Journal of Petroleum and Gas Exploration Research (ISSN 2276-6510) Vol. 2(8) pp. 152-160, September, 2012
Available online http://www.interesjournals.org/JPGER

Full Length Research Paper

Cleaner production in vinyl sulphone industry

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Accepted September 03, 2012

Cleaner production is proposed to develop cleaner technology in vinyl sulphone industry by adopting better technologies, better plants, better processing, better recoveries and better pollution control measures which is more convenient and viable for industry to increase their economical benefit in short time of payback period and also to satisfy Gujarat Pollution Control Board rules. Scope of this project is that it helps us to increase maximum recovery of byproducts , to decrease loss in storage of raw material and also to decrease excess amount of raw material usage by proposed alternative technology of vinyl sulphone to satisfy Gujarat Pollution Control Board rules, to improve process and economics. In proposed process, it is possible by modifying hydrochloric acid absorption system or using falling film absorber decreases hydrochloric acid emissions from vent of caustic scrubber and also increase concentration of hydrochloric acid than conventional process, modifying storage system by using ujarat r to recover ethylene oxide vapor and providing new process technology decrease usage of excess raw materials, effluent etc.

Keywords: Falling Film Absorption, Tail gas scrubber, Condensor, Ethylene oxide recovery system, 40% Spent Acid.

INTRODUCTION

Among the dye intermediates the highest exports are of vinyl sulphone and it is one of the most polluting industries, because some environmental hazards like as Hydrochloric acid is liberated in chlorosulphonation stage as gas and needs to be scrubbed. Due to poor absorption recovery system, concentration of hydrochloric acid as byproduct is continuously decreasing. Inefficient scrubbing and recovery may cause air pollution due to high concentration of hydrochloric acid gas in air from vent and does not satisfy ujarat pollution control board rules. For conventional neutralization of acidic mother liquor, large quantity of lime is required. Excess of ethylene oxide used in condensation is hazardous and it is to be used in excess as large quantity of the some hydrolyses to glycols in presence of water. Mother liquor and washings after condensation contain glycols, sodium sulphate and sodium chloride. Also liquid effluent generated is toxic having high biological oxygen demand(BOD), chemical oxygen demand (COD) and temperory dissolved solids (TDS), which is difficult to biodegrade, and solid waste generated is hazardous. Due to poor raw material storage and handling system, like as ethylene oxide which is transferred from ethylene oxide tanker to storage tank, large amount of ethylene oxide vapor escapes and it's diluted solution goes as effluent. Due to many hazards problems, it is finding increasingly difficult to compete in the world market, therefore, it is felt to take-up the study.

Conventional Manufacturing Process of Vinyl Sulphone

The original manufacturing process for vinyl sulphone, the development of which can be attributed to Hoechst, Germany, consists of the following unit processes (shown in Figure 1). The aromatic acetylamino substrate is chlorosulphonated with an excess of chlorosulphonic acid, the latter itself acting as a solvent to afford the sulphonyl chloride. The sulphonyl chloride derivative is isolated by dumping into ice-cold water and then reduced

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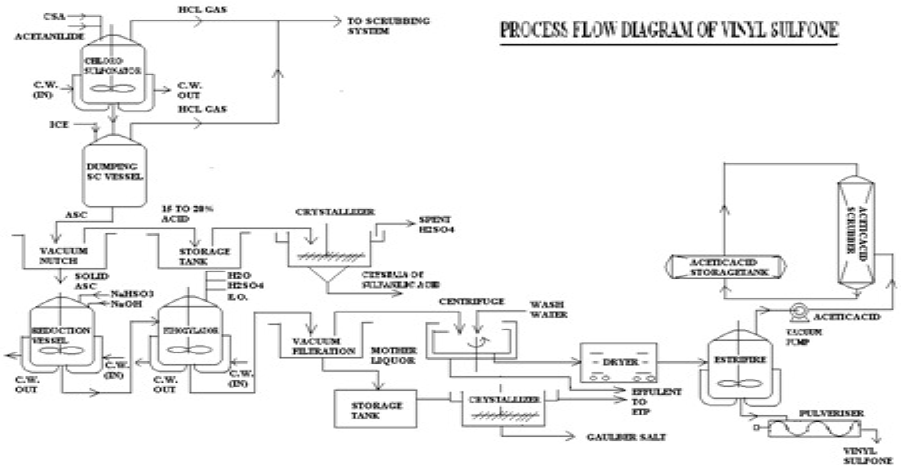

Figure 1. Process flow diagram of vinyl sulphone.

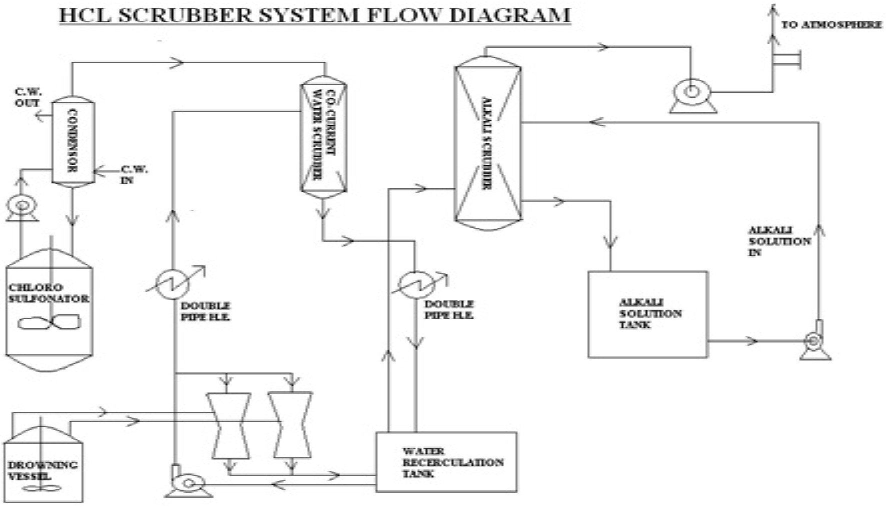

Figure 2. Conventional Hydrochloric acid Absorption System.

with alkaline sodium bisulphite to the corresponding sulphonic acid. The sulphonic acid derivative is then condensed with ethylene oxide in presence of sulphuric acid to give β-hydroxyethylsulphone. Heating the sulphone with concentrated sulphuric acid brings about sulphation andhydrolysis to yield β-sulphatoethylsulphone derivatives, which are marketed as such.

Sources of Emissions

i) Hydrochloric acid (HCl) emission from chiorosulphonation and drowning step.
ii) Acetic acid and water vapour emission from esterification step.
iii) Pulveriser air emission containing vinyl sulphone dust.

Current Methods For Recovery And Treatment of Hydrochloric Acid Emissions

Hydrochloric acid gas is emitted from chlorosulphonation and drowning step is scrubbed with water in packed bed scrubbers (shown in Figure 2). Hydrochloric acid solution is re-circulated by pump until it gets concentrated. Hydrochloric acid solution can be sold, if it is 30%. As the concentration of hydrochloric acid increases, recovery efficiency decreases. Packed bed scrubbers are not properly designed to provide effective surface area for absorption. No suction is provided for the gas. Packed columns are not properly cleaned and maintained.

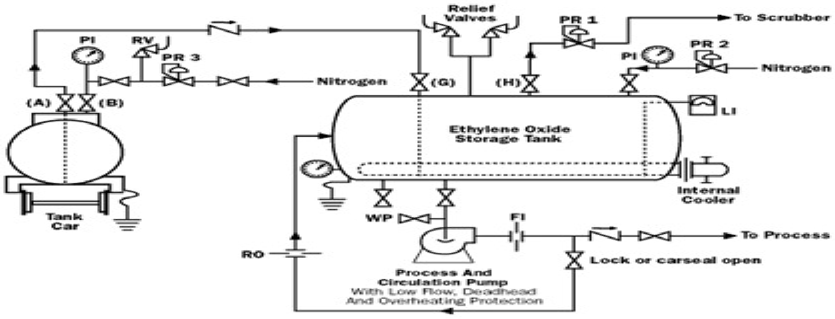

Figure 3. Sample Procedure For Unloading With Inert Gas Nitrogen.

Figure 4. Ethylene Oxide Storage Tank (Capacity 10 tonne).

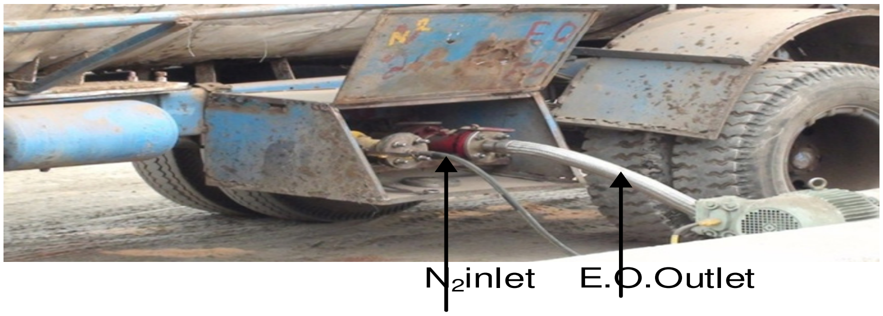

Figure 5. Transfer of E.O.

Recovery efficiency of hydrochloric acid is about 90%.

Disadvantages of Conventional hydrochloric acid Absorption System/Problem Formulation.

1) Poor design of scrubber.
2) Do not satisfy Gujarat pollution control board norms due to high concentration of HCl gas (more than 20 ppm) in vent from caustic scrubber.
3) HCl is circulated in single scrubber, it's maximum concentration is 25%-30%, and it continuously decreases recovery and efficiency of scrubber. Continuous make up of water is required.
4) High consumption of caustic in caustic scrubber increases quantity of effluent.

Storage/Unloading System of Ethylene Oxide

Before transfer ethylene oxide liquid from E.O. storage tanker to storage tank, first to check pressure, temperature and cooling system of E.O. storage tank (shown in Figure 3). If pressure in storage tank and storage tanker 4 kg/cm^2, then open the nitrogen outlet valve (PR 2) of storage tank (shown in Figure 3) to release the pressure of nitrogen. Generally pressure of E.O. storage tank is 3 kg/cm^2 and temperature is 10°C when it is filled in it. So that, due to high pressure in storage tanker of E.O., it is transferred to the storage tank without any addition of nitrogen in tanker. When pressure in both storage tank and tanker is equal, then to add extra nitrogen from nitrogen cylinder (shown in Figure 7) to tanker (shown in Figure 4 and 5). So nitrogen is

Figure 6. Top View of E.O.

Figure 7. N_2 cylinder.

Figure 8. Loss of Ethylene Oxide in Water During Tansfer From Storage Tanker to Storage Tank.

pressurized E.O. liquid. Pressure of nitrogen cylinder is maximum 200–250 psi (14 kg/cm^2). When N_2 transfer to tanker, at that time pressure is between 3 to 4 kg/cm^2.(Figure 6)

Problem Formulation During Transfer Ethylene Oxide From Ethylene Oxide Tanker To Storage Tank

i) N2 is filled in O2 cylinder. As per GPCB norms it is more dangerous for industry, because if O2 comes in contact with E.O., then explosion may occur.

ii) When E.O. is transferred from E.O. tanker to storage tank, the pressure is increased in storage tank. To reduced pressure, N2 valve is to be open.So, N2 along with E.O Vapor escape from storage tank . This N2 – E.O.

Vapor is directly dilute with water (shown in Figure 8). So that E.O. gets dilute in water and produce ethylene glycol. Ethylene glycol is more toxic and difficult to treat by conventional methods Loss of ethelyne oxide per tanker is 100 kg and 300 kg in winter – monsoon and tanker is 100 kg and 300 kg in winter – monsoon and summer (shown in Table 1).

Proposed Manufacturing Process Of Vinyl Sulphone

Chlorosulphonic acid is taken in M.S. jacketed reactor and cooled to 10℃. Acetanilide is added slowly with agitation and cooling, maintaining the temperature at 10℃. Then the temperature is raised to 55℃ by passin steam through the jacket, and maintained at 55℃ for 4 hours. The completion of reaction is checked by caustic solubility test. Liberated hydrochloric acid gas is sent to HCl absorption system (Figure 9,10 and 11). The reaction mass is cooled to 10℃. The cooled reaction mass is drained to jacketed glass contactor, in which it is continuously contacted with cooled 40% sulphuric acid, maintaining the temperature below 20℃. Liberated hydrochloric acid is sent to HCl scrubbing system. The reaction mass is drowned in an agitated mild steel glass lined drowning vessel in which ice water is taken. The vessel is cooled externally also to maintain temperature

Table 1. Loss of Ethylene Oxide.

Loss of Ethelyne Oxide/Tanker/month in winter or monsoon.	100 Kg/Tanker	8000 Rs/tanker /month
Loss of Ethelyne Oxide/Tanker/month in summer.	300 Kg/Tanker	24000 Rs/tanker /month
Loss of Ethelyne Oxide/10Tanker /month in winter or monsoon.	1000 Kg/10 Tanker	80000 Rs/10Tanker /month
Loss of Ethylene Oxide/10Tanker /month in summer.	3000 Kg/10Tanker	240000 Rs/10Tanker/ month
Loss of Ethylene Oxide/6 months in winter and monsoon.	6000 Kg/6 months	480000 Rs/6 months
Loss of Ethylene Oxide/4 months in summer.	12000 Kg/4 months	960000 Rs/4 months
Total Loss in Rs/annum	-	1440000 Rs/annum

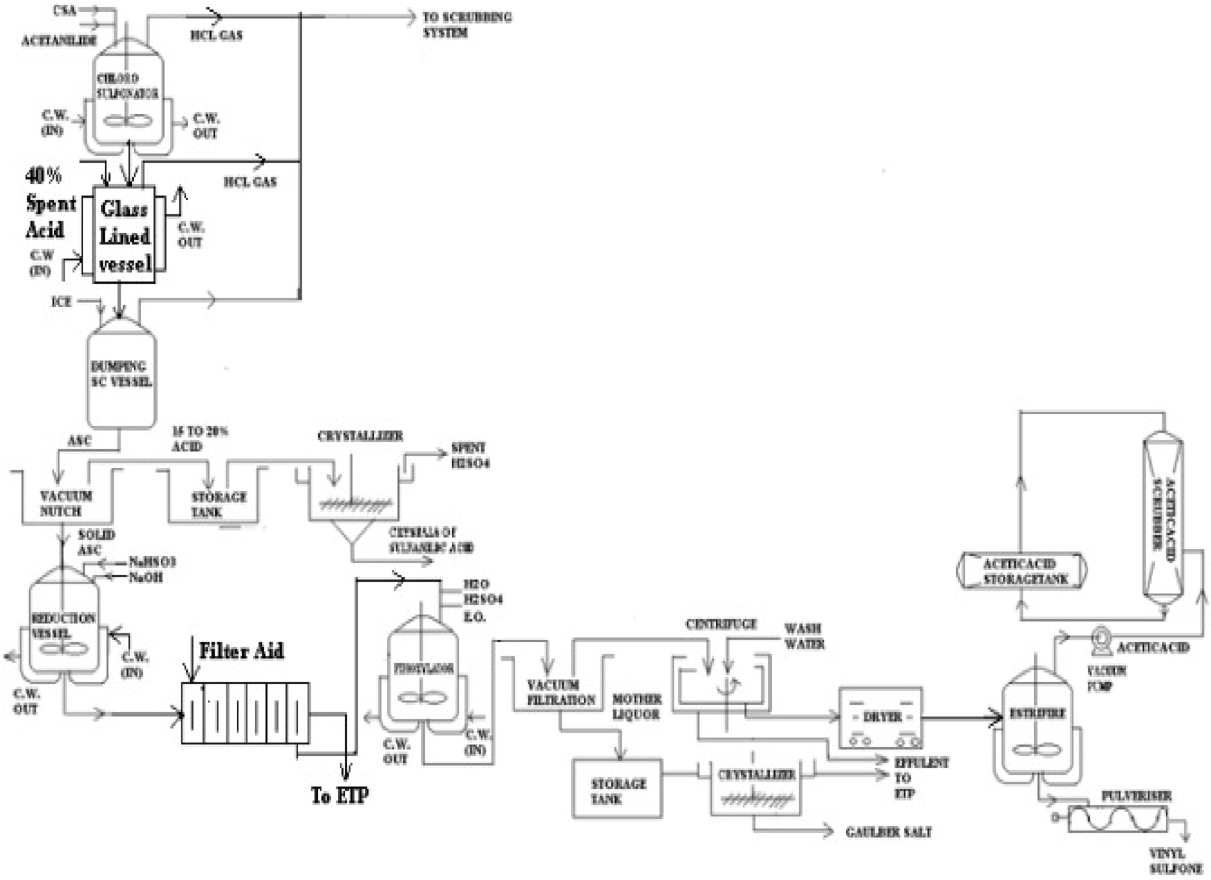

Figure 9. Proposed Process Flow Diagram of Vinyl Sulphone.

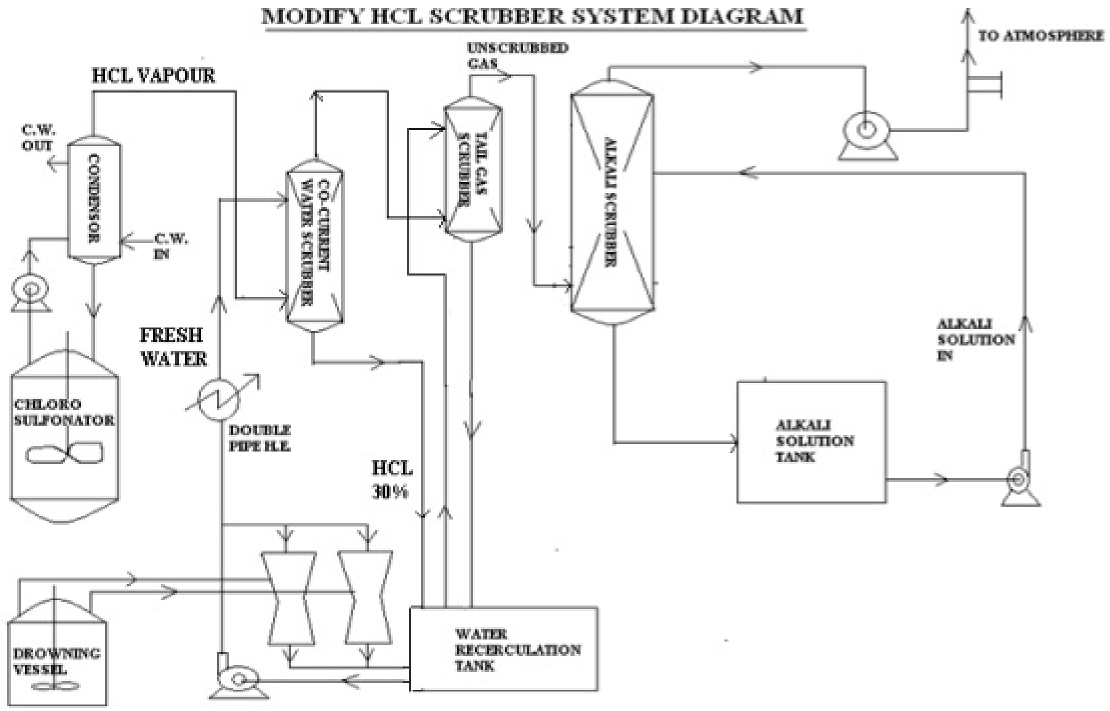

Figure 10. Proposed Process Flow Diagram of HCl Recovery.

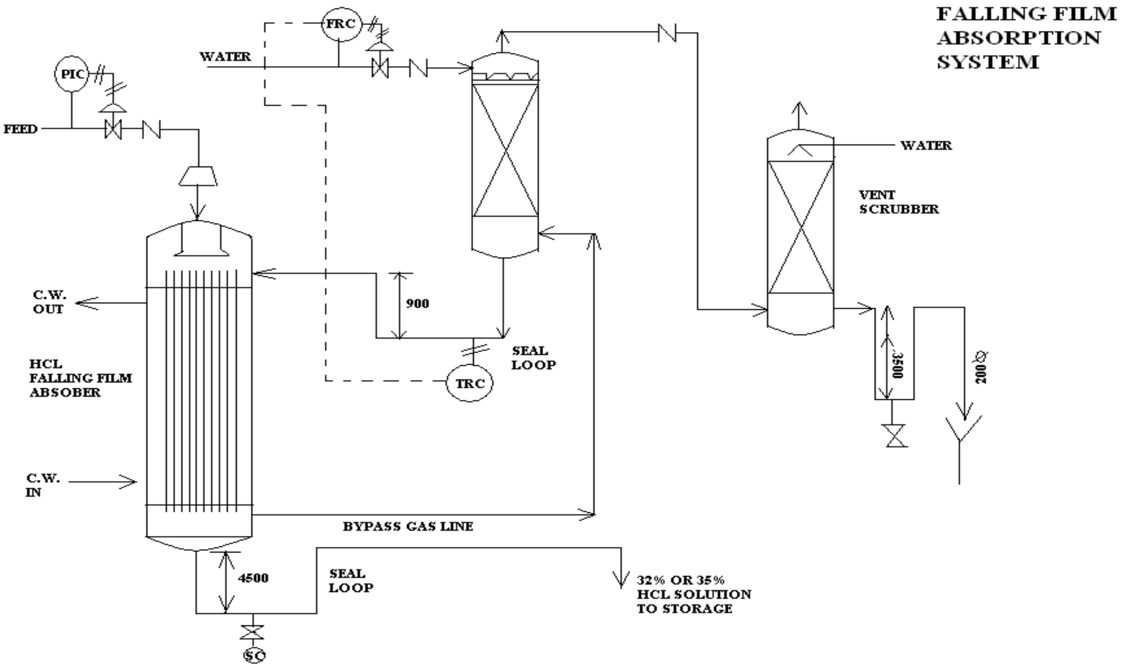

Figure 11. Falling Film Absorber.

at 10°C. This vessel also is connected to HCl absorption system. Acetanilide sulphonyl chloride (ASC) slurry is pumped to a pressure filter for filtering ASC. ASC cake is thoroughly washed with chilled water at 10°C in the pressure filter. Filtrated and washings are collected and sent for recovery of sulphanilic acid and spent acid. ASC cake is scraped and transfer to reduction reactor. Aqueous solution of sodium bisulphite is taken in jacketed stainless steel reduction reactor, to which ASC wet cake is added. Caustic lye is added simultaneously controlling the resulting pH at 7.0. Then it is heated to 55℃ and 48 maintained for 4 hours. The reaction mass is clarified by passing over a filter press coated with filter air. Clarified reaction mass is taken in condensation reactor. Filter cake is washed, removed and sent for disposal. Sodium salt of sulphanilic acid taken in jacketed stainless steel condensation reactor is maintained at 55℃. Ethylene oxide gas is passed at a controlled rate taking all necessary precautions. pH is controlled at 7.00 by addition of 40% sulphuric acid. The reaction mass is then cooled to 20℃. The reaction mass is filtered through a closed filter cum dryer where precipitated acetanilide hydorxy ethyl sulphone (AHES) is filtered, washed with water and dried. Filtrate and washings are collected and sent for glauber salt recovery. Dried AHES is transferred to sulphation reactor. AHES is taken in stainless steel sulphation reactor specially designed for sold handling. 100% sulphuric acid (monohydrate) is added and the reaction mass is heated to 170℃ and maintained. Acetic acid vapours are sent to condenser for recovery of acetic acid. Acetic acid evolution is stopped when the reaction is complete. The end of reaction is confirmed by TLC. The product is discharged and taken in a pulveriser. Pulveriser is fitted with elaborate dust collection system. pulverised vinyl sulphone is packed.

Proposed Methods For Recovery And Treatment Of HCl Emissions

Proposed absorption system for HCl gas is shown in Figure 10. HCl gas evolved in chlorosulphonation reactor, sulphuric acid contactor and drowning vessel is passed through two packed bed scrubbers in series. (shown in Figure 10) Concentration of HCl is allowed to rise upto 30% in the first scrubber with re-circulation and then it is sent for sale. HCl acid solution from the second absorber, which is about 10% concentration, is then taken for circulation in the first column. Fresh water is taken in the second column. If any quantity of unabsorbed HCl gas escapes the second column, it is scrubbed in the third column by caustic soda solution. Scrubber solution at the third column is sent to effluent treatment, when the strength of caustic soda solution fall below 3% wt/wt. The exit gas is analysed for traces of HCl.

New Technological Option For HCl Recovery by Using Falling Film Absorber

Advantages

(1) It satisfy GPCB norms by also decreases ppm of HCl in vent less than 50 ppm .
(2) Concentration of HCl from falling film absorber is 35% - 37% while the same from adiabatic packed tower ranges from 25% to 30% .(shown in Figure 11)
(3) Absorption is more efficient in falling film absorber for the given absorption duty.
(4) Falling film absorber requires less space compared to adiabatic packed tower type absorber.
(5) Other advantages of falling film absorber are lower temperatures, lower pressure drops and higher efficiency.
(6) Consumption of caustic in caustic scrubber for neutralization almost negligible.

Disadvantages

(1) More difficult to control and is sensitive to liquid and gas distribute on problems.
(2) It has greater tendency to absorb undesirable water soluble low boiling impurities.

Proposed Ethelyne Oxide Recovery Systen By Using Pump With Condensor Without Using Inert Gas

(1) Check pressure, temperature, inventory of storage vessel, and all pipe line-ups before unloading the EO railcar. While unloading, system pressure always remains in the inert region as determined by railcar and storage vessel temperatures (Figure 12 can be used as a guide for sites to establish minimum pressure(s) for unloading operations and onsite storage).
(2) Open liquid valves A, D, E, G
(3) Close liquid valve C
(4) Open vapor valves B, F
(5) Check that the transfer pump is properly primed and not vapor bound

Design Specification of Condensor For Recovery of Ethelyne Oxide Vapour Escapes With Nitrogen From Storage Tank

Problem

Nitrogen saturated with ethelyne oxide vapour at 2.5 kg/cm^2 and at 11℃ temperature is to be sent to shell and tube heat exchanger for recovering ethelyne oxide. Nitrogen – Ethelyne oxide vapour mixture is to be cooled to 10℃ by chilled brine as a ethylene glycol which enters at -20℃ and leaves the heat exchanger at -18℃.
Type of Heat Exchanger : BEM as per TEMA SS - 304
Shell ID = 180 mm
Tube length = 2000 mm
Tube ID = 15.748 mm

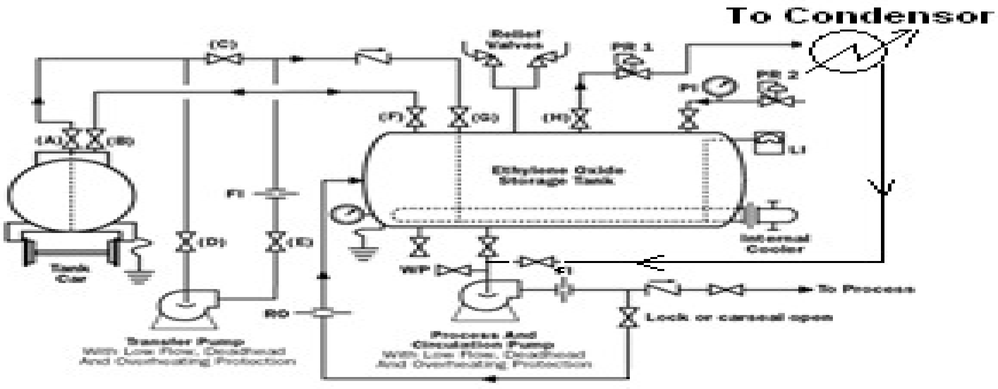

Figure 12. Sample Procedure For Unloading With Transfer Pump.

Table 2. Quantitative Comparison Of Raw Material Consumption Between Conventional And Proposed Process.

SR NO	Consumption of main raw materials	Conventional Process In Kg	Proposed Process In Kg
(1)	Acetanilide	3000	2680
(2)	Chlorosulphonic acid	13500	10965
(3)	Sodium Bisulphite	1849	1652
(4)	Caustic Soda	2133	1917
(5)	Ethylene oxide	1300	874
(6)	Sulphuric acid	835	835

Tube OD = 19.05 mm
Tube pitch = 25.04 mm
Type of tube pitch arrangement = Triangular
Number of tubes = 28
Number of tube side passes = 2
Number of shell side passes = 1
Baffle type = 25 % cut segmental
Baffle spacing = 75 mm
% Efficiency/Recovery = 66 – 70 %
Cost Saving = 10 lakh Rs/annum
PayBack Period = 6 months.

Design Specification Of Centifugal Pump For Transfer E.O. Liquid From Storage Tanker to Tank and Also To Transfer Condensed Liquid From Condensor.

Pump Type = MEGA 32 – 200
Nominal Speed = 2900 rpm
Frequency = 50 Hz.
Impeller Outlet width = 6 mm
Impeller Diameter = 186 mm
Pump Capacity = 10 m^3/hr.
Pressure = 4 kg/cm^2
Head = 45 m (max)
NPSH = 0.5 m
Delivery Pipe Size = 32 mm
Suction Pipe Size = 50 mm.
Electric motor = 7.5 HP
Powe Consumption = 5.5 kwatt
Cost of Pump = 16000 Rs.
Cost of 7.5 HP motor = 12000 Rs.
Cost of Unit power consumption/hr = 28 Rs/hr
Cost saving per annum = 1440000 Rs.
Payback period = 6 months.

RESULTS

Table 2 and 3

CONCLUSION

From above result, it is to be concluded that if chlorosulfonated mass after chlorosulphonation contact with 40% sulphuric acid, then negligible amount of hydro-

Table 3. Quantitative Comparison Of Effluent And Treatment For Vinyl Sulphone.

Particulars	Conventional Process In Kg	Proposed Process In Kg	
Gaseous			
Hydrochloric Acid Generated	811	2711	2711
Treatment	Single Absorber	Multiple absorber with tail gas scrubber	Falling Film Absorber
Hydrochloric acid emitted from water scrubber	81	27	Negligible Amount
Caustic Soda consumption in caustic scrubber	127	42	Negligible Amount
Liquid			
Water Consumption (including ice)	94547	57215	
Waste Water generated	1,06,940	68623	
Main Pollutants			
H_2SO_4	9178	10829	
HCl	730	2440	
Na_2SO_4	3734	3227	
NaCl	1040	938	
Glycols	775	175	

chloric acid goes into effluent. More quantity of hydrochloric acid is scrubbed by falling film absorber system than conventional process. So, consumption of caustic in caustic scrubber for neutralization of hydrochloric acid is negligible in falling film absorption system and decreases quantity of effluent. Condensor with centrifugal pump without using any inert gas is widely useful for recovery of ethelyne oxide vapor escapes with nitrogen from storage tanker and convert it into the liquid form about 66% to 70% for reuse.Total recovery of ehelyne oxide in terms of money is 10 lakh Rs. Total capital cost for installation of condenser and payback period are very less. From the above various technological options for hydrochloric acid absorption system, ethylene oxide recover system and to decrease excess raw materials by new technological routes, it is clear that liquid effluent, gaseous emissions which is generated in conventional process may be reduced or eliminated, The most advantage of this research work is to satisfy Gujarat pollution control board norms and do not create any environmental pollution by vinyl sulphone industries.

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