

CHEMSYSTEMS PERP PROGRAM

Vinyl Chloride Monomer (VCM)/ Ethylene Dichloride (EDC)

Ethylene- and Acetylene-Based VCM Process Technology, Cost of Producing VCM via Balanced Oxychlorination, Bioethylene, & Acetylene Routes. Cost of Producing EDC by Vinnolitt's Vin-Tec Boiling Reactor Process, & by Direction Chlorination Route. Safety, Health & Environmental Issues. Regional Supply/Demand.

PERP 08/09-4

Report Abstract

October 2009

6 Nexant

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For further information about these reports, please contact the following:

New York, Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: + 1-914-609-0315, e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, Multi-client Programs Administrator, phone: + 1-914-609-0381, e-mail: hcoleman@nexant.com. *London*, Dr. Alexander Coker, Manager PERP Program, phone: + 44-(20)-70950-1570, e-mail: acoker@nexant.com. *Bangkok*, Maoliosa Denye, Marketing Manager, Energy & Chemicals Consulting: Asia, phone: + 66-2793-4612, e-mail: mdenye@nexant.com.

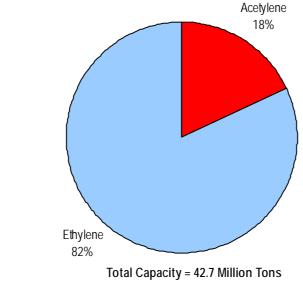
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INTRODUCTION

Historically, vinyl chloride monomer (VCM, chloroethene, chloroethylene) was not produced from ethylene dichloride (EDC), but by the reaction of acetylene with hydrogen chloride (HCl) in the presence of a mercuric chloride catalyst. Until the early 1950s, this acetylene-based technology predominated. The industry has spent several decades moving away from this technology due to the energy input necessary to produce acetylene and the hazards of handling it. Thereafter, ethylene-based routes have since become predominant. In addition, there seem to be no environmental or economic incentives to reverse this trend (i.e., there is a strong environmental incentive to cease the use of the mercury-based catalyst involved in the acetylene-based process). Today, this process is largely obsolete outside China, where the availability of relatively cheap local coal makes it economically attractive to continue with this technology. These historical economic drivers are unlikely to continue long-term, but there is still interest in this technology where supplies of oil are scarce or potentially scarce.

Currently, commercial VCM capacity can be categorized based on the feedstocks acetylene and ethylene. The Figure below shows the VCM capacity share of these two feedstocks. Ethylene is the dominant feed source for the production of VCM outside of China.



Global VCM Capacity by Feedstocks

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With the incentives of lower cost feedstock and simpler process scheme, the development of ethane-based technology for the production of VCM has been a long identified, albeit difficult to realize, target of VCM process research. A number of companies have been involved in the attempted development of an ethane-based process, several processes have been patented, but as yet none have been commercialized.

CONVENTIONAL TECHNOLOGY

Acetylene-Based VCM

The classical commercial route to acetylene is the calcium carbide route in which lime is reduced by carbon (in the form of coke) in an electric furnace to yield calcium carbide:

$$CaO + 3C \longrightarrow CaC_2 + CO$$

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The calcium carbide is then hydrolyzed to produce acetylene:

There are two principal methods for producing acetylene from calcium carbide, based on the type of generator used. In the wet generator, the reaction takes place in a cylindrical water shell attached below a carbide feed hopper. For larger scale plants, the dry generation design is more common. This design features a continuous feed of carbide mixed with enough water to complete the reaction and serve to dissipate the reaction exotherm. Acetylene production technology is described in the report, including a pertinent process flow block diagram.

The oldest and simplest commercial route to VCM is via the vapor phase addition to acetylene (C_2H_2) with anhydrous hydrogen chloride (HCl) over a mercuric chloride (HgCl₂) catalyst supported on activated carbon.

$$\begin{array}{c} \text{HC} \equiv \text{CH} + \text{HCI} & \xrightarrow{\text{HgCl}_2} & \text{CH}_2 = \text{CHCI} \\ \hline \text{Carbon} & \text{VCM} \\ \end{array}$$

Acetylene and hydrogen chloride are used in a 1:1 molar ratio. A commercial process for the production of VCM via acetylene/hydrogen chloride is described and schematically represented.

Ethylene-Based VCM

Commercial ethylene-based VCM technology utilizes direct chlorination of ethylene to produce EDC, followed by pyrolysis to VCM and hydrogen chloride and oxychlorination to utilize the hydrogen chloride.

Direct Chlorination	
$H_2C=CH_2 + CI_2 \longrightarrow CH_2CICH_2CI$	
Ethylene	1,2 - Dichloroethane (EDC)
EDC Pyrolysis	
$CH_2CICH_2CI \longrightarrow H_2C=CHCI + HCI$	
EDC	VCM
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In the oxychlorination step, the hydrogen chloride released in pyrolysis is reacted with ethylene (polymer grade) and oxygen (99.5 volume percent pure) to yield EDC and water:

 $H_2C=CH_2 + 2HCI + \frac{1}{2}O_2 \longrightarrow CH_2CICH_2CI + H_2O$ COMP. 20101.0009.4104..cdx

The commercialization of oxychlorination technology paved the way for the "balanced process", combining direct chlorination, oxychlorination, and EDC pyrolysis reactions. This widely used commercial process produces only VCM and water.

Using this balanced process (i.e., operating both the oxychlorination pathway and the direct chlorination pathway), VCM can be produced from ethylene without incurring the problem of hydrogen chloride disposal. The two processes operate synergistically and an efficient design for the manufacture of vinyl chloride involves both processes.

A high proportion of VCM production capacity is based on this technology. However, a number of producers operate unbalanced schemes drawing hydrogen chloride from other chlorination operations in an adjacent plant. A further variation runs in part on EDC brought in from other sources. Nevertheless, the balanced process is representative of the majority of the industry in the developed regions.

 Process description including pertinent process flow sheets for a generic balanced VCM production plant highlighting Direct Chlorination, EDC Cracking, Purification, Oxychlorination (catalyst, byproducts, fixed versus fluid-bed technology, air versus oxygen technology, other technology aspects). VCM purification etc.

EDC

The chemical compound 1,2-dichloroethane, commonly known by its old name of ethylene dichloride (EDC), is a chlorinated hydrocarbon, mainly used to produce VCM, the major precursor for PVC production. It is a colorless liquid with a chloroform-like odor. EDC is also used generally as an intermediate for other organic chemical compounds, and as a solvent.

In the direct chlorination process, EDC is produced by the exothermal addition of chlorine to ethylene in liquid EDC phase. In the Vinnolit process, a special complex is used as catalyst. Vinnolit-Uhde Boiling Reactor Technology including process flow diagram for the direct chlorination operation is included in the report.

SAFETY, HEALTH AND ENVIRONMENTAL (SHE)

VCM is a gas with a molecular weight of 62.5 g/mol and boiling point of -13.9°C (7°F), and hence has a high vapor pressure at ambient temperature. Therefore, it is manufactured under strict quality and safety control.

Ethylene dichloride (EDC) is a clear, manufactured liquid that is not found naturally in the environment. It is slightly soluble in water. The vapor pressure for EDC is 64 mm Hg at 20°C (68°F). EDC is thermally stable at typical use temperatures. However, exposure to elevated temperatures can cause the product to decompose.

Both ethylene dichloride and vinyl chloride are hazardous chemicals. Both are defined as flammable, with vapors that can explode when mixed with air, and both are potentially damaging to health.

• In addition to health and environmentally related issues to VCM, EDC and their production processes, this section pays particular attention to the significant and topical environmental issues surrounding PVC.

RECENT DEVELOPMENTS

EDC and VCM production processes are exemplary of very mature industry segments. Nexant has carried out a survey of selected patents from 2005 to the present.

ECONOMIC ANALYSIS

The cost of production estimates for the following are provided:

- VCM produced by a commercial balanced oxychlorination process.
- VCM produced from biotethylene the cost of production of bioethylene via ethanol dehydration and the cost of production of ethanol from corn are also provided.
- VCM produced by the commercial acetylene-based route.

In some situations, EDC is produced for export, to support VCM and PVC production in regions lacking an indigenous chlorine industry. EDC is more readily transported than chlorine, so moving EDC is the preferred means of getting chlorine equivalents to remote regions.

- A cost of production estimate for a stand-alone EDC facility employing direct chlorination is presented.
- Cost of production estimates for the VinTec boiling reactor process from Vinnolit show the economic position of the VinTec process either as (a) a stand-alone EDC operation or (b) as part of a balanced EDC/VCM operation.

Various sensitivities have been explored to illustrate the effects of variations in certain parameters on the based case economics presented in the previous section. These results can also be used to make approximate comparisons between cases for which detailed economics that have not been provided by adjusting for capacity differences, alternative feedstock valuation, etc. The sensitivity of the cost of production for VCM and EDC has been analyzed for pricing, economy of scale, capital investment, and operating rate in this section.

COMMERCIAL ANALYSIS

Vinyl chloride monomer (VCM) is used almost exclusively to produce PVC. PVC can be used in a multitude of applications by employing a number of fabrication methods including extrusion, calendaring, injection molding, blow molding, and coating. Most PVC is processed by extrusion to make pipe, siding and window or door profiles, wire and cable insulation and rigid film or sheet. Other applications include chlorinated solvents and polyvinylidene chloride; however the volumes involved are insignificant relative to PVC production.

EDC is consumed almost exclusively for VCM production. The remainder is consumed in the manufacture of chlorinated solvents, lead alkyls, and adhesives. A majority of the EDC capacity is integrated with VCM units on the same site.



- VCM and EDC Supply, Demand and Trade for the United States, Western Europe and Asia Pacific are discussed.
- Tables giving extensive listings of specific plant capacity, company and location for each of the regions denoted above are given.



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