

# CHAPTER 6

## ETHANE AND HIGHER PARAFFINS – BASED CHEMICALS

# INTRODUCTION

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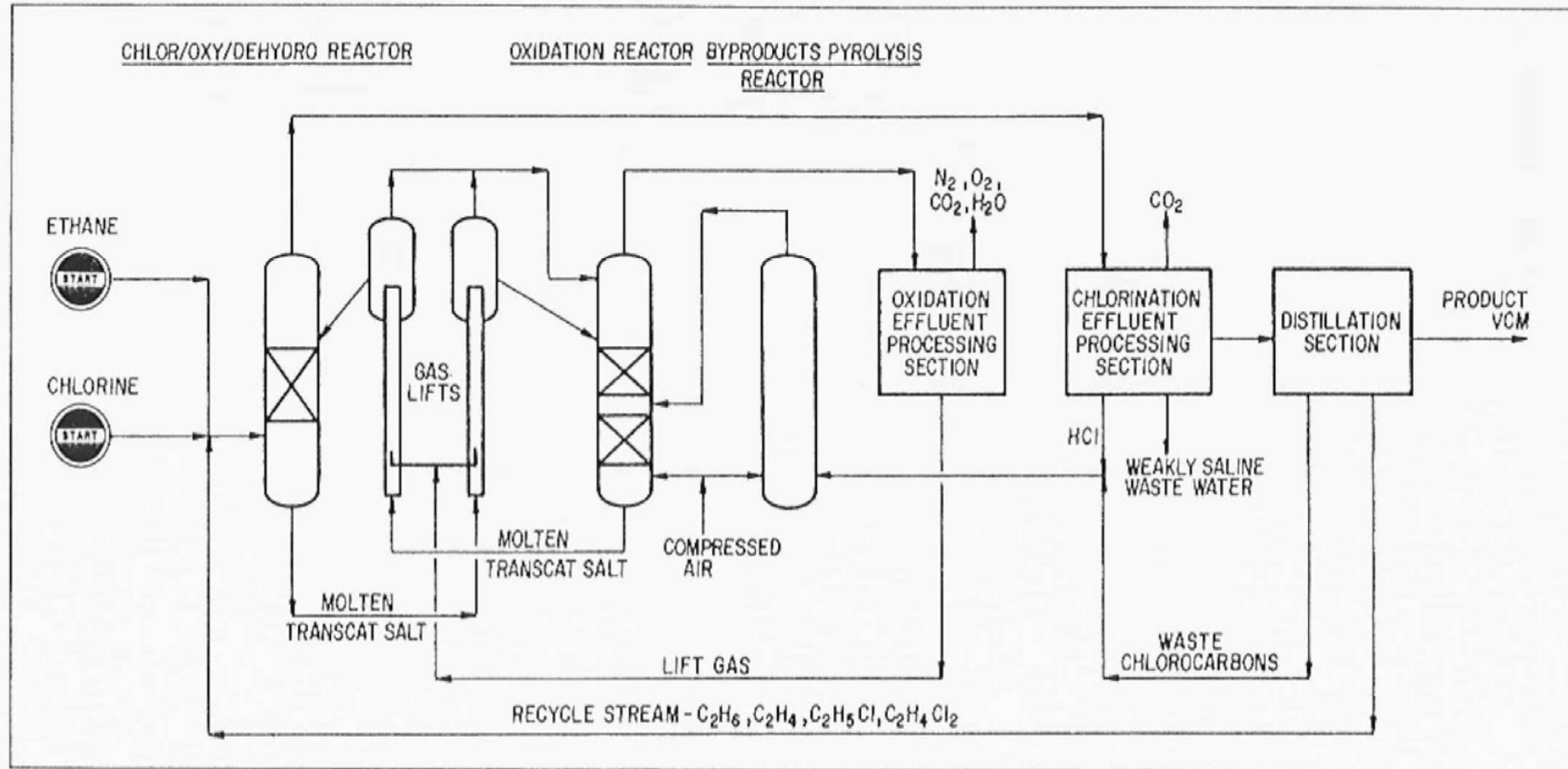
- Paraffinic hydrocarbons are less reactive than olefins.
- Paraffinic hydrocarbons are the starting materials for the production of olefins.
- Methane's relation with petrochemicals is primarily through synthesis gas.
- Ethane, on the other hand, is a major feedstock for steam crackers for the production of ethylene.
- The higher paraffins-propane, butanes, pentanes, and heavier-also have limited direct use in the chemical industry except for the production of light olefins through steam cracking.

# ETHANE CHEMICALS

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- The main source for ethane is natural gas liquids. Approximately 40% of the available ethane is recovered for chemical use.
- The only large consumer of ethane is the steam cracking process for ethylene production.
- A minor use of ethane is its chlorination to ethyl chloride:  
$$\text{CH}_3\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl}$$
- By-product HCl may be used for the hydrochlorination of ethylene to produce more ethyl chloride.

# ETHANE CHEMICALS



The Transcat process for producing vinyl chloride from ethane

# ETHANE CHEMICALS

- Hydrochlorination of ethylene is the main route for the production of ethyl chloride:



- Major uses of ethyl chloride are:
  - the manufacture of tetraethyl lead and the synthesis of insecticides, and
  - as an alkylating agent and as a solvent for fats and wax.
- A small portion of vinyl chloride is produced from ethane via the Transcat process.
- In this process a combination of chlorination, oxychlorination, and dehydrochlorination reactions occur in a molten salt reactor.

# ETHANE CHEMICALS

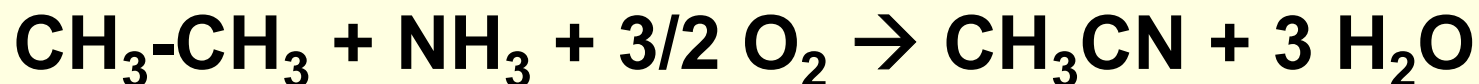
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- The reaction occurs over a copper oxychloride catalyst at a wide temperature range of 310-640°C.
- During the reaction, the copper oxychloride is converted to copper (I) and copper (II) chlorides, which are air oxidized to regenerate the catalyst.
- Vinyl chloride is an important monomer for polyvinyl chloride (PVC).
- The main route for obtaining this monomer, however, is via ethylene.

# ETHANE CHEMICALS

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- A new approach to utilize ethane as an inexpensive chemical intermediate is to ammoxidize it to acetonitrile.
- The reaction takes place in presence of a cobalt Beta-Zeolite.



# PROPANE CHEMICALS

## OXIDATION OF PROPANE

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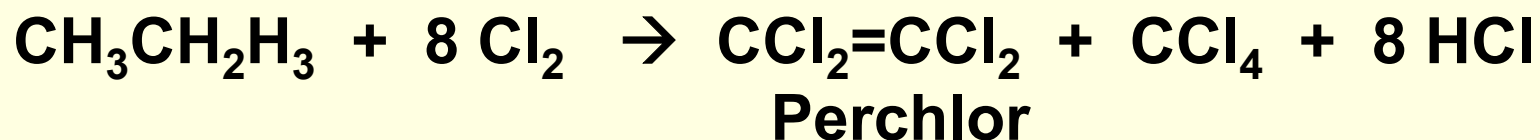
- The non-catalytic oxidation of propane in the vapor phase is nonselective and produces a mixture of oxygenated products.
- Oxidation at temperatures below 400°C produces a mixture of aldehydes (acetaldehyde and formaldehyde) and alcohols (methyl and ethyl alcohols).
- At higher temperatures, propylene and ethylene are obtained in addition to hydrogen peroxide.
- Due to the non-selectivity of this reaction, separation of the products is complex, and the process is not industrially attractive.



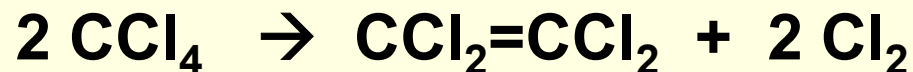
# CHLORINATION OF PROPANE (Production of Perchloroethylene)

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- Chlorination of propane with chlorine at 480-640°C yields a mixture of perchloroethylene (Perchlor) and carbon tetrachloride:



- Carbon tetrachloride is usually recycled to produce more perchloroethylene:



# CHLORINATION OF PROPANE (Production of Perchloroethylene)

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- Perchlor may also be produced from ethylene dichloride (1,2-dichloroethane) through an oxychlorination-oxyhydrochlorination process. Trichloroethylene (trichlor) is co-produced.
- Perchlor and trichlor are used as metal degreasing agents and as solvents in dry cleaning.
- Perchlor is also used as a cleaning and drying agent for electronic equipment and as a fumigant.

# DEHYDROGENATION OF PROPANE (Propene Production)

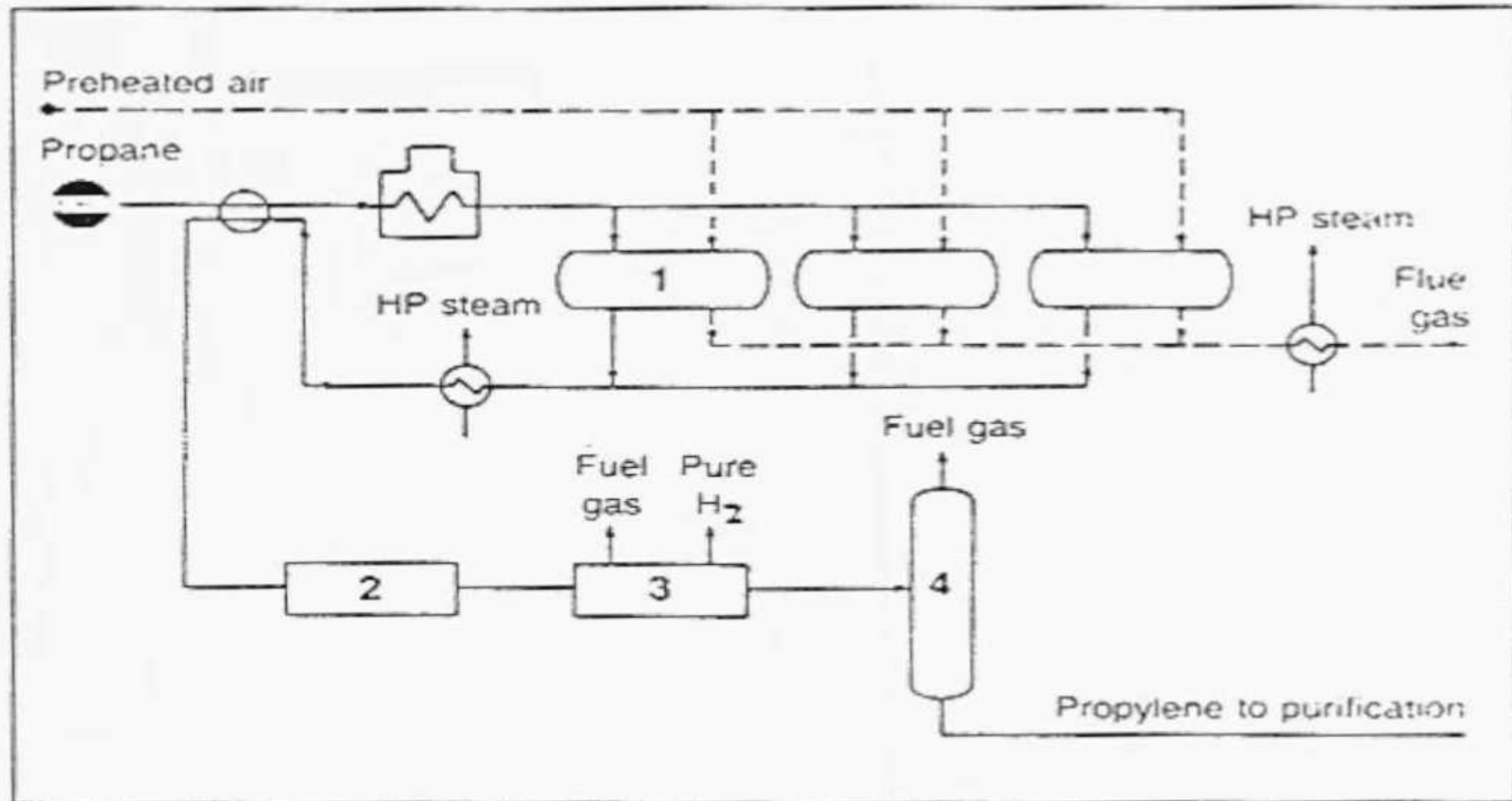
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- The catalytic dehydrogenation of propane is a selective reaction that produces mainly propene:



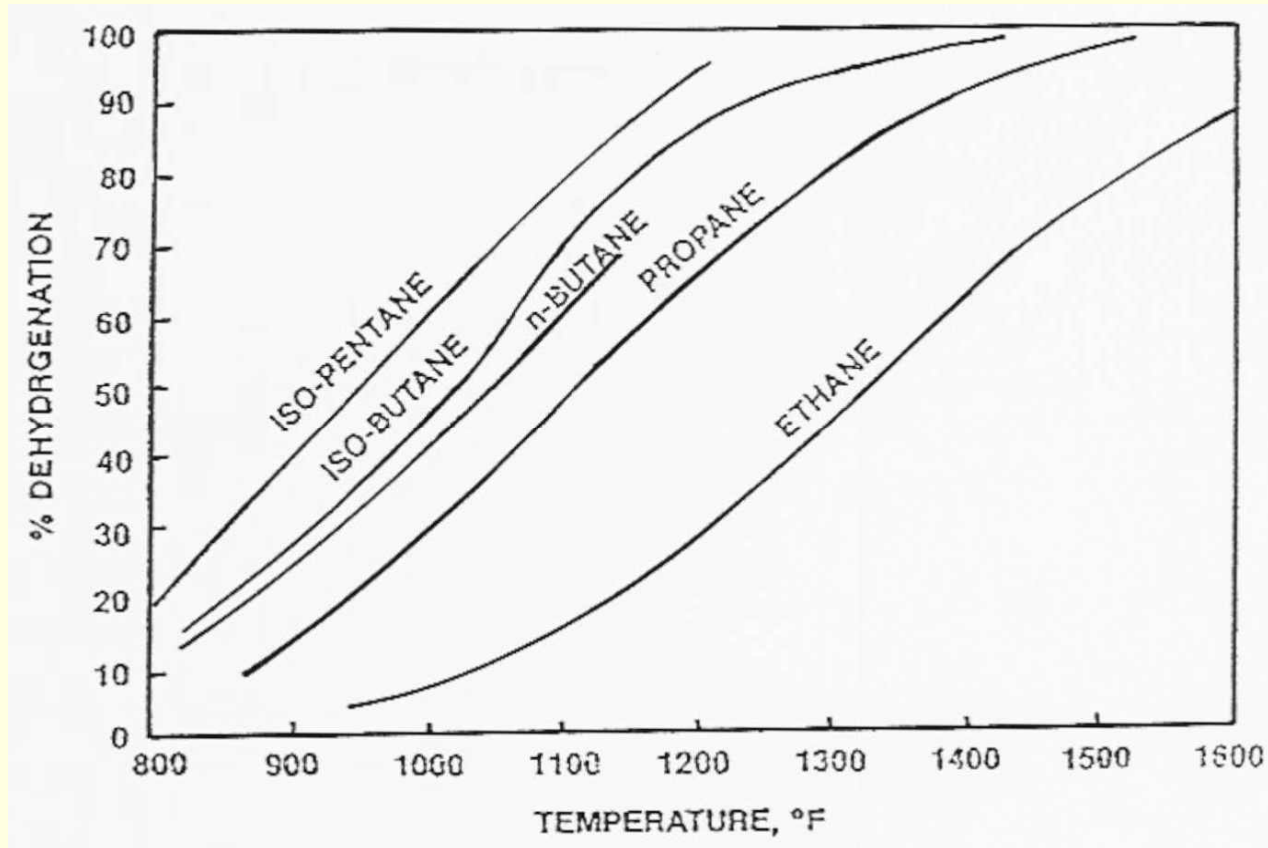
- The process could also be used to dehydrogenate butane, isobutane, or mixed LPG feeds.
- It is a single-stage system operating at a temperature range of 540-680°C and 5-20 absolute pressures.
- Conversions in the range of 55-65% are attainable, and selectivities may reach up to 95%.
- Lummus-Crest Catofin dehydrogenation process

# DEHYDROGENATION OF PROPANE (Propene Production)



The Lummus Crest Catofin dehydrogenation process: (1) reactor, (2) compressor, (3) liquid product recovery, (4) product purification.

# DEHYDROGENATION OF PROPANE (Propene Production)



Effect of temperature on the dehydrogenation of light paraffins at one atmosphere.

Dr. Bassam El Ali\_CHEM 453

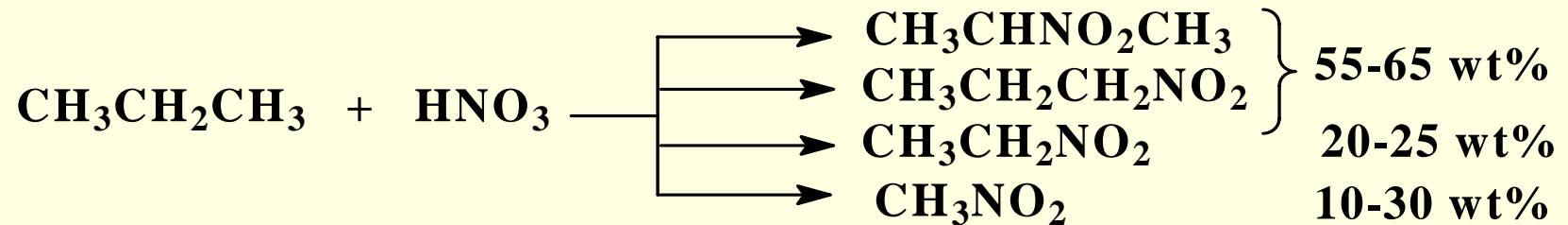
# NITRATION OF PROPANE (Production of Nitroparaffins)

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- Nitrating propane produces a complex mixture of nitro compounds ranging from nitromethane to nitropropanes.
- The presence of lower nitroparaffins is attributed to carbon-carbon bond fission occurring at the temperature used.
- Temperatures and pressures are in the range of 390°-440°C and 100-125 psig.
- Increasing the mole ratio of propane to nitric acid increases the yield of nitropropanes.

# NITRATION OF PROPANE (Production of Nitroparaffins)

- Typical product composition for 25:1 propane/acid ratio is:



- Nitropropanes are good solvents for vinyl and epoxy resins. They are also used to manufacture rocket propellants.
- Nitromethane is a fuel additive for racing cars.

# n-BUTANE CHEMICALS

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- Like propane, n-butane is mainly obtained from natural gas liquids. It is also a by-product from different refinery operations.
- The major use of n-butane is to control the vapor pressure of product gasoline.
- Surplus n-butane could be isomerized to isobutane, which is currently in high demand for producing isobutene.



# n-BUTANE CHEMICALS

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- Isobutene is a precursor for methyl and ethyl tertiary butyl ethers, which are important octane number boosters.
- Another alternative outlet for surplus n-butane is its oxidation to maleic anhydride. Almost all new maleic anhydride processes are based on butane oxidation.
- n-Butane has been the main feedstock for the production of butadiene.
- This process has been replaced by steam cracking hydrocarbons, which produce considerable amounts of by-product butadiene.

# n-BUTANE CHEMICALS

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- The chemistry of n-butane is more varied than that of propane.
- The noncatalytic oxidation of butane yields a variety of products including organic acids, alcohols, aldehydes, ketones, and olefins.
- Although the noncatalytic oxidation of butane produces mainly aldehydes and alcohols, the catalyzed oxidation yields predominantly acids.

# OXIDATION OF n-BUTANE (Acetic Acid and Acetaldehyde)

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- The oxidation of n-butane represents a good example illustrating the effect of a catalyst on the selectivity for a certain product.
- The noncatalytic oxidation of n-butane is nonselective and produces a mixture of oxygenated compounds including formaldehyde, acetic acid, acetone, and alcohols.
- Typical weight % yields when n-butane is oxidized in the vapor phase at a temperature range of 360-450°C and approximately 7 atm are: formaldehyde 33%, acetaldehyde 31%, methanol 20%, acetone 4%, and mixed solvents 12%.

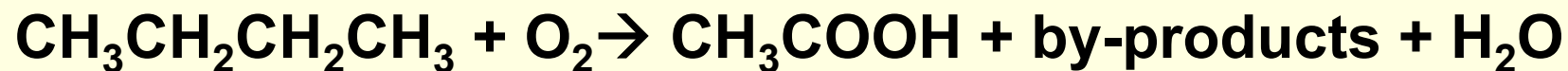
# OXIDATION OF n-BUTANE (Acetic Acid and Acetaldehyde)

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- The catalytic oxidation of a n-butane, using either cobalt or manganese acetate, produces acetic acid at 75-80% yield.
- Byproducts of commercial value are obtained in variable amounts.
- In the Celanese process, the oxidation reaction is performed at a temperature range of 150-225°C and a pressure of approximately 55 atmospheres.

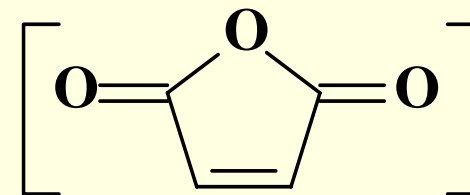
# OXIDATION OF n-BUTANE (Acetic Acid and Acetaldehyde)

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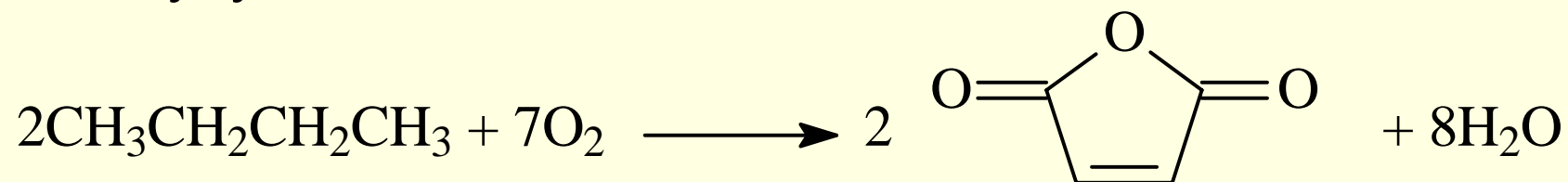


- The main by-products are formic acid, ethanol, methanol, acetaldehyde, acetone, and methylethyl ketone (MEK).
- When manganese acetate is used as a catalyst, more formic acid ( $\approx 25\%$ ) is obtained at the expense of acetic acid.

# MALEIC ANHYDRIDE

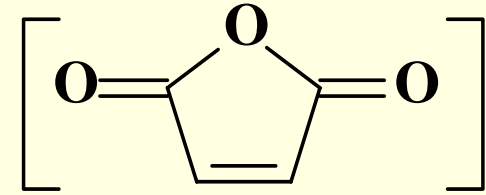


- The Catalytic oxidation of n-butane at 490° over a cerium chloride, Co-Mo oxide catalyst produces malefic anyhydride.



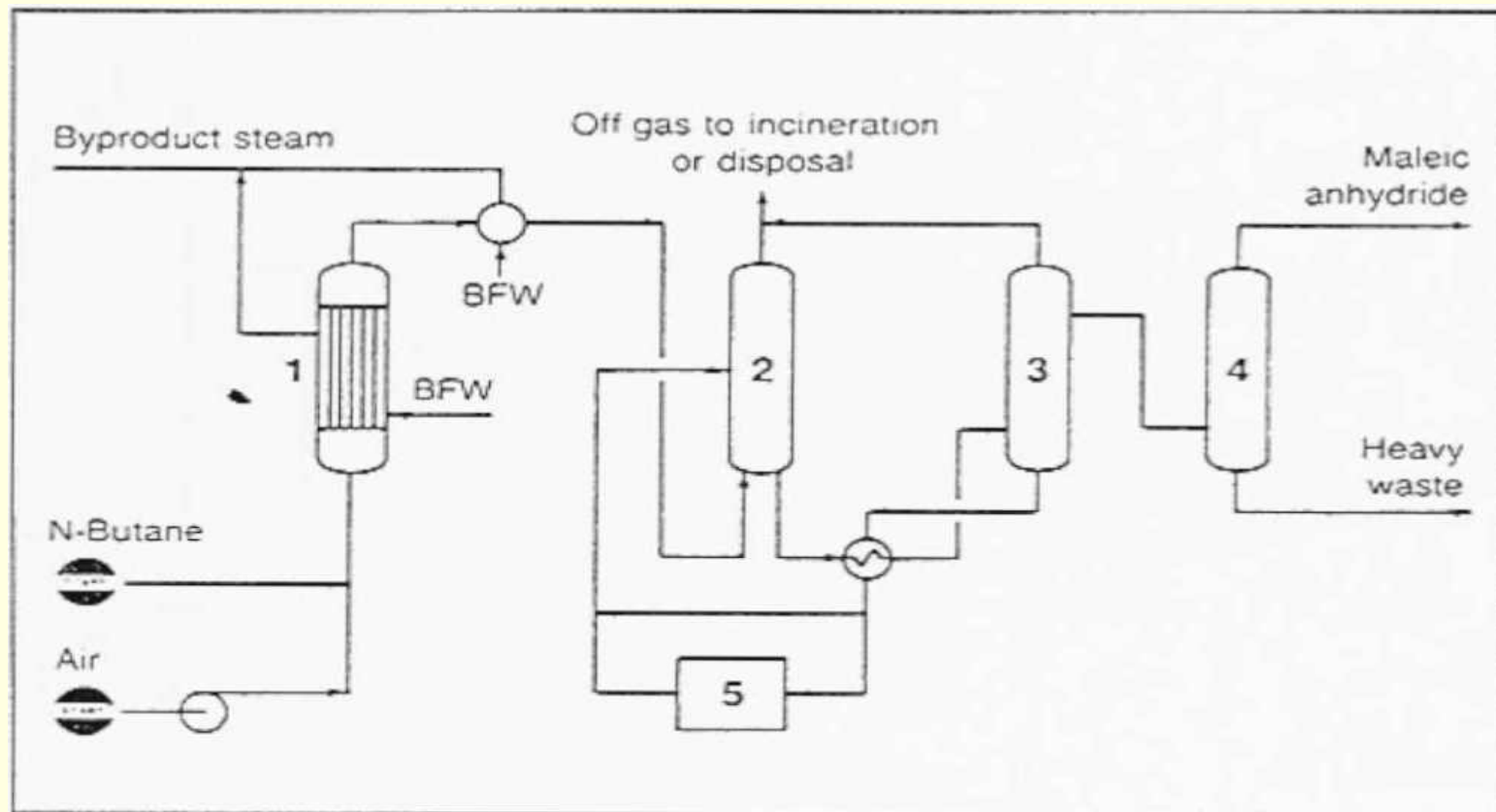
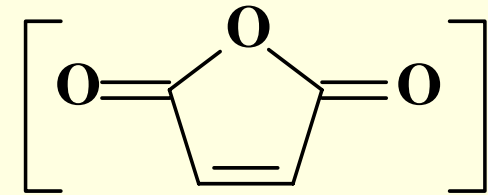
- Other catalyst systems such as iron  $\text{V}_2\text{O}_5$ - $\text{P}_2\text{O}_5$  over silica alumina are used for the oxidation.

# MALEIC ANHYDRIDE



- In the Monsanto process, n-butane and air are fed to a multitube fixed-bed reactor, which is cooled with molten salt.
- The catalyst used is a proprietary modified vanadium oxide.
- The exit gas stream is cooled, and crude maleic anhydride is absorbed then recovered from the solvent in the stripper.
- Maleic anhydride is further purified using a proprietary solvent purification systems.

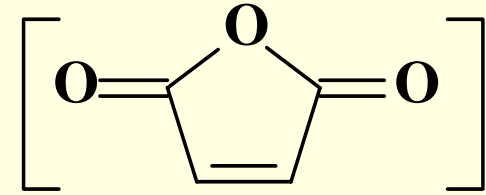
# MALEIC ANHYDRIDE



The Monsanto process for producing maleic anhydride from butane: (1) reactor, (2) absorber, (3) stripper, (4) fractionator, (5) solvent purification.

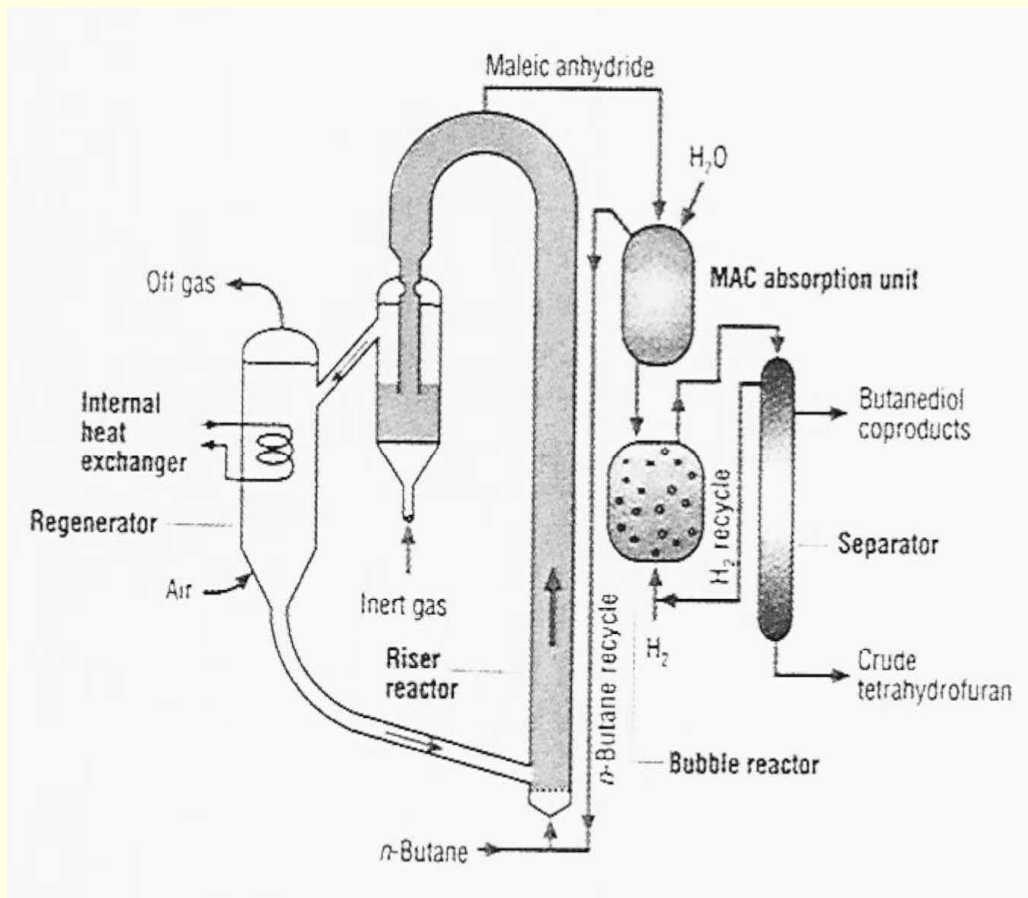
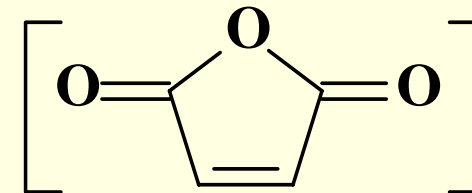


# MALEIC ANHYDRIDE



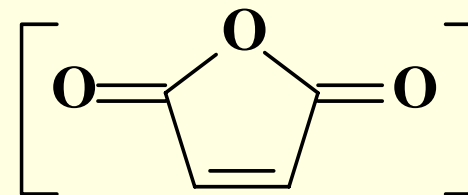
- A new process for the partial oxidation of n-butane to maleic anhydride was developed by **DuPont**.
- The important feature of this process is the use of a circulating fluidized bed-reactor.
- Solids flux in the riser-reactor is high and the superficial gas velocities are also high, which encounters short residence times usually in seconds.
- The developed catalyst for this process is based on vanadium phosphorous oxides  $(VO)_2P_2O_7$  type, which provides the oxygen needed for oxidation.

# MALEIC ANHYDRIDE



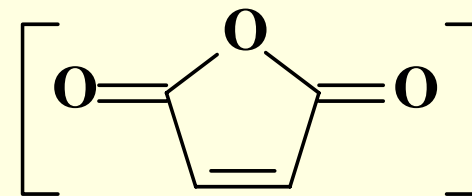
The DuPont butane to Maleic Anhydride process

# MALEIC ANHYDRIDE



- The selective oxidation of n-butane to maleic anhydride involves a redox mechanism where the removal of eight hydrogen atoms as water and the insertion of three oxygen atoms into the butane molecule occurs.
- The reaction temperature is approximately 500°C. Subsequent hydrogenation of maleic anhydride produces tetrahydrofuran.
- Oxidation of n-butane to maleic anhydride is becoming a major source for this important chemical. Maleic anhydride could also be produced by the catalytic oxidation of n-butenes and benzene.

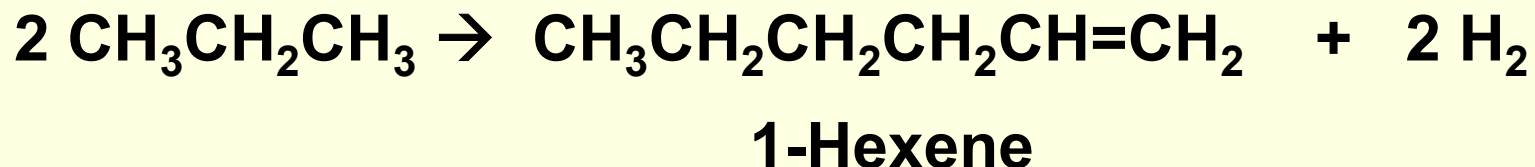
# USES OF MALEIC ANHYDRIDE



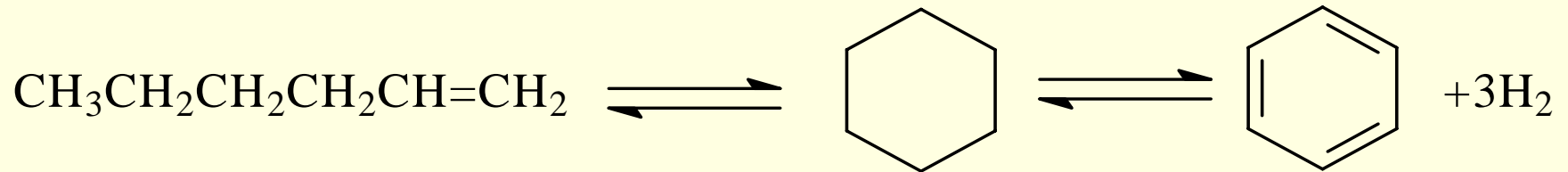
- The principal use of maleic anhydride is in the synthesis of unsaturated polyester resins.
- These resins are used to fabricate glass-fiber reinforced materials.
- Other uses include fumaric acid, alkyd resins, and pesticides.
- Maleic acid esters are important plasticizers and lubricants. Maleic anhydride could also be a precursor for 1,4-butanediol.

# AROMATICS PRODUCTION

- Liquefied petroleum gas (LPG), a mixture of propane and butanes, is catalytically reacted to produce an aromatic-rich product.
- The first step is the dehydrogenation of propane and butane to the corresponding olefins followed by oligomerization to C6, C7, and C8 olefins.
- These compounds then dehydrocyclize to BTX aromatics.



# AROMATICS PRODUCTION



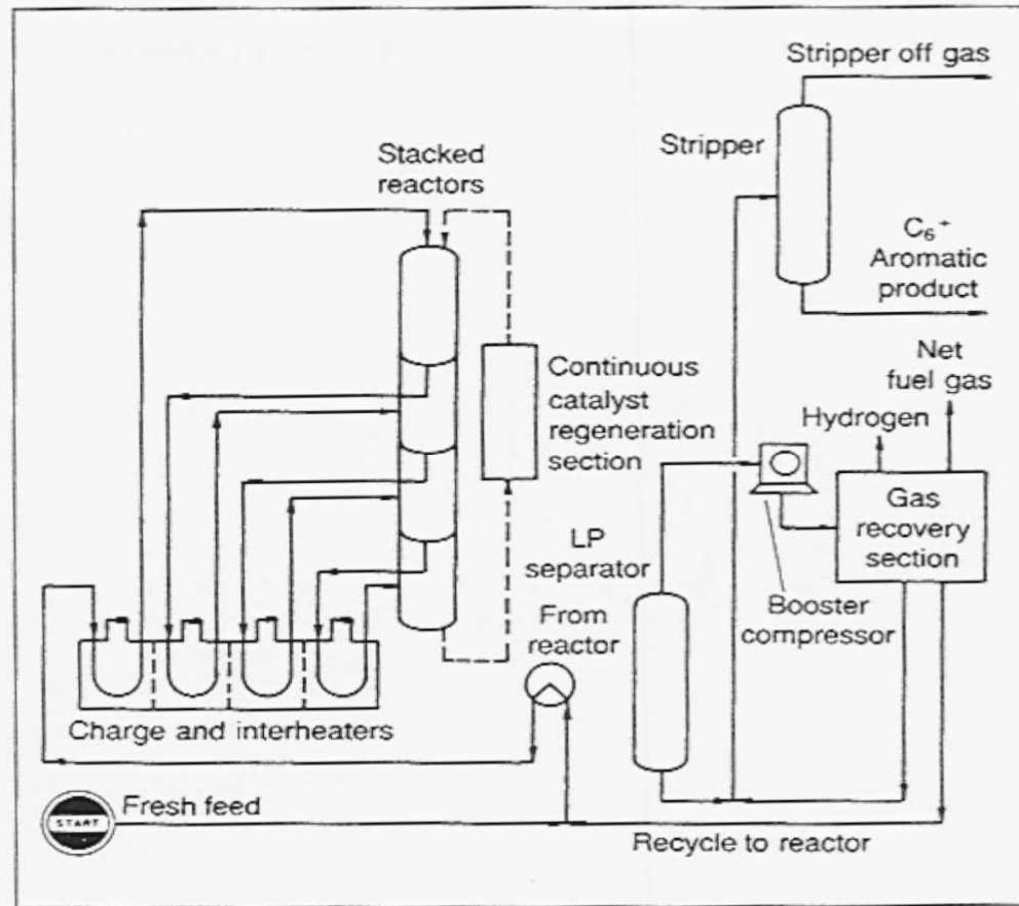
- Although olefins are intermediates in this reaction, the final product contains a very low olefin concentration.
- The overall reaction is endothermic due to the predominance of dehydrogenation and cracking.
- Methane and ethane are by-products from the cracking reaction.
- Example, the Cyclar process developed jointly by British Petroleum and UOP.

# AROMATICS PRODUCTION

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- The process consists of a reactor section, continuous catalyst regeneration unit (CCR), and product recovery section.
- The reactor feed consists solely of LPG plus the recycle of unconverted feed components; no hydrogen is recycled.
- The liquid product contains about 92 wt% benzene, toluene, and xylenes (BTX), with a balance of C9+ aromatics and a low nonaromatic content.
- Therefore, the product could be used directly for the recovery of benzene by fractional distillation (without the extraction step needed in catalytic reforming).

# AROMATICS PRODUCTION

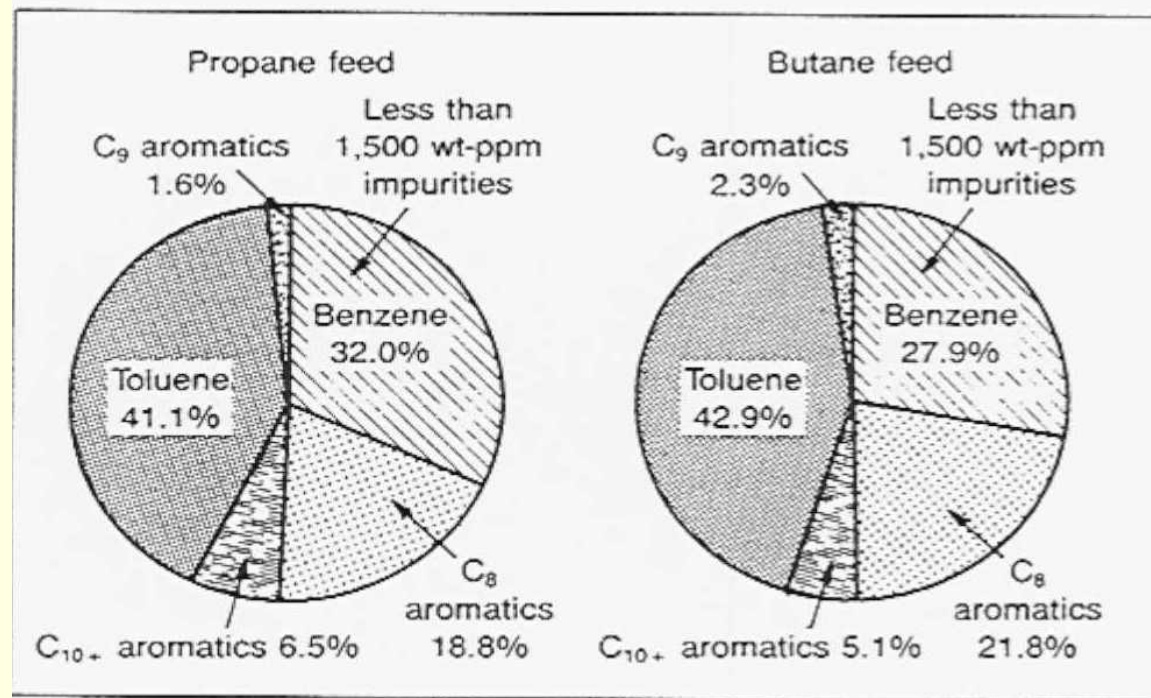


A flow diagram showing the Cyclar process for aromatics production of LPG.

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# AROMATICS PRODUCTION



The liquid ( $C_6^+$ ) product breakdown in weight units obtained from the Cyclar process.

# AROMATICS PRODUCTION

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**Product yield from saturated LPG feed to the cyclar process**

**Yields, wt% of fresh feed**

<b>Feedstock</b>	<b>Aromatics</b>	<b>Hydrogen</b>	<b>Fuel gas</b>
Propane (100%)	63.1	5.9	31.0
Butanes (100%)	65.9	5.2	28.9

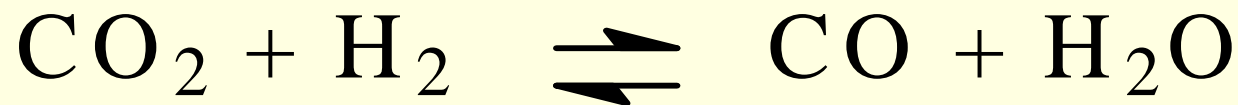
# AROMATICS PRODUCTION

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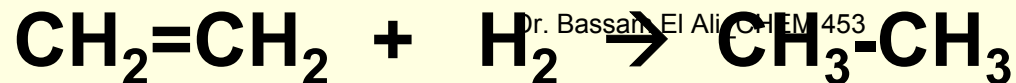
- Interest in the use of lower-value light paraffins for the production of aromatics led to the introduction of two new processes similar to the Cyclar process: the Z-forming and the Aroformer processes, which were developed in Japan and Australia, respectively.
- Research is also being conducted in Japan to aromatize propane in presence of carbon dioxide using a Zn-loaded HZSM-5 catalyst.

# AROMATICS PRODUCTION

- The effect of CO<sub>2</sub> is thought to improve the equilibrium formation of aromatics by the consumption of product hydrogen (from dehydrogenation of propane) through the reverse water gas shift reaction.

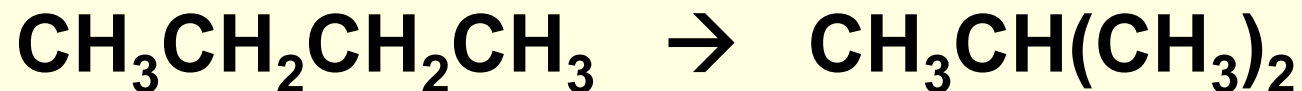


- A more favorable effect was found for the reaction between ethylene and hydrogen.
- The reverse shift reaction consumes hydrogen and decreases the chance for the reduction of ethylene to ethane byproduct.

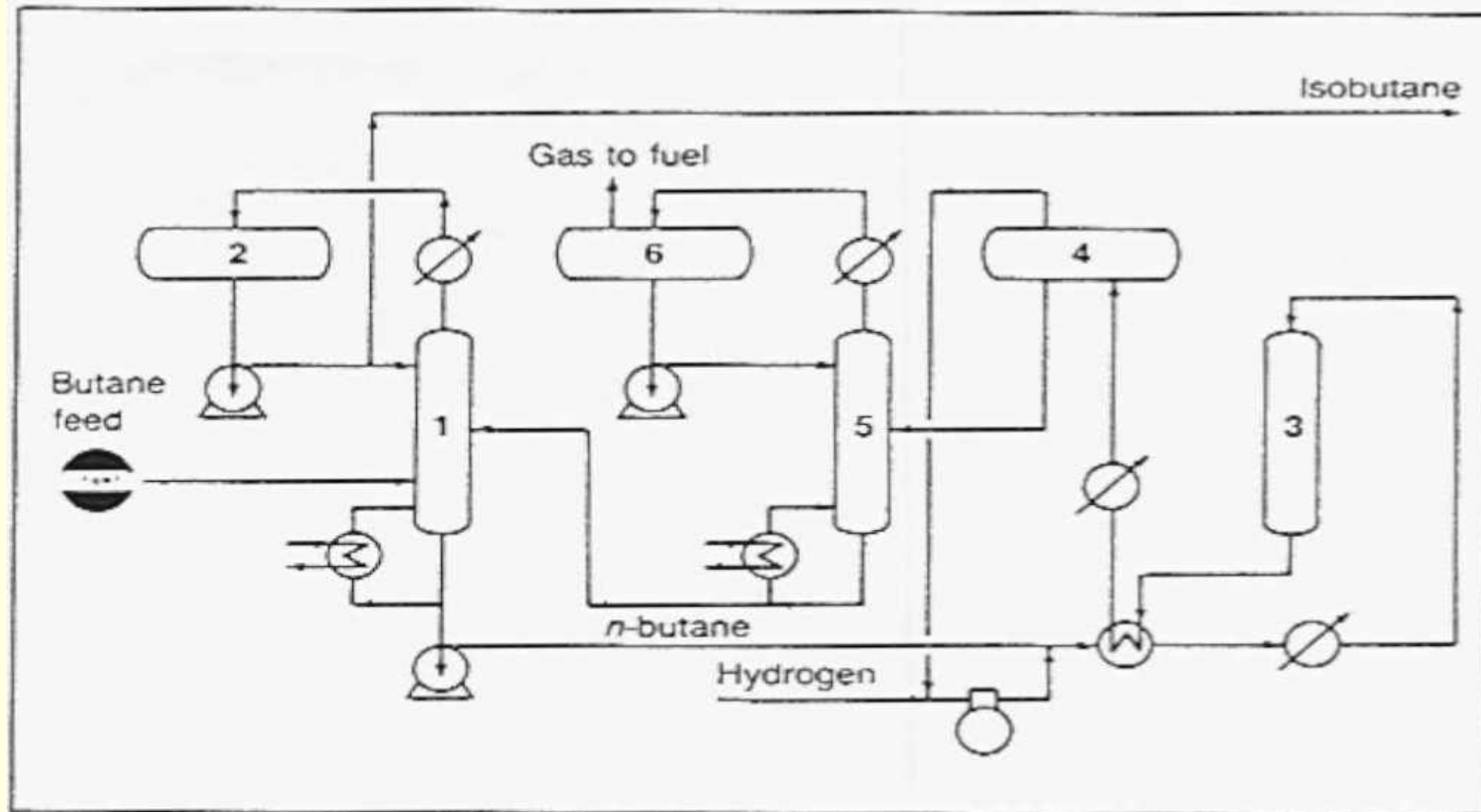


# ISOMERIZATION OF n-BUTANE (Isobutane Production)

- n-Butane is isomerized to isobutane, which is further dehydrogenated to isobutene.
- The Butamer process has a fixed-bed reactor containing highly selective catalyst that promotes the conversion of n-butane to isobutane equilibrium mixture.
- Isobutane is then separated in deisobutanizer tower. The n-butane is recycled with make-up hydrogen.
- The isomerization reaction occurs at a relatively low temperature:



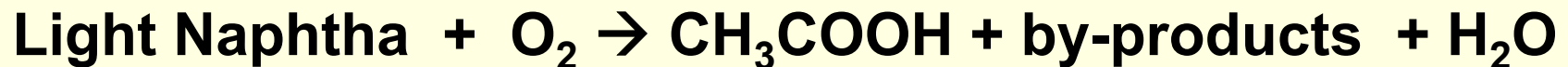
# ISOMERIZATION OF n-BUTANE (Isobutane Production)



The UOP Butamer process for isomerization of n-butane to isobutene:  
(1,2) desobutanizer, (3) reactor, (4) separator (for separation and recycling H<sub>2</sub>),  
(5,6) stabilizer.

# NAPHTHA-BASED CHEMICALS

- Light naphtha containing hydrocarbons in the C5-C7 range is the preferred feedstock in Europe for producing acetic acid by oxidation.
- The oxidation of light naphtha is performed at approximately the temperature and pressure ranges (170-200°C and  $\approx$  50 atmospheres) in the presence of manganese acetate catalyst. The yield of acetic acid is approximately 40 wt%.



# NAPHTHA-BASED CHEMICALS

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- The product mixture contains essentially oxygenated compounds (acids, alcohols, esters, aldehydes, ketones, etc.).
- As many as 13 distillation columns are used to separate the complex mixture. The number of products could be reduced by recycling most of them to extinction.
- Manganese naphthenate may be used as an oxidation catalyst.
- A yield of 83% of C1-C5 acids relative to n-hexane was reported.
- The highest yield of these acids was for acetic acid followed by formic acid. The lowest yield was observed for pentanoic acid.



# CHEMICALS FROM HIGH MOLECULAR WEIGHT n-PARAFFINS

- High molecular weight n-paraffins are obtained from different petroleum fractions through physical separation processes.
- Those in the range of C8-C14 are usually recovered from kerosenes having a high ratio of these compounds.
- Vapor phase adsorption using molecular sieve 5A is used to achieve the separation. The n-paraffins are then desorbed by the action of ammonia.
- Continuous operation is possible by using two adsorption sieve columns, one bed on stream while the other bed is being desorbed. n-Paraffins could also be separated by forming an adduct with urea.

# CHEMICALS FROM HIGH MOLECULAR WEIGHT n-PARAFFINS

- For a paraffinic hydrocarbon to form an adduct under ambient temperature and atmospheric pressure, the compound must contain a long unbranched chain of at least six carbon atoms.
- Ease of adduct formation and adduct stability increases with increase of chain length.
- As with shorter-chain n-paraffins, the longer chain compounds are not highly reactive. However, they may be oxidized, chlorinated, dehydrogenated, sulfonated, and fermented under special conditions.
- The C9-C17 paraffins are used to produce olefins or monochlorinated paraffins for the production of detergents.

# CHEMICALS FROM HIGH MOLECULAR WEIGHT n-PARAFFINS

Selected properties of paraffins from C5-C16

Name	Formula	Density	B.P. °C	M.P. °C
Pentane	$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	0.626	36.0	-130.0
Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	0.695	69.0	-95.0
Heptane	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3$	0.684	98.0	-90.5
Octane	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$	0.703	126.0	-57.0
Nonane	$\text{CH}_3(\text{CH}_2)_7\text{CH}_3$	0.718	151.0	-54.0
Decane	$\text{CH}_3(\text{CH}_2)_8\text{CH}_3$	0.730	174.0	-30.0
Undecane	$\text{CH}_3(\text{CH}_2)_9\text{CH}_3$	0.740	196.0	-26.0
Dodecane	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$	0.749	216.0	-10.0
Tridecane	$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_3$	0.757	234.0	-6.0
Tetradecane	$\text{CH}_3(\text{CH}_2)_{12}\text{CH}_3$	0.764	252.0	5.5
Pentadecane	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_3$	0.769	266.0	10.0
Hexadecane	$\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$	0.775	280.0	18.0

# OXIDATION OF PARAFFINS (Fatty Acids and Fatty Alcohols)

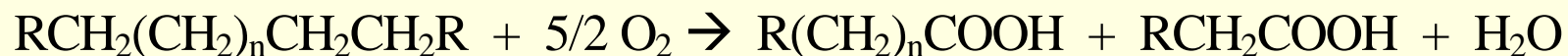
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- The catalytic oxidation of long-chain paraffins ( $C_{18}$ - $C_{30}$ ) over manganese salts produces a mixture of fatty acids with different chain lengths.
- Temperature and pressure ranges of 105-120°C and 15-60 atmospheres are used.
- About 60 wt% yield of fatty acids in the range of  $C_{12}$ - $C_{14}$  is obtained. These acids are used for making soaps.
- The main source for fatty acids for soap manufacture, however, is the hydrolysis of fats and oils (a non-petroleum source).

# OXIDATION OF PARAFFINS (Fatty Acids and Fatty Alcohols)

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- Oxidation of paraffins to fatty acids:

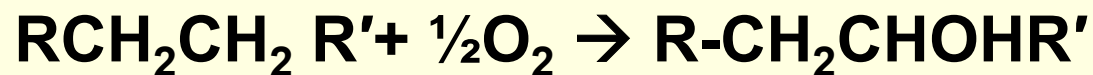


- Oxidation of C12-C14 n-paraffins using boron trioxide catalysts was extensively studied for the production of fatty alcohols.
- Typical reaction conditions are 120-130°C at atmospheric pressure.
- ter-Butyl hydroperoxide (0.5%) was used to initiate the reaction. The yield of the alcohols was 76.2 wt% at 30.5% conversion. Fatty acids (8.9 wt%) were also obtained.

# OXIDATION OF PARAFFINS (Fatty Acids and Fatty Alcohols)

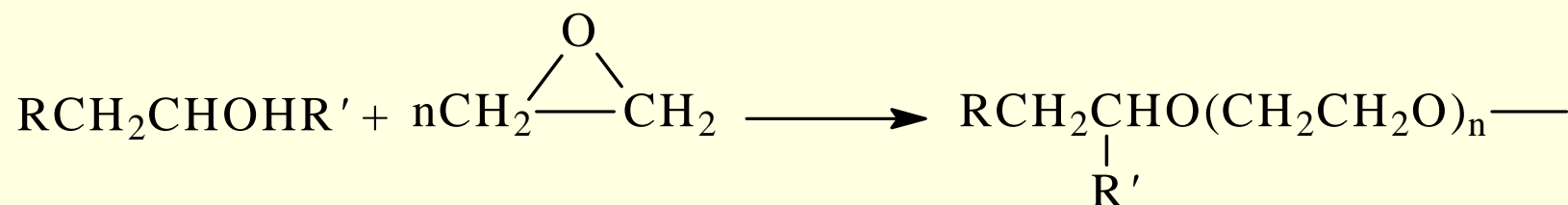
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- Product alcohols were essentially secondary with the same number of carbons and the same structure per molecule as the parent paraffin hydrocarbon.
- This shows that **no cracking** has occurred under the conditions used.
- The oxidation reaction could be represented as:



# OXIDATION OF PARAFFINS (Fatty Acids and Fatty Alcohols)

- n-Paraffins can also be oxidized to alcohols by a dilute oxygen stream (3-4%) in the presence of a mineral acid.
- The acid converts the alcohol to esters, which prohibit further oxidation of the alcohols to fatty acid. The obtained alcohols are also secondary.
- These alcohols are of commercial importance for the production of nonionic detergents (ethyoxylates):



# **CHLORINATION OF n-PARAFFINS (Chloroparaffins)**

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