Appendix 7

Technologies Under Development
Could Alter the Structure of the PVC Value Chain

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The Dehydration of Ethanol to Ethylene

Ethanol dehydration to produce ethylene is a multi-step, catalytic process that operates under relatively moderate conditions and has high yields and conversions. Approximately 1.7 tonnes of ethanol are required to produce 1.0 tonne of ethylene. Materials and energy requirements for the process are not excessive, and the process can operate efficiently at much smaller scales than can conventional crackers.

As currently practiced in Brazil, the process is based on sugar cane and does not abate process emissions. Implementation in the US at the current time would be based on ethanol derived from corn, although other carbohydrate sources could be utilized in the future if justified economically and environmentally.

In the base year the PVC chain consumed about 5.5 MMt of ethylene out of the 12.4 MMt produced by the crackers servicing the chain. Replacing the crackers would require about 9.3 MM t of ethanol, which was approximately 20% of US production in the base year. This would require the dedicated output of some 30-40 of the newer plants in the Iowa-Nebraska region.

If the technology is to be shown to be preferred to conventional crackers from the perspective of GHG emissions, both the production of ethanol and its dehydration would have to be decarbonized. The ethanol fermentation step generates 0.96 t CO_2/t ethanol while plant utilities typically generate an additional 0.47 t/t and the plant's grid emissions typically contribute an additional 0.21 t/t.

The dehydration process itself generates about 0.11 t CO_2/t ethylene, so total unabated emissions from ethanol production and dehydration are almost 2.9 t/t ethylene. Abating fermentation emissions is very efficient because they are nearly pure CO_2, and plant emissions can be abated by scrubbing. If so, total abated emissions would be reduced to about 0.8 t CO_2/t ethylene. More than 85% of the total abated emissions are from the grid.

The slate of crackers currently supplying the PVC chain emit on average 0.87 t CO_2/t ethylene. Abating the crackers by scrubbing the combustion gases would reduce total emissions to about 0.25 t/t ethylene, of which over 60% are from the grid.

In 2019 the average spot price of ethanol was $466/t FOB[1]. Assuming that IRS 45Q credits would cover the cost of CO2 transportation and sequestration, decarbonized ethanol delivered to the US Gulf Coast would cost about $600/t, equivalent to more than $1000/t of ethylene produced from it. Dehydration costs would increase that to more than $1100/t ethylene.

In 2019, the average spot price of ethylene was $408/t. Decarbonizing the emissions from the crackers in the PVC chain would impose costs of about $90/t, so that the price of decarbonized ethylene would have been almost $500/t.

The amounts of both unabated and abated CO2 emissions from the production of ethylene by dehydration of ethanol are more than three times those from ethylene produced by the crackers in the PVC chain. This is driven by the large amount of CO2 generated in the fermentation process as well as plant emissions in both fermentation and dehydration, and the fact that almost 1.7 tonne of ethanol are required to produce 1 tonne of ethylene. More than 85% of abated emissions from ethanol production and dehydration would arise from the grid, and more than 60% of those from the crackers would do so as well.

These estimates are based on the process operations and not life cycle analyses that consider emissions outside of the plant boundaries. Based on GHG emissions alone, ethanol dehydration would not be considered more favorably than cracker ethylene unless other credits were applied. Even if the ethanol were produced from alternative feedstocks that intrinsically produced far less CO2 in the conversion process, it would still require 1.7 tonnes of it to produce a tonne of ethanol. Consequently, extremely efficient processes, and/or significant offsetting credits, would be required.

Assuming that suitable feedstock sources and policy measures can be developed to incentivize its use, ethanol dehydration might become suitable for the dispersed, much smaller-scale production of ethylene for PVC production in regions other than the US Gulf Coast where smaller scale crackers or lack of suitable cracker feedstocks would make their operation uneconomic.

Electrification to Eliminate the Direct Use of Fossil Fuels in Process Applications

In 2020, about 23% of the unabated emissions from the PVC chain came from the crackers and 9% came from the combustion of fuels within the processes. 53% came from operation of the CHP plants, 14% were grid emissions, and 1% were attributed to the power required to produce the oxygen and hydrogen chloride consumed in the manufacture of EDC. Since the CHP plants themselves are producers of power as well as thermal energy they are not candidates for

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[1] FOB stands for "free on board" and indicates when the liability for goods is transferred from a seller to a buyer.

electrification. Neither, in this context, is the grid whose energy sources will be selected by different criteria than those used in the PVC chain.

Except for the CHP plants, ethylene crackers, and the VCM cracking furnaces, fossil fuels are consumed in boilers to raise the LP or IP steam that delivers energy to the various process steps. Electric boilers are available commercially to meet the process steam requirements of the PVC chain. The energy costs to operate them will be higher than for fossil fueled boilers, but they would not have to be decarbonized. Currently there are no commercially available electric VCM cracking furnaces, but they are smaller and operate under less severe conditions than ethylene crackers. There should be no intrinsic problems with producing suitable designs using electrical energy, but focused R&D programs will be required for their development.

Programs for the Design and Testing of Electrified Steam Crackers for Ethylene Production Have Been Announced

Recent announcements by consortia made up of Dow and Shell and of BASF, SABIC and Linde briefly describe the initiation of R&D programs for the development of e-crackers whose energy source would be electricity rather than fossil fuels. The efforts by Dow and Shell are being supported by the EU.

Naphtha currently is the dominant feedstock for steam crackers outside of the US, and they emit more than twice as much CO_2 per unit of ethylene produced than do crackers supplying the domestic PVC chain. Electrifying them using power from a decarbonized grid would achieve major reductions in CO_2 emissions. Since conceptual engineering has just begun on the design of test facilities for this concept, demonstration of successful operation at a scalable size is years away, and large-scale commercial adoption is unlikely before 2030.

Ethane is the dominant feedstock for crackers in the domestic PVC chain. Electrifying ethane crackers would require less energy than electrifying naphtha-fed crackers but would not generate as high reductions in the amount of CO_2 eliminated per unit of ethylene produced. Furthermore, electrifying the crackers alone would not decarbonize them completely since significant amounts of fuel gases, which are primarily methane, are generated in the cracking reactions and would be emitted unless they were abated. Abatement could be achieved by reforming them to produce blue hydrogen, which would reduce direct cracker emissions by about 97%.

The energy requirements of the cracking reactions depend on the size of the system and the details of its design and operation but are most sensitive to the composition of the feedstock. Heavier feedstocks such as naphtha require more energy than light ones such as ethane because more byproducts are produced in the cracking reactions. The energy requirements currently are provided by the efficient combustion of fossil fuels, including natural gas, and the fuel gases and hydrogen produced in the cracking process itself. A portion of this energy is

recovered when the cracked gases are quenched in an energy recovery system. This energy is converted into steam that is used to drive the compressors in the product separation train, and some steam may be exported to other operations on the site.

The designs of the fuel burners and of the metallic reactor tubes that contain the feedstock being cracked are sophisticated, having evolved over many years of experience to maximize thermal efficiency and process performance, minimize the extent of coke formation, and maximize the lives of the tubes, which operate near the limits of their mechanical stability. The reactor tubes will have to be replaced by ones that are electrically heated while maintaining the desired temperature profile and detention time so that the products of the cracking reactions have the desired composition. This most likely will require replacement of existing furnace structures, but not replacement of the product separation and purification chain, assuming that the energy recovery system remains unchanged.

In 2040 total emissions from grid power and combustion of fuels in the PVC chain crackers is estimated to be about 10 MM t/yr. of CO_2 . Most of the CO_2 produced in the fuel-gas reforming process would be captured and sequestered. The emitted CO_2 would be charged to the cracking process, along with the CO_2 produced in generating the electricity used as the cracker's energy source.

Replacing the cracking furnace with an electrically heated one and upgrading the power supply and distribution for the site to accommodate the greatly increased demand, could require capital investments of the order of 5–15% of the cost of a complete cracking system, depending on the details of the designs found to be required in the development process. In addition, the project would incur the cost of installing a relatively small fuel-gas-reforming and CCS system. Operating costs for the cracker would increase at the Reference Case prices projected for natural gas and electricity, since electricity would be about 4.7 times as expensive as natural gas on a contained energy basis.

Existing fossil-fueled boilers in other operations in the PVC chain can be replaced with electrically heated ones with capital requirements in the range of 100–250k $/MW of capacity. Capital requirements for the VCM cracking furnace may be higher, depending on the designs that evolve. As is the case with cracker, operating costs will increase with the use of electrical energy, but the need to abate emissions from the boilers and VCM furnaces will have been eliminated. Existing CHP plants might be decarbonized either by the installation of CCS systems or by substituting hydrogen for the natural gas currently used to fuel them. Use of hydrogen would minimize the capital requirements for a decarbonized CHP system but increase the operating costs since blue hydrogen would be about 2.7 times as expensive as natural gas on a contained energy basis.

Based on a mid-range estimate of the capital requirements to electrify crackers and the estimated capital requirements for relatively small ATR-CCS systems to reform the cracker fuel gases, the capital required to electrify the crackers in the PVC chain in 2040 would be about

$6.6 billion. Based on the reference case prices for natural gas, electricity and hydrogen, the net cost of converting from natural gas to electrically heated furnaces would be about $500/t ethylene. Almost 75% of the operating costs result from the high cost of electricity in the Reference Case. Elimination of fossil fuel consumption and reforming the fuel gas would result in a reduction in CO_2 emissions of about 9.6 MM t/yr. However, the CO_2 emissions from the grid would increase by about 26.7 MM t/yr. because of the greatly increased consumption of electricity so that the net result would be an increase of about 17 MM t/yr. from an undecarbonized grid.

These capital requirements and increased operating costs would have to be weighed against the alternatives of decarbonizing the crackers using either CCS systems or hydrogen as a fuel. Decarbonizing the cracker fleet in the PVC chain with CCS systems in 2040 would require investments of about $3.6 billion and incur operating costs of about $90/t ethylene. The CCS systems have limited capabilities to remove CO_2 from combustion gases and require significant amounts of grid power, so the net reductions in cracker CO_2 emissions would be about 7.7 MM t/yr. About half of the 2.3 MM t/yr. of CO_2 emitted would be from grid emissions.

Decarbonizing the crackers with merchant blue hydrogen in 2040 would require capital expenditures of about $3.8 billion and incur operating costs of about $180/t ethylene with merchant hydrogen priced at $1.38/kg. All fossil fuel emissions from the cracker would have been eliminated, but production of blue hydrogen from merchant sources, from fuel gas reforming, and from grid emissions would create emissions totaling about 2.1 MM t/yr. CO_2. Almost 60% of these emissions would come from the production of about 0.9 MM t/yr. of the merchant H_2 used as cracker fuel.

While there is significant uncertainty in estimating the costs for cracker electrification in the absence of any design or operation data, preliminary estimates indicate that the capital requirements for e-crackers and the associated fuel gas reforming plants would be of the order of 1.7–1.8 times the capital requirements for decarbonization by CCS or hydrogen. Total operating costs would be of the order of 2.7–5.5 times higher than decarbonization by CCS or hydrogen at the energy prices in the Reference Case, driven by the high cost of electricity. If the price of electricity were reduced enough to be equal to the price of fossil fuels and hydrogen on a delivered energy content basis, the total operating costs would be intermediate between those for CCS and hydrogen decarbonization.

Substituting electricity for the fossil fuels consumed by the crackers in the PVC chain in 2040 would require about 10.6 GW of connected power. The power required for the crackers and the associated fuel gas reforming plants would generate emissions from the grid of 2 t CO_2/t ethylene at the grid emission rates in the Reference Case. Consequently, cracker electrification is not a reasonable decarbonization strategy unless the grid is largely or completely decarbonized. Were the grid completely decarbonized, the e-cracker emissions would be reduced to about 300 kt/yr., whereas those from CCS and hydrogen decarbonization would be about 1.1 and 1.5 MMt/yr. respectively.

Thus, major reductions in the estimated capital requirements for e-cracker systems, the availability of decarbonized or nearly decarbonized electricity at prices equivalent to those of fossil fuels, or policy measures that offset the increased costs will be required to incentivize adoption of this technology.

Development of Technology to Produce EDC Without the Use of Chlorine or Hydrogen Chloride is Underway at a Demonstration Scale Plant

Chemetry, a process development company located in Moss Landing, California, has been developing electrochemical technologies that differ from conventional chlor-alkali processes. In one embodiment of the technology, byproduct sodium hydroxide and hydrogen are generated from sodium chloride, but the chloride is not oxidized to chlorine at the anode. Instead, copper is oxidized to its cupric state there, the cupric chloride solution is used to chlorinate ethylene to produce ethylene dichloride, and the resulting cuprous chloride is recycled to the electrochemical cell.

The developers of Chemetry's e-Shuttle EDC process expect to generate significant cost savings vis-à-vis the conventional chlor-alkali route to the production of chlorine gas for EDC by eliminating the oxidation of chloride, thereby reducing the electrochemical energy consumption. Energy consumption is projected to be 28% lower than that of conventional membrane chlor-alkali plants, which would reduce CO2 grid emissions by an equivalent amount. Instead, redox reactions based on copper are used to shuttle chloride from an electrochemical cell to a chlorination reactor where EDC is synthesized as the cupric ion is reduced to its cuprous state for recycle. The simplified electrochemical stoichiometry is:

$$2NaCl + 2H_2O + 2CuCl = 2CuCl_2 + 2NaOH + H_2$$
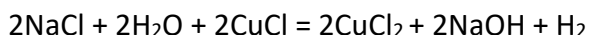
The aqueous cupric chloride solution is then contacted with ethylene gas, converting some of the gas to ethylene dichloride. The simplified stoichiometry of this reaction is:

$$2CuCl_2 + C_2H_4 = C_2H_4Cl_2 + 2CuCl$$
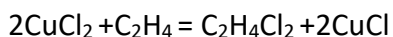
The resulting cuprous chloride solution is stripped to remove impurities and recycled to the electrochemical cell so that the overall result of this sequence is the conversion of salt, ethylene and water into ethylene dichloride, sodium hydroxide and hydrogen without the production of chlorine gas. The crude EDC is purified to remove high and low boiling impurities and unreacted ethylene is recycled, closing the process.

Because the chloride ion does not have to be oxidized, cell voltages will be lower than those in a conventional chlor-alkali plant. However, current densities will also be lower with current cell design so as many as twice as many cells will be required. Selective membranes are required to isolate the anode and cathode compartments. The cells will operate with highly purified brine

at 85–90° C and byproduct caustic soda will be produced at concentrations in the 30–32% range. The aqueous cupric chloride solution will be contacted with ethylene gas at temperatures and pressures in the range of 150° C and 10 bar respectively; the reactions proceeding without the need for an external catalyst.

The reduction in energy costs for membrane chlor-alkali plants projected by Chemetry amounts to about $26/t of chlorine with power priced at $0.04/kWh. The projected reduction in GHG emissions amounts to about 0.43t/t chlorine. This is comparable to the projected reduction in power consumption, although the bases for the estimate were not given. No estimates were provided for electricity, fossil fuel requirements or GHG emissions for Chemetry's EDC plant, but since conditions are more severe than in a conventional direct chlorination plant, they are unlikely to be lower.

The process has been tested extensively at the pilot scale and TechnipFMC has been retained as the EDC licensor for the process. A demonstration scale plant is currently under construction at Maceio, Brazil in cooperation with Braskem, and Permascand has been retained to conduct cell scale-up and manufacture. Integrated operations are expected to begin later this year and to continue into 2023. If the process technology can be demonstrated so that the projected energy savings can be realized, and if the process capital costs are manageable as well, full commercial scale operation might be achieved by 2030. The likely scale of a commercial operation is unclear given the undemonstrated state of the designs of the EDC reactor and the electrochemical cells.

Since both Chemetry's electrochemical cell design and its EDC production reactor design are fundamentally different from those of a chlor-alkali–EDC production-reactor sequence, estimates of the differences in capital requirements cannot be developed with a high degree of confidence. Chemetry's estimates of potential cost savings due to the reduction in energy requirements would amount to about $40/t of chlorine, or about $30/t EDC, at Reference Case power prices in 2030.

Chemetry's estimate of GHG reductions amounts to about 0.43 t/t chlorine, although the bases for this estimate, including the assumed carbon intensity of the grid and the contribution of any CHP plants, are not clear. If this ratio applies to the chlor-alkali-CHP plant suite in the PVC chain, emissions from them would be reduced by about 28%, which is consistent with the projected percent power reduction.

In the absence of reliable cost estimates, it is not clear that the projected reductions in energy requirements and GHG emissions would be sufficient to justify adoption of this technology solely by virtue of the projected reduction in the cost of abating 25–30% CO2. An advantage of the technology is that it is likely to be easier to scale to lower production rates than would be the case for conventional chlor-alkali–direct chlorination plants. This could permit it to be established in locations where EDC demand is relatively low. However, such a complex could

not be tied directly to smaller scale PVC production without the addition of a VCM cracker, which would generate large amounts of hydrogen chloride that would have to be managed.

Development of Technology for the Conversion of Natural Gas to Acetylene Using Plasma as an Energy Source Has Been Demonstrated in a Small Pilot Scale Plant, and Conversion of Acetylene to VCM Is Known Technology

Transform Materials has built a small pilot plant in Florida to demonstrate its plasma-based technology for the production of acetylene and hydrogen from natural gas. The process has been under development since 2014 and the 30-kW-scale pilot plant is used to produce material for customer evaluation as well as for process development. The company's target markets are the applications where acetylene currently produced from calcium carbide and various refinery sources are consumed. However, the process of converting acetylene to vinyl chloride monomer by reacting it with hydrogen chloride is well known and currently being practiced in China, where the acetylene is derived from coal.

The simplified stoichiometry for Transform Materials methane conversion process is:

$$2CH_4 = C_2H_2 + 3H_2$$
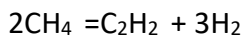
After separation and purification, the addition of hydrogen chloride to the acetylene results in an overall stoichiometry as follows:

$$2CH_4 + HCl = C_2H_3Cl + 3H_2$$
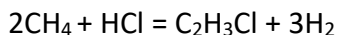
The net result is that methane plus hydrogen chloride is converted into VCM plus hydrogen without the requirement for ethylene and chlorine or the formation of intermediate products.

Transform Material's process operates at near atmospheric pressure and "moderate" temperatures. The company claims that conversion of methane to acetylene per pass can exceed 90%, and that selectivity can exceed 95%. Some of the methane disproportionates to form elemental carbon that coats the reactor tube and must be removed periodically by direct combustion. The reaction products are separated by proprietary technology that has not been described. Acetylene purities exceed 99.6% while the hydrogen may contain of the order of 5% other gases, mainly unreacted methane and inerts.

If natural gas is used as a feedstock, it must be purified to remove odorants that contain sulfur and any CO2 present. The higher hydrocarbons present in the gas will undergo the same types of reactions that methane does, being converted into other unsaturated compounds and hydrogen as well as forming carbon. Any inert gases in the natural gas, such as nitrogen, will build up in the circulating unreacted methane and will be purged with the hydrogen stream.

The need to focus the microwave radiation in a concentrated manner to produce the plasma that drives the reactions limits the size of the reactor tube to relatively small diameters. The pilot plant reactor is about 50 mm in diameter and 150 mm long, and reactant contact times are in the low millisecond range. This means that, unless the required microwave energy can be delivered in much larger diameter reactors, a plant of commercial size for VCM production would involve multiple reactors arranged in parallel. Transform Materials believes that the maximum practical plant capacity may be about 25 kt/yr. of acetylene, which then could be converted into about 60 kt/yr. VCM, which would require roughly 300 reactor systems. Commercialization at that scale likely would require the design, construction, and operation of a much larger scale pilot or demonstration-scale facility, which may be difficult to achieve before 2030.

The conversion of methane into acetylene and hydrogen is a highly endothermic process, requiring of the order of 20MWh/t acetylene to heat the reactants to temperature and to provide for losses in the generation of the microwaves. Additional power and thermal energy will be required to produce VCM, and the energy content of the hydrogen chloride should be included in accounting for emissions.

Given the small size of the existing pilot plant and the relatively undeveloped state of designs that could be commercialized it is not possible to estimate costs for Transform Materials natural gas to VCM process concept with any certainty. Capital requirements might be expected to be manageable because only two steps are involved rather than four in the existing route, but the requirement for 300 reactor systems will limit the ability to obtain scale economies. Credits from the sale of almost 0.1 t H2/t VCM could offset the cost of almost 0.6 t HCl/t VCM required, but the differences in other components of operating costs cannot be established with certainty at this time. Microwave power requirements will be high and the energy requirements of the hydrogen chloride reactant and the VCM conversion process must be considered as well, so that the emissions from an undecarbonized grid may be comparable to the total for the conventional route before decarbonization. If so, the process would require access to decarbonized power to be comparable to the existing technologies.

At the maximum capacity of the VCM plants of about 60 kt/yr., which is less than 10% the average size of the existing VCM plants, the technology could offer the possibility of developing dispersed PVC production facilities closer to the location of PVC product fabrication plants were a suitable supply of HCl available.

These Technologies Would Require Special Circumstances to Be Considered Economically and Environmentally More Beneficial than Current Technologies

The preceding technology evaluations were done assuming "normal" activities in the R&D sequence, with government or private sector support but without "Manhattan Project" levels of commitment of funding and technical resources.

Special credits or subsidy policies will be required to incentivize ethanol-to-ethylene production. Evaluation of much stricter requirements to abate natural gas and ethane production emissions is outside the scope of this study but could alter the balance of emissions between this and the conventional route. However, this technology scales down much more efficiently than crackers and could open the possibility of its employment at small scale in dispersed sites. The technology would be implementable by 2030, if the necessary CCS infrastructure exists

A decarbonized grid and very low-cost power would be required to incentivize the development of electrified crackers. Our best estimate is that e-cracker technology will not be implementable at full commercial scale until mid-2030s.

A combination of Chemetry's electrochemical chloride production technology with relatively small-scale ethylene production, as from ethanol to ethylene, might be employed to produce EDC outside of the existing large-scale locations in the US Gulf Coast. Implementation at large demonstration scale by 2030 is possible, but a special situation is required to complete the VCM-PVC chain without creating a problem of disposing of excess HCl.

Transform Materials' plasma-based technology to produce acetylene from natural gas could lead to economic VCM-PVC production at small, decentralized locations, assuming decarbonized grid power is available, HCl is available, and markets exist for the byproduct H2. Implementation at a large (for this technology) demonstration scale may be possible by 2030, but a special situation is required if it is to be coupled with PVC production, since HCl must be available to produce VCM.