

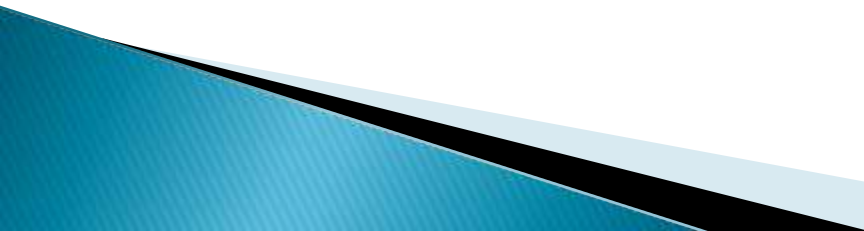
CATALYTIC ISOMERIZATION

PETROLEUM
TECHNOLOGY

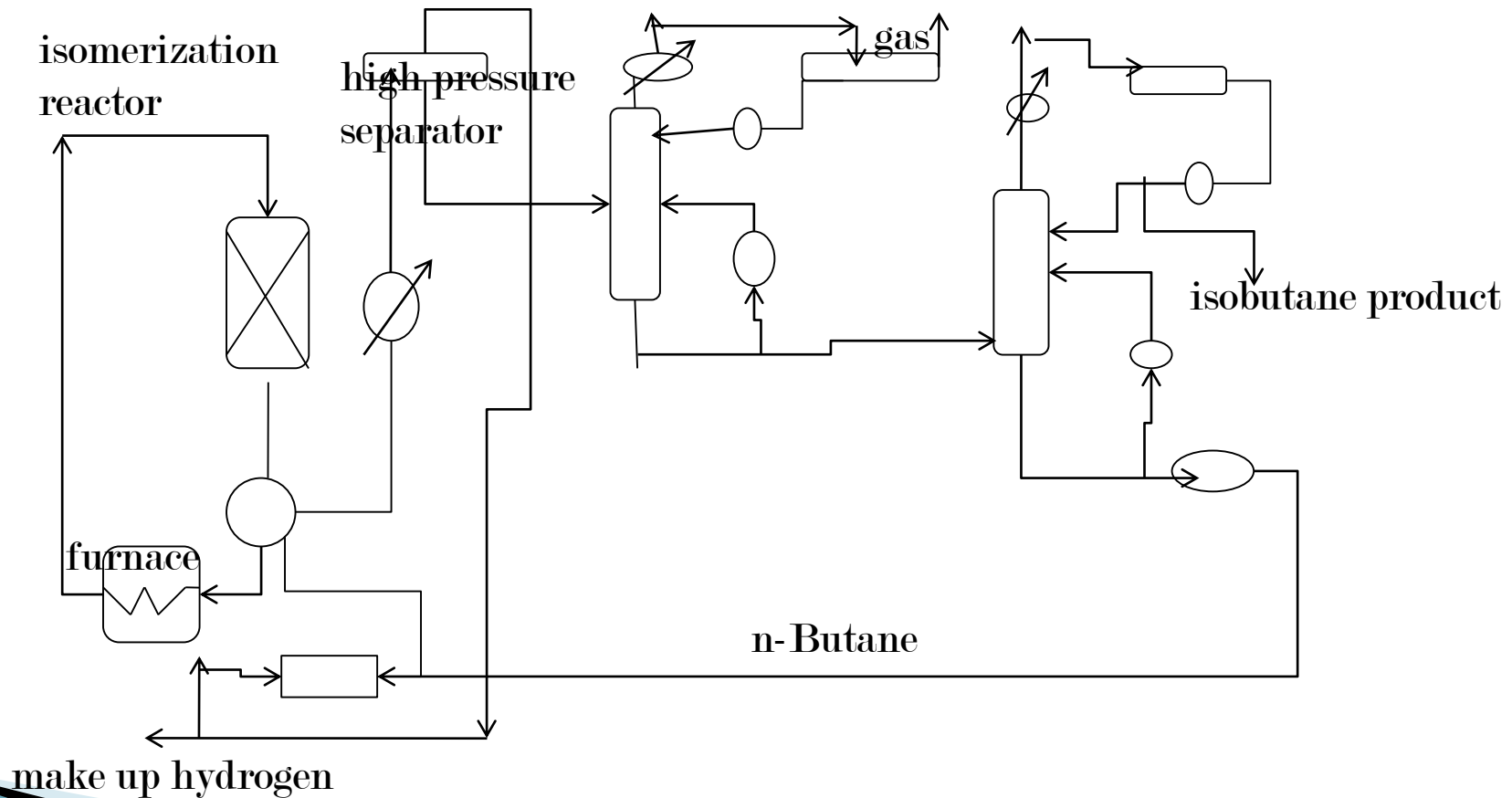
CHEMISTRY OF CATALYTIC ISOMERIZATION

- ❖ Catalytic isomerization is used to convert n-butane to isobutane, which may be alkylated to liquid hydrocarbons in boiling range of motor gasoline
- ❖ This process is used to convert relatively low octane number paraffins to more desirable isoparaffins which have high octane number

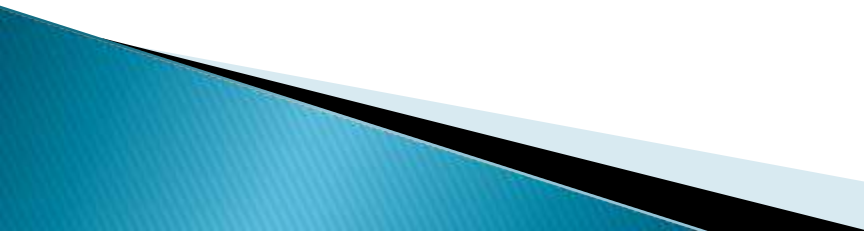
Isomerization reaction

- ❖ This reaction is mildly exothermic
 - ❖ it is reversible first-order reaction it requires catalyst to obtain significant yield of isomer
 - ❖ Isomerizing catalyst must ensure the optimal rate of reaction at as low temperature
 - ❖ Isomerization reaction carried out at elevated pressure
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UOP BUTAMER ISOMERIZATION PROCESS




Description of flow diagram

- ▶ n-butane stream is withdrawn from the bottom of column
 - ▶ It is mixed with hydrogen –rich recycle gas and preheated by heat exchange with reactor effluent
 - ▶ The mixed feed is heated to required reaction temperature in fired heater and then passed to the reactor containing a platinum catalyst
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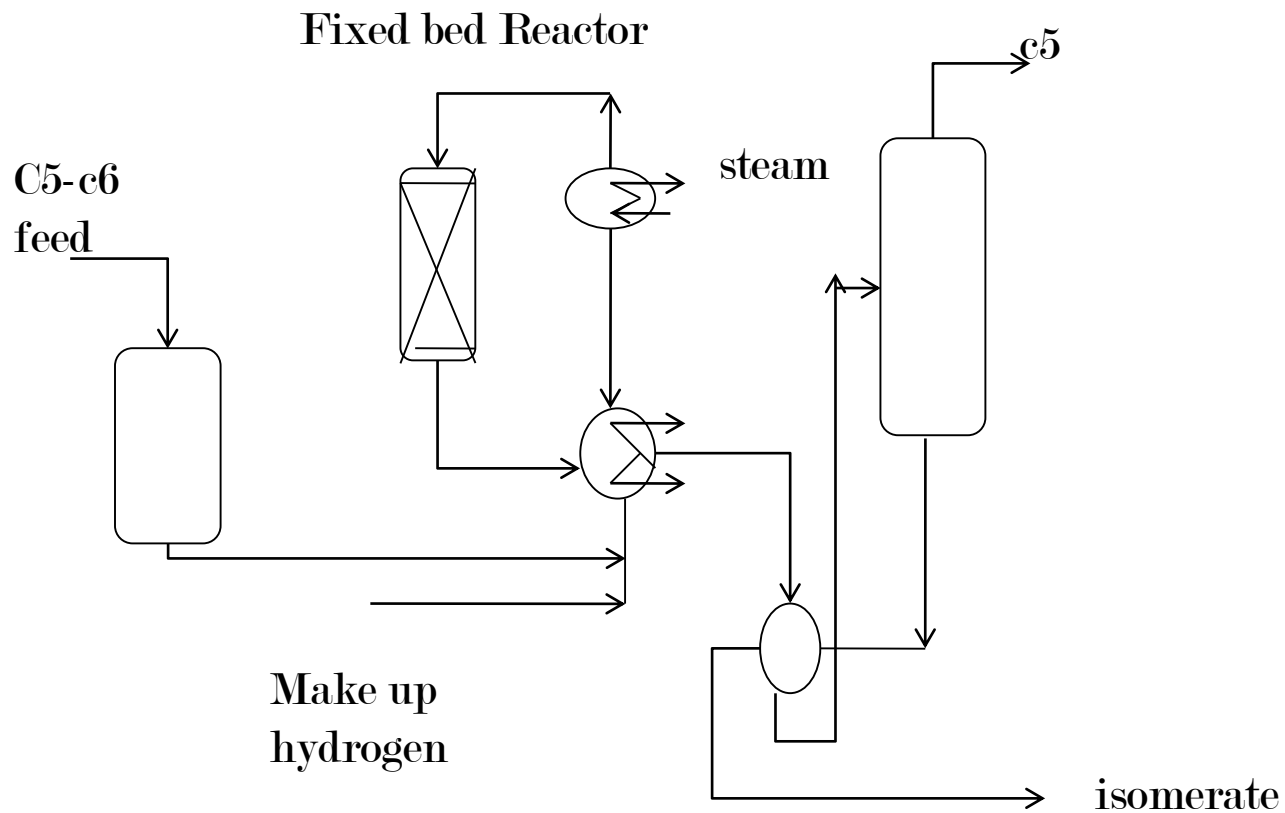
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- ▶ The n-butane is isomerized to isobutane
 - ▶ The hydrogen rich gas is separated from the reaction product in the high pressure separator and recycled back in the process
 - ▶ A small quantity of make-up hydrogen gas is mixed with the recycled gas to maintain the required percentage of hydrogen in it .
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continued

- ▶ The dissolved gas and breakdown product are removed in stabilization column
 - ▶ The bottom product from the stabilizer containing n-butane and isobutane is fed to the distillation column for the separation into isobutane and n-butane
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UOP PENEX PROCESS



FLOW DIAGRAM DESCRIPTION

- ▶ Isomerization increases the octane value of c5-c6 fractions by converting normal paraffins to their isomers using several options
 - ▶ Penex process is single pass isomerization using a high-activity chlorided alumina catalyst.
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continued

- ▶ Recycle options are available by adding product iso/normal paraffin separation consisting of molecular sieves or fractionation
 - ▶ TIP process-integrated recycle isomerization consisting of UOP's zeolite isomerization and isosiv processes for iso/normal paraffin separation .
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CATALYTIC POLYMERIZATION



CATALYTIC POLYMERIZATION

- ▶ Polymerization is a process by which two or more molecules combined to produce a single larger molecule.
- ▶ Catalytic polymerization in a petroleum refinery is used to convert light olefins, such as propane and butenes, into a high octane number motor gasoline component (polymer gasoline)


CHEMISTRY AND CATALYSTS OF THE PROCESS

- ▶ This process is also used for producing straight chain C_7-C_9 olefins which are subsequently used for the manufacture of speciality .
- ▶ This process can be used for the alkylation of aromatics with olefins to form products such as cumene and ethyl benzene.
- ▶ Catalytic polymerization most often carried out with the use of solid phosphoric acid supported are kieselguhr.

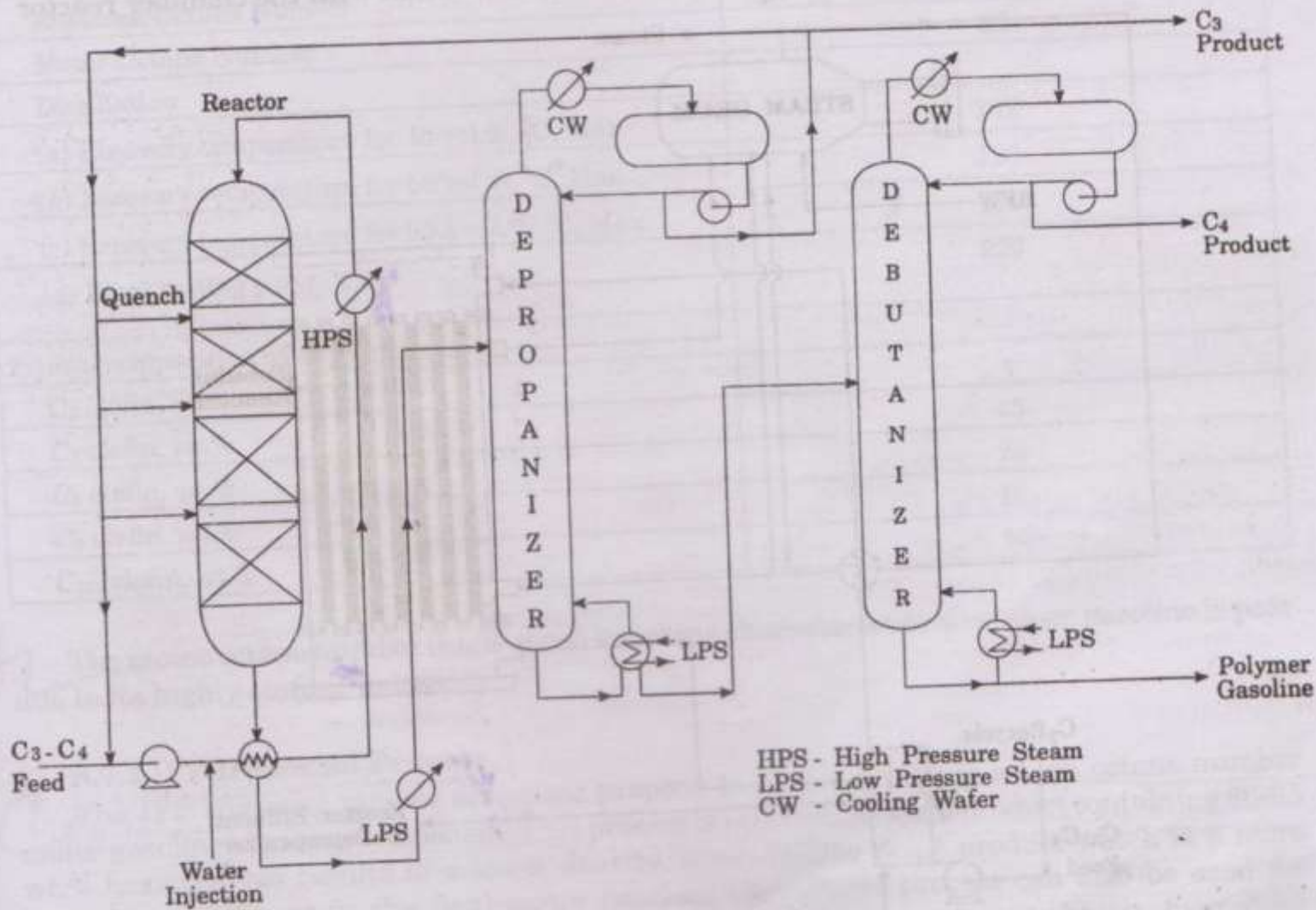
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- ▶ Feedstock catalytic polymerization unit consist of C_3-C_4
- ▶ Products from fluid catalytic cracking as well as visbreaking and coking operation.
- ▶ A final water wash removes presses of ammonia and other basic compound.

UOP CATALYTIC POLYMERIZATION PROCESS


- ▶ The catalytic polymerization reaction is exothermic. It release about 1550 kcal/kg and 920kcal/kg of olefin converted for propane and butene.
 - ▶ The catalytic is arranged in a series of separate weights.
 - ▶ This allows the injection of cold recycle propane as quench.
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UOP CATALYTIC POLYMERIZATION PROCESS DIAGRAM



CONTINUED

- ▶ This arrangement in ensures temperature control in the reactor. The reactor is maintained at 150 to 200°C. an increase in the temperature above about 200°C promotes the reaction of hydrogen transfer with the formation of diolefins.
- ▶ The polymerization causes the deactivation of the catalyst . The olefin content of the reactor feed is limited to about 30 volume % to control the temperature rise across each bed . This is achieved by recycling bag propane to the feed.

- ▶ Water is injected into the reactor feed to maintain the correct degree of hydration on the phosphoric acid catalyst.
 - ▶ An under hydrated catalyst promotes heavy polymer and coke formation, while over hydration results in softening of the catalyst. Therefore control of water injection is of great importance
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ALTERNATIVE UOP TUBULAR REACTOR DESIGN

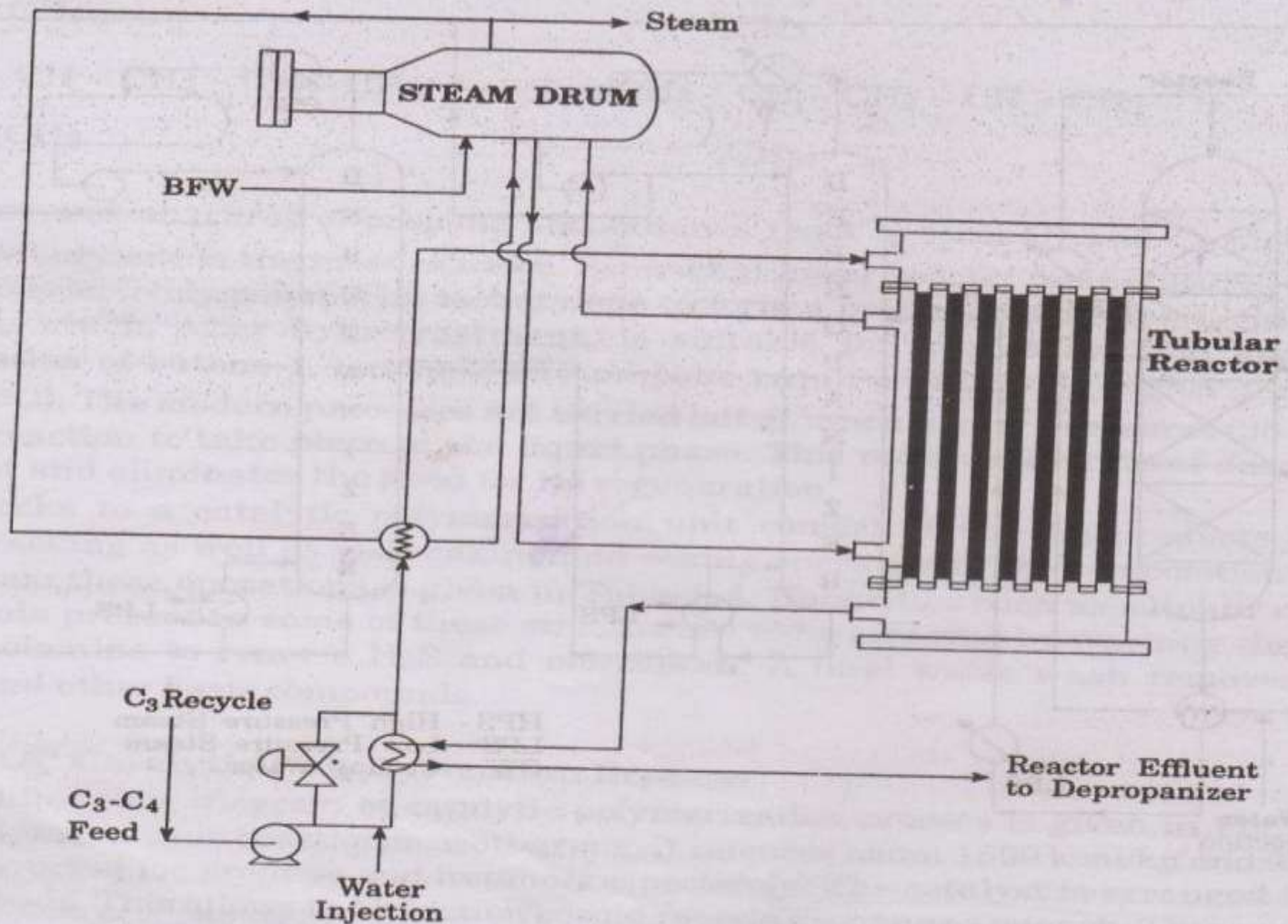
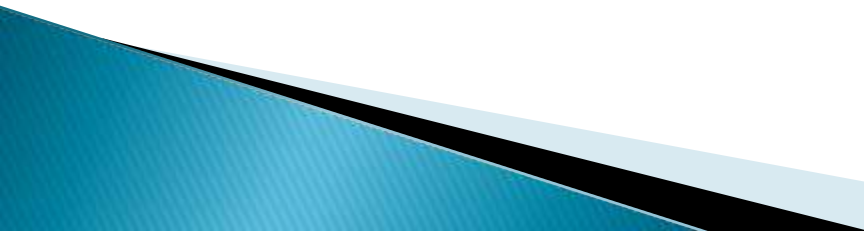


Fig. 8.16 Alternative UOP tubular reactor for polymerization

ALTERNATIVE UOP TUBULAR REACTOR DESIGN

- ▶ In this design, the catalyst is contained in large number of two inch vertical tubes this tubes are surrounded by a water jacket to remove the exothermic hit of reaction.
- ▶ The steam generated in the water jacket is then utilized to preheat the feed with C₄ and mixed C₃– C₄ feedstock, the olefin contents are allowed to 50 moles%, but the design can accept reactor feedstocks containing 45 mole % olefin with C₃ stream because of higher reaction.

CONTINUED

- ▶ The quantity of recycle required by the tubular reactor system and this results in reduced energy consumption in producing the recycle stream.
 - ▶ Depending on feedstock quality, operating condition and catalytic activity, olefin conversion of 85–95% can be achieved in the catalytic polymerization process.
 - ▶ The motor octane number (high-speed knocking characteristic) of polymer gasoline is poor due to its highly olefinic nature.
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Typical yields and product qualities

Feedstock– mixed C3 –C4 steam

Propene, wt%	21.4
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Butene, wt%	36.3
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Yield, wt%

Propane	12.8
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Butane	34.3
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Polymer gasoline	52.9
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Polymer gasoline quality

Density at 15°C ,kg/m ³	735
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Research Octane number	95.5
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Motor Octane number	82
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Typical yields and product qualities

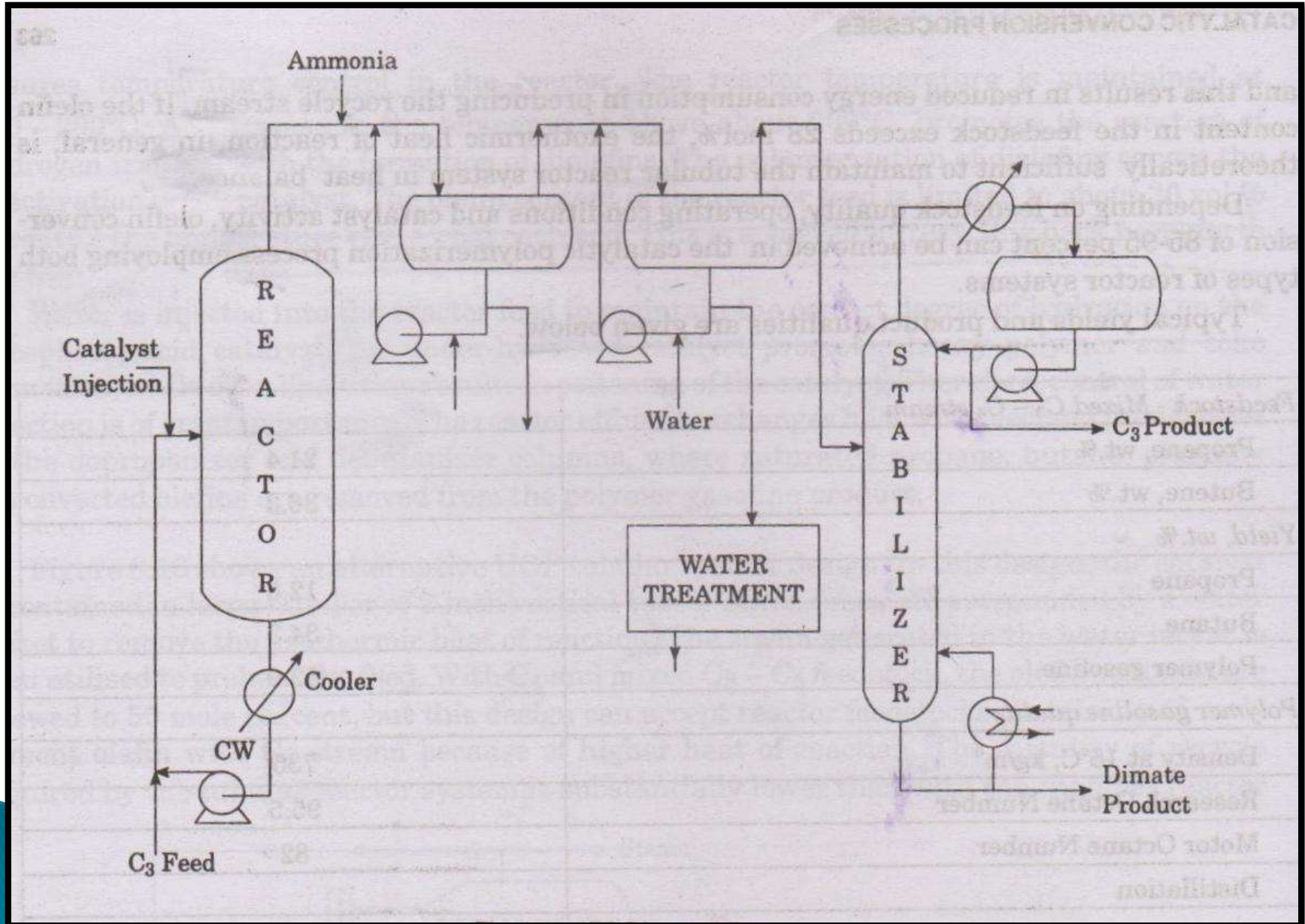
Distillation

(a) Recovery temperature for 10 vol.%, °C, Max	102
(b) Recovery temperature for 50 vol.%, °C, Max	120
(c) Recovery temperature for 50 vol.%, °C, Max	175
(d) Final boiling point, °C	220

Typical composition of Polymer gasoline


C ₆ olefin, wt%	4
C ₇ olefin, wt%	45
C ₈ olefin, wt%	25
C ₉ olefin, wt%	16

IFP DIMERSOL PROCESS



IFP DIMERSOL PROCESS

- ▶ The IFP dimersol process dimerizes propane to hexene which is a high octane number motor gasoline blending component, this process is reported to give a product containing 80 to 85 weight% hexene.
- ▶ This result in a lower density, lower boiling point which is a more desirable component in the final motor gasoline blend.
- ▶ This process can also be used for demerizing butene to produce linear C₈ olefins or co-demerizing propane and butene to produce C₇ olefin.

- ▶ The linear C₇ and C₈ olefins formed are used for specialty alcohols manufacture.
 - ▶ The catalyst comprises nickel co-ordination complex and aluminium alkyl which are continuously injected in small concentration into the feedstock.
 - ▶ The polymerization takes place at ambient temperature with sufficient pressure to maintain liquid phase
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- ▶ The exothermic heat of reaction is removed in the recycle cooler to control the reactor temperature. The ammonia is injected in the reactor and this destroys the catalyst.
- ▶ Inorganic material from the product stream are then extracted by water washing. The separation of C₃ stream(LPG) and the dimethyl product is done in the stabilizer.
- ▶ The dimethyl catalyst is believed to be very sensitive to feedstock impurities such as water, sulphur, ammonia, diolefins and acetylenes. Therefore, feedstock is usually given treatment including drying over molecular sieves.
- ▶ This process is unsuitable for feedstock containing significant concentration of isobutene and so cannot be used for C₄ or mixed C₃-C₄ streams from catalytic crackers.

Thanks

