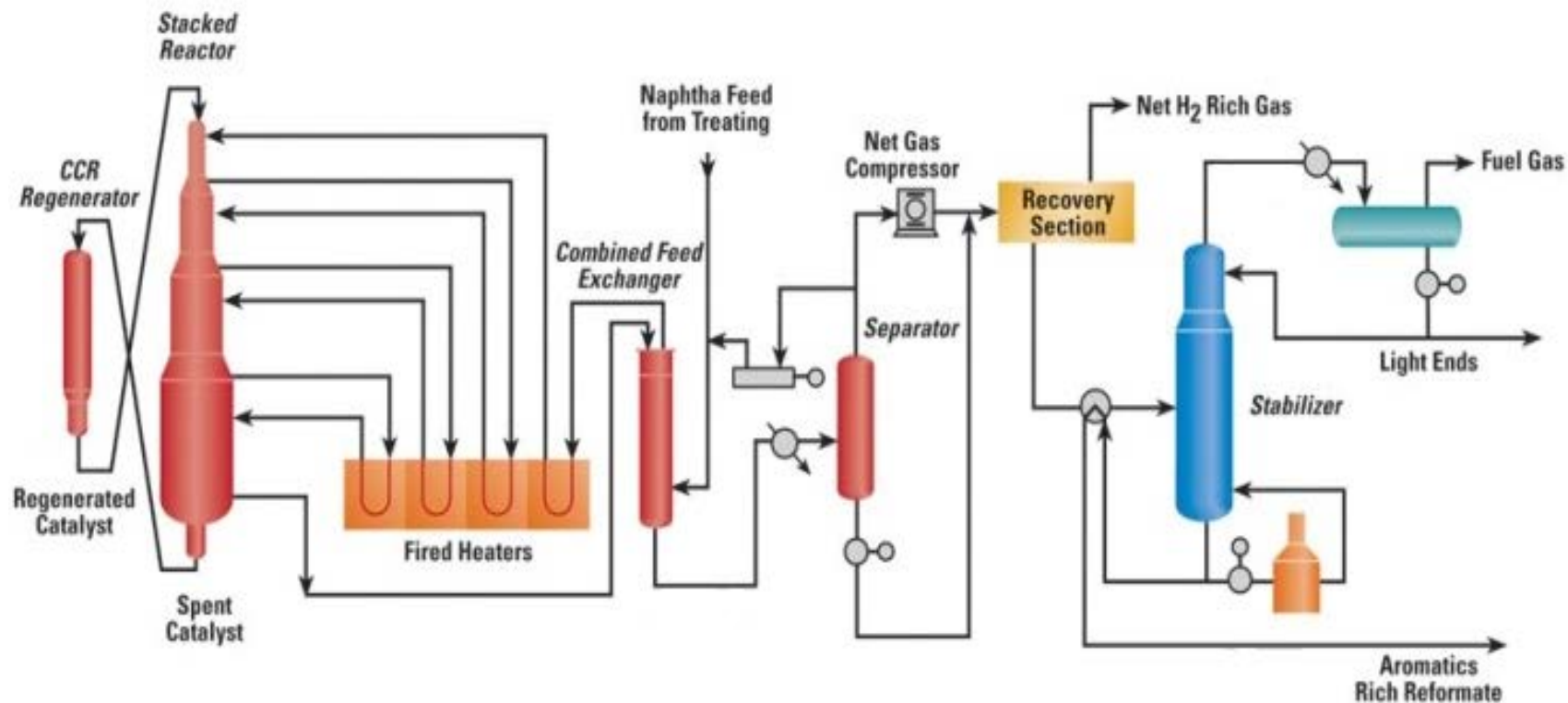
Magnaforming – British Petroleum (CCR)

Octanizing – IFP (CCR)

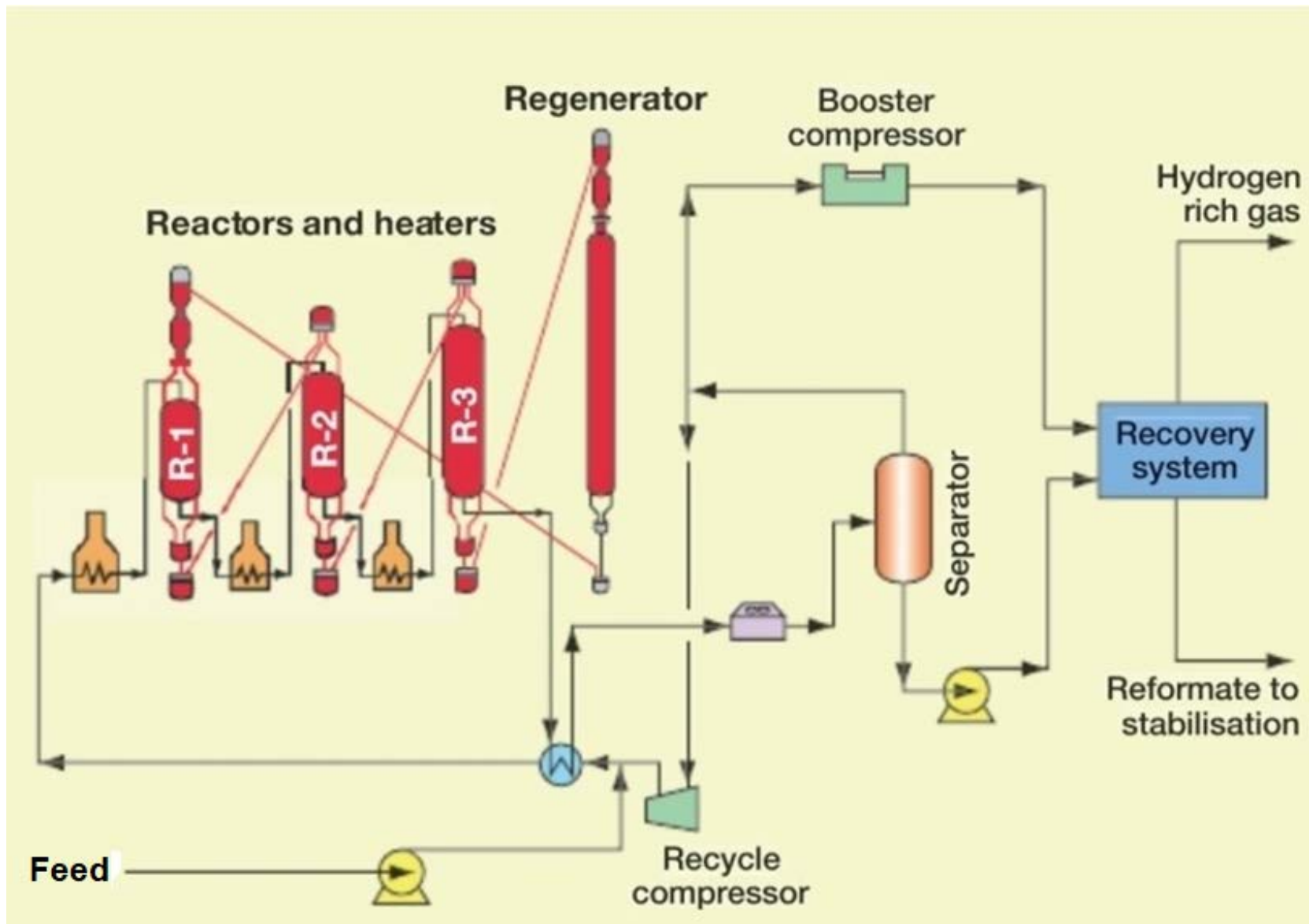
CCR - UOP



Semi-regenerative Reforming Process



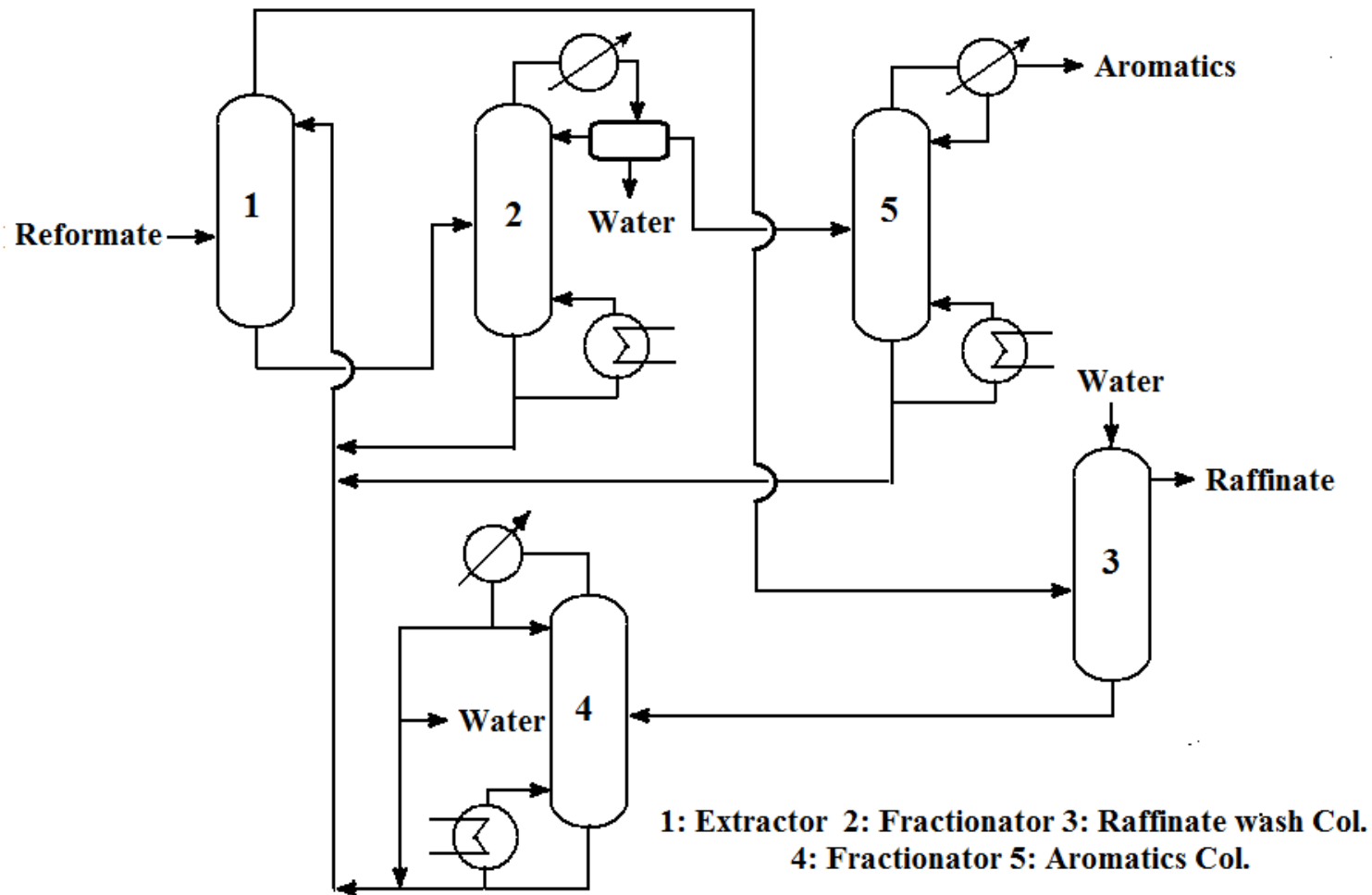
UOP's CCR (Stacked) Platforming Process



IFP's Octanizing Process (CCR:Side-by-Side)

Udex Process for Aromatic Extraction

In this process, aqueous ethylene glycol (80-90%) solution is used as solvent for aromatics. Aromatic-rich reformat stock, heated to 150 °C under a pressure of 8-10 atm, is sent to the extractor (1), where the Udex solution comes in contact with the aromatic-rich stock. The raffinate from the top goes to a water washer (3), where the solvent is washed off by water. From the top, raffinate is obtained; may be allowed to settle or by steaming the remaining solvent stains may be removed. The extract from the extractor goes into a fractionator (2), where the top product containing aromatics and small amount of solvent is finally distilled in a column (5) to get aromatics and solvent from the bottom of the column to join the extractor. Raffinate washings are collected and separately fractionated in a column (4) to drive off excess water to maintain the degree of dilution of the solvent, i.e., 80-90%. Solvent recycling is 5-6 times of hydrocarbon feed.



Solvent: 80-90% Aqueous Ethylene Glycol
150 °C, 8-10 atm

Udex Process for Extraction of Aromatics

Critical physical properties for different solvents for LLE

	Boiling point, °C	Density, g/cm ³	Aromatics solubility	Solubility difference of aromatics/non-aromatics
Glycols	280–330	1.1–1.2	Low to medium	Medium
NFM	244	1.15	Medium to high	Medium
NMP	206	1.03	High	Low
Sulfolane	287	1.26	Medium	High
TECHTIV	280–290	1.24–1.27	Medium to high	High

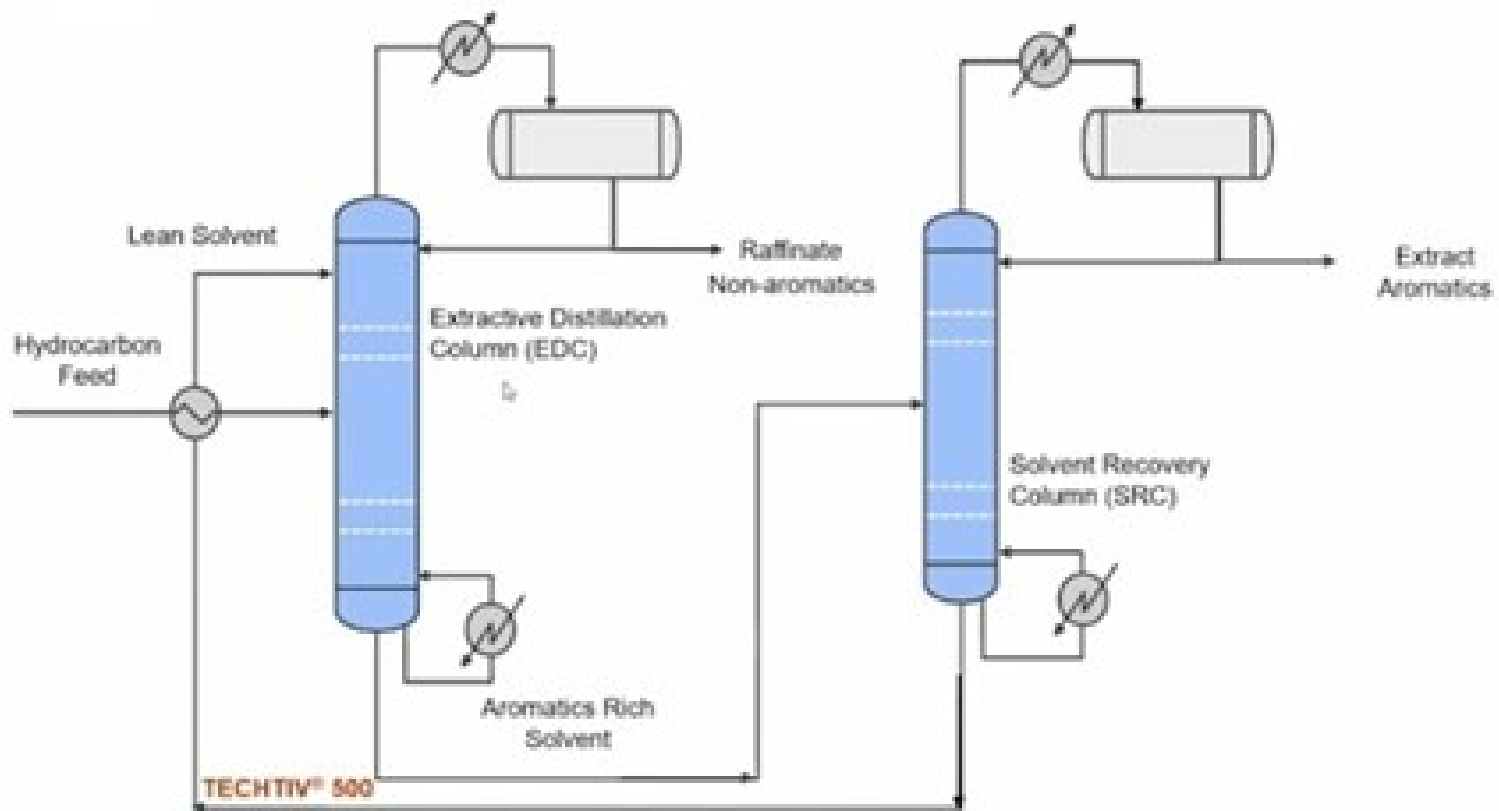
NFM = N-Formyl morpholine; **TECHTIV** : Extractive distillation solvent developed by GTC Technology Corporation and used on GT-BTX process.

Earlier Glistch Technology Corporation, GTC Technology Corporation, headquartered at Houston, TX merged with Sulzer in 2019 to become SULZER-GTC.

GT-BTX® Process for Aromatic Separation

GT-BTX® is an aromatics recovery technology that uses extractive distillation to remove benzene, toluene and xylene (BTX) from refinery, petrochemical or coke oven aromatics streams such as catalytic reformat, pyrolysis gasoline or coke oven light oil (COLO). GT-BTX® has no special feed preparation requirements and is capable of handling a wide-range (BTX) feedstock while producing very high aromatics purities (99.99 wt.% plus) at high recoveries (99.9 % plus).

Sulzer-GTC's GT-BTX process is a result of extensive testing of extractive distillation solvents and blends. Certain combinations of solvent components is shown to enhance extraction performance. Co-solvents also provide an additional parameter for the optimization of unit performance (e.g., stability, mass transfer efficiency). GT-BTX utilizes the TECHTIV-500® extractive distillation solvent which provides optimum extractive distillation performance.

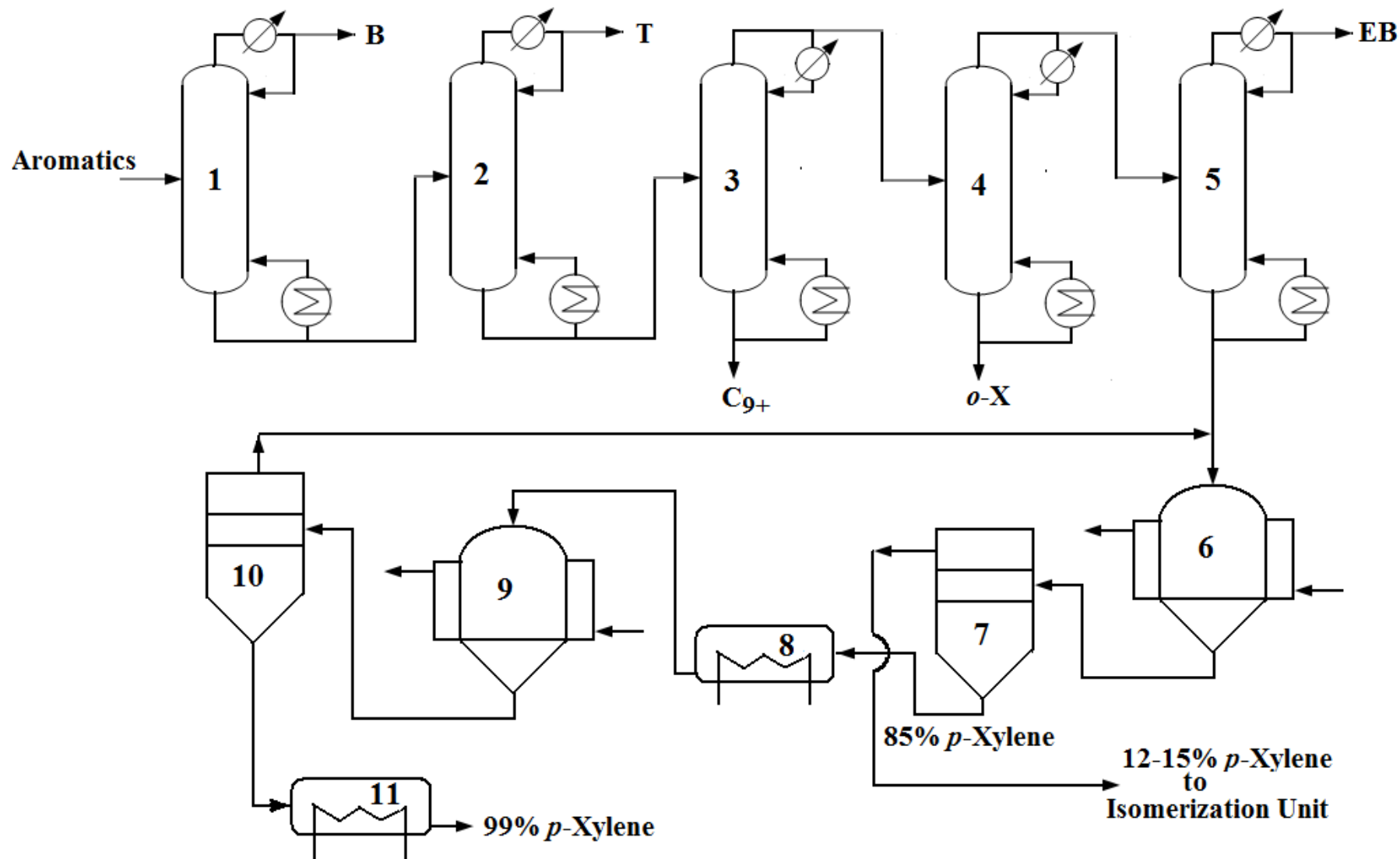


GT-BTX Process Scheme for Separation of Aromatics by Extractive Distillation

Physical Properties of Light Aromatics

Aromatic	Normal BP (°C)	Freezing Pt. (°C)
Benzene	80.1	-
Toluene	110.8	-
Ethyl benzene	136.0	-95.0
<i>p</i> -Xylene	138.3	13.2
<i>m</i> -Xylene	139.1	-47.9
<i>o</i> -Xylene	144.3	-25.2

Based on the physical properties (boiling point & freezing point) of the light aromatics, the separation scheme is designed.

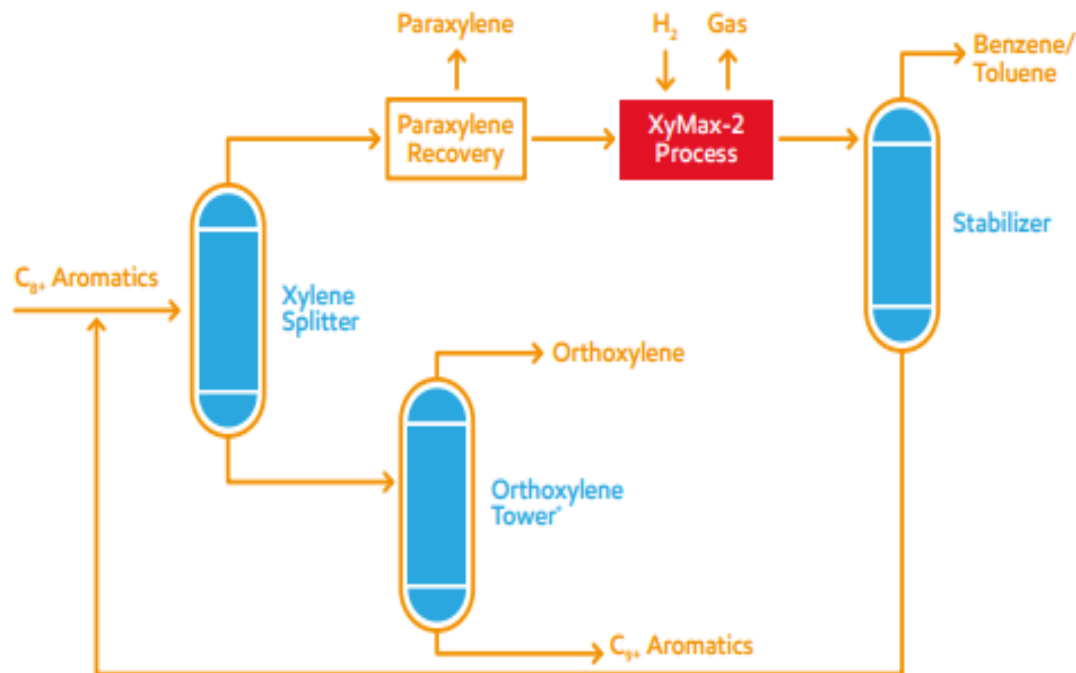


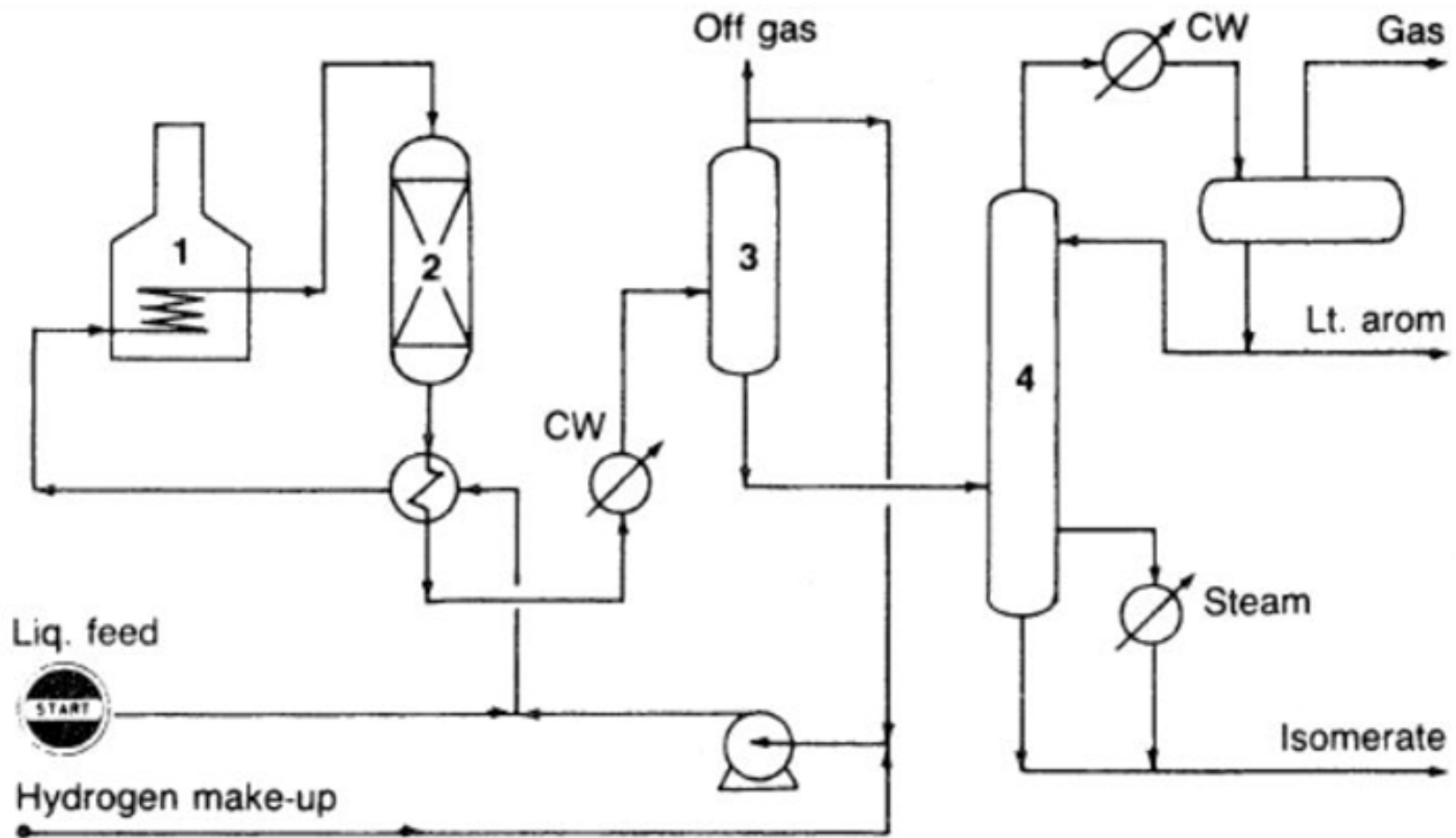
1: Benzene Col. 2: Toluene Col. 3: Hy. Aromatics Col. 4: *o*-Xylene Col. 5: EB Col.
 6: Crystallizer 7: Centrifuge 8: Heater 9: Crystallizer 10: Centrifuge 11: Heater

Separation Scheme for Light Aromatics

ExxonMobil's XyMax-2 Process

XyMax-2 process is the seventh generation of vapor-phase isomerization technology licensed by ExxonMobil. The process features a higher activity catalyst, higher weight hourly space velocity (WHSV) and expanded temperature window compared to prior ExxonMobil vapor phase isomerization technologies. The XyMax-2 process is ideal for debottlenecking xylenes isomerization units as it requires lower catalyst volumes than any process currently in service, achieves higher ethylbenzene (EB) conversion per pass and offers the flexibility of operating at temperatures similar to or lower than existing processes.





1: Furnace; 2: Reactor; 3: G-L Separator; 4: Fractionator

Flow Diagram of ExxonMobil's XyMax-2 Process

Liquid Phase Isomerization (LPI) of Xylene by ExxonMobil

The LPI process is the latest addition to ExxonMobil's portfolio of xylenes isomerization processes available for license. The technology operates at low temperature with xylene losses less than the best performing vapor phase isomerization technology, the XyMaxSM-2 process. The LPI process can be deployed in parallel with vapor phase isomerization units in existing plants, yielding both energy savings and debottlenecking opportunities. Because of its very low EB conversion per pass, the LPI process is often operated in combination with a vapor phase isomerization process, where most EB removal is achieved. However, in situations where the C8 aromatics stream to be isomerized contains very low EB, xylenes isomerization can be carried out via the LPI process only, and EB purge is managed by other means.

LPI advantages:

Significant energy savings

- Low temperature operation
- Elimination of two costly steps - (1) raffinate vaporization and (2) isomerate condensing
- Reduced traffic through the high temperature vapor phase isomerization unit

Ultra-low xylene losses

Low catalyst costs

Low metallurgy costs

Debottlenecking opportunity for existing plants or significant reduction of the vapor phase isomerization unit size in grassroots facilities

High p-xylene selectivity

Long cycles consistent with modern aromatics complexes turnaround schedule



Thank you!