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THE MONSANTO/SD VINYL CHLORIDE PROCESS

INTRODUCTION

The importance of vinyl chloride as a monomer and its spectacular market growth to over 4 billion lbs/yr in the United States alone are well known and need not be reviewed here. Its major use -- in the manufacture of polyvinyl chloride and vinyl chloride copolymers -- has been exploited in the production of film, extruded goods, molded items, coatings, latexes and the like.

Historically, vinyl chloride has been manufactured from acetylene and hydrogen chloride by a classical organic synthesis technique. This technology is still employed in many parts of the world. However, the decreasing cost of ethylene, relative to acetylene, prompted the investigation of alternate methods for making vinyl chloride. The first major departure from the total use of acetylene occurred through the chlorination of ethylene to 1, 2-dichloroethane, followed by pyrolysis to vinyl chloride and hydrogen chloride. In many plants, the hydrogen chloride produced by pyrolysis has been reacted with acetylene to produce additional vinyl chloride. Nevertheless, complete elimination of the use of acetylene has been a major objective of vinyl chloride producers for many years. An early approach to this problem involved the investigation of the Deacon process, whereby hydrogen chloride is oxidized to chlorine, which, in turn, can be used for chlorination of ethylene. This approach proved to be unattractive economically because of the thermodynamic limitations of hydrogen chloride oxidation. Therefore, the next logical approach involved the catalytic oxidation of hydrogen chloride in the presence of a chlorine acceptor (ethylene) to overcome the equilibrium limitation on HCl oxidation. Such investigations resulted in a process which has come to be known as oxychlorination. The mechanism of oxychlorination has not been completely defined and is outside the scope of this paper.

This paper describes pioneering work conducted first by Monsanto alone, and then in collaboration with Scientific Design Company, in the development and commercialization of a unique oxychlorination process. In this process, either air or oxygen reacts with hydrogen chloride and ethylene in a modified fluidized bed reactor to produce 1, 2-dichloroethane. The latter is combined with dichloroethane produced by a simplified chlorination process and then dehydrochlorinated (cracked or pyrolyzed) to high-purity vinyl chloride and to hydrogen chloride for recycle.

BACKGROUND

Monsanto began the manufacture of vinyl chloride at Texas City in 1950 using ethylene and acetylene in a "balanced operation". This operation utilized the classical combination of ethylene chlorination, cracking of dichloroethane, and hydrochlorination of acetylene. In 1958, Monsanto initiated research directed toward the development of an economical ethylene oxychlorination process.

In 1959, after successful laboratory and pilot plant studies, a commercial oxychlorination unit having an annual capacity of 30 million pounds of dichloroethane was installed at Texas City. This oxychlorination unit was used primarily to supplement the acetylene hydrochlorination unit. In 1964, Monsanto and Scientific Design entered into an agreement providing for cooperative further development of the vinyl chloride process and for the licensing of the process by SD on behalf of Monsanto. Licenses were granted to Kasei Mizushima (a joint venture of Mitsubishi Chemical Industries, Ltd. and Nippon Carbide Company) in Japan and to Pemex in Mexico. The former license provided for an oxychlorination unit using oxygen and the latter was based on the use of air. Additional licenses were granted later.

In 1968, the first plant designed by SD to use the Monsanto process was started up in Japan. Unexpected startup problems occurred in the oxychlorination section, but a joint effort by Kasei Mizushima, Monsanto and SD isolated and solved the problem. After simple modification, the oxychlorination unit has operated very successfully and the entire plant has been operating as designed.

In late 1968, SD designed and Monsanto installed a complete oxychlorination pilot plant at Texas City for additional process development and for the study of any plant problems which might occur in future plants for licensees. The use of this pilot plant has resulted recently in the testing and approval of a new and superior oxychlorination catalyst which is now being installed in a licensee's plant. During the same period of time, through cooperation between Monsanto and SD, other improvements in the process were developed and are included in the process described in this paper.

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Process Development Objectives

In the development of an oxychlorination process, a number of objectives must be accomplished. Primary attention should, however, be applied to reactor design and catalyst characteristics.

Several basic types of reactors were considered. A conventional fixed-bed reactor was eliminated because of the severe heat-transfer problem. Oxychlorination is highly exothermic and hot-spot temperatures in a fixed bed were too high to achieve good yields and to employ low-cost materials of construction. Heat-transfer problems can be mitigated in fluidized bed reactors, but scale-up was considered to be too unreliable to justify adoption of this technique. On the other hand, fluidization of catalyst in tubes allows good heat transfer and ease of scale-up, so maximum effort was devoted to development of such a reactor design.

The catalyst development program had several objectives. The catalyst must enable the achievement of high conversions of both ethylene and hydrogen chloride at no sacrifice in yield. It must have sufficient activity so that high gas velocities can be employed and so that reaction temperatures can be

reasonably low. The latter criterion is necessary if carbon steel is to be used in reactor construction, as well as to prevent volatilization of copper salts (the active catalytic component) and thus maintain long catalyst life. The catalyst must also demonstrate very low attrition loses and must be adaptable to the use of either oxygen or air.

Finally, the process must be safe, especially from the standpoint of avoidance of combustible or explosive mixtures under reaction conditions.

All of these objectives were met, as will be observed from the following process description.

Chlorination (Figure 1)

Ethylene and chlorine vapors are charged to a carbon steel reactor containing liquid dichloroethane which acts as reaction medium and coolant. The following reaction occurs:

$$CH_2=CH_2 + Cl_2 \rightarrow CH_2Cl-CH_2Cl$$

The heat of reaction is removed by circulating liquid dichloroethane through external water-cooled exchangers. The reaction takes place at mild temperatures (50°-65°C) and low pressure. Chlorine is completely reacted, with ethylene conversion ranging from 97-99% depending on the operating conditions and ethylene purity. The product dichloroethane is of high purity, containing less than 0.5 wt. percent of chlorinated by-products, mainly trichloroethane.

The reactor overhead gas is treated to recover dichloroethane and remove hydrogen chloride. The crude dichloroethane is washed to remove acidic compounds.

Cracking and Purification

Dichloroethane Purification (Figure 2)

Dichloroethane from chlorination and oxychlorination is dried and purified by distillation. The major by-product is a heavy chlorinated hydrocarbon stream which can be sent to waste disposal or used as a feedstock for conversion to perchloroethylene and/or carbon tetrachloride by a well-known process developed by SD. The purified dichloroethane is pumped to the cracking section.

Dichloroethane Pyrolysis (Figure 3) CBY 1017526

Purified dichloroethane is vaporized and pyrolized in a fired heater to produce vinyl chloride and hydrogen chloride. The reaction is as follows:

$$CH_2Cl-CH_2Cl \rightarrow CH_2=CHCl + HCl$$

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The furnace operates at moderate outlet temperatures (450°-500°C) and medium pressure. Conversion per pass is controlled at 50-60% to minimize production of coke and undesired chlorinated hydrocarbons, resulting in a high yield (greater than 99% efficiency to vinyl chloride).

Furnace decoking is infrequent - when required it is carried out using air. The hot furnace effluent gas is quenched by direct contact with a recirculated dichloroethane-rich liquid. The quenched cracking effluent streams are then sent to the HCl recovery section.

Hydrogen Chloride Recovery - Vinyl Chloride Refining (Figure 4)

Anhydrous hydrogen chloride gas is recovered from the quenched cracking effluent using a novel absorption/stripping process. The high-purity HCl by-product is recycled to oxychlorination or can be used for acetylene hydrochlorination.

Unreacted dichloroethane is separated by distillation from vinyl chloride and intermediate-boiling impurities and recycled back to dichloroethane purification. The crude vinyl chloride is then refined by distillation to a product of greater than 99.99 wt. % purity, which meets the severest industrial specification.

Oxychlorination (Figure 5)

Reactor feed gas, containing HCl, ethylene, and oxygen in controlled concentrations, is charged to a tubular, modified fluid bed (slugging) reactor. The over-all reaction that occurs is:

$$CH_2=CH_2 + 2\,HCl + \tfrac{1}{2}O_2 \longrightarrow ClH_2C\text{-}CH_2Cl + H_2O$$

The oxychlorination catalyst consists of a copper salt on a special refractory support. The high activity of this catalyst allows the oxychlorination reaction to occur at moderate temperatures (200°-250°C) and permits the use of a carbon-steel reactor.

The slugging fluid bed is used for efficient heat removal from the highly exothermic reaction. Medium-pressure steam is generated in the reactor shell and used to provide heat in the cracking and purification sections.

The yield in the reactor is high; HCl conversion is in excess of 99%, with 99% selectivity to dichloroethane; ethylene losses by oxidation to carbon oxides are small. The reaction products are treated to remove unconverted HCl and then processed to recover crude dichloroethane and unconverted ethylene.

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Description of Slug Flow

The flow patterns in a fluidized bed vary depending on the bed dimensions, particle size distribution and gas velocity. Fluidized-bed reactors are usually operated with low height-to-diameter ratios so that bubbles of gas will flow up

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through the bed and burst at the surface. For relatively deep beds, the bubbles may grow to the diameter of the containing vessel, even for beds a few feet in diameter (1). When this occurs, the bed is called a slugging bed and the flow pattern-slug flow.

In the small diameter fluidized beds used in laboratories, slug flow occurs commonly and has been studied in detail (2,3). A typical slug flow pattern is shown in Figure 6. The slugs rise at regular intervals with a dense phase of particles between them. The particles rain down the sides of the large bubble to allow it to move upward.

The regular pattern of slug flow lends itself to theoretical analysis. For simple reactions, overall conversions can be predicted with reasonable accuracy (3).

Reactor Scale-Up

Since the bubble size and flow patterns in large-diameter fluidized beds are difficult to predict, the scaling-up of massive beds can be a problem. A slug flow reactor uses multiple tubes of fixed diameter and height. Since the capacity range of each tube is set by the operating conditions, the capacity of the reactor will vary linearly with the number of tubes. Scale-up is therefore no problem, and the results obtained in the pilot-plant reactor can be duplicated in any size of commercial reactor.

Design variables

The capacity and efficiency of each tube depend on a number of variables, the most important of which are:

Reaction Temperature: Shell-side pressure is adjusted to control reaction so that the tube operates within the range 200°-250°C. This temperature range permits the use of carbon-steel reactors and results in optimum yields and minimal catalyst loss.

Ratio of Reactants: The stoichiometric ratios of HCl/ethylene/oxygen are 2/1/0.5. The Monsanto reactor can operate over a wide range of reactant ratios, but for optimum HCl conversion and selectivity, operates with ethylene and oxygen ratios slightly in excess of stoichiometric.

Velocity: The Monsanto slug flow reactor can operate satisfactorily with HCl conversions of 99% over a wide velocity range as shown in Figure 7. At very high velocities, the HCl conversion slowly decreases, Dichloroethane purity is essentially constant at 99 wt. % plus, over the entire operating range shown in Figure 7.

Use of Air or Oxygen

The Monsanto oxychlorination process can operate with air or oxygen. When air is used, the gas flow is once-through. With oxygen, the unreacted gases are recycled back to reaction feed. The selection between the two processes is based on the particular economics of a proposed project, since the higher cost of oxygen (relative to air) in one is offset by the increased capital and utilities costs of the other.

PROCESS FEATURES

Market expansion, improved technology and increased plant size have all contributed to the development of the modern vinyl chloride plant. In summary, these features are:

1. Vinyl chloride purity in excess of 99.99%, which results in improved polyvinyl chloride quality and reduced polymerization costs.

2. Use of ethylene and chlorine and/or HCl has reduced raw material costs. Better reaction yields and improved product recovery have reduced raw material requirements per unit of vinyl chloride.

3. Total recycle of by-product HCl and high yields have reduced quantity of by-products. Chlorination processes (for example, to produce perchloroethylene) permit the profitable utilization of by-products.

4. The increased capacity of the modern plant has made it economical to introduce process refinements which reduce utilities requirements.

5. The trend to large plants has reduced the capital investment per unit production. In addition, improved technology based on continued development work has increased process capabilities and hence, reduced capital costs.

SUMMARY

In summary, vinyl chloride technology has advanced significantly over the past decade, with the major development being the commercialization of economical ethylene oxychlorination processes. The use of all-ethylene plants has now become entrenched and resulted in significant reduction in vinyl chloride cost of production. The efficient utilization of hydrogen chloride and the reduction of by-products and waste are of great importance in the current drive to reduce pollution. Evolution of the present Monsanto/SD all-ethylene vinyl chloride process is a good example of how chemical manufacturers and process-oriented engineering companies can collaborate in the improvement of chemical processes and commercialization of these processes through licensing.

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REFERENCES

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(3). Hovmand, S. and Davidson, J. F., "Chemical Conversion in a Slugging Bed," Trans Instn. Chem. Engrs., Vol. 46, 1968, Page T-190.

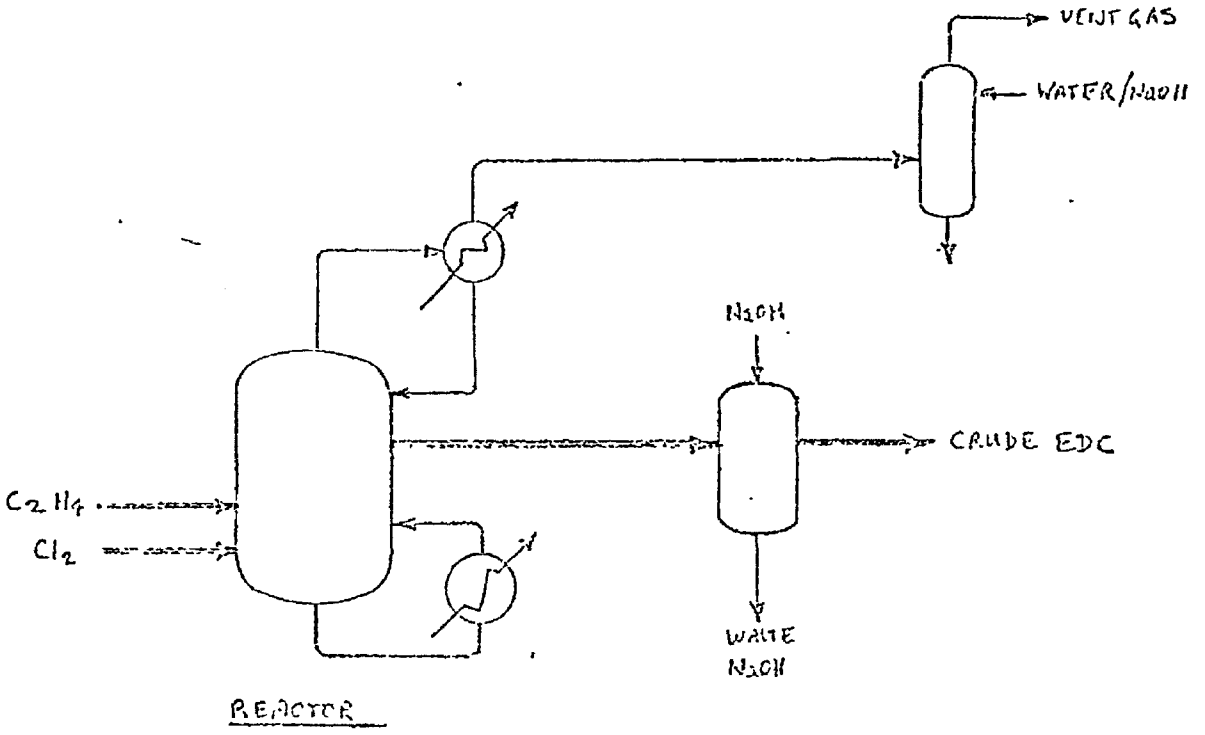
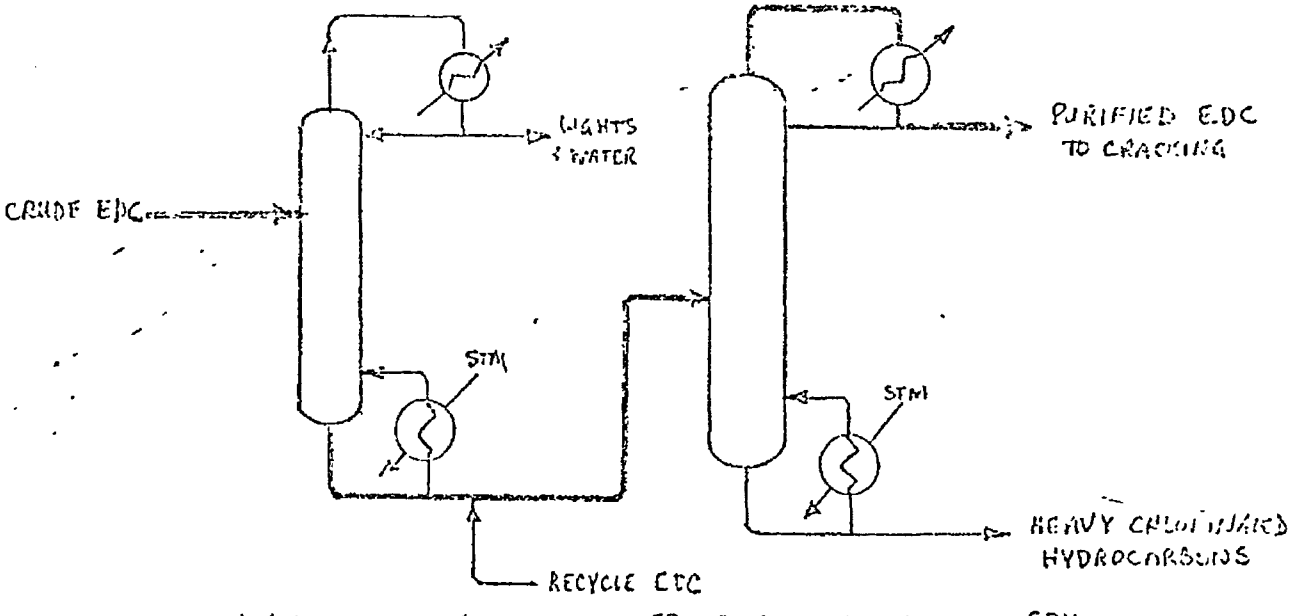


FIGURE 1. - DIRECT CHLORINATION



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DICHLOROETHANE (EDC)

FIGURE 2. - EDC PURIFICATION

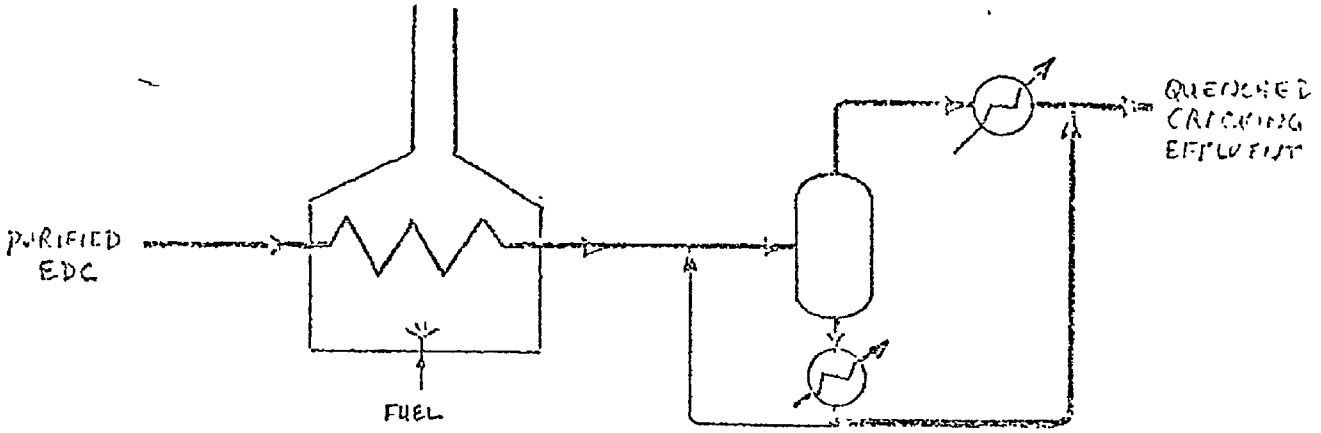

FIGURE 3 - EDC CRACKING

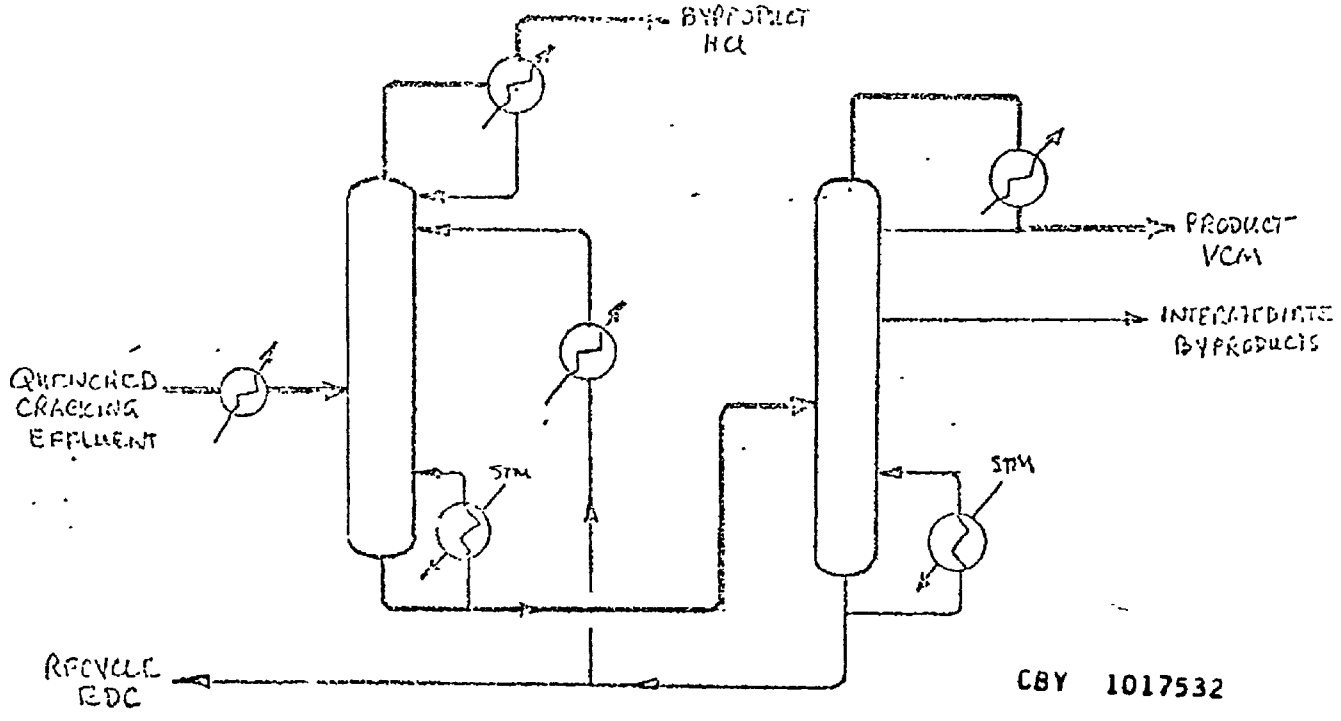

FIGURE 4 - HCl RECOVERY AND VCM REFINING

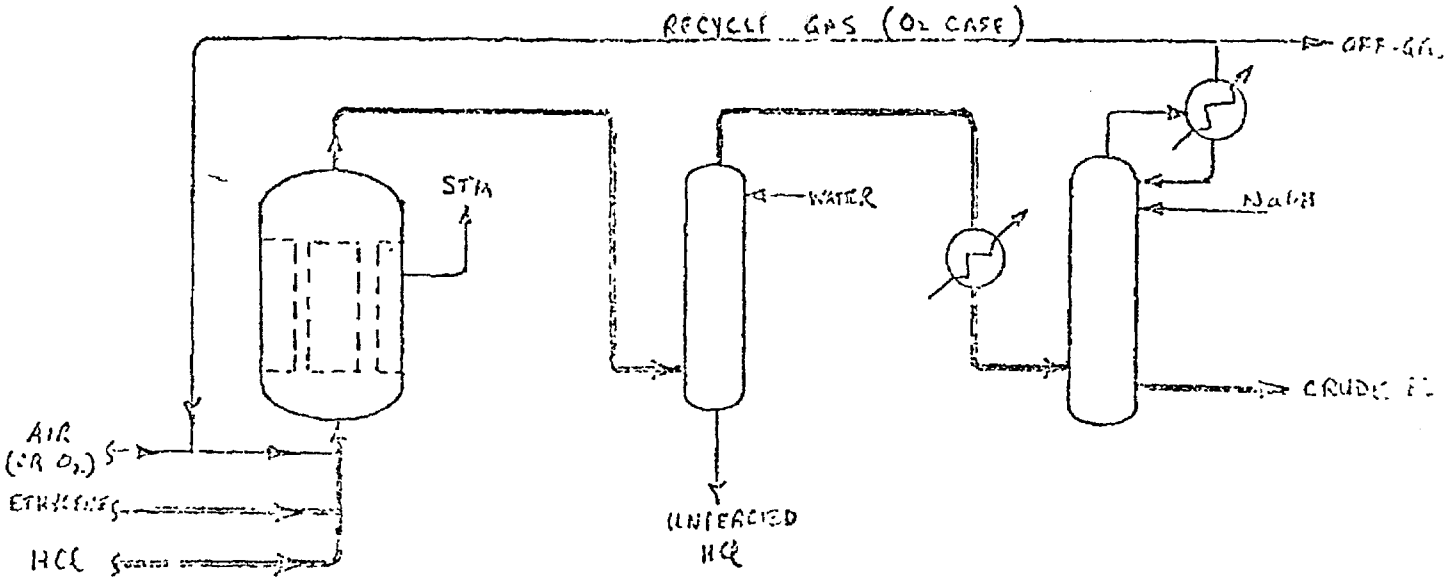

FIGURE 5 - OXYCHLORINATION

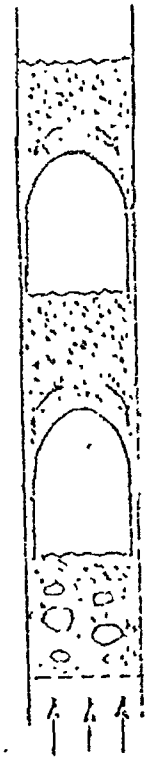

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FIGURE 6 - A TYPICAL SLUG FLOW PATTERN

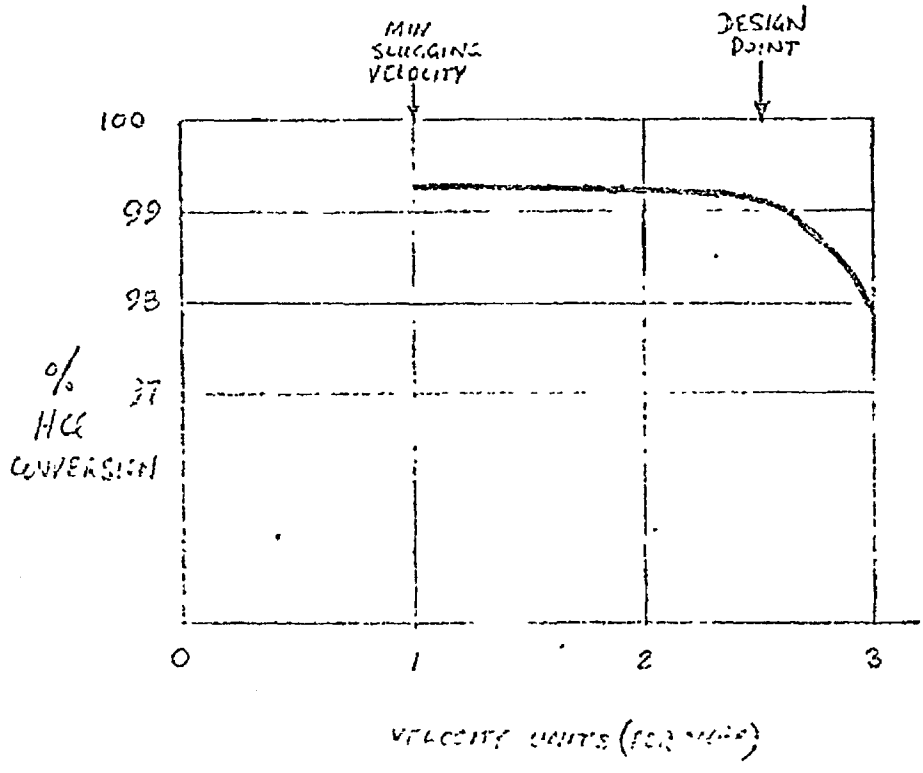

FIGURE 7 — HC CONVERSION VS. TRAY VELOCITY IN OXYCHLORINATION REACTOR

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