

Evaluation on Production and Economics of Acrylonitrile by Sohio Process

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Abstract-- Acrylonitrile is a highly reactive monomer and unsaturated hydrocarbon. It is used as a raw material in the production of fibers, dyes; anti-oxidants. Industrial production of acrylonitrile is done by Sohio process. Worldwide production of acrylonitrile is through Sohio process that is vapour phase ammoxidation of propene. The advantage of the process is the high conversion of reactants with minimum residence time. Air, ammonia and propene are fed into the reactor operating at 0.3- 2 atm pressure and 350°C-510°C. Ammonia and air should be supplied to the reactor in excess of stoichiometric proportions as excess air is needed for the regeneration of the catalyst and excess ammonia drives the reaction closer to the completion. Reaction is highly exothermic. The gaseous phase product stream is quashed in liquid phase through counter current water absorber to remove inert gases and recover reaction products. Mixture of acrylonitrile, acetonitrile, carbon oxides and hydrogen cyanide are formed. Product surge is sent to fractionator to remove hydrogen cyanide. Acrylonitrile is separated from acetonitrile by extractive distillation. Acrylonitrile obtained after extractive distillation is subjected for drying. Acetonitrile and hydrogen cyanide which are the primary by-products of the process are subjected to incineration. Incineration leads to the formation of nitrogen oxides, carbon oxides which are the primary pollutants.

INTRODUCTION

Acrylonitrile is a major organic chemical which is widely accepted in the chemical industries, drug intermediates as solvent and intermediate in various chemicals. Acrylonitrile also known as 2-propenenitrile, propene nitrile, vinyl cyanide, cyano-ethene, ACN is a chemical compound with formula $\text{CH}_2=\text{CH-CN}$ registered with the CAS number 107-13-1.5 [1] It has been largely manufactured in continuous process. There are three main routes of manufacturing, among them sohio process is mainly adopted because of its merits with respect to other processes. Our project is to design a plant to manufacture 200 tons/day of acrylonitrile and we have adopted Sohio process as the project task. Acrylonitrile is a clear, colourless flammable liquid with sweet, pungent, irritating odour. Acrylonitrile is slightly soluble in water, whereas acrylonitrile is soluble in organic solvents such as ethanol, acetone, ethyl acetate, carbon tetrachloride and benzene. Acrylonitrile is highly reactive molecule because of the presence of both carbon-carbon double bond and carbon – nitrogen triple bond in the same molecule. Nitrile in ACN can undergo hydrolysis to acrylamide (partial hydrolysis) and to acrylic acid; ACN and primary alcohol react in

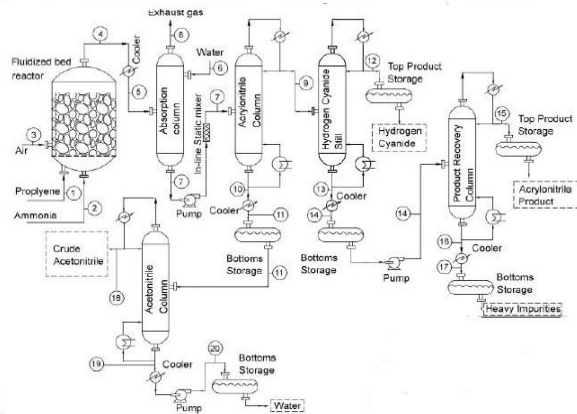
presence of acids to acrylic esters [2]. In the presence of alkalis or peroxide and when exposed to light, violent polymerization takes place. Charles Moure was the first person to prepare acrylonitrile in 1893 by dehydration either with acryl amide or with ethylene cyanohydrin in the presence of phosphorous pentoxide up to 1960. Process based on hydrogen cyanide and ethylene oxide or acetylene was used to produce acrylonitrile. At present, acrylonitrile is produced worldwide because of its various applications. The total world production capacity of acrylonitrile manufacturing is approximately 4000 tons per year. Acrylonitrile is used in the manufacturing of synthetic fibers, plastics and elastomers. It is also used to produce acrylonitrile, nylon intermediate. Most prominent among these are catalysts for ammoxidation of propene to acrylonitrile that are utilized for the production of 10 billion pounds of acrylonitrile annually [3] An indication of the difficulty here is that the major breakthroughs in the 1990s by BP-America [4] (formerly SOHIO) and Mitsubishi [5] in discovering catalysts (e.g. MoVNbTeO) that convert propane (not propene) directly to acrylonitrile have not yet led to commercially viable catalysts
Propene –ammoxidation process [6-8]: In this process acrylonitrile is manufactured by vapour phase catalytic propene ammoxidation process. Ammonia, propene and air are fed into a reactor containing solid catalyst. The reactor is maintained is maintained at 350 – 450 C temperature and 1-2 Kg/cm (gauge) pressure. In catalyst bed reactor propene oxidized with ammonia in vapour phase. The hot effluent is then quenched in water where unreacted ammonia is neutralized with sulphuric acid and form ammonium sulphate. Cooled vapour is passed to the absorber. Unreacted gases pass to incinerator. The absorbed liquid is sent to distillation column (recovery column), where crude acrylonitrile is found as top product which is then sent to fractionating column to get pure acrylonitrile. Bottom product from the recovery column is sent for further processing to remove the by-product acetonitrile. Different chemicals were studied to find alternative precursors to acrylonitrile. It is found that there is a yield of acrylonitrile when ethylene, propene, and butane react with ammonia at high temperature. Monsanto, Power gas, and ICI have developed catalytic ammoxidation processes based on propene. Propene is of particular importance because of a cost advantage over propene. It is found that when ethylene reacts with hydrogen cyanide and oxygen in the presence of palladium-based catalyst, high conversions to acrylonitrile is obtained.

EXPERIMENTAL SECTION

Raw materials and catalyst: The main raw materials used for the reaction are Propene obtained from petrochemical process, Air naturally available, Ammonia is obtained in synthetic process, Water naturally available.

Material balance: Total production 200 tons/day, Production rate 0.019758 kmol/s, Molar feed ratio Propene: ammonia: air (1:1.1:8.1)

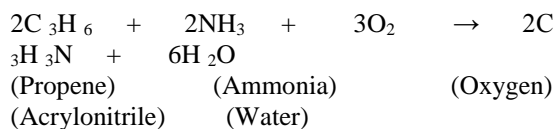
PROCESS DESCRIPTION



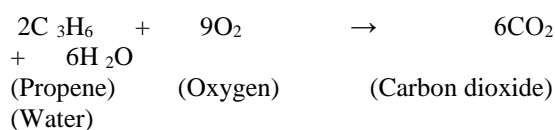
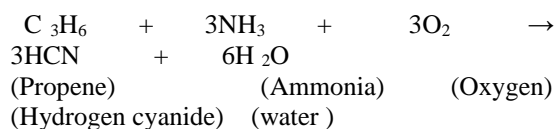
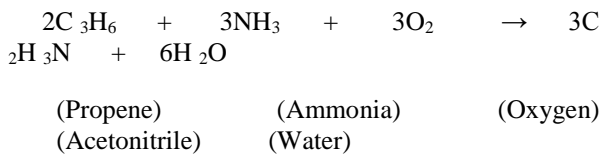
The air is introduced below the bottom grid whereas mixed propene and ammonia are introduced through the spiders above the grid. Residence time in the reactor is between 2 to 20 seconds. There is almost complete conversion of propene and the selectivity of acrylonitrile is around 80% [9-10].

The main reactions and side reactions of the process in reactor are as follows:

Main reaction:



Side reactions:



The gaseous phase product stream is quashed in liquid phase through counter current water absorber to remove inert gases and recover reaction products. Mixture of acrylonitrile, acetonitrile, carbon oxides and hydrogen cyanide are formed. Product surge is sent to fractionator to remove hydrogen cyanide. Acrylonitrile is separated from acetonitrile by extractive distillation. Acrylonitrile obtained after extractive distillation is subjected for drying. The acrylonitrile obtained after drying is 99% pure. Acetonitrile and hydrogen cyanide which are the primary by-products of the process are subjected to incineration. Incineration leads to the formation of nitrogen oxides, carbon oxides which are the primary pollutants. Other emission sources involve the volatilization of hydrocarbons through process leaks and from the deep well ponds, breathing and the working losses from the product storage tanks and losses during product loading operations. Primarily propene and propane are emitted in the fugitive and deep well or pond emissions, whereas storage tank and product loading emissions consists of acrylonitrile.

Fluidized bed reactor:

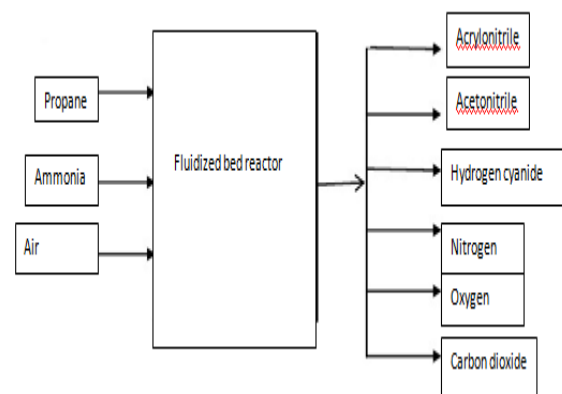


Figure 1: Block diagram for Fluidized Bed Reactor

From main reaction:
 $2C_3H_6 + 2NH_3 + 3O_2 \rightarrow 2C_3H_3N + 6H_2O$

TABLE 1: PARAMETERS OF FLUIDIZED BED REACTOR

Parameters	Value
Acrylonitrile exit from fluidized bed reactor	0.019758 kmol/s
For 85% conversion of propene charged	0.023245 kmol/s
Ammonia requirement 2kmol of ammonia ≡ 2kmol of acrylonitrile	0.0276612 kmol/s
Oxygen requirement 3kmol of O ₂ ≡ 2kmol C ₃ H ₃ N	0.04 kmol/s
Water produced during the reaction	0.071147kmol/s
Propene unreacted	0.000232kmol/s
Ammonia unreacted	0.007932 kmol/s
Oxygen unreacted	0.010363 kmol/s
Theoretical air required	0.190476 kmol/s
Nitrogen in air	0.150476kmol/s

From side reaction 1 (2% conversion)
 $2C_3H_6 + 3NH_3 + 3O_2 \rightarrow 3C_2H_3N + 6H_2O$

3.9516×10^{-4} kmol propene = 0.000697 kmol/s acetonitrile

From side reaction 2: (2% conversion)
 $C_3H_6 + 3NH_3 + 3O_2 \rightarrow 3HCN + 6H_2O$

3.9516×10^{-4} kmol of propene = 0.001394 kmol/s of hydrogen cyanide

From reaction 3: (10% conversion)
 $2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$

0.002324 kmol propene = 0.006973 kmol/s of carbon dioxide

ENERGY BALANCE

Working = 24 hours per day
 Base temperature is taken as 300°K(27°C)

Heat capacity and enthalpy data

TABLE 2: HEAT CAPACITY AND ENTHALPY DATA

Component	ΔH_f° (kJ/mol)	C_p (kJ/mol)
Propene	+20.41	0.05
Ammonia	-46.19	0.03
Oxygen	-	0.03
Nitrogen	-	0.03
Acrylonitrile	+184.93	1.204
Acetonitrile	+74.56	0.06
Hydrogen cyanide	+130.5	0.035
Carbon dioxide	-393.5	0.039
Water (g)	-241.83	2.013
Water (l)	-285.83	4.184

TABLE 3: ENTHALPY OF FORMATION OF REACTION

For main reaction	$2C_3H_6 + 3NH_3 + 3O_2 \rightarrow 3C_2H_3N + 6H_2O$	$(2 \times 184.93 + 6 \times (-241.83)) - (2 \times (-46.19) - (2 \times 20.41))$	$\Delta H_f^\circ = -1029.56$ kJ/s
For side reaction 1		$(3 \times 74.56 + 6 \times (-241.83)) - (2 \times 20.41 + 3 \times (-46.19))$	$\Delta H_f^\circ = -1047.85$ kJ/s
For side reaction 2	$C_3H_6 + 3NH_3 + 3O_2 \rightarrow 3HCN + 6H_2O$	$3 \times 130.5 + 6 \times (-241.83) - (3 \times (-46.19) + (-20.41))$	$\Delta H_f^\circ = -941.32$ kJ/s

For side reaction 3	$2C_3H_6 + 9O_2 \rightarrow 6CO_2 + 6H_2O$	$(6 \times (-241.83) + 6 \times (-285.83)) - (2 \times 20.41)$	$\Delta H_f^\circ = -3852.8$ kJ/s
Total enthalpy of formation			$\Delta H_f^\circ = -6871.53$ kJ/s
Enthalpy of reactants $\Delta H_R = [(nc_p)_{propene} + (nc_p)_{ammonia} + (nc_p)_{oxygen} + (nc_p)_{nitrogen}] \Delta t$			2.87438 kJ/s
Enthalpy of products $\Delta H = [(nc_p)_{propene} + (nc_p)_{ammonia} + (nc_p)_{oxygen} + (nc_p)_{nitrogen} + (nc_p)_{acetonitrile} + (nc_p)_{acrylonitrile} + (nc_p)_{HCN} + (nc_p)_{water}] \Delta t$			72.2060 kJ/s
$\Delta H_{reaction} = \Delta H_f + \Delta H_R + \Delta H_P$			-6796.4497 kJ/s

Therefore heat of reaction is as follows $\Delta H_{reaction} = -6796.4497$ kJ/s, negative sign indicates that reaction is exothermic. Hence water is needed to remove the heat. So assume water enters at 25oC and leaves at 80oC, so $Q = n c_p \Delta T$, n forms 29.53 kmol/s.

Design of Fluidized Bed Reactor

Since it is ammoxidation process [9-10], the equipment is subject to corrosion. Now a days, various steels like SS316, SS316L, and (High tensile steel) are available to suit the conditions. SS316 has given good results at low concentration of halides and sulphates provided sufficient corrosion allowance d is given. Since the operation is at high pressure and temperature, in the moderately corrosive atmosphere, SS316 is chosen as M.O.C reactor.

TABLE 4: SUMMARY OF DESIGN

Fluidized bed catalyst reactor	
Reaction time	10 Seconds
Catalyst bed height	8 m
Diameter	2.1m
Height –vessel (Total)	9.75m
Temperature	400°C
Pressure	2kg/cm ²
Bottom disc	Triangular
Top disc	Elliptical
Cooling coil (Total length)	47.98 m
Inner diameter of the tube	75 mm

Design of Fractionation Column

The feed to the distillation column consists of acrylonitrile, water and other impurity like hydrogen cyanide. The top product consists of acrylonitrile and small part of water and uncondensed gas. The bottom product consists of rest of water and entire part of acrylonitrile.

TABLE 5: MATERIAL BALANCE FOR DISTILLATION COLUMN

Serial No.	components	Input (kmol/s)	Output (kmol/s)		Total
			Distillate	Bottom product	
1	Acrylonitrile	3.7534	2.4134	1.30	3.7134
2	Water	1.6007	1.57	0.0307	1.6007
Total		5.3541			5.3141

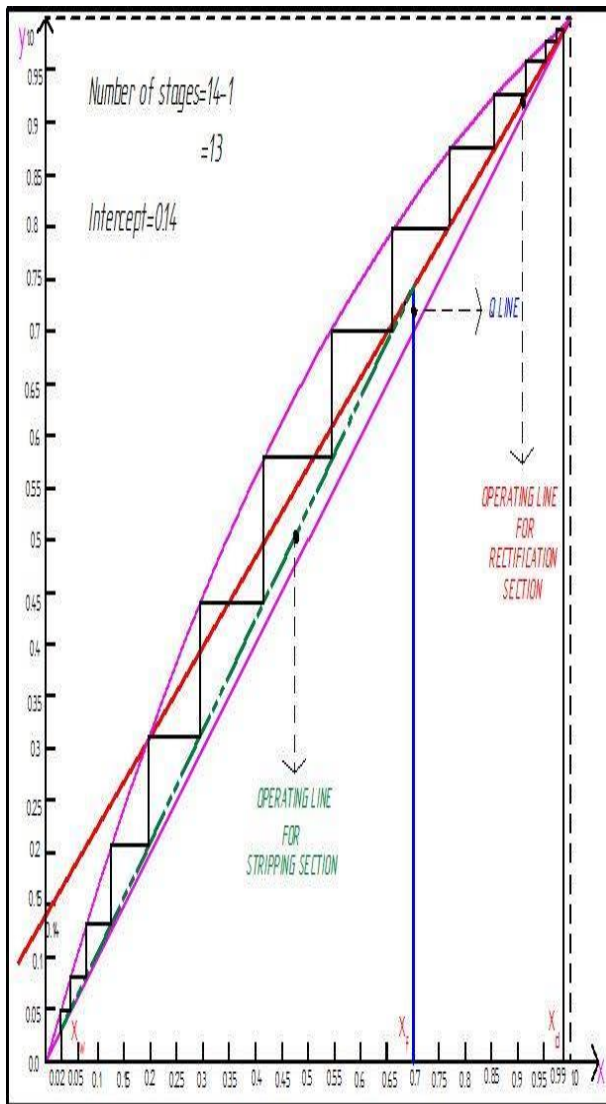


Figure 2: Graph showing number of theoretical stages

For hydrocarbon fractionation, commonly used efficiency is about 60% so the actual number of plates is 21.

TABLE 7: COST ESTIMATION

Number of working days	300
Cost of 1000kg of acrylonitrile	Rs 85,000
Production of acrylonitrile	60000 tons /year
Total income	Rs 5,10,00,00,000
Direct cost is 70%	Rs 3,57,00,00,000
Indirect cost	Rs 1,53,00,00,000
60% of total product cost	Rs 2,75,40,00,000
5% of total product cost	Rs 22,95,00,000
15% of total product cost	Rs 6,88,50,000
20% of operating labour cost	Rs 13,77,00,000
10% of total product cost	Rs 4,59,00,000
3.6% of fixed capital investment cost	Rs 18,36,00,000
6.7% of operating labour cost	Rs 4,61,29,500
1.5% of fixed capital cost	Rs 7,650,0,000
10% of product cost	Rs 45,90,00,000
5% of total product cost	Rs 22,95,00,000
Depreciation for machinery is 10% of fixed capital cost + depreciation for building ,3% of land cost	Rs 1,22,40,00,000
1% of fixed capital cost	Rs 5,10,00,000
General expenses 4%	Rs 18,36,00,000
6% of total product cost (sales)	Rs 27,54,00,000
1% Research and development cost	Rs 4,59,00,000
2% financing	Rs 9,18,00,000
Net profit	Rs 20,40,00,000

Direct cost is 70% of fixed capital investment says Rs 3,57,00,00,000. Total costs involved are equipment cost (35%), installation and piping cost (6 %), instrumentation cost (9 %) Electrical cost (10%), piping cost (9 %), Building, process and auxiliary cost (7%), Service facilities cost (4%) and Land cost (20%).

Indirect cost = fixed capital investment – direct cost = 1,53,00,00,000

Indirect cost consists of following terms engineering supervision cost (6 %), Contingency (2%), Working capital (22%),

Gross earning is 10% of annual income = 51, 00, 00,000

Product cost = Total annual income – gross earnings = 4,59,00,00,000

RESULTS AND DISCUSSION

In the current paper, the process selected is appropriate for the efficient production. It has the entrenched intend parameters those covered within the plant for the expansion in future to increase the production. Besides, the process selected is very suitable to adopt environmental rules imposed by government agencies, worldwide. The other alternate routes of production Ethylene cyanohydrin pyrolysis process is based on the catalytic dehydration of ethyl cyanohydrins. Ethylene cyanohydrin was produced from ethylene oxide and aqueous hydrocyanic acid at 6°C in the presence of basic catalyst. The intermediate was then dehydrated in the liquid phase at 200 C in the presence of magnesium carbonate and alkaline of alkaline earth salt of formic acid. The process is slightly longer route wherein the production of Acrylonitrile is delayed. This in turn has effect on the raised cost of production. Moreover the cyanide chemical, handling and by product, effluents are all leading the environmental pollution, besides occupational

hazards to the technical team who are involved in the production process.

Over view production: The method of preparing this compound involves the following steps: (1) reaction of commercial methyl cyclopropyl ketone with liquid HCN in the presence of a basic catalyst to produce the cyanohydrin, alpha-methyl-alpha-cyclopropyl glycolonitrile; (2) acetylation of the cyanohydrin with acetic anhydride and sulfuric acid catalyst to produce alpha-acetoxy-alpha-cyclopropyl propionitrile; and (3) pyrolysis of this acetate at a temperature of 430-450 C. to eliminate acetic acid and produce the desired alpha-cyclopropyl acrylonitrile. The acetic acid may be removed by distillation or by washing with soda solution. The product is then vacuum distilled to purify it and is obtained as a water-white liquid of rather acrid odor which somewhat-resembles nitrobenzol in smell.

Hence such methods adoptability is not possible. In our present case a process route is chosen as described. Propene – ammoxidation process is most preferred route for large-scale production of acrylonitrile given by soho since 1958 due to high selectivity, faster rate of reaction, control of operating parameters , by products productions and simplicity compared to the other routes of production. Moreover the economic conditions and environmental aspects are favourable in our present methods. Market conditions, plant location and energy costs are the factors that influence the recovery of these by-products. Hydrogen cyanide and acetonitrile are usually incinerated as the production of these by-products has effect on the economics of producing acrylonitrile. Hence the optimally selected process is the Sohio process.

Effect of environmental conditions: Though there are four methods for the production of Acrylonitrile (described earlier in our literature survey), Sohio process is most

favourable due to the reasons of low environmental damage and ease of access for the productions and gang-men friendly. Hence the selectivity of the process is justified.

Effect of economic conditions: Besides the points as discussed above this Sohio process is economically feasible for the investment for safe and continuous production.

CONCLUSION

The focus of this study was to develop a methodology using multi objective optimization that would enhance a chemical process by increasing the overall revenue and also reduce the waste generated. This research has been done using the acrylonitrile process as a case study. A general methodology involving process modelling, generation of process alternatives and incorporation of multi objective optimization was formulated. Manufacture of Acrylonitrile by Sohio Process deals with the production of Acrylonitrile 200 tons/day, in a continuous process. Literature survey has been done and Sohio process has been selected for this academic work. The relative advantages of this process are considered with respect to other manufacturing methods for the same. Manufacture and mechanism of ammoxidation of propene process is explained in details. Various design parameters are considered for the optimal design of a Fluidized bed reactor and also a distillation column. Structural design for the best material of construction and plant layout feasibilities are reported in this project. In addition to these points, cost of production and little marketing strategies are included. The details of environmental effect and safe production aspects of chemical engineering are given importance and the same has been included appropriately. The project is designed in such there should be scope for expansion and such criteria also notified in the project.

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