Cleaner Production of Vinyl Chloride Monomer (VCM)

Jemish Dattani, Darshan Devani, Omprakash Sahu

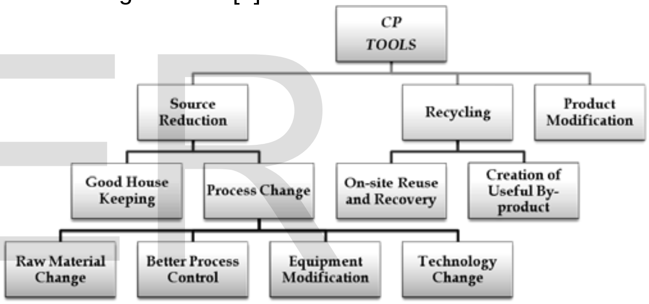
Abstract - Cleaner production eliminates pollution throughout the entire production process. It is a way of reducing pollution damage to both the environment and the human population by increasing the efficiency of resource use – decreasing pollution discharge by improving management and technology. Cleaner production is implemented at the factory level. The factories get both economic and environmental benefits from implementing cleaner production. The implementation of cleaner production involves a combination of reorganization, improved technology in the factories, power saving and decreasing consumption, improved management and competent resource use. The eventual goal of clean production is to achieve a 'closed loop' operation in which all excess materials are recycled back into the process, which is utmost necessary in today's world. ..Here we have included a case study of vinyl chloride monomer (VCM) production using cleaner production (CP), which includes Material Balance, Energy Balance, Cost Estimation and Simulation.

Index Terms- cleaner production, vinyl chloride monomer, eco efficiency

◆

1 INTRODUCTION

Cleaner Production (CP) is the continuous application of an integrated preventive environmental strategy to processes, products, and services to increase overall efficiency, and reduce risks to humans and the environment. Cleaner Production can be applied to the processes used in any industry, to products themselves and to various services provided in society [1]. It is a broad term that encompasses terms such as eco-efficiency, pollution prevention and green productivity. In essence, applying cleaner production protects the environment, the consumer and the worker while improving industrial efficiency, profitability and competitiveness. The Key element of the CP is to reach the precautionary, preventive, integrated and holistic approach with democratic control. The basic principle of CP is focus on the primary function of the economic activities for process input resources (raw material, energy, water, etc.) into usable outputs [2]. However, all the inputs are not transformed into the usable outputs. The portion that does not get transformed into useful outputs comes out as waste. This transformation of waste depends on the technology employed and efficiency of the process. However, with the growth of the economic activities, on one hand the withdrawal of resources from nature has increased, while on the other hand the discharge of the wastes into the environment as amplified. The current trends as well as the pace in the economic activity of our country are resulting in the generation of wastes at a much higher pace than the assimilative capacity of the environment. This new & creative approach to enable the production process less waste intensive is based on different techniques. These techniques are classified into three main categories as which are shown in figure no.1 [3].



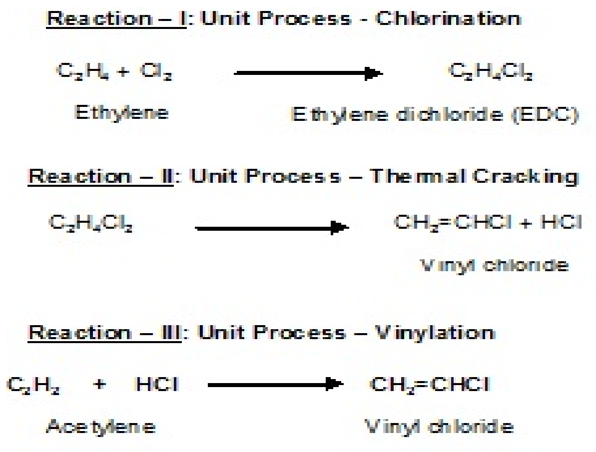
F ig.1: Technique of Cleaner production

In 1993, a CP demonstration project targeting SMEs was initiated by UNIDO, in cooperation with the Indian National Productivity Council and other industry associations. This desire project focused on different sectors such as agro-based pulp and paper, textile dying and printing, polymeric material and pesticides formulation [4]. From the all other product we choices the polymeric Vinyl chloride for the cleaner production, Vinyl chloride (CH_2=CHCl) is a haloginated alkane. It is the building block for its polymer poly-vinyl chloride (PVC) and other co-polymers with acetate and vinyl chloride. Poly (vinyl chloride), PVC, is a common commodity plastic, and its production is the third largest, after polyethylene and polypropylene [5]. It is cost-effective, highly versatile and is used in many construction applications as water, sewage and drainage pipes, and a variety of extruded profiles [6]. Thousands of rigid, semi-flexible and flexible (plasticized) materials and products based on PVC are widely used in practically all spheres of the world economy and will remain so for a very long time. From volume estimates, the world production of PVC grew from a few hundred million pounds to about 44 billion pounds in 2000 [7] as new uses and markets were developed. However, it is known that PVC degrades at elevated temperatures, giving off hydrochloric acid (HCl) that in turn accelerates the degradation process. Depending on the number of conjugated double bonds formed, it becomes yellow, orange, red, brown and finally black [8]. The splitting-off of HCl from the polymer backbone affects the physical, chemical and the mechanical properties of the polymer. Until the discovery of thermal stabilizers, PVC was not an industrially very useful polymer, as it could not be processed to useful articles without degradation at elevated temperatures. Quantum improvements in extrusion and injection moulding machinery and extrusion die design, together with significant improvements in stabilizers and lubricant technology have all contributed to increased tonnage production and usage of PVC. The goal of this study is to produce an environmentally friendly, safe, and economically profitable vinyl chloride production in plant and to achieve a 'closed loop' operation in which all excess materials are recycled back into the process.

2. MATERIAL AND METHODS

Vinyl chloride was first produced using the process of dehydrating ethylene dichloride (EDC) with alcoholic caustic potash. However, the first effective industrial process was based on the hydro-chlorination of acetylene. Until the late 1940s, this process was used almost exclusively. The normal method of producing acetylene was from calcium carbide. “The high-energy requirement for carbide production was a serious drawback to the continuing mass production of vinyl chloride by this method”. However, as ethylene became more plentiful in the early 50’s, commercial processes were developed to produce vinyl chloride from chlorine and ethylene via EDC, namely, the balanced ethylene route. Today the balanced ethylene is responsible for well over 90% of the world’s vinyl 6 chloride production. “This process has been refined and the scale of operation has greatly increased, but no fundamentally new processes have achieved commercial viability”. Although this is true, it is still necessary to examine the alternative processes and determine if they can still be utilized. All current production plants for vinyl chloride depend on the use of a C_2 hydrocarbon feed stocks, specifically, acetylene, ethylene, or ethane. Commercial operations using these compounds are confined to gas-phase processes. “Manufacture from acetylene is a relatively simple single-stage process, but the cost of acetylene is high”. Ethane is by far the least expensive C2 hydrocarbon, but it cannot be converted to vinyl chloride with high selectivity.

2.1 Chlorination followed by Thermal Cracking and Vinylation



2.2 PROCESS DESCERIPTIONS

Ethylene dichloride (EDC)

For the production of Vinyl chloride from ethylene is allowed to react with gaseous ylene is reacted with Chlorine gas at temperature of 65□C in the presence of FeCl2, the resultant product is Ethylene dichloride (Reaction - 1). The reaction is highly exothermic in nature. The conversion is 100% and selectivity for this step is above 99% for this reaction. To produce Vinyl chloride from EDC, thermal pyrolysis process is carried out at a temperature of 480-550°C and 4 atmospheric pressure(Reaction-2). At this operating condition, thermal cracking of EDC is taking place in tubular pyrolysis (cracking) furnace. Additionally Vinylation (Reaction – 3) is carried out to utilize co – product HCl produce in thermal cracking reaction (Reaction – 2).In vinylation reaction, acetylene and HCl (produced in thermal pyrolysis reaction) are allowed to react at temperature 200°C and 1 atmospheric pressure. The reaction of acetylene and hydrogen chloride is carried out in the vapor phase at 150–250°C over a mercuric chloride catalyst. The acetylene route is usually coupled with ethylene chlorination unit so that the hydrogen chloride derived from cracking dichloroethane can be consumed in the reaction with acetylene. HCl being now a raw material, the entire environment in a plant producing vinyl chloride has to be kept perfectly dry atmosphere. Since the tubular reactor containing carbon pellets impregnated with HgCl2 is used, initially temperature used is 160°C which is increased to 2□□C progressively depending on the deactivation of catalyst due to carbon deposition. Proper heating of raw material must be done to avoid deactivation.

Control of temperature is the most essential parameter to increase the conversion level. Thus one mole each of ethylene, acetylene, and chlorine give two moles of vinyl chloride with a minimum of by-products. Hard cracking of hydrocarbons to a 1:1 molar mixture of ethylene and acetylene for use as feedstock for vinyl chloride production is done. The crude stream from the tubular reactor contains the main product, as well as unreacted amount of acetylene and HCl, the unreacted amount is stripped off in a stripper and recycled to the reactor to reduce the raw material requirements. Hence at the end more amount of vinyl chloride is obtained, as a result the overall plant production capacity can thus be increased. The flow diagram is shown in figure 2.

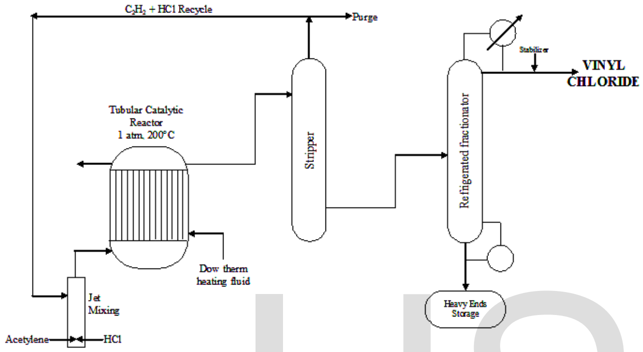


Fig.2: Production of VCM via Acetylene-HCl route

3. RESULT AND DISCUSSION

3.1 Production by route-III: The vinyl chloride is produced by the unit processes namely chlorination, thermal pyrolysis and vinylation respectively. To produce 1000 TPD (16000 kgmoles / day) of Vinyl chloride, process is initiated by chlorination using raw material as ethylene and chlorine (equimolar) in a quantity 224 TPD (8000 kgmoles / day) and 568 TPD (8000 kgmoles / day) respectively. These raw materials for chlorination process are preheated and fed to the rector. During preheating, energy requirement is 0.106 x 107 kJ / day. Since chlorination is highly exothermic in nature, the amount of heat that must be removed from the reactor is 145 x 107 kJ / day. As the conversion is 100% for chlorination process, the product ethylene dichloride (EDC) come out of reactor is 792 TPD (8000 kgmoles / day). Here, energy that must be required in terms of cooling is 23.26 x 107 kJ / day to cool the product. In second step, thermal pyrolysis is done with the raw material EDC. In this stage, fresh EDC 792 TPD (8000 kgmoles / day) from chlorination process with recycled quantity 465.1 TPD (4698.4 kgmoles / day) is preheated and sent to thermal cracking. Energy required for preheating is 74.8 x 107 kJ / day. Since the cracking reaction is thermodynamically highly endothermic in nature. Energy required in terms of heating 58 x 107 kJ / day. Since the conversion of the process is 63%, the product comes out of the reactor at the end of reaction contains main product vinyl chloride 500 TPD (8000 kgmoles / day), by – product HCl 292 TPD (8000 kgmoles / day) and unreacted EDC 465.1 TPD (4698.4 kgmoles / day). This product stream is allowed to cool and separate in separation unit. Energy that must be required in terms of cooling is 74.8 x 107 kJ / day to cool the product stream. In this reaction, unreacted quantity of EDC 465.1 TPD (4698.4 kgmoles / day) is recycled with fresh EDC. Hence the raw material requirement can thus be reduced. By – product – HCl generated is also fully utilized in this route. In vinylation, reaction is carried out by using acetylene as a raw material with HCl produced in thermal pyrolysis reaction i. e. in second step. Acetylene 208 TPD (8000 kgmoles / day) and HCl 292 TPD (8000 kgmoles / day) is allowed to preheat initially before reaction to takes place. Heat required to preheat the raw material is 1.92 x 107 kJ / day. The vinylation is exothermic reaction, so as to remove the exothermic heat 79.49 x 107 kJ / day; energy is required in terms of cooling. The conversion of this process is considered as 100%. The product leaving the reactor contains main product vinyl chloride 500 TPD (8000 kgmoles / day). The product stream is allowed to cool and impurities are separated in the separator. Hence 19.57 x 107 kJ / day of energy is required in terms of cooling to cool and separate the product. Hence, finally in this route total 1000 TPD (16000 kgmoles / day) of vinyl chloride is obtained. Here, HCl produced is fully utilized to react with acetylene so that liquid waste generated is zero. Hence, raw material requirement reduces to half and also energy requirement in terms of cooling and heating also reduces to half. Thus this is the most favorable route in terms of energy conservation and waste minimization.

3.2 Comparison of routes based on Material Balance Principles:

Finally we can summarize the entire three routes in common table by material balance principles for the production of 1000 TPD of vinyl chloride as under:

TABLE 1:
COMPARISON OF MATERIAL BALANCE

Route		Product		Intermediate	Reactants			Reactants	
	Unit	VCM	HCl*	EDC	C_2H_4	Cl_2	C_2H_2	HCl*	O_2
R - I	TPD	1000	584	2514.3	448	1136	--	--	--
	Kgmoles / day	16000	16000	25396.9	16000	16000	--	--	--

	Unit	VCM	HCl*	EDC	C_2H_4	Cl_2	C_2H_2	HCl*	O_2
R -II	TPD	1000	**584**	2514.3	448	568	--	**584**	64
	Kgmoles / day	16000	**16000**	25396.9	16000	8000	--	**16000**	4000
	Unit	VCM	HCl*	EDC	C_2H_4	Cl_2	C_2H_2	HCl*	O_2
R - III	TPD	1000	**292**	1257.1	224	568	208	**292**	--
	Kgmoles / day	16000	**8000**	12698.4	8000	8000	8000	**8000**	--

As could be seen from above table, Route – II and Route – III can be considered as environmentally friendly route. Since by – product – HCl comes out at the end of pyrolysis reaction is being fully utilized in these above mentioned routes. Raw material requirement as compared to other conventional route also reduces to half. Chlorine quantity requirements in route - II are reduced to half; as a result intensity of pollutant-Cl2 in gaseous effluent stream also gets reduced considerably. Quantity of CO2 emission in atmosphere gets reduced to half quantity – equivalent carbon credits are obtained. Thus, Route-III is more environmentally friendly in comparison to Route-II.

3.3 Comparison of routes based on Energy Balance Principles: The Energy requirement for entire three routes can be summarized with respect to energy balance in a common table as under:

TABLE 2:
COMPARISONS OF ENERGY BALANCE

Route		Preheating (kJ / day)	Heat to be absorbed / removed (kJ / day)	Separation (kJ / day)	TOTAL (kJ / day)
R- I	Step:1 Chlorination	0.213 x 10^7	291 x 10^7	46.54 x 10^7	337.75 x 10^7
	Step: 2 Thermal Pyrolysis	149.6 x 10^7	116 x 10^7	149.6 x 10^7	415.2 x 10^7
TOTAL ENERGY REQUIRED (kJ / day)					**752.95 x 10^7**
R – II	Step:1 Chlorination	0.106 x 10^7	145 x 10^7	23.27 x 10^7	168.4 x 10^7
	Step: 2 Thermal Pyrolysis	149.6 x 10^7	116 x 10^7	149.6 x 10^7	415.2 x 10^7
	Step: 3 Oxychlorination	6.51 x 10^7	191 x 10^7	61.39 x 10^7	258.9 x 10^7
TOTAL ENERGY REQUIRED (kJ / day)					**842.5 x 10^7**
R- III	Step:1 Chlorination	0.1065 x 10^7	145 x 10^7	23.27 x 10^7	168.4 x 10^7
	Step: 2 Thermal Pyrolysis	74.8 x 10^7	58 x 10^7	74.8 x 10^7	207.6 x 10^7
	Step: 3 Vinylation	1.92 x 10^7	79.49 x 10^7	19.57 x 10^7	100.98 x 10^7
TOTAL ENERGY REQUIRED (kJ / day)					**476.98 x 10^7**

It can be seen from above table that among three routes for the production of 1000 TPD of vinyl chloride, the energy requirement in Route – III is the lowest than the conventional route i. e. Route – I. Route – II requires 10% additional energy than the conventional route though it is considered as environmentally friendly route as the emission of pollutant (Cl2) quantity reduces to half and the liquid effluent (HCl) is also fully utilized by this route. If comparison can be made between Route – I and Route – II, then energy requirement in step – 1 of Route – II is approximately half to that of step – 1 of Route – I, but oxychlorination step in Route – II needs more energy. Hence, Route – II almost needs more energy (10%) than Route – I. Finally, if one can analyses and compare the entire three routes, Route – III is more energy efficient as well as eco – friendly route. More energy conservation compared to other two routes can be obtained in this Route – III and also the by – product – HCl generated is fully utilized by this route. The requirement of energy is also reduced by 66%. Hence more carbon credits can be earned. So, Route – III can be considered as the more environmentally route than Route – II.

4 CONCULSION

This route is more environmental friendly than the other routes in terms of waste minimization and energy conservation. Vinylation reaction (step – 3) is carried out to utilize the by – product – HCl generated in pyrolysis reaction, as a result the quantity of liquid waste generated in this route is zero. The most important conclusion for this route can be drawn by material and energy balance calculation, when compared with other routes. To produce 1,000 TPD of vinyl chloride, 224 TPD of ethylene and 568 TPD of chlorine is required in chlorination (step – 1) to produce EDC. In thermal pyrolysis (step – 2), 1257.1 TPD of EDC is fed to reactor to produce vinyl chloride, 292 TPD of HCl as a by – product and some unreacted amount of EDC which is recycled to the reactor, so that requirement of fresh raw material EDC is reduced. To utilize by – product HCl generated in thermal pyrolysis, this by – product becomes the feed stock for vinylation reaction and is allowed to react with 208 TPD of acetylene to produce vinyl chloride. Thus total 1,000 TPD of vinyl chloride is er routes produced. So, in this route also quantity of liquid effluent generated is practically zero, also intensity of pollutant – Cl2 gets reduced to half compared to ot. Here, in this route, as compared with other two routes, raw material requirement also gets reduced to half, although plant capacity for the production of vinyl chloride remains the same. The total energy requirement for this entire route for vinyl chloride production is 476.98 x 107 kJ / day. Compared with the energy requirement in other two routes, the energy requirement in this route gets reduced almost to 50%. Thus, from the environmental point of view, this route has provided the best platform for implementation of Cleaner Production Principles. This route is thus, a more environmentally friendly route in terms of waste minimization, reduction in raw material requirements and energy conservation than other routes. Hence, in this industrial case study for production of vinyl chloride Cleaner Production Principles can be implemented successfully.

ACKNOWLEDGEMENTS:
Authors acknowledge to department of chemical engineering KIT Jamnagar and Ministry of Technical Education Gujarat (India) for their support.

Reference

[1]Puranik, S.A.; “Capacity Building for Students And Academicians In Environment Related Issues With Special Emphasis On Cleaner Production”, 2nd International Conference on Cleaner Production (Deptt. Of Forests & En.) February 6-8, 2012.

[2]Gujarat Cleaner Production Centre, “Cleaner Production Manual”, p: 5 – 14, 65 – 78, 117 – 125(2010).

[3]Gujarat Cleaner Production Centre, “Draft of Cleaner Production Manual”, www.gcpcgujarat.org, P15-29(2011).

[4]“Implementation Cleaner Production” Pollution Prevention and Abatement Handbook World Bank Group, July 1998.

[5] Yoshioka T, Kameda T, Leshige M, Okuwaki A ; Dechlorination behaviour of flexible poly(vinyl chloride) in NaOH/EG solution. Polym. Degrad. Stab., 93: 1822-1825 (2008).

[6]Van Es DS, Steenwijk J, Frissen GE, van der Kolk HC, van Haveren J, Geus JW, Jenneskens LW (2008). The compatibility of (natural) polyols with heavy metal- and zinc- free poly(vinyl chloride): Their effect on rheology and implications for plate-out. Polym. Degrad. Stab., 93: 50-58(2008).

[7]Skip.T.;“WhatisPVC”,http://www.plastics.com/articlelive/articles/5/1/ p. 3(2006).