Unipar Oxo Alcohols Plant

Start Up: August, 1984
Location: Mauá - São Paulo - Brasil

Nameplate Capacity:

⇒ Oxo plant: 33 KTA in Isodecyl Alcohol [106 t/day of Isodecyl Alcohol or 70 t/day of Tridecyl Alcohol (ISO)].
⇒ SynGas plant: 2300 Nm3/h syngas and 1200 Nm3/h of hydrogen reforming propane.

Note: Unipar has equipment available but not installed for an expansion of capacity from 33 to 42 KTA (44 KTA in Isodecyl alcohol). After expansion, the syngas unit would produce 2800 Nm3/h of syngas and 1500 Nm3/h of hydrogen.

Manufacturing Process (attachment 1)

⇒ Oxo Alcohol - PCUK technology
⇒ Synthesis Gas - KTI Technology

Raw Materials (attachment 2)

⇒ Nonene to produce Isodecyl Alcohol
⇒ Propylene Tetramer to produce Tridecyl Alcohol (ISO)
⇒ Propane and Steam to produce syngas and hydrogen. The raw material can be shifted to natural gas with small modifications in the syngas plant

Products (attachment 3)

⇒ Isodecyl Alcohol
⇒ Tridecyl Alcohol (ISO)

Process Flow Schemes

⇒ General Process Flow Scheme (attachment 4)
⇒ Oxo Alcohol - PCUK technology (attachment 5)
⇒ Synthesis Gas - KTI Technology (attachment 6)

Attachment 1. - Manufacturing Process Description -

Oxo Alcohol - PCUK technology

The Oxo processes is based on the addition of synthesis gas to an olefin via hydroformilation, followed by the hydrogenation of the resultant aldehydes to the respective alcohol. In the case of C9 and C12 olefins, the oxo reaction takes place at 155 - 175 °C and pressure of about 200 to 230 Bar. The catalyst used is gaseous cobalt-hydrocarbonyl dissolved in the olefin feed. After the cobalt has been removed by contacting the aldehydes with an aqueous solution of sodium hydroxide, the aldehydes are water washed to remove the remaining sodium and cobalt. The aldehydes are then hydrogenated in a series of jacketed fixed bed reactors at a temperature of 140 to 200 °C and a pressure of around 45 to 60 bar using Copper-Chromite, Cobalt on kieselguhr and Nickel on kieselguhr as solid tablets. The unreacted olefins are hydrogenated to form saturated hydrocarbons or remain as olefin structures. Other side reactions involve the formation of acetals, esters, ethers and polymers of the aldehydes, acids, etc.
The by-products are separated from the alcohols by distillation on sieve tray columns. The first column allows the separation of a mixture containing practically all the hydrocarbons and water at its overhead. For an overhead pressure of 100 mm Hg and temperature of 80-90 °C we have 3 to 5 % of alcohol in the overhead. The second column operates at 20 mm Hg and allows the separation of the alcohols at its overhead while the heavy ends containing 2 to 5 % of alcohol are drawn at its bottom.
The distilled alcohols are then sent for final hydrogenation on a reactor containing nickel catalyst at 45 Bar and 70 to 130 °C. This operation allows the production of purified alcohol. The heavy ends recovered at the bottom of the alcohol column are sent to the polymer cracking section which consists of a furnace, an activated alumina reactor and a steam stripping column, thus allowing the recovery of some alcohol which is sent back to the hydrogenation reactors.

Synthesis Gas - KTI Technology

Liquid Propane is fed to a steam heater and then to heat exchangers installed in the convection section of the reforming furnace. The vaporized stream is hydrogenated in a CoMox reactor to saturate the olefins and to convert to H2S any eventual sulfur content. Absorption of eventual sulfur compounds takes place in a zinc oxide reactor. The desulfurized feedstock is mixed with steam and the hot recycled CO2 and fed to the reformer. The heat content from the hot reformer effluent is then recovered in the process gas boiler and in the MDEA stripper reboiler. The process stream goes through an MDEA system, consisting of absorption and stripping columns for the removal of Carbon Dioxide which is recycled back to the reformer to maximize the formation of Carbon Monoxide. Raw gas from MDEA system is compressed to 77 bar and fed to the two stage Prism separator which is licensed by Air Products. In the first stage of the Prism separator, a hydrogen to CO ratio adjusted Oxo Syngas will be separated from the hydrogen rich raw gas and compressed to feed the oxoalcohols unit. In the second stage, the hydrogen rich raw gas will be further purified to 98.5 volume percent hydrogen. The hydrogen product from Prism Separator still contains slightly less than one percent CO which is removed in a Methanation reactor. The effluent from the methanator is compressed to 78 bar in order to supply the aldehyde hydrogenation section.

Attachment 2. - Raw Material Specification -

Nonene

APPEARANCE: Clear liquid, colorless and free of sediment.

PROPERTY	SPECIFICATION Minimum	Maximum	TEST METHOD
Monoolefins, vol. %	97.0		ASTM D - 1319
Pt-Co Color		5	ASTM D - 1209
Relative Density 20/4 ºC	0.734	0.745	ASTM D - 1298
Distillation Range, ºC			ASTM D - 86
IBP	131.5		
DP		146.0	
Bromine Number, g/100g	100	130	ASTM D - 1159
Water Content, mg/kg	200		ASTM D - 1744

For temperatures below -30 °C, storage heating devices are necessary.

Propylene Tetramer

APPEARANCE: Clear liquid, colorless and free of sediment.

PROPERTY	SPECIFICATION Minimum	Maximum	TEST METHOD
Monoolefins, vol. %	97.0		ASTM D - 1319
Pt-Co Color		30	ASTM D - 1209
Relative Density 20/4 ºC	0.760	0.770	ASTM D - 1298
Distillation Range, ºC			ASTM D - 86
IBP	171.0		
FBP		208.0	
Bromine Number, g/100g	80	100	ASTM D - 1159
Water Content, mg/kg		200	ASTM D - 1744

For temperatures below -30 °C, storage heating devices are necessary.

Attachment 3. - Product Specification -

Isodecyl Alcohol

APPEARANCE: Clear liquid, colorless and free of sediment.

PROPERTY	SPECIFICATION Minimum	Maximum	TEST METHOD
Alcohol Content, wt %	99.0		I - 150.180
Acidity, milimole/kg		5	ISO 1843/II
Aldehydes Content, milimole/kg		10	ISO 1843/III
Pt-Co Color		10	ASTM D - 1209
Relative Density 20/4 °C	0.834	0.842	ASTM D - 1298
Distillation Range, °C			ASTM D - 1078
IBP	215.0		
DP		226.0	
Water Content, wt %		0.10	ISO 760

For temperatures below -10 °C, storage heating devices are necessary.

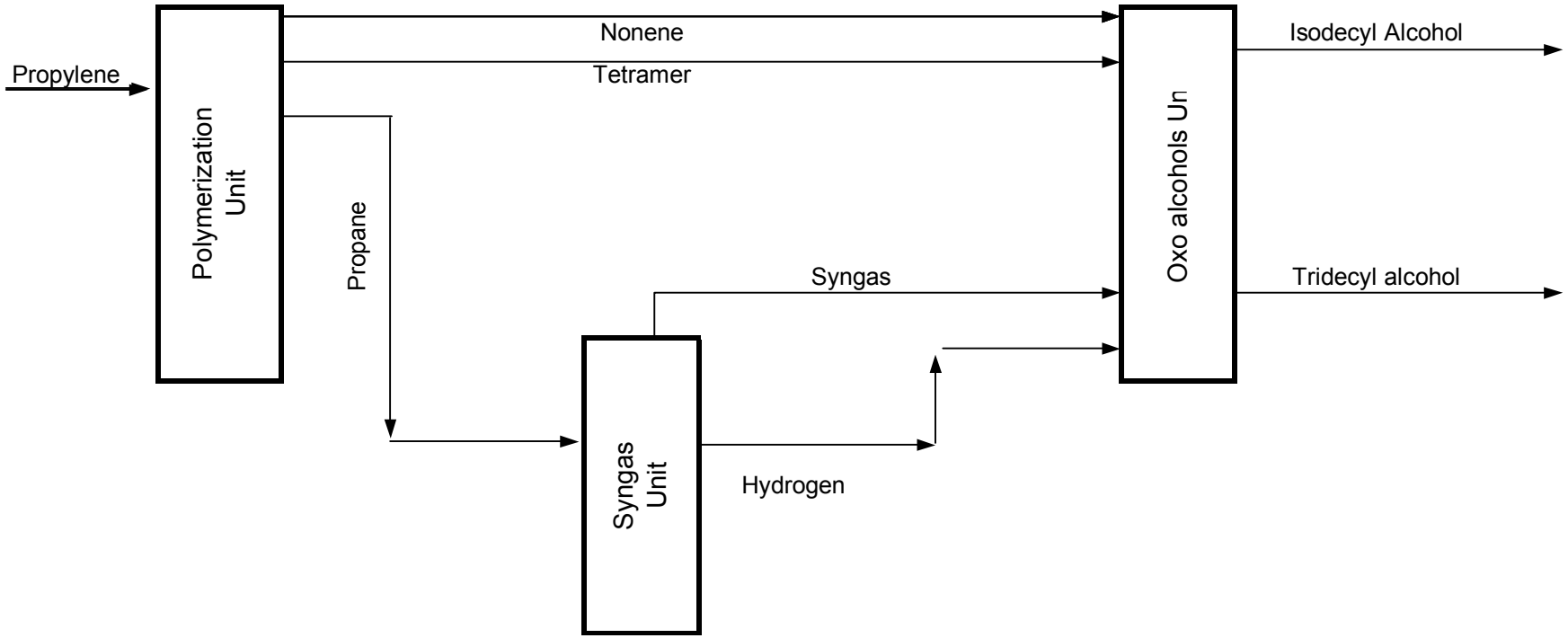
Tridecyl Alcohol (ISO)

APPEARANCE: Clear liquid, colorless and free of sediment.

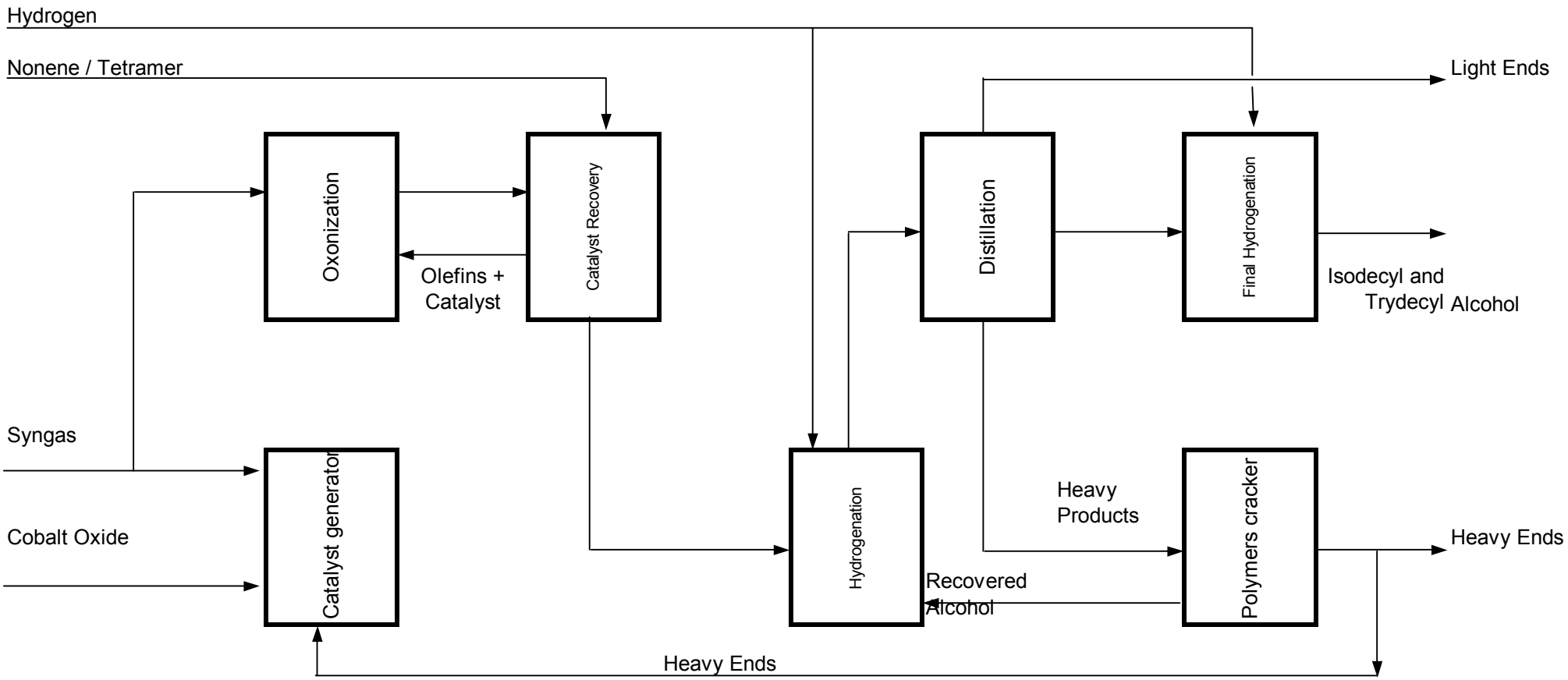
PROPERTY	SPECIFICATION Minimum	Maximum	TEST METHOD
Alcohol Content, wt %	99.0		I - 150.180
Acidity, milimole/kg		2	ISO 1843/II
Aldehydes Content, milimole/kg		10	ISO 1843/III
Pt-Co Color		10	ASTM D - 1209
Relative Density 20/4 °C	0.842	0.848	ASTM D - 1298
Distillation Range, °C			ASTM D - 1078
IBP	250.0		
DP		268.0	
Water Content, wt %		0.10	ISO 760

For temperatures bellow -10 °C, storage heating devices are necessary.

Attachment 4. - General Process Flow Scheme -



Attachment 5. - Oxoalcohol Process Flow Scheme -



Attachment 6. - Syngas Process Flow Scheme -