Appendix 3

Industry Structure and Technology for Polyvinyl Chloride Production

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Introduction

This section describes the structure of that segment of the Chemical Processing Industry (CPI) that manufactures polyvinyl chloride (PVC) resins. While all the participants in the PVC manufacturing segment use the same basic technologies, the specific ways in which each technology is implemented differs from one participant to another and even among the various sites operated by each participant. In this regard the PVC segment mirrors operations in the entire CPI, where common technologies are implemented in different ways.

The first part of this section describes the overall structure of the PVC manufacturing segment. The second part describes the major players in this segment, how they are organized, and their capacities. The third part describes the process technologies that are employed in the major production steps used in the manufacture of PVC resins.

Overall Structure

All manufacturers in this segment produce PVC by reacting the basic raw materials - ethylene with chlorine or hydrogen chloride - to produce the intermediate compound ethylene dichloride (EDC). The EDC is then pyrolized, or cracked, to produce the vinyl chloride monomer (VCM) that, in turn, is polymerized to produce PVC resins. PVC resins are compounded with various additives and then processed into the final forms that consumers are familiar with, such as pipes, profiles, sheathing for cables, etc. This analysis is limited to the production of PVC in resin form: *its fabrication into the many commercial forms in which it is sold is beyond the scope of this study.*

Ethylene is produced by the high-temperature thermal cracking of hydrocarbon feedstocks such as ethane, natural gas liquids, naphthas, gas oils, and others. In 2019 US production of ethylene was approximately 31.4 million tonnes.[1] Almost 80% of the ethylene produced was derived from ethane, nearly 17% was derived from propane and butane, and the balance was derived from heavier hydrocarbons. Almost 59% of the ethylene produced was consumed in the

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[1] American Chemistry Council. "2021 – Guide to the Business of Chemistry"

production of various types of polyethylene while only about 14% was consumed in the production of PVC. The balance, about 27% of the total, was consumed in the production of all other ethylene-based chemicals.

Chlorine is produced by the electrolysis of chloride-containing brines, mainly sodium chloride, and results in the production of the co-products sodium hydroxide, or caustic soda, and hydrogen. In 2019 US production of chlorine was 10.9 million tonnes.[2] About 44% of the chlorine produced is consumed in the manufacture of PVC, while the balance is consumed in the production of other chlorinated materials and chemical intermediates, as a facilitator in the production of other metals and materials, and in the purification of drinking water and wastewater.

Ethylene dichloride is produced either by the direct reaction between ethylene and chlorine or by the oxychlorination of ethylene using hydrogen chloride and oxygen. In 2019 US EDC production was almost 10.0 million tonnes. Because of its advantageous cost position, the United States is a major exporter of EDC, with about 8% of total production being exported, and almost 99% of the remainder was consumed in the production of vinyl chloride monomer, VCM.[3]

Almost 8.8 million tonnes of VCM were produced in the US in 2019, of which almost 15% was exported and more than 99% of the remainder was consumed in the manufacture of PVC resins.[4] The VCM is produced by high temperature pyrolysis of EDC and results in the formation of coproduct hydrogen chloride. Most of this material is recycled within the manufacturing process to produce EDC by oxychlorination.

In 2019 US manufacturers produced over 7.4 million tonnes of PVC resins, of which almost 98% were made by suspension polymerization with the balance being produced by emulsion-type polymerization techniques.[5] Almost 73% of these resins were fabricated into rigid forms such as pipes and profiles, 14% were fabricated into flexible forms such as sheathing for wire and cable. The rest were consumed in the production of all other PVC products.[6]

Ethylene is a major building block chemical and is produced at more than two dozen sites in the US, most of which are located along the Gulf Coast. Although there are more than four dozen crackers at these sites only four were operated by producers of PVC in 2019, although a fifth one was being commissioned.

While the largest single use of chlorine is the production of PVC, most of the chlorine produced in the US is consumed in the purification of drinking water and wastewater, the production of

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[2] Op cit. Some chlorine is produced by the electrolysis of potassium chloride-containing brines, and some is produced as a byproduct of the manufacture of magnesium metal.
[3] Op cit. and Whitfield & Associates estimates.
[4] Op cit. and Whitfield & Associates estimates
[5] Op cit. and Whitfield & Associates estimates.
[6] Op cit. and Whitfield & Associates estimates.

inorganic chemicals such as titanium dioxide, and the production of chlorine-containing organic compounds and intermediates. Chlorine plants are located in many parts of the country. Electrolytically produced chlorine and chlorine-containing bleach is produced at 42 sites, more than half of which are operated by five integrated producers of PVC and its intermediates and are located along the Gulf Coast. The rest are operated by independent producers of chlorine or chlorine-containing bleach.

There are five integrated producers of EDC, VCM, and PVC, and one small producer of PVC manufactured from purchased VCM. The integrated producers operate plants at 20 sites, mostly along the Gulf Coast. They account for more than 98% of US production capacity.

The operations of the integrated producers of PVC and its intermediates are described in the following section.

Integrated Producers of PVC and its Intermediates

The salient characteristics of the integrated producers of PVC and its intermediates are summarized in Table A3-1. While all are integrated into chlorine production, only Shintech, Westlake and Formosa are partially integrated into ethylene as well. All producers operate at multiple sites, and all except Olin produce PVC resins as well as its intermediates. The overall characteristics of each producers' businesses, its US PVC chain plant locations and capacities and the indicated flows of materials to and from each location are summarized below.

Table A3-1: Characteristics of Integrated Producers

Producer	Integrated to Ethylene	Integrated to Chlorine	Number of Sites	Produces EDC	Produces VCM	Produces PVC
Shintech	Partially	Yes	3	Yes	Yes	Yes
Westlake	Partially	Yes	5	Yes	Yes	Yes
OxyChem	No[a]	Yes	7	Yes	Yes	Yes
Formosa	Partially	Yes	2	Yes	Yes	Yes
Olin	No	Yes	3	Yes	Yes	No

Note: In addition to these integrated producers, there is one small non-integrated producers of specialty PVC resins.

[a]OxyChem is a joint venture partner in the Ingleside LLC ethylene cracker and takes its production.

Shintech. Shintech is the US subsidiary of Japanese diversified chemical company Shin-Etsu Chemical. Shin-Etsu is the largest producer of PVC resins in the world and its US subsidiary is the largest PVC producer in the US. Worldwide production capacity of Shin-Etsu amounts to 3.2 million metric tons of PVC resin. Outside the US, Shin-Etsu operates PVC and chlor-alkali facilities in Europe and Asia. Global net sales of Shin-Etsu amounted to $13.5 billion dollars in fiscal year 2021 which includes sales from its other business lines of semiconductor silicon,

silicones, specialty chemicals, and electronic and functional materials business. US sales represented 23% of global sales.

In the US, Shintech operates plants in Plaquemine and Addis, Louisiana, and Freeport, Texas.[7] In 2020 the site at Plaquemine commissioned a cracker and today requires additional ethylene from other crackers. The site has about 10% more capacity for chlorine than can be consumed in the manufacture of EDC. Total EDC capacity was about 3.1 Mt/yr. and was in balance between the direct and oxychlorination routes so as to consume all of the hydrogen chloride produced when EDC is converted into VCM.[8] The VCM capacity, about 1.8 Mt/yr., was sufficient to meet the production of PVC of 0.6 Mt/yr. on site and to provide the VCM required for production of almost 0.9 Mt/yr. of PVC at Addis. The site at Freeport, has capacity to produce almost 1.5 Mt/yr. of PVC and does not produce PVC intermediates. The required amount of VCM must be acquired from other producers, most likely OxyChem and Olin.

Shintech has the capacity to produce about 2.9 Mt/yr. of PVC at its three US sites, and this will increase to about 3.7 Mt/yr. with announced capacity additions.

Westlake. Westlake is the second largest producer of PVC in the world and the second largest in the US. As a fully integrated producer along the PVC value chain, it has facilities to produce ethylene, chlorine, and caustic soda, EDC/VCM, PVC resin and compounds, and vinyl building products. The company's vinyl products business segment also produces chlorinated derivative products and has manufacturing facilities in Europe and Asia. Westlake's second business segment, the olefins unit, manufactures polyethylene, styrene monomer, and propylene. Global sales in 2020 amounted to $7.5 billion, of which the vinyls business unit represented 80% of sales.

In the US, Westlake operates plants in Plaquemine, Lake Charles and Geismar, Louisiana, Calvert City, Kentucky, and Aberdeen, Mississippi. It operates crackers at Lake Charles, Louisiana, and Calvert City; the Calvert City cracker has somewhat more capacity than can be consumed on site to produce EDC, and the Lake Charles crackers have the capacity to produce as much as 70% more ethylene than can be consumed on site. The chlorine plants at Lake Charles also have the capacity to produce about 70% more chlorine than can be consumed in the production of EDC there. The production of EDC at Lake Charles is balanced between direct and oxychlorination, and the total capacity exceeds that required to produce almost 1 Mt/yr. of VCM on site by almost 15%. No PVC is produced at Lake Charles.

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[7] For this and all other integrated producers, estimated material flows when stated are based on estimated nameplate capacities except where noted. In 2019 across the industry ethylene and chlorine were produced at about 86% of capacity, EDC at about 83%, and VCM and PVC at about 91% of capacity. The percentage of capacity attainment may have been quite different at individual plants.

[8] Shintech has recently announced capacity expansions at the Plaquemine site for chlorine, EDC, VCM, and PVC that will be completed before 2023.

The plant at Calvert City is nearly in balance with respect to ethylene and chlorine production as well as direct and oxychlorination and has the capacity to produce almost 0.65 Mt/yr. of PVC. The plant at Plaquemine acquires ethylene from one of the nearby crackers, is in balance on site with respect to the supply of chlorine and the production of EDC by direct and oxychlorination, but would have to import almost 15% of the VCM required to produce PVC at its capacity of about 0.85 Mt/yr. This material might be available from some of Shintech 's nearby excess capacity.

The Geismar plant must acquire ethylene from other crackers located there and has 15–20% or so excess capacity for chlorine, EDC, and VCM given a capacity limit of about 0.33 Mt/yr. for PVC at the site.[9] Direct and oxychlorination would not be in balance to produce VCM at capacity on site, so the required additional amount of hydrogen chloride would have to be produced on site or acquired elsewhere. The plant at Aberdeen has the capacity to produce about 0.45 Mt/yr. of PVC, probably from captive VCM produced at the Lake Charles site.

Westlake has the capacity to produce about 2.3 Mt/yr. of PVC at its five sites, which will increase to about 2.5 Mt/yr. with announced capacity additions.

OxyChem. OxyChem is the chemical business unit of Occidental Petroleum Corporation, which occupies a significant position in the production and transportation of oil, natural gas, and natural gas liquids. Its international operations extend from on-shore and off-shore operations in North America to the Middle East and Africa. OxyChem operates in the basic chemical and vinyls segments of the petrochemical industry. Its principal operations are in the US and at two international sites in Canada and Chile. It produces ethylene, chlor-alkali and derivative products, EDC/VCM, and PVC. **.** OxyChem's Low Carbon Ventures is the business unit that is developing and commercializing new products and technologies for capturing, transporting, and permanently and safely storing CO2 in subsurface reservoirs. Sales of Occidental Petroleum Corp amounted to $17.8 billion in 2020 and the chemicals business unit sales were $3.7 billion.

OxyChem operates plants at Deer Park, Ingleside, La Porte, and Pasadena, Texas; Convent and Geismar, Louisiana; and Pedricktown, New Jersey. The plant at Deer Park must acquire all its requirements for both ethylene and chlorine from nearby sources. The production of EDC by direct and oxychlorination is in balance, and the site can produce about 40% more VCM than is required to produce about 0.3 Mt/yr. of PVC at capacity. The Ingleside plant also must acquire ethylene, plus about 40% of its requirements for chlorine to produce EDC, which is in balance between direct and oxychlorination when VCM production is operating at about 90% of capacity. At that condition the site would have about 30% more capacity for EDC than is required to produce about 1 Mt/yr. of VCM.

The La Porte plant must acquire ethylene and about 15% of its total chlorine requirements. The production of EDC by direct and oxychlorination are not in balance when VCM is produced at its

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[9] Westlake has announced an expansion of PVC production capacity at Geismar to about 0.5Mt/yr.

capacity of almost 1.1 Mt/yr. When operating at capacity, the plant at Geismar must acquire ethylene from sources located nearby and can produce about 0.28 Mt/yr. of EDC by direct and oxychlorination. Since there is no VCM production at that site, the amount of hydrogen chloride required for oxychlorination must be purchased or possibly manufactured there from the excess chlorine produced at the site.

The Convent plant produces only EDC by direct chlorination of purchased ethylene and chlorine produced on site. About 20% of additional chlorine, which could be captive material from a plant at Taft, Louisiana, is required to produce EDC at capacity of 0.68 Mt/yr. The plants at Pasadena and Pedricktown have the capacity to produce about 0.94 and 0.19 Mt/yr. of PVC from captive VCM respectively.

OxyChem has the capacity to produce about 1.4 Mt/yr. of PVC at its seven sites.

Formosa. Formosa Plastics Corp, USA, is a privately held company that is part of the Formosa Plastics Group, a large conglomerate of companies headquartered in Taiwan. In addition to their significant position in the PVC value chain, the parent company and its affiliates are involved in such industries as petrochemicals, plastics, textile, fibers, electronics, energy, transportation, and steel. The aggregate worldwide sales amounted to $59 billion in 2020. In the US, it is a fully integrated producer along the PVC value chain and its industrial facilities also produce polyethylene, polypropylene, and other chlorine derivatives. Its PVC involvement extends into specialty PVC resins and fabricated PVC products such as pipe, fencing, and flooring.

Formosa operates plants at Baton Rouge, Louisiana, and Point Comfort, Texas. The plant at Point Comfort has a cracker with a capacity that is three times the amount required to produce EDC on site and produces sufficient chlorine on site to meet the requirements for EDC production. EDC production by direct and oxychlorination are in balance when VCM is produced to balance production of 0.75 Mt/yr. of suspension PVC, and total EDC production is more than 25% more than the amount required for that amount of VCM. The plant also has the capacity to produce almost 0.1 Mt/yr. of specialty PVC resins.

The Baton Rouge plant has the capacity to produce about 0.54 Mt/yr. of PVC as well as VCM and EDC and must acquire all the required ethylene and chlorine from other plants in the vicinity.[10] The plant must also acquire additional EDC, possibly merchant material from Plaquemine, to supplement the EDC made on site by oxychlorination. With onsite VCM production limited to about 80% of capacity to match PVC production capacity, additional chlorine is required to meet the hydrogen chloride requirements in oxychlorination.

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[10] Formosa has announced an increase in PVC capacity at Baton Rouge of 0.13 Mt/yr.

Formosa has the capacity to produce about 1.3 Mt/yr. of suspension PVC at its two sites, which will be increased to about 1.4 Mt/yr. It also has the capacity to produce about 0.1 Mt/yr. of emulsion PVC.

Olin. Olin Corporation is the leading producer of chlor-alkali and derivative products in the US and the world. Its facilities operate six chlor-alkali facilities in the US, one in Canada, and two EDC/VCM facilities in the US. It also produces chlorinated organic intermediates to produce fluoropolymers, silicones, and agricultural chemicals. Olin operates two other business segments: epoxy resins (used to produce wind turbines) and Winchester (the manufacturer of small firearms and ammunition). In 2020, Olin sales amounted to $5.8 billion, and the chlor-alkali and vinyls segment reported sales of $3.0 billion.

Olin operates plants at Freeport and Oyster Creek, Texas, and Plaquemine, Louisiana, that produce chlorine, EDC, and VCM. Olin does not produce PVC resins. The plant at Oyster Creek must acquire both ethylene and chlorine to produce the EDC made on site. When operating at its capacity to produce about 0.77 Mt/yr. VCM, the plant can produce about 30% more EDC than is required. Since 90% of the EDC is made by oxychlorination, the plant is not balanced and almost 85% of the chlorine consumed is required to produce the necessary hydrogen chloride.

The Freeport and Plaquemine plants both have the capacity to produce chlorine far in excess of their requirements for the production of EDC by direct chlorination, and both must acquire ethylene from adjacent sources. EDC capacities at these plants are about 0.75 and 0.42 Mt/yr. respectively.

Orbia. Orbia (formerly Mexichem) is a holding company with headquarters in Mexico City. Its business segments have interests in agricultural services (Netafin, a leader in precision micro-irrigation solutions), data communications, building and infrastructure (water management systems), and chemical products (fluorinated material products). In the US, Orbia has grown through acquisition. It has consolidated its vinyls assets into the Polymer Solutions division. This division operates two specialty PVC resin facilities and several PVC compounding and fabrications facilities in the US. In addition, Polymer Solutions owns and operates PVC resin and related facilities in South America and Europe. PVC resin is produced under its Vestolit brand and compounds under its Alphagary brand. Sales of Orbia amounted to $6.4 billion in 2020; Polymer Solutions account for $2.2 billion in sales.

Orbia operates plants in Henry, Illinois, and Pedricktown, New Jersey, that produce specialty PVC resins from purchased VCM. The total capacity of these two sites is about 116 kt/yr.

Process Technologies

The five major technologies employed in the production of PVC resins (cracking of hydrocarbons to produce ethylene, electrolytic production of chlorine, production of ethylene dichloride, production of vinyl-chloride monomer, and production of polyvinyl-chloride resins)

are described in more detail in this section. First an overall description of each technology is presented, and then the major technical variants that are practiced currently are described. Finally, the way the technologies are incorporated specifically into the PVC value chain is summarized.

It is important to emphasize that these are all mature technologies, having been practiced in earlier embodiments for many decades. Numerous improvements in their designs and operations, both substantial and incremental, have been made over the years, and are still underway, that have resulted in improved efficiencies in materials and energy consumptions, improved product qualities, and reduced environmental impacts. Such improvement will continue to be made, and the technology descriptions presented here should not be viewed as the final versions that will be employed in future decades.

Ethylene Crackers

Ethylene crackers are complex, multi-step systems that produce ethylene, hydrogen, and other relatively low-molecular-weight hydrocarbons by the thermal decomposition of ethane or other hydrocarbons in the presence of steam in high-temperature furnaces. The products of the cracking reactions are cooled quickly and separated into various fractions that are either recycled within the process, transferred as products to other operations, or disposed. The cracking process itself, which takes place at temperatures in the vicinity of 850° C, is energy-intensive, and the product separation section of the plant employs cryogenic temperatures to produce the individual product streams. Energy flows within a cracker are highly integrated, with steam generated by cooling the hot reactor off gases being used to drive the compressors used in the separation section.

The design requirements for a cracker depend on the feedstock that is being treated. The product separation sequence for ethane crackers is simpler than that for crackers that treat naphtha because fewer byproducts are formed in the cracking reactions.

Ethane feedstock is pretreated, if required, to ensure that deleterious impurities are reduced to acceptable levels and steam is introduced to obtain a ratio of steam-to-carbon in the range of 0.3–0.4. Uncracked ethane is recycled from the product-separation sequence, the chemical dimethyl sulfoxide is added in small amounts to reduce the formation of carbon monoxide and coke in the cracking reactions, and the steam-hydrocarbon mixture is introduced to the cracking furnaces where it is heated to temperatures in the vicinity of 850° C. Cracking temperatures are achieved by the combustion of the fuel gases, mainly methane (as well as hydrogen) that are produced in the cracking reactions. The residence time in the furnaces is short, of the order of 250 to less than 500 milliseconds, to limit the formation of undesired byproducts.

The cracked gases are cooled rapidly, or *quenched,* and energy is recovered from this process in the form of superheated, high-pressure steam that is used within the process to drive the compressors in the product separation and recovery section of the plant. Cooling to the final

cracked gas temperature is achieved through the direct use of quench water, and some heavy byproducts, such as pyrolysis gas oils, may be condensed here as well. The cooled gases are compressed and scrubbed with caustic soda to remove the acid gases carbon dioxide and hydrogen sulfide, and they are then compressed again and dried to remove water vapor carried over from the previous steps.

The hydrocarbons in the compressed, dried cracked gases are separated in a sequence of distillation towers operating at cryogenic temperatures. The refrigeration required to achieve these temperatures is achieved by compressing, cooling and then expanding the ethylene and propylene gases themselves in a multistep refrigeration train. The gases contain small amounts of acetylene and other diolefins that are removed by catalytic hydrogenation. Byproduct hydrogen and methane are the first products separated from the mixture, and they are, in turn, separated with the methane-rich stream and often hydrogen used as fuel gases in addition to purchased natural gas to heat the cracking furnaces. The next products separated out are ethylene and uncracked ethane which are, in turn, separated into the ethylene product and ethane which is recycled back to the cracking furnaces.

The remaining gases consist of C3 and C4 hydrocarbons and some heavier hydrocarbon byproducts that are separated into their constituent compounds or transferred as mixed streams to other operations in the complex as required. The cracking reactions also produce coke, which adheres to the walls of the reactor and eventually increase pressure drop and impair its ability to transfer energy at the required rate. Furnaces are taken off-line periodically to remove the coke deposits and restore performance.

Most crackers are a part of a larger petrochemical complex and employ this sequence of operations, changing operating conditions and specific design requirements as required to integrate material and energy flows into the complex most efficiently. Design details such as the number, size and thermal design of individual furnaces, management of the high temperature energy recovery operations, and the degree of separation of the C3 and heavier byproducts vary. In addition, operators can select operating conditions such as steam-to-carbon ratio, cracking temperature, and residence time to control the degree of severity obtained, which influences the yield of ethylene and byproducts and the rate of coke build-up in the furnace and its available stream time.

The greatest determinant of cracker design, cost, and product slate, however, is the choice of feedstock to be treated: the heavier the feedstock, the more costly it is to build and operate the cracker and the more complex the product slate is. Approximately one quarter of all crackers in the US were designed to take ethane as a feedstock, one quarter were designed to take a mixture of ethane and propane, and the rest were designed to be flexible enough to take ethane-propane-butane mixtures as well as naphtha, gas oil or other feedstocks. The impact of feedstock choice on cracker materials flows is summarized in Table A3-2.

Table A3-2

Typical Materials Flows for Various Cracker Feedstocks[11]

Feedstock	Ethane	Ethane/Propane	Butane	Naphtha
Feedstock t/t[1]	1.3	1.7	2.6	3.5
H2 produced, t/t	0.08	0.07	0.03	0.03
Fuel gas, t/t	0.12	0.25	0.5	0.5
Crude C3s, t/t	0.06	0.15	0.38	0.59
Crude C4s, t/t		0.06	0.47	0.31
Pyro gas, t/t		0.05	0.25	0.9
CO2 released, t/t	0.75+/-0.2	0.95+/-0.2	1.5+/-0.2	1.8+/-0.2

[1] Tonnes per tonne ethylene

While half of the crackers in the US have been designed to accept both the lighter and heavier feedstocks, the availability of relatively large supplies of ethane recovered from natural gas has resulted in it becoming the favored cracker feedstock. Only about 5% of current ethylene cracker production in the US is based on naphtha or heavier feedstocks, about 15% is based on propane and butane, and almost 80% is based on ethane. The proportions are similar for the crackers that are associated with the PVC value chain, except that about two thirds of these crackers were designed initially to accept naphtha as well as the lighter hydrocarbons.

The average capacity of crackers in the US is almost 700 kt/yr. ethylene, and capacities range from almost 2.6 Mt/yr. to about 70 kt/yr., with a median size of almost 600 kt/yr. The size distribution of the crackers associated with the PVC value chain is more compressed, with capacities ranging from 1.5 Mt/yr. to about 130 kt/yr. and average and median capacities of 670 and 650 kt/yr. respectively.

Given the distribution of feedstocks to the crackers, and the resulting differences in flows or materials through them shown in Table A3-2, the wide range of their sizes, and the differences in their ages and operational and maintenance histories, it must be expected that they will show a range of energy consumptions and CO2 emissions. Under these circumstances it

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[11] Values depend on furnace design, cracking severity, and feedstock compositions. CO2 emissions assume byproduct H2 is burned as fuel

becomes difficult to define the characteristics of a "typical" cracker for purposes of describing the costs and performance of CO2 abatement technologies in the PVC chain.

While the crackers may be integrated to exchange thermal energy with other operations within a complex, they typically are net consumers of fossil energy to heat the cracking furnaces and are consumers of electricity for various process drives. They may also be net exporters of steam, depending on how the integration is done.

Electrolytic Production of Chlorine

Chlorine is produced by the electrolysis of potassium or sodium chloride-containing brines, but all chlorine associated with the PVC value chain is produced from purified brines of sodium chloride. In this process the chloride ions in the brine are oxidized at an anode to produce chlorine gas and water is reduced at a cathode to produce hydroxide ions and hydrogen gas. The sodium ions in the brine combine with the hydroxide ions to produce sodium hydroxide, which is commonly called caustic soda. The overall chemical reaction for the process may be written as follows:

$$2NaCl + 2H_2O = Cl_2 + 2NaOH + H_2$$
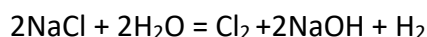
According to this stoichiometry, approximately 1.65 t of salt would be converted into 1 t of chlorine with coproduction of 1.127 t of caustic plus 0.028 t of hydrogen, and this essentially is achieved in commercial production.

The ways in which chlorine is produced differ mainly in the way the chlorine gas and sodium hydroxide produced in the electrolytic cells are prevented from mixing with each other. Two types of cells are in use for PVC chain chlorine production: membrane and diaphragm type cells.

The main differences between the process flowsheets for these technologies lie in the way the brines are prepared for electrolysis and how the caustic solutions are recovered and concentrated.

The diaphragm cell process has been in use for more than a century, although its efficiency has been improved greatly. Diaphragms originally were made of asbestos but are now made of polymer modified asbestos materials or a synthetic fluoropolymer material. Raw brines, often obtained from deep wells, are typically treated with soda ash and caustic to precipitate calcium and magnesium and the solids are removed by sedimentation and filtration.

Purified, saturated brine is introduced into the anolyte chamber in which the chloride is oxidized. The chlorine gas typically contains a small amount of air in-leakage and oxygen that is formed by the decomposition of water in the cell. The level of brine in the anolyte chamber is maintained higher than that in the catholyte chamber on the other side of the diaphragm, and the hydraulic gradient induces a flow of depleted brine through the membrane and into the catholyte chamber. There, water is reduced to form hydrogen gas and the hydroxide ions that reacts with the sodium ions contained in the depleted brine.

The caustic concentration in the catholyte withdrawn from the cell to maintain the hydraulic gradient typically is in the range of 12%, and the solution is normally concentrated to 50% for sale as a commercial product. The catholyte contains a higher concentration of salt than caustic, and it must be removed and recovered to produce caustic with less than about 1% salt. This is possible because salt has a relatively low solubility in concentrated caustic solutions so that it precipitates and is separated as the caustic is concentrated. Concentration is done in multiple effect evaporators designed to remove the precipitated salt mechanically. The recovered salt is recycled in the process to re-saturate the brine that is fed to the anode chamber of the cell.

The chlorine leaving the cell is saturated with water, which must be removed to produce chlorine that is dry enough to be non-corrosive to ordinary materials of construction. The gas is cooled and dried by contacting it with a highly concentrated solution of sulfuric acid in a multistage countercurrent scrubber, and the acid is regenerated by evaporation of the water picked up from the chlorine. The chlorine may then be compressed and liquefied by cooling if it is to be stored or transported by rail for sale. The byproduct hydrogen is also saturated with water and is dried by cooling.

Membrane cells, developed almost 50 years ago, differ from diaphragm cells in the way the anolyte and catholyte chambers are separated and in the flows of solutions through them. The membranes themselves are typically thin, fiber reinforced ion selective bi-layer structures with a perfluorocarboxylic acid film on the catholyte side and a perfluorosulfonic acid film on the anolyte side. This type of membrane permits sodium ions to cross it from anolyte to catholyte with a minimum of ion flow in the reverse direction and the transport of a minimum amount of water from the anolyte to the catholyte. This results in the production of a low-sodium caustic product at concentrations of around 32% and permits the depleted brine to be recycled directly from the anolyte compartment.

The membranes can be coated or fouled by impurities in the brine, and this would degrade their performance and increase electrical consumption so they must be reduced to very low levels. Removal of calcium, magnesium, sulfates, and other impurities is achieved by a series of ion exchange and polishing filtration steps, the degree of removal depending on the cell operating parameters. The recirculated brine is dechlorinated to protect the ion exchange media, and the purified brine's pH is adjusted to maximize the lives of anode coatings and the diaphragms.

The treatment of the chlorine and hydrogen gases from membrane cells is essentially the same as in diaphragm cells, but treatment of the caustic is simpler. Because caustic from membrane cells has a low salt content and is more concentrated, it can be converted to a saleable 50% product with less energy consumption and in simpler evaporators than is possible for diaphragm-produced caustic.

There is a significant difference in practice among plants on how byproduct hydrogen is treated and how steam for caustic concentration is produced. Some plants may sell the hydrogen for its chemical value, some may use hydrogen to produce hydrogen chloride, some may burn the hydrogen along with purchased fuels to generate steam, and others may vent some or a portion of the hydrogen if it cannot be sold or used on site.

Also, different plants may take different approaches to providing the steam required for caustic concentration and acquiring the electricity required for chlorine production and general plant use. In some circumstances steam may be available from an adjacent cracker or from elsewhere within a chemical complex. Some plants may use a conventional boiler to raise only the amount of steam required, while others may cogenerate the steam and power for plant use in so-called CHP plants.[12] The choice among these options is site and situation specific.

The theoretical energy consumption for chlorine production, 1700 kWh/t, is not achieved in practice because competing reactions require additional energy and real systems impose electrical resistances that must be overcome, requiring additional energy. The current density in a cell, in units of kA/m^2, is a measure of how fast the electrolytic reactions are being driven; the higher the current density the smaller the cell may be per unit of chlorine produced, but the higher the consumption of electrical energy will be. The cell design is chosen to achieve an optimum balance between the investment required and the cost of energy. Current densities are typically higher in membrane than in diaphragm cells.

Cell designs of each type may differ in other aspects as well. All cells use dimensionally stable electrodes, typically coated titanium anodes and coated nickel cathodes of proprietary design that resist corrosion and promote gas release thereby reducing cell electrical resistance. Groups of cells, called electrolysers, may be connected in what are called either monopolar or bipolar arrangements to provide the current required for electrolysis, and typically operate at different voltages and with different numbers of cells in an electrolyser stack. Bipolar configurations require less energy than monopolar ones because the electrical resistance through the circuit is lower. Typical performance characteristics for diaphragm and membrane cells are summarized in Table A3-3.

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[12] All CHP plants in the PVC chain use natural gas as a fuel, and most of them employ combined cycle technology to generate power and steam. Their ages and sizes vary widely.

Table A3-3

Cell Performance Characteristics[13]

Cell Type	Diaphragm	Membrane
Cell Voltage	3-4.5	2.9-3.4
Current Density kA/m^2	1-2	3-5
AC Power kWh/t	2800	2600
Comment	Lower for non-asbestos membranes	Lower for bipolar electrolysers

The average and median capacities of electrolytic chlorine plants in the US, excluding those that produce bleach, are about 260 kt/yr., but the capacities range from 11 kt/yr. to over 1.4 Mt/yr. The size range for plants in the PVC value chain is compressed because the smallest one has a capacity of 165 kt/yr., and the average and median capacities are about 690 and 580 kt/yr. respectively.

About 67% of these plants' capacity comes from the use membrane cells, and they will require less electrical energy for chlorine production and less thermal energy for caustic concentration than will the plants using diaphragm cells. Furthermore, the membrane cell plants tend to be larger than diaphragm cell plants and so should benefit from efficiencies of scale as well. Finally, the choices with respect to providing steam for concentrating caustic or cogenerating steam and electricity are based on site specific technical and economic factors. As is the case with the ethylene crackers described previously, there is no single type of "typical" chlorine plant in the PVC chain; distinction must be made at least between those using diaphragm and those using membrane cell technologies as well as in those generating steam or cogenerating steam and electricity.
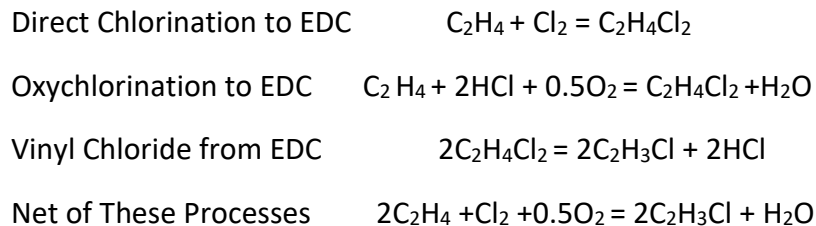
Chlorine plants are large consumers of electricity, whether purchased or generated on site, both for electrolysis and for process drives. They are consumers of fossil energy to raise steam for caustic concentration as well as for cogeneration of steam and electricity if that is practiced on site.

Production of Ethylene Dichloride

Two processes are employed to produce EDC, direct chlorination and oxychlorination, and they are often conducted simultaneously and tied to the production of vinyl chloride monomer from EDC. The reason for this is shown in the stoichiometries of the reactions in the production sequence.

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[13] BAT reference document for chlor-alkali production.

Direct Chlorination to EDC $\quad\quad C_2H_4 + Cl_2 = C_2H_4Cl_2$

Oxychlorination to EDC $\quad C_2H_4 + 2HCl + 0.5O_2 = C_2H_4Cl_2 + H_2O$

Vinyl Chloride from EDC $\quad\quad 2C_2H_4Cl_2 = 2C_2H_3Cl + 2HCl$

Net of These Processes $\quad\quad 2C_2H_4 + Cl_2 + 0.5O_2 = 2C_2H_3Cl + H_2O$

Plants where the capacities to produce EDC and VCM by these routes are consistent with the stoichiometries shown are said to be in balance with respect to the production and consumption of hydrogen chloride, but not all plants in the PVC chain are configured that way. Some plants practice only either direct or oxychlorination alone and some practice both but do not have capacities that are in balance with the production of VCM. This may occur in plants that produce some EDC for sale rather than for on-site conversion to VCM, and in these cases any additional requirements for HCl must be made up by on-site production or purchases.

Two processes are practiced for the direct chlorination of ethylene to produce EDC; a low temperature and a high temperature process. Both the low and high temperature processes take place in the liquid phase in the presence of solid catalysts, typically ferric chloride, and at pressures below 5 bar. The chlorination reaction is exothermic, and the processes differ in how their energy requirements are managed. Byproduct formation is lower for the low temperature process, which may operate in the vicinity of 50 C, than it is for the high temperature one which may operate in the vicinity of 100 C or higher.

In the low temperature process, ethylene and chlorine react in a circulating flow of EDC and suspended catalyst. Inert gases and volatile byproducts such as ethyl chloride are vented, scrubbed, and sent to treatment. The EDC formed in the reactor carries suspended catalyst and must be washed with caustic to remove it. The wet EDC is dried by distillation, which also removes residual lower boiling impurities. If the washed, dried EDC contains an objectionable amount of heavy ends, it must be redistilled to remove them since the subsequent VCM production process may be susceptible to fouling and inhibition by them. The exothermic heat of reaction is removed by cooling water and is unavailable for use in other process steps.

The high temperature process operates at temperatures above the normal boiling point of EDC, which is vaporized from the circulating liquid-catalyst suspension by using some of the heat of reaction. The balance of the reaction energy, more than 80% of the total, can be recovered in the form of low-pressure steam for use elsewhere in the process. The EDC vapors are condensed and treated to remove both light and heavy byproducts as required but washing and drying is not required because the nonvolatile catalyst remains in the reactor.

Oxychlorination takes place at about the same pressure as direct chlorination but at temperatures in the vicinity of 250-300 C and in the vapor phase. The reaction is catalyzed by cupric chloride supported on an inert substrate and may be carried out in either fixed or fluidized bed reactors, and the latter provides for easier recovery of the exothermic heat of reaction. Both air and separated oxygen can be used as the oxidant in the reaction.

Oxygen and ethylene are fed to the reactor in excess of the amount required to insure essentially complete conversion of the hydrogen chloride. The heat of reaction is about one third higher than for the direct chlorination process and is recovered in the form of IP steam that can be used elsewhere. Entrained catalyst is removed from the reactor off gases, and they are quenched and cooled in stages to first separate lower volatility impurities and the water formed in the reaction. The water must be treated further to remove dissolved chlorinated compounds prior to discharge.

Additional cooling permits separation of non-condensable gases from the condensed, crude EDC. The non-condensable gases include the excess ethylene and oxygen fed to the reactor, and nitrogen if air is used, and most are recycled to the reactor, although a purge stream is vented to remove high volatility impurities. The vent stream will be quite large if air is used as the oxygen source since the nitrogen, argon and other inert gases must be removed, and must be treated to remove chlorinated hydrocarbons and other objectionable compounds.

While per-pass conversions in the reactor may be as high as 98-99%, the selectivity for EDC is lower than for direct chlorination and byproduct formation may be of the order of 2- 5%. While some byproducts will be removed in the water condensate and gas purge streams, the crude EDC will have to be treated further by distillation to remove them, as is the case with direct chlorination.

There are fourteen direct chlorination and twelve oxychlorination plants in the PVC value chain, with total and announced capacities of about 9.8 Mt/yr. and 9.6 Mt/yr. respectively. The direct chlorination plants' capacities range from 75 kt/yr. to over 1.4 Mt/yr., with average and median sizes of about 660 and 580 kt/yr. respectively. The oxychlorination plants' capacities range from 200 kt/yr. to almost 1.6 Mt/yr., with average and median sizes of about 740 and 580 kt/yr. respectively. Comparing the cohort of plants in 1990 to the present day, the number of companies producing EDC has been reduced by half, the average size of an EDC plant has doubled, three plants have been retired, and the average age of the cohort is over 30 years.

Table A3-4

Characteristics of EDC Industry, 1990-2019

EDC (direct & oxy)	1990	2019
Companies	10	5
Avg. size, oxy & direct (kt)	382	725
Total capacity (mt)	9.2	19.4
# of plant sites	24	28
# Retirements of 1990 plants		3
Avg age of cohort	--	>30 years

There are three different process options to produce EDC, each with different energy requirements and yields, and their capacities in the PVC chain installations vary by a factor of more than 20. They are utilized in a variety of ways; in addition to being balanced with respect to HCl in VCM production, they are also used in unbalanced combinations and as individual entities. The situation at each PVC chain site must be characterized individually to recognize the differences properly.

All EDC production processes require electricity for process drives and consume fossil energy to raise the steam used in reboilers in the EDC purification sections of the plants. The high temperature direct chlorination process and the oxychlorination process can generate some of their steam requirements by capturing high temperature energy within the process.

Production of Vinyl Chloride Monomer

Vinyl chloride monomer, the precursor from which PVC is made, is produced by the thermal decomposition of ethylene dichloride in high temperature furnaces. The EDC cracking furnaces differ in design from those used to crack ethane to ethylene in that they operate at lower temperatures, about 500 C, higher pressures, from 20-40 bar, and have much longer residence times at reaction conditions, from 10-20 seconds. As is the case with ethylene crackers, however, the pyrolysis reactions are complex, and significant amounts of light and heavy byproducts are formed, which must be removed from the VCM product. As is the case with ethylene crackers, carbon that can foul the reactors is also formed and is deposited as coke on furnace surfaces.

Operators control furnace conditions to minimize the extent of formation of chlorinated byproduct and coke. This requires that EDC conversions per pass be limited to no more than 50-65%, which means that the furnace feed can consist of from a third to as much as a half-recycled EDC. The cracking furnaces are designed to use the energy from fuel combustion to

vaporize the EDC, heat it to reaction temperature, and provide the energy for the endothermic cracking reactions. Certain compounds can act as initiators or promoters to improve reaction selectivity and may be added in small amounts to the furnace feed.

The reaction products exiting the furnace are quenched rapidly with recycled, crude EDC produced in a series of pressure let-down and cooling steps to limit the formation of tars. The HCl-VCM-EDC mixture passes to a series of distillation columns, the first of which removes the HCl and low boiling impurities and returns them to the oxychlorination process. High purity VCM is separated from the EDC and higher boiling impurities in the next column in the sequence. The VCM may need additional treatment to remove traces of HCl or other compounds that would interfere with the polymerization process. The final purification steps remove byproducts that are lighter and heavier than the EDC, which is returned to the cracking furnaces to limit the extent of coke formation in the furnaces.

As is the case with crackers, EDC cracking plants use multiple furnaces since formation of some coke is inevitable and eventually builds up to the extent that it limits furnace performance. When the furnace can no longer attain the required performance, it is taken offline, and the coke is burned off using steam and air. The formation of byproducts with a range of boiling points complicates the purification scheme for this process and generates waste streams that must be destroyed or treated further before they can be disposed.

There are eleven plants in the PVC chain that produce VCM by cracking EDC, and their total and announced capacity is about 10.6 Mt/yr. Individual plant capacities range from about 330 kt/yr. to 1.8 Mt/yr., and average and median capacities are about 880 and 770 kt/yr. respectively. Comparing the cohort of plants in 1990 to the present day, the number of companies producing VCM has been reduced from nine to five, the average size of a VCM plant has more than doubled, four plants have been retired, and the average age of the cohort is over 29 years.

Table A3-5

Characteristics of VCM Industry, 1990-2019

VCM	1990	2019
Companies	9	5
Avg. size (kt)	403	884
Total capacity (kt)	4.8	9.8
# of plant sites	12	12
# Retirements of 1990 plants		4
Avg age of cohort	--	>29 years

All VCM plants employ the general sequence of operations described above, but differences in furnace designs and operating conditions lead to differences in byproduct formation rates and the sequence of operations to purify the HCl and VCM produced. About 15% of the VCM that is produced is not tied directly to the production of PVC but is exported.

VCM plants use electricity in process drives and consume fossil energy both to heat the cracking furnaces and to raise steam for reboilers in the VCM separation and purification section of the plant

Production of Polyvinyl Chloride Resin

Polyvinyl chloride resins are made by polymerizing vinyl chloride monomer under carefully controlled conditions to produce products with the desired molecular weight distribution, particle size distribution and porosity. There are two types of processes for polymerizing VCM: the suspension and emulsion processes. PVC capacity among the integrated producers is almost 99% devoted to suspension polymerization. The capacity for PVC production by emulsion polymerization, including the independent producer, is about 2.5% of the total, but the production share is lower than that at about 2.2%. The relatively small amounts of PVC produced by emulsion polymerization are incorporated into specialty products and will not be considered in detail here.

The process description that follows describes the production of resins that contain only polymerized vinyl chloride, which are called homopolymer resins. However, the same techniques can be used to produce resins that are copolymers of VCM and other monomers such as vinyl acetate. Also, PVC can be chlorinated further to produce CPVC, a product that has better mechanical properties than the homopolymer material and is widely used in piping systems. Since these products are still based on the polymerization of VCM they are not considered further here.

Polymerization by the suspension process is done batch wise in an aqueous medium that has its dissolved oxygen content reduced to low levels. Emulsifiers and polymerization initiators are added to the medium and VCM is introduced into the reactor at a controlled rate to maintain a pressure of 5-15 bar. The reactors are agitated vigorously, and the exothermic heat of polymerization is removed to maintain the reaction temperature in the range of 40-60 C. When the reaction has been completed and about 90% of the VCM has been consumed, the excess VCM is vented to a gas holder.

The slurry of PVC particles in the medium contains dissolved VCM that must be removed, and this may be done batch wise while it is still in the reactor, or the slurry may be transferred to an external stripping operation. In either case the VCM is removed by passage of nitrogen or steam through the slurry at atmospheric pressure or under vacuum and goes to a VCM recovery system. This system removes water from the recovered VCM by condensation and the dried, oxygen free monomer is returned to VCM storage.

The stripped PVC slurry is partially dewatered by centrifugation and final water removal takes place at relatively low temperatures in one of a variety of types of dryers. The dried solids are sieved to produce the particle size distribution desired and conveyed to packaging and storage. Water recovered from the VCM drying operation and water recovered from PVC slurry dewatering and drying are treated to remove residual VCM and fine PVC particulates before release.

Integrated producers operate twelve suspension process PVC plants that have a total and announced capacity of about 9.1 Mt/yr. of PVC. The plant sizes range for 190 kt/yr. to more than 1.4 Mt/yr., with average and median sizes of about 570 and 540 kt/yr. respectively. Comparing the cohort of plants in 1990 to the present day, the number of companies producing VCM has been reduced from fourteen to five, the average size of a PVC resin plant has more than quadrupled, twenty-four plants have been retired, and the average age of the cohort is over 28 years.

Table A3-6

Characteristics of PVC Industry, 1990-2019

PVC resin	1990	2019
Companies	14	5
Avg. size (kt)	135	556
Total capacity (kt)	4.6	8.4
# of plant sites	34	15
# Retirements of 1990 plants		24
Avg age of cohort	--	>28 years

While PVC resin might be viewed as a commodity product, the operators control conditions in the PVC polymerization process to produce materials that meet the specifications required by their customers, particularly with respect to molecular weight, particle size distributions, and surface characteristics that are important is subsequent processing steps. A typical plant will have multiple reactors and employ reactors of different sizes to be able to produce resins with a range of properties that meet the customers' requirements.

PVC plants use electricity for process drives and fossil energy to heat reactor contents and dry the PVC and, in some cases, as a stripping agent to remove unreacted VCM from the product.

Summary

Products produced in the PVC value chain include EDC, VCM, and PVC resin. All three products are exported in significant amounts. They are manufactured by five producers in twenty sites,

most of which are located along the US Gulf coast. Three producers are partially integrated into ethylene production, and all purchase ethylene from external sources. All producers are integrated into chlorine production, however, and its consumption in the manufacture of PVC resins is a major outlet for the product. While four of the producers manufacture EDC, VCM and PVC resins, one producer manufactures only the intermediates EDC and VCM.

All producers in the PVC chain use the same basic technologies but employ them in different ways. Plant sizes differ greatly, even within individual producers' different sites. The various merchant and captive crackers that supply the ethylene to the PVC chain use different feedstocks and have different materials and energy requirements and byproduct production suites.

The chlorine plants in the chain use both diaphragm and membrane type cells and have different arrangements by which they produce steam to concentrate caustic and generate, or cogenerate, electricity for use in the plants. The disposition of byproduct hydrogen also differs from plant to plant.

All manufacturers in the PVC chain produce EDC by either low or high temperature direct chlorination as well as by oxychlorination. However, these technologies are employed in a variety of ways, either separately or in combinations that may or may not be in balance with PVC production with respect to the disposition of HCl. All manufacturers produce VCM by the high temperature pyrolysis of EDC, with differing furnace designs and product purification sequences being used as conditions require.

Only four of the manufacturers in the chain produce PVC resins. Almost all resins are produced by the suspension process in batch reactors. Conditions are chosen so that the resin products have the chemical and physical properties desired by their customers.

Decarbonization of the PVC chain will require a variety of approaches since the technologies currently in use consume large amounts of electricity, fossil fuels for delivering energy for high temperature cracking processes, and fossil fuels for raising steam for process use. Because plant sizes differ so greatly, and the technologies are employed in different ways among the sites there can be no "one size fits all" solution to eliminate carbon emissions from the chain.

Works Cited

American Chemistry Council. "2021 – Guide to the Business of Chemistry"