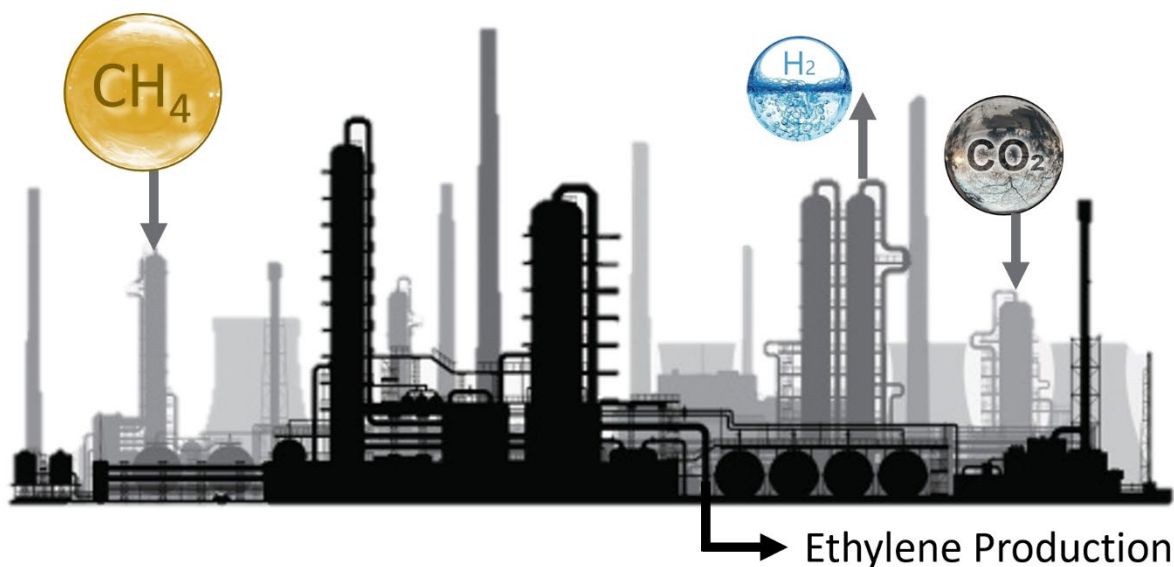


Prospects of hydrogen cogeneration and carbon dioxide utilization in electrochemical refineries for ethylene production via oxidative coupling of methane: A techno-economic assessment

Fabian Rosner, Boxun Hu, Michael Tucker, Hanna Breunig

Energy Technologies Area

June 2024



This work was supported by a Laboratory Directed Research and Development (LDRD) Energy Technology Area/Divisional Priority topics: Electrochemical Refinery & Negative Emissions Technologies Initiatives. This work was supported by the U.S. Department of Energy under Lawrence Berkeley National Laboratory Contract No. DE-AC02-05CH11231. Co-PIs: Hanna Breunig, Michael Tucker. Thanks to Drs. Adam Weber and Corinne Scown for their leadership of the LDRD priority topic.

Report #: LBNL-2001597

OSTI ID: 2372625

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory is an equal opportunity employer.

Table of Contents

List of Figures	5
List of Tables	6
1. Introduction	8
2. Methodology	8
2.1 Design Basis	8
2.1.1 Site Characteristics.....	8
2.1.2 Feedstock Specifications	9
2.2 Economic Analysis.....	10
2.2.1 Capital Cost Estimation.....	10
2.2.1 System Analysis.....	12
2.3 Environmental Impact Assessment	13
2.4 Property Methods	13
2.5 Process Description and Modeling of Process Units unique to the Ethane Steam Cracker Plant	14
2.5.1 Steam Cracker.....	14
2.5.2 Acetylene Hydrogenation.....	15
2.6 Process Description and Modeling of Process Units unique to the OCM Plant.....	16
2.6.1 Natural Gas Desulfurization.....	16
2.6.2 Combustion Furnace.....	16
2.6.3 Solid Oxide Cell for Electro-chemical Coupling of Methane	17
2.6.4 Carbon Dioxide Separation	18
2.6.5 Methanation	18
2.7 Process Description and Modeling of Common Plant Process Units.....	20
2.7.1 Cooling Tower	20
2.7.2 Cryogenic Gas Separation	20
3. Results and Discussion	21
3.1 Ethane Steam Cracker Plant	21
3.1.1 Technology Performance Analysis.....	21
3.1.2 Economic Performance Analysis	25
3.2 Electrochemical OCM Plant with Air as Oxidant	28
3.2.1 Technology Performance Analysis.....	28
3.2.2 Economic Performance Analysis	32
3.3 Electrochemical OCM Plant with Steam as Oxidant.....	36
3.3.1 Technology Performance Analysis.....	36
3.3.2 Economic Performance Analysis	39
3.4 Electrochemical OCM Plant with Carbon Dioxide Utilization via Methanation	43
3.4.1 Technology Performance Analysis.....	43
3.4.2 Economic Performance Analysis	48
4. Summary, Conclusions and Recommendations	57
4.1 Summary.....	57

4.2	Conclusions	57
4.3	Recommendations	60
5.	References.....	61

List of Figures

Figure 2-1:	Steam cracker carbon deposition equilibrium.....	15
Figure 3-1:	Simplified flowsheet of the ethane steam cracking process for ethylene production.	24
Figure 3-2:	Breakdown of the ethane steam cracker total-plant-cost (TPC).....	26
Figure 3-3:	Economies of scale of the ethane steam cracker plant.	28
Figure 3-4:	Breakdown of the OCM (air oxidant) total-plant-cost (TPC).	33
Figure 3-5:	Simplified flowsheet of the electrochemical OCM plant with air as oxidant (OCM-A) for ethylene production.	34
Figure 3-6:	Simplified flowsheet of the electrochemical OCM plant with steam as oxidant (OCM-S) for ethylene production.	40
Figure 3-7:	Breakdown of the OCM (steam oxidant) total-plant-cost (TPC).	42
Figure 3-8:	Simplified flowsheet of the electrochemical OCM plant with CO ₂ utilization (OCM-C) for ethylene production.	47
Figure 3-9:	Breakdown of the OCM (CO ₂ utilization) total-plant-cost (TPC).	49
Figure 3-10:	Cost of ethylene by scenario.	51
Figure 3-11:	Economies of scale of the ethane steam cracker and OCM plants.....	52
Figure 3-12:	Impact of solid oxide cell cost and costs of power electronics upon the cost of ethylene. ..	53
Figure 3-13:	Impact of current density and operating voltage upon the cost of ethylene.....	53
Figure 3-14:	Impact of single pass yield upon the cost of ethylene.....	55
Figure 3-15:	Cost of ethylene for the OCM-S case at a single pass yield of 69%.	56

List of Tables

Table 2-1:	Site Characteristics.....	9
Table 2-2:	Natural Gas Composition.....	9
Table 2-3:	Total Plant Cost (TPC)* Correlations for Major Process Units in US\$ (2022).....	11
Table 2-4:	Cost Summary of Fuel and Consumables	13
Table 3-1:	Ethane Steam Cracker Plant Performance	21
Table 3-2:	Ethane Steam Cracker Plant Electric Power Consumption at Full Load Operation	22
Table 3-3:	Ethane Steam Cracker Plant Emissions	23
Table 3-4:	Ethane Steam Cracker Plant State-Point Stream Data	25
Table 3-5:	Ethane Steam Cracker Plant Economics	27
Table 3-6:	OCM (Air Oxidant) Plant Performance	29
Table 3-7:	OCM (Air Oxidant) Plant Electric Power Consumption at Full Load Operation	30
Table 3-8:	OCM (Air Oxidant) Plant Emissions	32
Table 3-9:	OCM (Air Oxidant) Plant State-Point Stream Data	35
Table 3-10:	OCM (Air Oxidant) Plant Economics.....	36
Table 3-11:	OCM (Steam Oxidant) Plant Performance.....	37
Table 3-12:	OCM (Steam Oxidant) Plant Electric Power Consumption at Full Load Operation	38
Table 3-13:	OCM (Steam Oxidant) Plant Emissions	39
Table 3-14:	OCM (Steam Oxidant) Plant State-Point Stream Data	41
Table 3-15:	OCM (Steam Oxidant) Plant Economics	43
Table 3-16:	OCM (CO ₂ Utilization) Plant Performance	44
Table 3-17:	OCM (CO ₂ Utilization) Plant Electric Power Consumption at Full Load Operation	45
Table 3-18:	OCM (CO ₂ Utilization) Plant Emissions	46
Table 3-19:	OCM (CO ₂ Utilization) Plant State-Point Stream Data	48
Table 3-20:	OCM (CO ₂ Utilization) Plant Economics	50
Table 3-21:	Faraday Efficiency	54
Table 3-22:	OCM Y69 (Steam Oxidant) Plant Emissions.....	55

1. Introduction

Ethylene is recognized as one of the most significant chemicals globally.¹ The projected ethylene production for 2023 stands at 227.6 million tonnes, with expectations of continued demand growth. The primary use of ethylene, accounting for over 76%, lies in the production of plastics such as polyethylene, polyvinyl chloride, and polystyrene.² Despite the enduring carbon retention potential of plastics themselves, traditional ethylene feedstock production from fossil resources contributes substantially to greenhouse gas emissions, ranging from 0.29 to 2.29 kg_{CO2}/kg_{Ethylene} depending on various factors like feedstock and process design.³⁻⁵ Various decarbonization strategies, including the utilization of hydrogen as a primary heat source, have been proposed to reduce the carbon footprint of ethylene production,⁶ but their efficacy remains limited, offering at best a 0–30% reduction in on-site CO₂ emissions.⁵

Looking ahead to a future abundant in renewable energy, there's potential for refineries to transition from conventional thermochemical methods to electrochemical synthesis routes. Proton-conducting high-temperature membranes to produce ethylene from ethane,⁷ and the oxidative coupling of methane (OCM) in solid oxide cells have emerged as promising alternatives. OCM presents a particularly groundbreaking opportunity as it allows for the upgrading of simple organic molecules like methane; and as such, the utilization of methane from biogenic sources, thereby reducing reliance on fossil resources and mitigating emissions from ethane feedstock production. However, despite these promising developments, there's a significant gap in our understanding of the performance, costs, and competitive advantages associated with practical electrochemical system implementations.

Recent advancements in electrochemical OCM,^{8,9} including demonstrations with metal-supported cells¹⁰, indicate progress towards enhancing flexibility in operating conditions and system integration. To accelerate and better guide solid oxide OCM cell development, a comprehensive system-level analysis is conducted to evaluate the potential implications of operating conditions on both performance and economics in prospective OCM-based ethylene refineries. This work builds upon previous work by the authors¹¹ and further investigates possibilities of H₂ co-production and CO₂ utilization.

2. Methodology

2.1 Design Basis

2.1.1 Site Characteristics

The plant site is considered to be in the United States (U.S.). Due to the variety of geographical climate zones within the U.S., ISO conditions are chosen as basis for ambient conditions. In this study, all plants will use the same ambient conditions to facilitate an objective comparison between the state-of-the-art (SOTA) technology – ethane steam cracking – and an electrochemical system incorporating the oxidative coupling of methane. At ISO conditions, the ambient air has a temperature of 15 °C at a pressure of 1.01325 bar (0 m elevation). The air composition used in this work is: 79% N₂ and 21% O₂ adjusted to a relative humidity of 60%. The resulting wet bulb temperature is 10.8 °C. Using a 5 °C temperature approach in the cooling tower,¹² a cooling water temperature of 15.8 °C is obtained. Conventional heat exchangers are simulated with a pinch temperature of 11 °C (unless specified otherwise, see steam cracker and cold box). The site characteristics are summarized in **Table 2-1**.

Table 2-1: Site Characteristics

Parameter	Value	Unit
Elevation	0	m
Barometric Pressure	1.01325	bar
Design Ambient Temperature, Dry bulb	15.0	°C
Design Ambient Temperature, Wet bulb	10.8	°C
Design Ambient Relative Humidity	60	%
Design Cooling Water Temperature	15.8	°C

2.1.2 Feedstock Specifications

For the steam cracking process, pure ethane with a lower heating value of 47.2 MJ/kg is assumed to be supplied at a pressure of 15 bar via pipeline at ambient temperature. To meet the energy demand of the steam cracker, natural gas is burned together with undesirable side products produced in the plant. The natural gas composition used in this study is an averaged value representative for natural gas in the U.S.¹³ The composition is slightly modified to account for trace components.¹⁴ The natural gas has a lower heating value of 47.5 MJ/kg and is supplied at 4 bar and 15 °C.

Table 2-2: Natural Gas Composition

Component	Mole-%
Methane	93.08746
Ethane	3.19957
Propane	0.69991
n-Butane	0.39995
Carbon Dioxide	0.99987
Nitrogen	1.59978
Water	0.00329
Oxygen	0.01000
Hydrogen Sulfide	0.00004
Tert-Butyl Mercaptan	0.00013

The CO₂ feedstock used in this study is sourced from a nearby fossil fuel power plant or a direct air capture system. Since the electrochemical cell is working close to ambient pressure, the CO₂ can be supplied to the plant at substantially lower pressure compared to scenarios where underground CO₂ storage is considered, which typically requires CO₂ compression to approx. 150 bar. Since gas compression is a considerable cost driver, a lower supply pressure will be beneficial for the economics of lower-pressure CO₂ utilization processes. In this work pure CO₂ is assumed to be available at the plant site at a pressure of 4 bar and ambient temperature. The degree of CO₂ purity required is not investigated in this study and depends on factors such as process design and catalyst selection. For CO₂ methanation over a Ni-Al₂O₃ catalyst, as chosen in this work, major concerns for catalyst poisoning are sulfur compounds, phosphorous compounds, chlorine compounds and oxygen. In the context of flue gas capture and direct air capture, controlling sulfur compounds and oxygen content will be most relevant, which can be accomplished with available technologies.

2.2 Economic Analysis

2.2.1 Capital Cost Estimation

To evaluate the economics of the plants on a 2022-dollar cost basis, Equation (E 2-1) is used with an annual escalation rate of 3%.

$$EC = RC \cdot (1 + AER)^{SY-RY} \quad (\text{E 2-1})$$

EC is the escalated cost, RC the reference cost, AER the annual escalation rate, SY the scaled year and RY the respective reference year. In order to obtain cost estimates at plant scale, the following equation is used.

$$SC = EC \left(\frac{SP}{RP} \right)^u \left(\frac{TS}{TR} \right)^{0.9} \quad (\text{E 2-2})$$

SC represents the scaled cost, EC represents the escalated cost, SP is the scaled parameter and RP is the reference parameter used to scale the equipment. u is the scaling exponent. The scaling exponent is equipment specific and typically around 0.6. Equipment specific scaling exponents be found in literature¹⁹ for a large variety of plant equipment. TS is the number of trains/purchased quantity of each equipment of the scaled plant and TR is the number of trains/purchased quantity of each equipment in the reference case. The exponent 0.9 accounts for the cost reduction when more than one of the same piece of equipment is purchased and installed.

The sum of all equipment at relevant scale is the total plant cost (TPC) which includes cost of process equipment, on-site facilities and infrastructure in support of the plant, both direct and indirect labor, and engineering services, procurement and construction (EPC). Detailed equipment design, contractor permitting and project/construction management costs are included in the EPC. The TPC also includes process contingencies and project contingencies, which typically vary between 0–30% depending on the type and novelty of equipment and application. Data found in literature^{17,18} have been used to establish the basis for contingencies. The expected accuracy of this methodology for cost estimation is expected to be in the range of -30% to +50%; however, scaling by more than a factor of two can increase the error margin.

Steam Cracker Plant Equipment

Several cost correlations exist for estimating the plant cost of a steam cracker plant for ethylene production.²⁰⁻²² Also, recent news coverage provides some insights into overall plant costs,²³ however, detailed break downs of unit operations are not readily available. A more detailed analysis of two U.S.-based ethane steam crackers in Pennsylvania and the Gulf Coast has been conducted by FCBI Energy¹⁸ at a 1.5-million-ton-per-year scale. In their work, the plant is divided into 19 individual equipment categories (Columns, Process Vessels, Pumps, Compressors & Fans & Blowers, Heat Exchangers, Tanks, Material Handling, Water Treatment, Miscellaneous Equipment, Electrical Equipment, Instrumentation Devices, Site Improvements, Buildings & Foundations & Platforms, Refractory, Piping, Insulation, Electrical & Instrumentation, Paintings & Coatings, Other Miscellaneous Cost). In this work unit operations were sized based on individual equipment cost relationships^{19,24-26} informed by thermodynamic and kinetic modelling. Additionally, some auxiliary equipment categories from FCBI Energy¹⁸ were used to estimate costs for non-process-related equipment such as Tanks, Material Handling, Water Treatment, Miscellaneous Equipment, Electrical Equipment, Site Improvements, Buildings, Foundations & Platforms, Electrical & Instrumentation as well as some other miscellaneous cost, which were scaled to the according plant size

using scaling exponents from.¹⁹ After applying the respective scale correction factors, fees, contingencies, etc., the equipment is categorized into the following major categories: Steam Cracker, Steam Cycle, Cooling Tower, Gas Processing and Compression, Refrigeration Cycles, Cryogenic Gas Separation, Materials Handling, Electrical & Instrumentation, Site Improvements, Structures & Foundations, and Misc. Equipment & Expenses. Individual maintenance factors are applied to derive the annual maintenance costs whereby 35% of the maintenance cost accounts for maintenance labor and the remaining 65% for maintenance materials.¹² The resulting plant cost from this approach falls within the expected range of the above-mentioned overall plant cost estimates. Cost correlations of the form $Constant \cdot Basis^{Exponent}$ for major process units have been derived and are presented in **Table 2-3**.

Table 2-3: Total Plant Cost (TPC)* Correlations for Major Process Units in US\$ (2022)

Process Unit	Basis (based on design capacity)	Constant	Exponent
Steam Cracker	Heat Absorbed, MW	1,861,977	0.870
Steam Cycle	Electric Power Generation, MW	2,081,527	0.732
Cooling Tower	Water Flow Rate, kg/s	185,870	0.652
Gas Processing and Compression	Compression Power, kW	29,152	0.839
Refrigeration Cycles	Total Cooling Load, kW	65,956	0.770
Cryogenic Gas Separation	Gas Flow Rate of Mixture Entering, kmol/h	470,463	0.612
Water Treatment	Raw Water Intake, t/year	24	0.800
Materials Handling	Feedstock, metric tonnes/year	7,313	0.614
Electrical & Instrumentation	Feedstock, metric tonnes /year	29,761	0.600
Site Improvements	Feedstock, metric tonnes /year	26,979	0.600
Structures & Foundations	Feedstock, metric tonnes /year	34,205	0.600
Misc. Equipment & Expenses	Feedstock, metric tonnes /year	23,068	0.600

*TPC includes EPC, process contingencies, project contingencies, etc.

OCM Plant Equipment

Most of the gas processing and product separation equipment in the OCM plant is the same as in the ethane steam cracker plant and the same costing methodology is used. Electrochemical cells that support the OCM reaction are still in an early development stage and an active area of research, meaning that no commercial cells for this application are available. The materials for anode, electrolyte and cathode are ceramics commonly employed in commercial solid oxide fuel cells, such as lanthanum strontium manganite (LSM), lanthanum strontium gallium magnesium oxide (LSGM), lanthanum strontium cobalt ferrite (LSCF) or yttrium-stabilized zirconia (YSZ).^{8,9,27,28} Thus, cost estimates are based on current anode supported SOFC cells using LSM, LSCF, YSZ²⁹ (due to this uncertainty a cell cost sensitivity analysis is included in this study). For this study the cells are designed to have an active area of 30 cm x 30 cm whereby 200 cells are combined to a stack in reference to current development goals for large scale SOFC applications. The stacks are assumed to be installed in modules of 22 stacks whereby each module has its own housing with insulation. Based upon a medium production capacity as defined in literature,²⁹ the respective stack cost is \$16,856 (excl. engineering, procurement, contingencies, housing, balance-of-stack (BOS), installation, power electronics, etc. which are accounted for separately to arrive at the total cost). No economies-of-scale is assumed for the modular BOS installation. Power electronics, housing, balance-of-plant (BOP) and installation costs are based upon values presented in literature.²⁹ Other BOP equipment, such as blowers and heat exchangers, are estimated using individual cost correlations, as previously mentioned. As SOCs are susceptible to sulfur poisoning, an expandable adsorption process is used upstream of the OCM unit. It is a lead-lag unit using TDA's SulfaTrapTM R2F sorbent. Cost for the unit is based on inhouse estimates. The monoethanolamine (MEA) process for CO₂ removal is integrated into the simulation to determine performance and energy consumption. The cost basis for the unit is provided in literature.³⁰ Lastly, the

methanation section is sized based on catalyst requirement (also see Methanation section) of the individual reactors and heat exchanger needs using the above-mentioned cost approach applied to process vessels and heat exchangers.

2.2.1 System Analysis

The operating period for all plants is assumed to be 30 years with a capital expenditure period of 4 years for a scale of 400,000 metric tonnes per year (MTPY). For reference, this expenditure period is one year less than the construction period of a 1,500,000 MTPY facility in Pennsylvania (including site improvements) which is 5 years.³¹ The distribution of overnight capital over the capital expenditure period is assumed to be: 20%, 35%, 25%, 20% (similar to large scale energy projects¹⁷). The financing structure is assumed to be similar to DOE's integrated gasification combined cycle (IGCC) and energy systems studies. The total overnight capital is assumed to be 100% depreciable (20 years, 150% declining balance).¹⁷ The project is assumed to be financed with 45% equity and 55% debt.¹⁷ With a real dollar cost of 7.84% and 2.94%, the after-tax weighted average cost of capital is 4.74%.¹⁷ Tax rates are 21% (federal) and 6% (state).¹⁷ Investment tax credits are not considered in the financial analysis as well as tax holidays are assumed to be 0 years. The resulting capital charge factor (CCF) is 0.080 and the following equation can be used to calculate the real first-year levelized cost of ethylene (COE).

$$COE = \frac{(CCF)(TOC) + OC_{\text{fix}} + (CF)(OC_{\text{var}})}{(CF)(MTPY)} \quad (\text{E 2-3})$$

where *COE* is the first year's levelized cost of ethylene, *CCF* the capital charge factor, *TOC* the total overnight capital, *OC_{fix}* the total fixed annual operating costs, *OC_{var}* the total variable annual operating costs, *CF* the plant capacity factor and *MTPY* the annual ethylene production at 100% CF.

The TOC includes the TPC, preproduction costs (6 months labor, 1 month maintenance materials, 1 month non-fuel consumables, 1 month waste disposal, 25% of 1 month energy & feedstock cost at 100% CF and others accounting for an additional 2% of the TPC),³² inventory capital cost (60 day supply of consumables as well as spare parts which are estimated to be 0.5% of the TPC),³² initial catalyst, sorbent & chemical costs, land (assumed to be \$900,000 in total),³² other owner's costs (preliminary feasibility studies, economic development, legal fees, permitting costs, etc. are assumed to be 18.4 % of TPC),^{18,32} and financing costs (2.7% of TPC).³²

Fixed operating costs (*OC_{fix}*) are annual operating costs that are independent of the capacity factor and include labor costs as well as property tax and insurance. Ethylene plants with naphtha as feedstock built between 1955-1972 had between 43 and 63 operators (capacity: 10,000 – 450,000 tons/year).²⁰ Considering the lower complexity of plants with ethane feedstock and the higher degree of automation of today's plants, the steam cracker plant is assumed to be controlled by 45 skilled operators per shift (3 shifts per day) who are paid an hourly salary of 40.85 \$/h (escalated from literature).¹²

For the OCM plants, the same number of operators is assumed as most of the plant equipment between the two cases remains identical. Differences in plant design are the cracking section of the ethane steam cracker furnace, which is replaced with an SOC unit and its additional equipment for the cathode oxidant stream, as well as an MEA CO₂ removal unit. SOC control is assumed to be highly automated, similarly to today's SOFC systems, and that the same number of operators controlling the cracking section of the furnace in the steam cracker plant is sufficient to operate the SOC and CO₂ removal unit in the OCM scenarios.

The operating labor burden is estimated at 30% and the overhead charge rate is assumed to be 25% at a plant capacity factor of 1.0.¹⁷ Labor related to maintenance activities is accounted for separately as 35% of the maintenance cost. The maintenance cost itself is based on individual cost relationships.¹⁷ Administrative

and support labor are projected to be 25% of operating and maintenance labor. Other fixed costs include property tax and insurance costs, which are typically around 2% of the TPC.¹⁷

Variable operating costs (OC_{var}) such as maintenance costs are dependent on the availability of the plant. Other variable costs that must be considered are consumables such as fuel, sorbents and catalysts. Fuel costs for the various fuels used in this study are summarized in **Table 2-4**. All costs shown in the table are escalated to the year 2022 using a 5% annual escalation rate.

Table 2-4: Cost Summary of Fuel and Consumables

Fuel	Value	Unit	Cost Year	Reference
Natural Gas	4.00	\$/MMBtu	2021	33
Ethane	0.26	\$/kg	2021	33
Hydrogen (Sales Price)	1.80	\$/kg	2022	34
Carbon Dioxide Feedstock	0.20	\$/kg	2022	assumed
Electricity	48.92	\$/MWh	2021	35
Raw Water	0.441	\$/tonne	2011	17
32% NaOH	0.661	\$/kg	2018	12
MEA Solvent	2.48	\$/kg	2007	36
Pt-Ag Cat. (C ₂ H ₂ -Hydrog.)	24.28	\$/kg	2016	37
Desulfurization Sorbent	23.75	\$/kg	2017	26
Methanation Catalyst	21.55	\$/kg	2016	38
Solid Waste Disposal	0.20	\$/kg	2017	39
Liquid Waste Disposal	0.03	\$/L	2018	40

2.3 Environmental Impact Assessment

Local plant site sulfur emissions are estimated based on typical sulfur concentrations found in natural gas, which are assumed to be emitted as SO₂. Moreover, direct plant site CO₂ emissions are established in the process analysis of the individual chemical consumption and utilization rates. Indirect CO₂ emissions from electricity production are based on an average US grid emission factor of 386 kg_{CO2}/MWh,¹⁵ from natural gas production are based on an average US high-pressure natural gas emission factor of 0.441 kg_{CO2}/kg_{NG},¹⁶ and from ethane production are based on an average global CO₂ emission factor of 0.750 kg_{CO2}/kg_{Ethane}.¹⁶

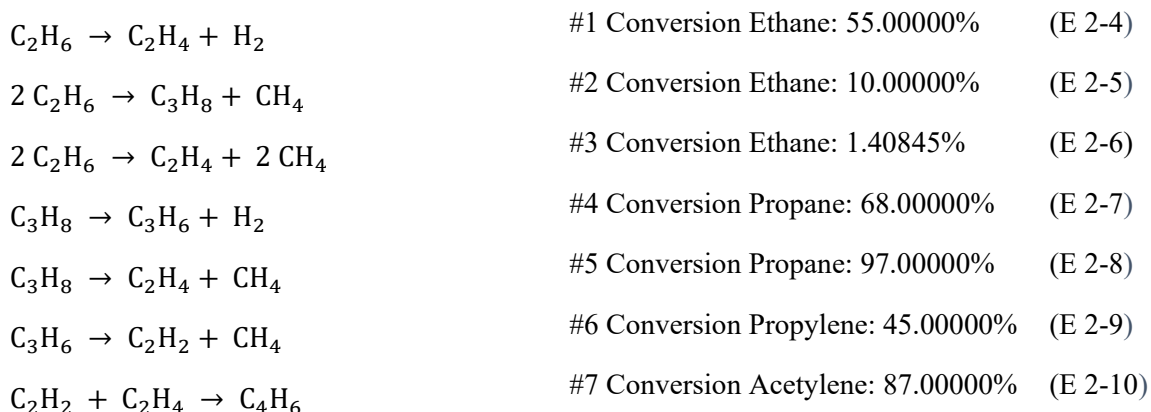
2.4 Property Methods

For the simulation, various thermodynamic property methods are selected based upon the component properties. These property methods are readily available in ProSim. For the cracked gas and hydrocarbons, the Peng-Robinson equation-of-state is used with Boston-Mathias alpha functions. However, ideal gas behavior is assumed for the quench tower, gas compression and intercooling to predict water condensation more accurately. The MEA-based CO₂ removal unit uses the Amines and Acid Gas model, and the caustic wash tower uses the Electrolyte NRTL model. Pure water and steam are represented by the NBS/NRC steam tables.

2.5 Process Description and Modeling of Process Units unique to the Ethane Steam Cracker Plant

2.5.1 Steam Cracker

The steam cracker operates near ambient pressure (cracking reactor and firebox). Single pass conversion rates of 60% are typical for industrial scale ethylene cracker plants.⁴¹ The reactions and conversion rates are adopted from literature⁴² and are summarized below (chemical reaction 8 from literature has been dropped since it's a combination of reactions 1, 2, 3 & 4). The sequential conversion rates and reaction sequence is provided below.



The inlet temperature to the cracker is 596 °C and the cracker outlet temperature is 865 °C which was established based on available literature data from a steam cracker that uses naphtha as feedstock.⁴³ The feedstock is preheated using the furnace flue gas. Gas-gas heat transfer coefficients are typically low and a pinch temperature of 17 °C has been assumed.⁴³ Steam cracking is kinetically controlled and the reaction products need to be quenched to a temperature of about 427 °C to stop the reactions.⁴³ Heat from the transfer line exchanger and the furnace's flue gas are recovered by generating steam for a steam cycle. The steam turbine inlet temperature is 540 °C (at 120 bar), which is typical for today's 20-60 MW-class steam turbines, such as Siemens' SST-400/300/200. The steam turbine back pressure is assumed to be 0.06 bar (water-cooled condenser). For a 400,000 MTPY ethylene plant the steam cycle generates approximately 30–35 MW of electricity; thus, a design with 2 feedwater heaters (+1 deaerator) is chosen for heating the water to 190 °C prior to the economizer (80 MW PC plants use typically 4, while 550 MW plants typically use 7)⁴⁴. Assumed compressor efficiencies (isentropic) for the cracked gas compressors are 72–74% (based on centrifugal compressors, gas-flows of smaller than 100,000 m³/h).

Steam to Hydrocarbon Ratio. Literature reports steam to hydrocarbon ratio values ranging from 0.3–1.0 kg/kg. Borralho⁴⁵ reports a steam to propane ratio of 0.3 kg/kg, and Karimzadeh⁴³ reports a steam to hydrocarbon ratio of 0.7 kg/kg using naphtha as feedstock. Froment et al.^{41,46} experimented with ethane and propane mixtures with steam to hydrocarbon ratios ranging from 0.4–1.0 kg of steam/kg of hydrocarbon and references an industrial ethane cracking unit that uses a steam to ethane ratio of 0.4 kg/kg.⁴¹ The quantity of steam needed varies not only by feedstock but also depends upon the severity of the cracking reactions and the design of the heat coils.⁴⁷ In general, steam dilution lowers the partial pressure of the hydrocarbons, which improves the olefin yield. Furthermore, steam helps to reduce the amount of carbon deposition and helps to reduce the catalytic effects of the metallic reactor walls.⁴⁷ Insufficient amounts of steam can lead to significant coke deposition and increases reactor downtime (coke needs to be burned off in regular intervals). An analysis of the thermodynamic gas stability shows that the operating regime of the cracker is almost always in the unstable gas region, where carbon deposition is thermodynamically favored (see **Figure 2-1**). Operating the cracker in the unstable gas region does not mean that carbon deposition

will occur, it is simply an indicator that carbon deposition can occur if reaction mechanistic pathways to solid carbon are accessible and retention times are sufficiently long. The green line in **Figure 2-1** represents the ethane-steam dilution curve. While steam dilution is favorable with respect to reaction yield and carbon deposition, large amounts of steam dilution are undesirable due to the thermal penalty associated with feed dilution using steam, resulting in a reduced electricity generation of the steam cycle. In this work a conservative steam-to-ethane-ratio of 0.70 kg of steam/kg of ethane is chosen to reduce carbon deposition, reduce reactor downtime and maximize olefin yield.

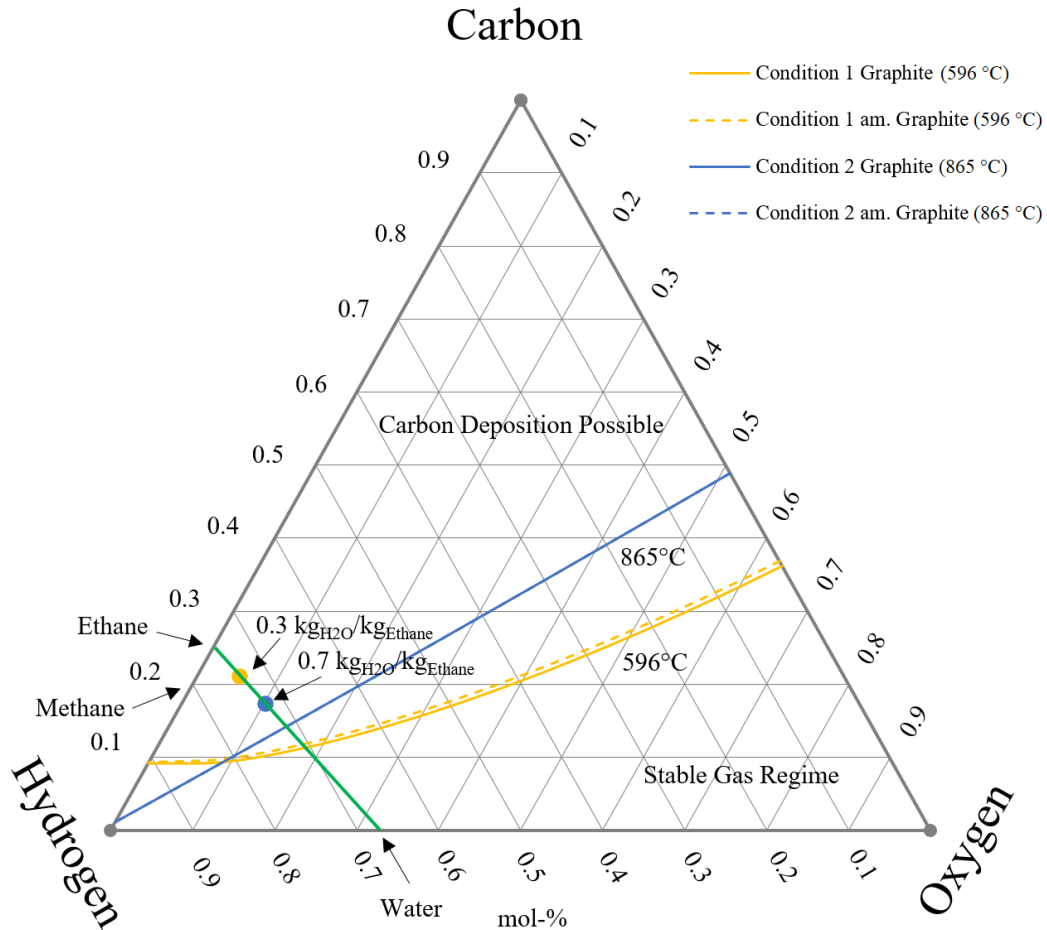


Figure 2-1: Steam cracker carbon deposition equilibrium.

2.5.2 Acetylene Hydrogenation

Acetylene hydrogenation is needed downstream of the deethanizer and is part of the product separation process. It is accomplished using a Pt-Ag catalyst supported on α -Alumina (e.g. Südchemie Olemax 201). Carbon monoxide is a poison for the catalyst and the hydrogen feed stream needs to be purified in a PSA system before adding it to the hydrogenation reactor.⁴⁷ The reactions considered in this work are the hydrogenation reactions of acetylene and ethylene.



Conversion rate and amount of catalyst required are based upon reaction kinetics developed by Dehghani et al.⁴⁸

$$r_{acetylene} = 0.0197 \frac{\text{mol}}{\text{g s bar}^{1.3}} \exp \frac{11641.3 \text{ J/mol}}{RT} \frac{p_{C_2H_2}^{0.4} \cdot p_{H_2}^{0.9}}{(1 + K_{C_2H_2} \cdot p_{C_2H_2})^{1.1}} \quad (\text{E 2-13})$$

$$r_{ethylene} = 0.0098 \frac{\text{mol}}{\text{g s bar}^{2.8}} \exp \frac{6067.7 \text{ J/mol}}{RT} \frac{p_{C_2H_4}^{1.4} \cdot p_{H_2}^{1.4}}{(1 + K_{C_2H_4} \cdot p_{C_2H_4})^{1.6}} \quad (\text{E 2-14})$$

With

$$K_{C_2H_2} = 2.128 \frac{1}{\text{bar}} \exp \frac{2983.8 \text{ J/mol}}{RT} \quad (\text{E 2-15})$$

$$K_{C_2H_4} = 0.7295 \frac{1}{\text{bar}} \exp \frac{3621.0 \text{ J/mol}}{RT} \quad (\text{E 2-16})$$

For model simplification, a catalyst effectiveness of 0.3 has been assumed and the logarithmic mean partial pressures have been used. A system sizing factor of 50% has been applied to account for catalyst deactivation over a 6-year operating period. The resulting acetylene and ethylene conversions are 99.3000% and 0.0498% respectively.

2.6 Process Description and Modeling of Process Units unique to the OCM Plant

2.6.1 Natural Gas Desulfurization

In the steam cracker scenario, natural gas is used as supplemental fuel in the steam cracker furnace and desulfurization is not needed. In the OCM plant, however, natural gas is used as feedstock for the OCM reaction in the electrochemical cell, which requires desulfurization in order to prevent catalyst poisoning. The desulfurization unit is a two-vessel lead/lag system filled with an expandable sorbent that uses a highly dispersed metal oxide phase deposited on the outer surface of a porous ceramic support. The bed is designed for 365 days and can reduce sulfur compounds, such as hydrogen sulfide and mercaptans, down to less than 0.1 ppm.

2.6.2 Combustion Furnace

Similarly to the firebox of the steam cracker, the combustion furnace in the OCM plant operates near ambient pressure. In the combustion furnace undesirable side products are converted to heat necessary for feedstock preheating and steam co-generation. Furthermore, a fraction of the product gas recycle stream needs to be purged and combusted to avoid the buildup of inert gases and trace components. Gas-gas heat transfer coefficients are typically low and a minimum pinch temperature of 17 °C has been assumed.⁴³ To minimize cracking side reactions, preheating of the hydrocarbon feedstock for the OCM reaction is limited to 596 °C (consistent with ethane steam cracker since the recycle contains a significant amount of ethane). The solid oxide cell operates at 750-850 °C (similar to the cracking section of the ethane steam cracker) and the anode outlet gas, which contains the ethylene product, quickly needs to be quenched to a temperature of about 427 °C⁴³ to prevent side reactions. To achieve sufficiently high cooling rates, the anode off-gas is cooled in a transfer line exchanger while raising steam rather than using the anode off-gas to pre-heat the hydrocarbon feedstock (boiling heat transfer coefficients are orders of magnitude higher than gas-gas heat transfer coefficients). The furnace wall is protected by water tubes acting as an economizer. Additional heat from the transfer line and the furnace's flue gas are recovered by generating

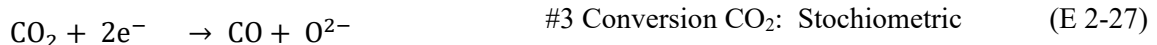
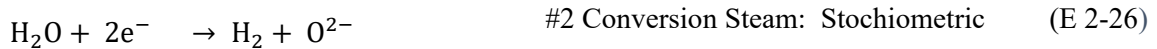
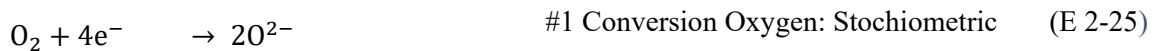
steam for a steam cycle. The steam turbine inlet temperature is 540 °C (at 120 bar), which is typical for today's 20-60 MW-class steam turbines, such as Siemens' SST-400/300/200. The steam turbine back pressure is assumed to be 0.06 bar (water-cooled condenser). For the OCM-based ethylene plant the steam cycle design is kept consistent with the ethane steam cracker design, and a design with 2 feedwater heaters (+1 deaerator) is chosen for heating the water to 190 °C prior to the economizer.

2.6.3 Solid Oxide Cell for Electro-chemical Coupling of Methane

The electro-chemical half reaction for the cell can be written as shown below. The methane conversion rates are based on experimental data from literature⁹ at 850 °C for the single pass 1.6 V case with 0.075Fe-SFMO. The overoxidation of CO and H₂ are assumed to be the same as the CH₄ overoxidation which is established based on the aforementioned experimental data. The ethane dehydrogenation reaction conversion rate is based on experimental data from literature²⁷ at 1.6 V and the same conversion rate has been assumed for the C₃₊ components (data are at 600 °C with CO₂ as oxidant). The water gas shift reaction is assumed to be in equilibrium at these temperature as suggested by literature⁴⁹; yet, small discrepancies in gas outlet composition persist. The maximum permissible temperature increase across the cell is limited to 100 °C, which is typical for current SOFC technology. The cell inlet temperature is assumed to be 750 °C, leading to a maximum outlet temperature of 850 °C. The oxidant flow rate, and thus, the oxidant utilization, is adjusted to meet this temperature constraint. The pressure drop across the cell is assumed to be 3% for both anode and cathode.



The OCM anode conversion rates are established for a voltage of 1.6 V (vs. NHE) using air as oxidant. To account for changes on the cathode when switching from air to steam as oxidant, it has been found that the activation overpotential for H₂O reduction is comparable to O₂,⁵⁰ and thus, only the voltage needs to be adjusted according to the Nernst equation to maintain the respective overpotentials.



The current density for all cases is assumed to be 0.95 A/cm^2 ,⁹ since corrections for the H_2O overpotentials and thermodynamics have been applied, resulting in operating voltages of 1.60 V (vs. NHE) for air, and 2.48 V (vs. NHE) and 2.51 V (vs. NHE) for H_2O as oxidant (H_2 co-production and CO_2 utilization scenarios respectively, both use H_2O as oxidant). Carbon dioxide reduction, as shown in reaction (E 2-27), has initially been considered for the CO_2 utilization scenario; however, it became clear from the plant integration that generating CO in this plant configuration is not particularly attractive as CO cannot be converted to ethylene via OCM as seen from equations (E 2-28)–(E 2-29). Thus, for the CO_2 utilization scenario, CO_2 is instead methanized using H_2 , generated via (E 2-26), rather than directly reduced to CO in the solid oxide cell. Also note, that CO methanation is highly exothermic making it challenging to thermally integrate CO-methanation reactors without exceeding thermal catalyst constraints. Furthermore, even if this heat integration challenge is solved, sufficient quantities of H_2 are needed for the methanation of CO. Reaction (E 2-30) is not able to provide sufficient H_2 for such a scenario. Direct CO_2 reduction would be more attractive if the OCM plant is coupled with another process that utilizes CO e.g. methanol production (if H_2 is available) or carbonylation syntheses.

Cell degradation is estimated with a first-order degradation of 0.2% per 1000 h (commonly used for SOFC technology). Thus, stacks will be replaced after an operating period of 10 years which requires a spare stack installation of 14.6% to compensate for the performance loss during this period.

Pre-heating of the anode inlet gas in the combustion furnace via heat exchangers is limited to $596 \text{ }^\circ\text{C}$ due to concerns about cracking side reactions. To further increase the anode inlet temperature, an anode recycle is used employing ejectors, which raises the inlet temperature to about $685 \text{ }^\circ\text{C}$ (moreover anode off-gas recirculation reduces the risk of carbon deposition). Ejectors are inexpensive and are installed upstream in close proximity to each stack to minimize the time the high temperature gas has to travel to the solid oxide cell. The anode inlet temperature of $685 \text{ }^\circ\text{C}$ is still lower than the target inlet temperature of $750 \text{ }^\circ\text{C}$; however, considering that the cathode mass flow is approximately 10 – 25 times larger than the anode mass flow and that the anode gas has to travel through the stack housing/channels before reaching the actual ceramic cell, it is assumed that the anode gas will reach its desired inlet temperature as it enters the actual cell.

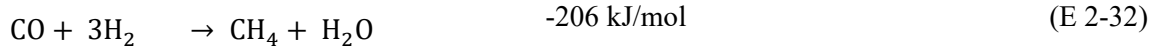
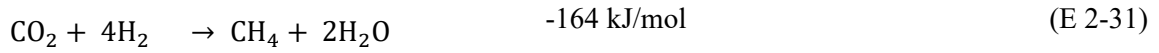
2.6.4 Carbon Dioxide Separation

Carbon dioxide needs to be removed upstream of the cryogenic gas separation unit as CO_2 has vapor pressure properties between those of ethane and ethylene, and a triple point of $-56.4 \text{ }^\circ\text{C}$ and 5.2 bar, which makes it difficult to separate CO_2 in the cryogenic gas separation unit and poses a risk of forming solid CO_2 in the low temperature section of the cold box. Thus, a MEA process has been selected for bulk CO_2 removal from the syngas upstream of the gas compression section, which further reduces compressor size and compression power. Any CO_2 trace amounts will be removed in the caustic scrubber downstream of the compression train. The absorber, which requires a chemical solvent such as MEA, operates near ambient pressure with a syngas inlet temperature below $35 \text{ }^\circ\text{C}$. The stripper operates at 2 bar to reduce downstream CO_2 compression work and the reboiler bottoms temperature is $119 \text{ }^\circ\text{C}$. The resulting MEA concentration is around 11 mol-%, which is cooled to below $40 \text{ }^\circ\text{C}$ before it is reintroduced into the absorber. These operating parameters are consistent with other MEA literature⁵¹ and achieve CO_2 removal down to trace amounts with a CO_2 product purity of greater than 96 mol-%.

2.6.5 Methanation

While CO co-production on the cathode has been ruled out as a means of CO_2 utilization in this plant due to the above-mentioned reasons, CO is still produced on the anode which will eventually be used in the methanation section together with a CO_2 feed. The methanation reactions of CO_2 and CO to CH_4 are

strongly exothermic (CO is 26% more exothermic than CO₂) and the reactor needs to be thermally controlled to not exceed the operating range of the catalyst. While chemical reactors can be cooled internally (often referred to as isothermal reactors), it is often preferred to use adiabatic bed reactors due to their simplicity. For reactions like the CO₂ and CO methanation reactions, these reactors are governed by chemical equilibrium. Thus, to control the temperature increase in the first bed for feed streams high in H₂ and CO, it is common practice to recycle some of the product gas back to the reactor inlet to dilute the reactants.⁵² Most methanation catalysts are limited to an operating temperature of 550 °C; however, recent developments have shown successful pilot scale testing of catalysts up to 675 °C.⁵³ The inlet temperature for methanation catalysts is typically around 300 °C.⁵⁴ To maximize CO₂ conversion, multiple reactors are used with intercooling. While for the OCM scenarios with air as oxidant and H₂ co-generation three reactor stages were sufficient, the OCM with CO₂ utilization requires four stages in order to reach satisfactory CO₂ conversion. This is because there is a higher CO₂ and H₂ concentration in the feed gas which leads to higher reactor outlet temperatures and less conversion.



To estimate the required catalyst volume, rate equations developed by Choi et al.⁵⁵ are used which are based on the Xu and Froment Model.

$$r_{\text{CO}_2} = \frac{15.1 \frac{\text{mol}}{\text{g s MPa}^{1.5}} \exp\left(-\frac{17800 \text{ J/mol}}{RT}\right) \frac{1}{p_{\text{H}_2}^{3.5}} \cdot \left(p_{\text{H}_2}^4 p_{\text{CO}_2} - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2}{K_{eq}}\right)}{\left(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4} + \frac{K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}\right)^2} \quad (\text{E 2-33})$$

$$r_{\text{CO}} = \frac{4290 \frac{\text{mol}}{\text{g s MPa}^{1.5}} \exp\left(-\frac{50900 \text{ J/mol}}{RT}\right) \frac{1}{p_{\text{H}_2}^{2.5}} \cdot \left(p_{\text{H}_2}^3 p_{\text{CO}} - \frac{p_{\text{CH}_4} p_{\text{H}_2\text{O}}}{K_{eq}}\right)}{\left(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4} + \frac{K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}}\right)^2} \quad (\text{E 2-34})$$

The calculation of the component specific van't Hoff adsorption equilibrium constants is described in literature.⁵⁵ The equilibrium constants for the methanation of CO₂ and CO have been derived from NIST data and can be approximated using the equations below (valid for 473–973 K, temperature unit used in the equation is K).

$$K_{eq,\text{CO}_2} = \frac{5.40 \cdot 10^{14}}{T^{6.52}} \cdot \exp\left(\frac{17400}{T} - 10\right) \quad (\text{E 2-35})$$

$$K_{eq,\text{CO}} = \frac{2.95 \cdot 10^9}{T^{5.52}} \cdot \exp\left(\frac{22850}{T} - 10\right) \quad (\text{E 2-36})$$

For model simplification, a catalyst effectiveness between 0.2 and 0.6 has been assumed depending upon the temperature range and approach to equilibrium, and logarithmic mean partial pressures have been used. System sizing factors between 4 and 1.5 have been applied to account for catalyst sintering effects (particularly relevant for high temperature reactors) and deactivation over the 4-year operating period (catalyst life).

2.7 Process Description and Modeling of Common Plant Process Units

2.7.1 Cooling Tower

Based upon the ambient conditions, the wet bulb temperature is 10.8 °C. Using a 5 °C temperature approach in the cooling tower,¹² a cooling water temperature of 15.8 °C is obtained. The cooling tower range is assumed to be 11 °C.¹² Evaporative losses in the cooling tower account for 0.8 % of the water circulation flow rate per 5.5 °C of range.⁵⁶ Drift losses are assumed to be 0.001% of the recirculation flow rate.⁵⁶ Blow down losses are estimated based on the assumption that drift losses are very small compared to other losses. Therefore, the following equation can be used to calculate the blowdown:⁵⁶

$$\text{Blowdown} = \frac{\text{Evaporative Losses}}{\text{Cycle of Concentration} - 1} \quad (\text{E 2-37})$$

Cycles of Concentration is a function of the water quality and describes the ratio of the concentration of dissolved solids in the blowdown water compared to the make-up water, a mid-range value of 4 is assumed in this study.¹² Water is internally recycled and the blowdown from steam drums is used as cooling tower makeup.

2.7.2 Cryogenic Gas Separation

For the propylene-ethylene cascade refrigeration cycle and the cold box, a pinch temperature of 4 °C is chosen⁵⁷ (ranges from 3–5 °C in the reference). The propylene refrigeration cycle uses a three-stage compressor to provide cooling at 5 °C, -20 °C and -36 °C. The ethylene refrigeration cycle provides cooling at two temperature levels: -71 °C and -102 °C. These are the typical temperature levels found in ethylene plants⁵⁷ and lower temperatures are only achievable if vacuum expansion would be considered; however, this would make the equipment significantly more expensive. The design of the cascade refrigeration cycle is consistent with literature.⁵⁷ To reach a condensate temperature of -121 °C in the last stage of the cold box, an expander/turbine is used.⁴⁵ An expander is able to extract more energy from the expansion gas than a throttling valve and allows the gas to reach lower temperatures. On the other hand, the overhead product from the demethanizer is only throttled in a valve, since this gas flow rate is comparatively small and sufficient cooling can be supplied by the gas stream expanded in the expander/turbine (reduction in capital cost, expanders are expensive). In the OCM scenarios, an expander/turbine is not needed at all as the lowest cold box temperature in these scenarios is set to -112 °C in order to improve the H₂ yield in the cold box off-gas (which is used for methanation). In the OCM scenarios significantly more CH₄ is present in the syngas, which is recovered in the overhead product of the demethanizer. The higher Joule-Thomson coefficient of CH₄ together with the higher mass flow in the OCM scenarios are able to provide sufficient cooling, after throttling, to cool the incoming gas stream in the last stage of the cold box down to -112 °C.

Using ethane as feedstock for ethylene production (ethane steam cracker scenario) leads to significantly higher ethylene yields as compared to other feedstocks, such as gasoil, naphtha, propane or butane and only small fractions of C₃₊ compounds.⁵⁸ Similarly, in the OCM scenarios only small amounts of higher hydrocarbons are produced. Thus, it is not worth it to separate the C₃₊ fraction to produce salable byproducts⁵⁹ and these undesirable side products are rather burned to offset some of the energy demand. The product separation is achieved in a demethanizer, deethanizer and a C₂-splitter. The tray efficiency of the distillation columns is assumed to be 0.70.⁶⁰ The demethanizer (48 trays) overhead product has a temperature of -97.5 °C and the bottoms product has a temperature of -0.7 °C. These values are in good agreement with literature (note: literature uses a variety of feedstocks): 30⁴², 65⁴⁵, 65⁶¹ trays; -113 °C⁴², -97.0 °C⁴⁵, -97.0 °C⁶¹ overhead; -4 °C⁴², 10.5 °C⁴⁵ bottoms. The deethanizer (50 trays) overhead product has a temperature of -8.8 °C and the bottoms product has a temperature of 81.3 °C. These values are in good

agreement with literature: 45⁴², 60⁴⁵, 60⁶¹ trays, -11 °C⁴², -17.6 °C⁴⁵, -11.0 °C⁶¹ overhead, 80 °C⁴², 76.2 °C⁴⁵ bottoms. The C₂-splitter (120 trays) overhead product has a temperature of -30.8 °C and the bottoms product has a temperature of -9.3 °C. These values are in good agreement with literature: 100⁴², 120⁴⁵, 71⁶¹ trays, -31 °C⁴², -31.1 °C⁴⁵, -30.0 °C⁶¹ overhead, -9 °C⁴², -9.7 °C⁴⁵ bottoms.

3. Results and Discussion

3.1 Ethane Steam Cracker Plant

3.1.1 Technology Performance Analysis

This section introduces the performance results of the ethane steam cracker plant which serves as the benchmark scenario for the electrochemical OCM cases presented in the following sections. The ethylene plant is designed for a capacity of 400,000 MTPY. Considering a capacity factor of 90% (plant downtime is due to maintenance and repairs) an annual ethylene production of 360,000 metric tonnes is obtained. In order to produce 360,000 MTPY, an ethane feed rate of 432,970 MTPY is necessary (resulting in a carbon yield of 85.7%), and an additional 19,230 MTPY of natural gas, equivalent to 28,770 kW_e, and 142,030 MWh/year of electricity are needed to satisfy the heat and electricity demand. At the same time, a heat load of 1,281,970 MWh/year is rejected in the cooling tower. The Rankine cycle is responsible for 30% of the cooling tower's heat rejection, the refrigeration cycle accounts for 28% and the remaining 42% are attributed to cracked gas quenching, inter-cooling and after-cooling. With 2,151,250 metric tonnes of annual water consumption, the cooling tower is responsible for 98% of the raw water withdrawal as well as the overwhelming majority of surface water discharge due to blowdown. The ethane to ethylene efficiency (based on LHV) of this plant is 82.53% and the overall efficiency (accounting for natural gas LHV and electricity) is 77.21%. A summary of the ethane steam cracker plant performance can be found in **Table 3-1**. A simplified process flow diagram that illustrated the plant configuration and heat integration can be seen in **Figure 3-1**. The corresponding state point stream data are provided in **Table 3-4**.

Table 3-1: Ethane Steam Cracker Plant Performance

Plant Design Capacity	Value	Unit
Ethylene Production Capacity	400,000	metric tonnes/year
Plant Capacity Factor	90	%
Actual Ethylene Production	360,000	metric tonnes/year
Consumables at 90% Capacity Factor	Value	Unit
Ethane	432,970	metric tonnes/year
Natural Gas	19,230	metric tonnes/year
Electricity	142,030	MWh/year
Raw Water Withdrawal	2,151,250	metric tonnes/year
NaOH Solution, 32%	620	metric tonnes/year
Energy Metrics at Full Load Operation		Unit
Ethane Feedstock Energy (LHV)	724,800	kW _e
Methane Feedstock Energy (LHV)	31,970	kW _e
Ethylene Product Energy (LHV)	598,180	kW _e
Electricity Consumption	18,010	kW _e
Cooling Tower Heat Rejection	162,600	kW _t
Efficiency Metrics	Value	Unit
Ethane to Ethylene Thermal Efficiency	82.53	%
Ethylene Overall Thermal Efficiency	77.21	%

A more detailed breakdown of electricity generating units and auxiliary power consumers is provided in **Table 3-2**. The Rankine cycle is a simple cycle without reheat operating at subcritical conditions (540 °C and 121.7 bar). To accommodate boiler feedwater heaters, deaerator, and other steam utilities inside the plant, steam extraction at three intermediate pressure levels is considered and the four steam turbine stages generate a combined power of 35,305 kW_e. An additional 315 kW_e of electricity is generated by an expander installed downstream of the last heat exchanger in the cracked gas cooling train; however, the main purpose of this expander is to provide additional cooling by extracting energy from the expanded gas rather than generating electricity. The largest auxiliary power consumer with 26,965 kW_e (50.2%) is the refrigeration system consisting of a propylene and an ethylene refrigeration cycle. The cracked gas compression accounts for 17,740 kW_e (33.1%) leaving 8,930 kW_e (16.7%) for other auxiliaries as shown in **Table 3-2**.

The design of the ethane steam cracker is based on state-of-the-art industrial facilities that make use of full thermal plant integration and on-site steam generation for additional power generation. While this co-produced electricity is not sufficient to cover the entire plant’s power consumption, it can increase the furnace efficiency. Typical gas fired furnace efficiencies range from 94% to 95%.⁶² With a sophisticated flue gas heat recovery system, an operating range described as “highly efficient” (up to 97%) can be achieved.⁶³

Additionally, the furnace fuel and ethane feedstock are pre-heated using waste heat, cooling the flue gas to an outlet temperature of 101 °C. As a result, the overall furnace efficiency is 96%-LHV in this work. The high furnace efficiency is further supported by using an excess air of 15%,⁴³ which is at the lower end of the typical 15–20% range. Furnace efficiency is an important factor contributing to the CO₂ intensity of ethylene production as the fuel is a mixture of natural gas (27% of flue gas carbon) and undesirable hydrocarbon byproducts (73% of flue gas carbon) mainly higher hydrocarbons, but also CO together with some H₂, which are side products of the cracking process.

Table 3-2: Ethane Steam Cracker Plant Electric Power Consumption at Full Load Operation

Electricity Generation	Value	Unit
Steam Cycle	35,305	kW _e
Cold Box Expander	315	kW _e
Total Electricity Generation	35,625	kW _e
Auxiliary Load		Unit
Furnace Air Blower	910	kW _e
Induced Draft Fan	2,000	kW _e
Steam Cycle Feedwater Pumps	920	kW _e
Quench Water Circulation Pump	175	kW _e
Quench Vent Compressor	50	kW _e
Caustic Recirculation Pump	5	kW _e
Cracked Gas Compression	17,740	kW _e
Cooling Water Circulation Pumps	1,075	kW _e
Cooling Tower Fans	790	kW _e
Hydrogen Boost Compressor	5	kW _e
Propylene Refrigeration Cycle	18,615	kW _e
Ethylene Refrigeration Cycle	8,350	kW _e
Miscellaneous Balance of Plant	3,000	kW _e
Total Electric Load	53,635	kW _e
Net Electricity Usage		Unit
Net Electricity Consumption	18,015	kW _e

With an ethylene design capacity of 400,000 MTPY and 90% utilization, the local CO₂ point source emissions are 188,634 MTPY, which equates to 0.524 kg_{CO2}/kg_{Ethylene}. This is in good agreement with literature data³⁻⁵ and close to the current EU benchmark case (more information in next paragraph). Sulfur emissions are small at this plant as the only source of sulfur are odorants from natural gas. Considering indirect CO₂ emissions from methane, ethane, and grid electricity, the CO₂ emission factor increases to 1.602 kg_{CO2}/kg_{Ethylene}. A summary of the ethane steam cracker plant emissions is provided in **Table 3-3**.

Other current efforts to reduce CO₂ emissions from ethylene production in the U.S. are options, such as replacing natural gas fuel with renewable, emission-free hydrogen.⁶ While this will certainly reduce the carbon footprint of ethylene by a considerable amount, this option will only be able to reduce the emission factor by 27% down to 0.383 kg_{CO2}/kg_{Ethylene} (based on this plant design). A new 1,500,000 MTPY ethylene mega project in Belgium – Project ONE, which is expected to come online in 2026 – aims to cut specific CO₂ emissions to 0.289 kg_{CO2}/kg_{High Value Chemicals}.³ This is possible by: 1) using ethane as feedstock over naphtha, 2) maximizing byproduct recovery (e.g. propylene, etc.) yielding in a carbon-efficiency of 86%, which appears to only be profitable at large scales, 3) “hyper-efficient clustering” with plant infrastructure (plant utilities, offices and workshops) to make use of waste heat from the furnace, 4) using H₂ produced during the cracking process as fuel to displace fossil fuels, and 5) by using renewable off-shore wind energy. With these measures Project ONE will be the lowest carbon footprint steam cracker in Europe within the European Emission Trading System, with a 53% CO₂ emission reduction versus the European emission benchmark case, which is currently at 0.680 kg_{CO2}/kg_{High Value Chemicals} (calculated by the 10% best performing plants¹). Once Project ONE comes online, this will lower the benchmark and encourage competitors to improve their carbon footprint, or they will have to purchase more emission rights.

Table 3-3: Ethane Steam Cracker Plant Emissions

Point Source Emissions at 90% Capacity Factor	Value	Unit
Carbon Dioxide	188,634	metric tonnes/year
Specific CO ₂ Emission	0.524	kg _{CO2} /kg _{Ethylene}
Sulfur Oxides (as SO ₂)	121	kg/year
Specific SO ₂ Emission	0.336	ppm-wt.SO ₂ /kg _{Ethylene}
Catalyst and Sorbent Disposal	3	metric tonnes/year
Caustic Discharge (Disposal)	2,291	metric tonnes/year
Surface Water Discharge	542,687	metric tonnes/year
Indirect Carbon Dioxide Emissions at 90% Capacity Factor	Value	Unit
Electricity-related CO ₂ Emissions	54,823	metric tonnes/year
Specific Electricity-related CO ₂ Emissions	0.152	kg _{CO2} /kg _{Ethylene}
Ethane-related CO ₂ Emissions	324,730	metric tonnes/year
Specific Ethane-related CO ₂ Emissions	0.902	kg _{CO2} /kg _{Ethylene}
Methane-related CO ₂ Emissions	8,483	metric tonnes/year
Specific Methane-related CO ₂ Emissions	0.024	kg _{CO2} /kg _{Ethylene}

¹ Note: most steam crackers in Europe currently use naphtha as feedstock

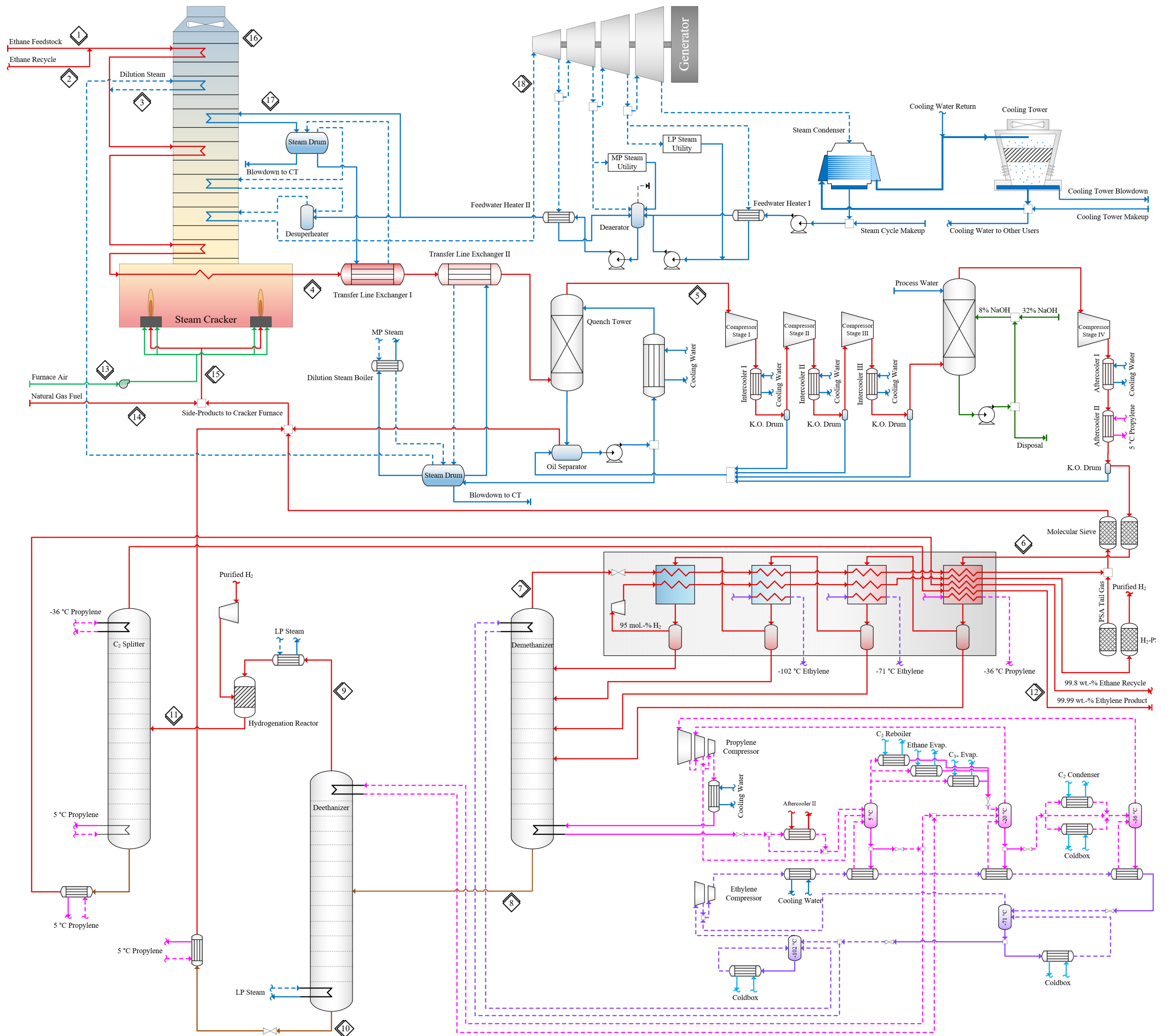


Figure 3-1: Simplified flowsheet of the ethane steam cracking process for ethylene production.

Table 3-4: Ethane Steam Cracker Plant State-Point Stream Data

Stream Number	Unit	1	2	3	4	5	6	7	8	9
Temperature	°C	15	12	192	865	32	16	-97	-1	-9
Pressure	bar	15.0	18.3	3.5	1.7	1.3	35.2	32.0	32.0	26.0
Mole Flowrate	kmol/h	1,826	1,192	3,528	8,299	4,967	4,738	154	2,864	2,820
Mass Flowrate	kg/h	54,918	35,868	63,563	154,716	94,665	90,156	1,569	83,597	81,523
Molar Vapor Fraction	–	1	1	1	1	1	1	1	0	1
Composition	mole-basis									
O ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
N ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
H ₂ O	–	0.00000	0.00000	1.00000	0.42513	0.04068	0.00000	0.00000	0.00000	0.00000
H ₂	–	0.00000	0.00000	0.00000	0.20586	0.34396	0.36057	0.49849	0.00000	0.00000
CO	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CH ₄	–	0.00000	0.00000	0.00000	0.01540	0.02569	0.02692	0.40635	0.00002	0.00002
C ₂ H ₆	–	1.00000	0.99853	0.00000	0.14541	0.24256	0.25168	0.00009	0.41565	0.42196
C ₂ H ₄	–	0.00000	0.00053	0.00000	0.20217	0.33672	0.35081	0.09507	0.56776	0.57666
C ₂ H ₂	–	0.00000	0.00002	0.00000	0.00034	0.00056	0.00058	Trace	0.00096	0.00098
C ₃ H ₈	–	0.00000	Trace	0.00000	0.00008	0.00013	0.00013	0.00000	0.00022	Trace
C ₃ H ₆	–	0.00000	0.00091	0.00000	0.00316	0.00536	0.00541	0.00000	0.00895	0.00039
C ₂ H ₃ -C ₂ H ₃	–	0.00000	Trace	0.00000	0.00244	0.00433	0.00389	0.00000	0.00644	Trace
SO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Total	–	1	0.99999	1	1	1	1	1	1	1
Stream Number	Unit	10	11	12	13	14	15	16	17	18
Temperature	°C	81	35	12	15	15	75	101	190	540
Pressure	bar	26.0	22.0	18.3	1.0	4.0	2.0	0.9	128.5	121.7
Mole Flowrate	kmol/h	44	2,820	1,628	9,912	141	2,106	11,199	8,210	8,277
Mass Flowrate	kg/h	2,075	81,530	45,662	285,072	2,439	12,226	297,299	147,901	149,120
Molar Vapor Fraction	–	0	1	1	1	1	1	1	0	1
Composition	mole-basis									
O ₂	–	0.00000	0.00000	0.00000	0.20824	0.00010	Trace	0.02403	0.00000	0.00000
N ₂	–	0.00000	0.00000	0.00000	0.78338	0.01600	0.00107	0.69360	0.00000	0.00000
H ₂ O	–	0.00000	0.00000	0.00000	0.00838	0.00003	0.01416	0.23381	1.00000	1.00000
H ₂	–	0.00000	Trace	0.00001	0.00000	0.00000	0.80937	0.00000	0.00000	0.00000
CO	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CO ₂	–	0.00000	0.00000	0.00000	0.00000	0.01000	0.00067	0.04855	0.00000	0.00000
CH ₄	–	0.00000	0.00002	0.00003	0.00000	0.93087	0.12286	0.00000	0.00000	0.00000
C ₂ H ₆	–	0.01290	0.42224	0.00006	0.00000	0.03200	0.00764	0.00000	0.00000	0.00000
C ₂ H ₄	–	Trace	0.57734	0.99990	0.00000	0.00000	0.02255	0.00000	0.00000	0.00000
C ₂ H ₂	–	Trace	Trace	Trace	0.00000	0.00000	0.00001	0.00000	0.00000	0.00000
C ₃ H ₈	–	0.01416	Trace	0.00000	0.00000	0.00700	0.00077	0.00000	0.00000	0.00000
C ₃ H ₆	–	0.55567	0.00039	0.00000	0.00000	0.00000	0.01176	0.00000	0.00000	0.00000
C ₂ H ₃ -C ₂ H ₃	–	0.41727	Trace	0.00000	0.00000	0.00000	0.00888	0.00000	0.00000	0.00000
SO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	Trace	0.00000	0.00000
Total	–	0.99999	0.99998	1	1	0.99600	0.99973	1	1	1

3.1.2 Economic Performance Analysis

In this section economic key parameters impacting capital cost, operating cost and the cost-of-ethylene (CoE) are discussed. The total plant cost (TPC) of the ethane steam cracker is \$1,113,565,000, which results in a specific plant cost of 2,784 \$/metric tonne of ethylene at a 400,000 MTPY plant scale. The cracker furnace with \$200,724,000 is the second most expensive process unit in the plant and has a share of 18.0% on the TPC. Steam cycle, cooling tower, and gas processing and compression account for \$28,252,000, \$37,982,000 and \$106,468,000 respectively. The refrigeration system is the most expensive process unit costing \$330,031,000 or 29.6% of the TPC. The cryogenic gas separation with its distillation columns costs \$83,525,000. Other plant units are 1) water treatment, 2) materials handling, 3) electrical and instrumentation, 4) site improvement, 5) structures and foundations, and 6) miscellaneous equipment and expenses, which account for 1) \$2,979,000, 2) \$23,146,000, 3) \$78,430,000, 4) \$71,099,000, 5) \$90,140,000, and 6) \$60,790,000. An illustration of the TPC breakdown can be found in **Figure 3-2**. Other

costs contributing to the total overnight capital are: preproduction cost, inventory capital cost, initial costs of catalysts, sorbents and chemicals, land, other owner’s expenses (such as project management, procurement and subcontracts, EPC warranty and EP fees) and financing costs which are summarized in **Table 3-5**. This leads to a total capital expenditure of \$1,404,353,000.

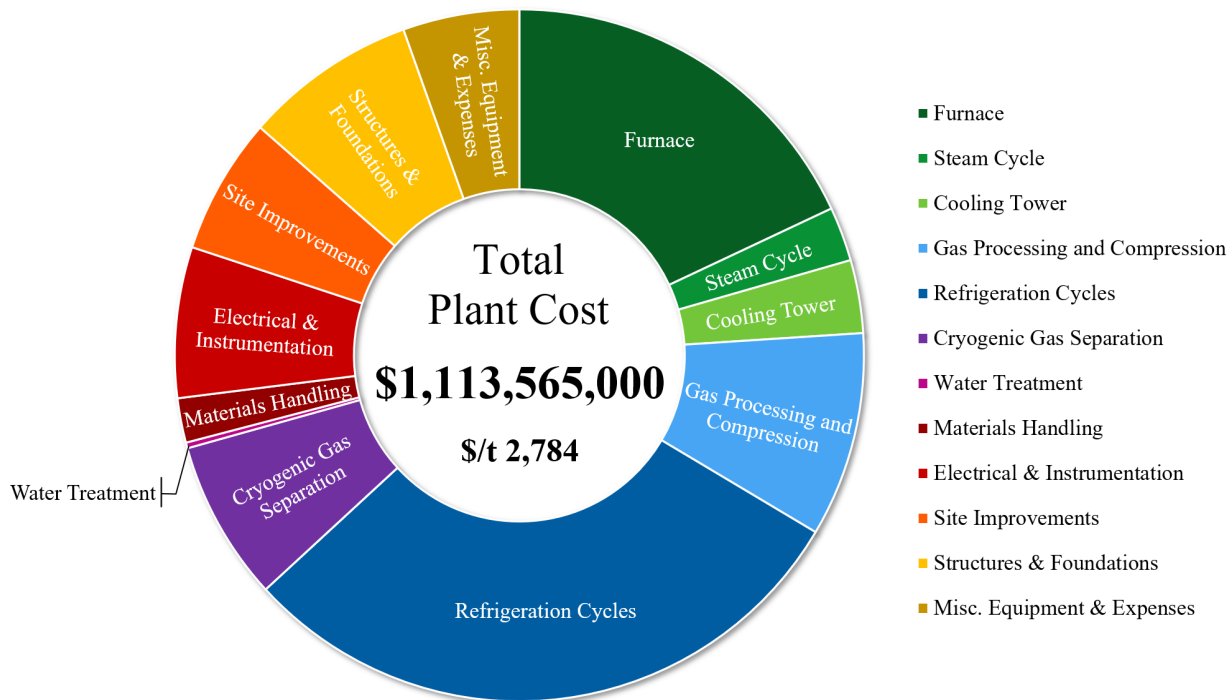


Figure 3-2: Breakdown of the ethane steam cracker total-plant-cost (TPC).

The operating costs can be divided into two categories; fixed operating costs that incur even when the plant is down, such as labor, tax and insurance, and variable operating costs that are coupled to the operation of the plant, such as feedstock cost, chemicals and maintenance materials. The annual labor costs are \$44,076,000, which includes operating labor with 45 operators per shift (59.4%), maintenance labor (20.6%) and administrative and support labor (20.0%). Property tax and insurance are estimated with 2% of the TPC which results in an annual cost of \$22,271,000.

The total variable operating costs are \$139,575,000 annually. As the primary feedstock for ethylene, ethane has the highest contribution to the variable operating costs with \$111,681,000 per year. The annual natural gas and electricity costs are \$3,463,000 and \$6,948,000. The levelized annual costs of the acetylene hydrogenation catalyst is \$74,000 assuming a six-year operating period before replacement. The annual water bill is \$1,623,000 and NaOH costs are \$502,000. Waste disposal accounts for \$84,000 per year. A summary of the results can be found in **Table 3-5**.

The resulting 1st-year levelized costs of ethylene for this 400,000 MTPY ethylene plant is \$884.09 per metric tonne of ethylene. The overnight capital cost is responsible for 35.3% of the CoE, the variable operating costs for 43.9% of the CoE and the fixed operating costs for 20.8% of the CoE. An illustration of the breakdown of the CoE with respective values is provided in **Figure 3-10**. In comparison, the average market price for ethylene in the years from 2017–2022 ranged from 697 \$/metric tonne in 2020 to 1,235 \$/metric tonne in 2022. While this analysis is based on the year 2022, with current ethane feedstock prices,

Table 3-5: Ethane Steam Cracker Plant Economics

Overnight Cost	Value	Unit
Total Plant Cost	1,113,565	\$ (thousands)
Preproduction Cost	48,754	\$ (thousands)
Inventory Capital Cost	5,956	\$ (thousands)
Initial Catalyst, Sorbent & Chemicals Cost	619	\$ (thousands)
Land	900	\$ (thousands)
Other Owners' Costs	204,493	\$ (thousands)
Financing Costs	30,066	\$ (thousands)
Fixed Operating Cost	Value	Unit
Annual Labor Cost	44,076	\$ (thousands)
Annual Tax and Insurance Cost	22,271	\$ (thousands)
Variable Operating Cost	Value	Unit
Annual Ethane Feedstock Cost	111,681	\$ (thousands)
Annual Natural Gas Cost	3,463	\$ (thousands)
Annual Electricity Cost	6,948	\$ (thousands)
Annual Maintenance Materials Cost	15,198	\$ (thousands)
Annual Chemical, Catalyst & Disposal Costs	2,284	\$ (thousands)
Economic Performance Metrics	Value	Unit
Specific Ethylene Plant Cost	2,784	\$/metric tonne ethylene
1 st Year Levelized Cost of Electricity	884.09	\$/metric tonne ethylene

this illustrates how competitive the ethylene market is; high impact of ethane feedstock prices, which account for 35.1% of the total CoE, as well as price uncertainty on the market. Just earlier this year (June 2022) margins for U.S. ethane steam crackers turned negative after recovering from negative profit margins in 2020 due to the pandemic and the near-term outlook for ethylene remains pessimistic for both supply and demand.⁶⁴ These thin profit margins drive the industry to larger and larger plant scales leading to the

commissioning of new mega projects with 1,500,000 MTPY and more. Larger plants profit from the economies of scale helping companies to gain a competitive edge over its competitors. In a 1,500,000 MTPY scale ethylene plant, the cost of ethylene can be reduced by over 22.3% to \$686.50 per metric tonne of ethylene solely due to the economies of scale without considering performance improvements in components such as compressors which can operate more efficiently at larger scales and further based on the assumption that the process train configuration and heat integration will not change. It also does not capture changes in operating labor/number of operators in the control room and assumes that the number of trains and unit operations remains constant; thus, same number of operators is needed. However, it captures changes in maintenance labor. The effects of the economies-of-scale upon the ethylene production price is shown in **Figure 3-3**.

When interpreting the cost analysis, it is important to understand that this cost estimation does not capture capital market dynamics such as demand and supply response as this analysis levelizes expenditures over a defined operating period of 30 years. While it is important to compare the results to real ethylene cost data to make sure the numbers are in the right ballpark, this analysis should be taken with a grain of salt when compared to real market data. The greater value of this economic analysis is that it enables a fair comparison between technologies based upon the same economic base parameters and environment.

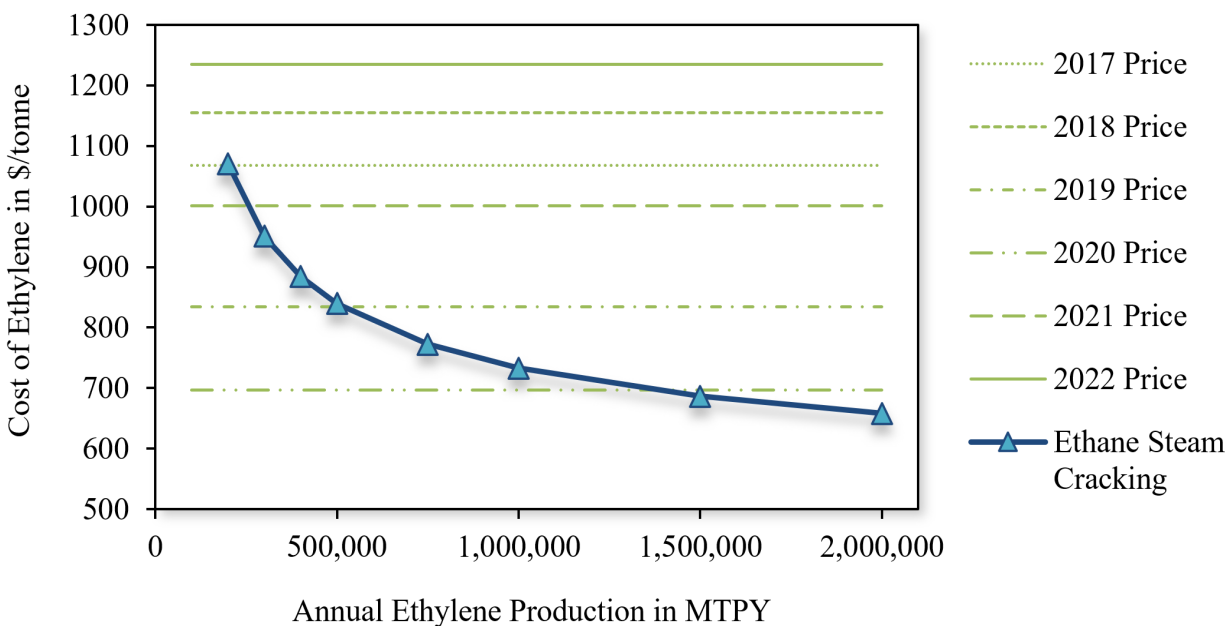


Figure 3-3: Economies of scale of the ethane steam cracker plant.

3.2 Electrochemical OCM Plant with Air as Oxidant

3.2.1 Technology Performance Analysis

The electrochemical OCM plant uses a very similar plant design as the ethane steam cracker plant, consisting of a furnace for preheating (however, without ethane cracking section which is replaced by the OCM unit), steam cycle, cracked gas processing and product separation. An overview of the system integration is shown in **Figure 3-5** together with state-point stream data, **Table 3-9**. Despite the fact that in the OCM plant no endothermic cracking reactions have to be supported by the furnace, the size of the furnace increased from 217 MW (incl. 107 MW for cracking) to 253 MW. This increase is due to the low single pass yield of the OCM process, which increases the recycle and as a consequence the recycle purge (necessary to avoid the buildup of trace components in the systems), as well as due to the formation of CO and H₂ byproducts that can only partially be converted back to CH₄ in a methanation section integrated into this plant design as shown in **Figure 3-5**. Because of this increase in byproducts and purge stream, which can only be utilized as fuel in the furnace to preheat feed streams or to generate steam, the furnace size has to be increased in the OCM scenario. With the substantial increase in furnace fuel gas, no supplemental natural gas fuel is needed in this case. In the OCM plants the additional heat is utilized by increasing the steam production, which increases the electric power generation from 35,305 kW_e (SOTA) to 98,700 kW_e. However, as a result of higher steam generation, which impacts the heat integration and exchanger design (constant pinch temperature), the furnace efficiency decreased to 94% in this scenario. All the 610,810 metric tonnes of natural gas used per year are used as feedstock in the OCM unit to produce ethylene. However, the OCM unit requires an additional 429,540 kW of electricity (at full load) to facility the OCM reaction. The cathode air supply alone is responsible for over 23.3% of this electric load in order to supply the cathode air at the required pressure of 1.6 bar. The challenge with current anode supported SOCs is that pressure differentials between the anode and cathode compartment are not acceptable due to the risk of cracking. Since the plant design requires the ethylene-rich product gas to be supplied at pressures of around 1.55 bar, there is no flexibility with respect to the cathode air supply pressure. However, future

metal supported SOC's could allow for more flexibility with respect to supply pressures as they are less prone to cracking. Another factor contributing to this high energy demand of the cathode air mover is the quantity of air needed in order to maintain acceptable thermal gradients within the SOC during operation (max. 100 °C temperature increase). The resulting air utilization is only 2.2%. The root of the problem is that current OCM cells operate at a voltage of 1.6 V (vs. NHE)⁹ in order to achieve appreciable reaction rates. Considering that the Nernst voltage of the reaction is -0.81 V (vs. NHE) and the thermoneutral voltage is -0.72 V (vs. NHE), the overpotentials are 2.41 V and the heating potential at this operating point is 2.32 V. Also, it is worth mentioning that operating the cell under such high overpotentials, which leads to electricity consumption rather than electricity production, leads to negative SOC efficiencies. In this specific case an efficiency of -233.5% is obtained. The interpretation of this is that 2.3 quantities of electricity are needed to degrade 1 quantity of chemical energy in the anode gas. Thus, electricity is really just used to accelerate the reaction kinetics and reduce the number of SOC's needed. However, this negative SOC efficiency does not mean that the overall plant efficiency is negative, although, the SOC efficiency certainly contributes to the overall plant efficiency. The plant's NG (LHV) to ethylene (LHV) conversion efficiency is 58.90%-LHV and considering the electric load (including the SOC electricity consumption) the plant efficiency is 40.47%-LHV. Key performance parameters of the OCM plant are summarized in **Table 3-6**.

Table 3-6: OCM (Air Oxidant) Plant Performance

Plant Design Capacity	Value	Unit
Ethylene Production Capacity	400,000	metric tonnes/year
Plant Capacity Factor	90	%
Actual Ethylene Production	360,000	metric tonnes/year
Consumables at 90% Capacity Factor	Value	Unit
Natural Gas Feedstock	610,810	metric tonnes/year
Electricity	3,646,220	MWh/year
Raw Water Withdrawal	6,080,390	metric tonnes/year
NaOH Solution, 32%	8,890	metric tonnes/year
MEA	1,440	metric tonnes/year
Energy Metrics at Full Load Operation	Value	Unit
Natural Gas Feedstock Energy (LHV)	1,015,610	kW _c
Ethylene Product Energy (LHV)	598,180	kW _c
Electricity Consumption	462,480	kW _c
Cooling Tower Heat Rejection	447,490	kW _t
Efficiency Metrics	Value	Unit
NG to Ethylene Thermal Efficiency	58.90	%
Ethylene Overall Thermal Efficiency	40.47	%

As mentioned before, the power generation in the steam cycle of the OCM plant increases due to the increased production of by-products (increase in H₂, CO, and bottoms product of deethanizer for C₂₊ separation remains almost constant), which are converted to heat for steam generation in the furnace. The cold box expander is eliminated in this design and no additional power is generated. The purpose of the cold box expander is primarily to provide additional cooling, however, with the high methane content of the ethylene-rich SOC product gas, this expander is no longer needed as methane has a very high Joule-Thomson coefficient. At the same time, the cooling temperature of the last cold box stage in the OCM case is increased from -121 °C (SOTA) to -111 °C (OCM-A) to increase the H₂ recovery from the last stage to maximize CO and CO₂ methanation (this is not CO₂ utilization as only CO and CO₂ byproducts produced

in the OCM unit are methanized). Hydrogen is the limiting factor for methanation in the OCM plants, and thus, a critical factor impacting carbon yield and CO₂ emissions.

The auxiliary load of the plant with 561,180 kW_e increased by more than a factor of 10 compared to the SOTA case. Primary electricity consumer is the OCM unit, 323,015 kW_e for the SOCs which incur an additional 6,460 kW_e of inverter losses and 100,065 kW_e for the air supply. The air supply power consumption is the net power consumption of the compressor and expander, whereby the compressor power is approximately double the size of the net power, and thus, close to 200,000 kW_e. As one might expect, auxiliaries related to the furnace operation and steam cycle operation increase at a similar scale as the furnace heat load and a more detailed breakdown can be found in **Table 3-7**.

Table 3-7: OCM (Air Oxidant) Plant Electric Power Consumption at Full Load Operation

Electricity Generation	Value	Unit
Steam Cycle	98,700	kW _e
Cold Box Expander	0	kW _e
Total Electricity Generation	98,700	kW_e
Auxiliary Load	Value	Unit
Solid Oxide Cell	323,015	kW _e
Inverter Loss	6,460	kW _e
Cathode Air System	100,065	kW _e
Furnace Air Blower	1,855	kW _e
Induced Draft Fan	3,040	kW _e
Steam Cycle Feedwater Pumps	2,545	kW _e
Quench Water Circulation Pump	245	kW _e
Quench Vent Compressor	100	kW _e
MEA CO ₂ Removal	120	kW _e
CO ₂ Compression	305	kW _e
Caustic Recirculation Pump	50	kW _e
Syngas Compression	48,700	kW _e
Cooling Water Circulation Pumps	2,930	kW _e
Cooling Tower Fans	2,180	kW _e
Propylene Refrigeration Cycle	44,515	kW _e
Ethylene Refrigeration Cycle	22,050	kW _e
Miscellaneous Balance of Plant	3,000	kW _e
Total Electric Load	561,180	kW_e
Net Electricity Usage	Value	Unit
Net Electricity Consumption	462,485	kW_e

A new process unit needed in the OCM plant is a MEA CO₂-removal unit. This unit is needed to remove CO₂ upstream of the cold box where CO₂ poses a risk of forming dry ice and blocking gas flow in critical process equipment. While cryogenic CO₂ separation can be used in some scenarios, which is typically done at conditions close to the triple point of CO₂ (5.1 bar, -56.6 °C),⁶⁵ it is a major challenge integrating this CO₂ separation into the cooling train used for ethylene separation. The separation of CO₂ from this mixture is particularly challenging as the vapor pressure curve of CO₂ lies in between ethane and ethylene. Thus, it is more effective to remove the CO₂ upstream of the gas compression section using a chemical solvent such as MEA. The power consumption of the MEA process is small 120 kW_e and an additional 305 kW_e for compressing a portion of the recovered CO₂ from 1.9 bar (regeneration pressure) to 20.0 bar for methanation. The CO₂ that is not internally reused can be considered as “capture-ready” with a purity of greater than 96.4 mol.-% (3.5 mol.-% water). While the electric power consumption of the MEA process is

low, it requires 29,810 kW_t of thermal energy, which is supplied by MP steam. The power consumption of the ethylene-rich product gas compression increased from 17,740 kW_e (SOTA) to 48,700 kW_e, a 175% increase. Again, this is due to the relatively low CH₄ and C₂H₆ conversion in the OCM unit, which leads to large recycle streams. This becomes apparent when comparing the mole flowrates entering the compression section, 4,967 kmol/h (SOTA) and 12,840 kmol/h (OCM-A). This high recycle flowrate not only impacts the compression but also the refrigeration cycles which are experiencing an increase in power consumption of 147%. Especially, the high methane content is detrimental as methane is separated in the demethanizer where the overhead product is cooled to -97 °C, the lowest temperature supplied by refrigeration cycle. The increase of cooling tower size and power consumption is mostly driven by the increased Rankine cycle power generation, but refrigeration cycles plus compressed gas cooling account for a similar increase in cooling demand. A detailed breakdown of the various power producers and consumers of the OCM plant with air as oxidant is provided in **Table 3-7**.

The local CO₂ point source emissions for this 400,000 MTPY OCM plant with air as oxidant are 480,996 MTPY which corresponds to 1.336 kg_{CO2}/kg_{Ethylene}. Twenty % of these emissions are from a pure “capture-ready” CO₂ stream equivalent to 0.267 kg_{CO2}/kg_{Ethylene}. The rest of the CO₂ emissions are from the furnace flue gas, whereby 0.755 kg_{CO2}/kg_{Ethylene} of the specific CO₂ emissions have their origin in the recycle purge stream. While the exact amount of purge necessary to eliminate the buildup of trace components can only be determined in pilot or pre-commercial demonstration projects, a substantial reduction of the purge stream can be expected as the single pass yield of the OCM unit increases and the methane recycle decreases. Other indirect CO₂ emissions include electricity and NG. Ethane-related emissions are not relevant to this case as the ethane feedstock is replaced by NG. Based on current US grid emission values an additional 1,407,440 MTPY of CO₂ or 3.910 kg_{CO2}/kg_{Ethylene} are emitted by this process. Natural gas-related emissions account for an additional 269,475 MTPY or 0.749 kg_{CO2}/kg_{Ethylene}. This leads to a total of 5.994 kg_{CO2}/kg_{Ethylene}. Considering current state-of-the-art OCM cells, a plant based upon this technology utilizing air as oxidant leads to a 274% increase in CO₂ emissions. Even in a future scenario with 100% CO₂-free electricity, the emission factor increases by 30% (2.085 kg_{CO2}/kg_{Ethylene}). Using biogenic methane as feedstock over NG; however, could make this process emission free or even carbon negative if the ethylene is used in PE production. The carbon yield of this process is 69.9% and approximately 1.85 kg_{CO2,eq}/kg_{bioCH4} could be sequestered. While for market introduction NG is most likely the preferred feedstock for OCM, due to price and availability, the ability to run on a commonly available renewable feedstock is a clear advantage of this technology as finding renewable ethane feedstocks for steam cracking will be a major hurdle for continued steam cracker operation. Sulfur emissions from this process are essentially zero as sulfur compounds need to be removed upstream of the OCM unit to avoid cell poisoning. Thus, any sulfur contained in NG is disposed together with the sorbent. The disposal of the sorbent accounts for 55 MTPY. An additional 12 MTPY of methanation catalyst need to be disposed of. Liquid disposal includes the caustic discharge at a rate of 16,730 MTPY, which is substantially higher than in the SOTA case due to higher trace amounts of CO₂ present in the ethylene-rich product gas (even with MEA CO₂ removal). The surface water discharge increases according to the cooling tower duty and is 1,593,184 MTPY in the OCM-A case. A summary of the various emission values is presented in **Table 3-8**.

Table 3-8: OCM (Air Oxidant) Plant Emissions

Point Source Emissions at 90% Capacity Factor	Value	Unit
Carbon Dioxide	480,996	metric tonnes/year
Specific CO ₂ Emission	1.336	kg _{CO2} /kg _{Ethylene}
Sulfur Oxides (as SO ₂)	0	kg/year
Specific SO ₂ Emission	0	ppm-wt. _{SO2} /kg _{Ethylene}
Catalyst and Sorbent Disposal	66	metric tonnes/year
Caustic Discharge (Disposal)	16,730	metric tonnes/year
Surface Water Discharge	1,593,184	metric tonnes/year
Indirect Carbon Dioxide Emissions at 90% Capacity Factor	Value	Unit
Electricity-related CO ₂ Emissions	1,407,440	metric tonnes/year
Specific Electricity-related CO ₂ Emissions	3.910	kg _{CO2} /kg _{Ethylene}
Ethane-related CO ₂ Emissions	0	metric tonnes/year
Specific Ethane-related CO ₂ Emissions	0.000	kg _{CO2} /kg _{Ethylene}
NG-related CO ₂ Emissions	269,475	metric tonnes/year
Specific NG-related CO ₂ Emissions	0.749	kg _{CO2} /kg _{Ethylene}

3.2.2 Economic Performance Analysis

The TPC of the OCM plant with air as oxidant is \$2,288,179,000, and more than double the cost of the SOTA ethane steam cracker plant. Accordingly, the specific plant cost increases to 5,720 \$/metric tonne ethylene at a 400,000 MTPY scale. Also in the OCM-A case, the furnace is one of the most expensive items with \$229,171,000; however, its share on the TPC reduced from 18.0% (steam cracker) to 10.0%. As expected, steam cycle equipment cost increased due to the higher steam and power generation and account for \$60,850,000. The cooling tower load increase has been discussed earlier and results in a cooling tower cost of \$72,933,000, almost double the cost of the cooling tower in the steam cracker case. The OCM process unit, consisting of the SOC modules, power electronics and cathode air supply, accounts with \$451,511,000 for 19.7% of the TPC, whereby the SOC modules contribute \$86,979,000, the power electronics contribute \$177,801,000 and the cathode air supply system \$186,731,000. It is uncommon that the air supply system constitutes such a large cost factor in an electrochemical system but this is attributed to the fact that the SOC operates at extremely high overpotentials, substantially increasing the cooling demand, and the elevated operating pressure. The SOC cost on the other hand is relatively low as the system operates at a current density of 0.9 A/cm², which is current state-of-the-art and a result of very high overpotentials.⁹ In comparison, modern solid oxide fuel cell systems like the BlueGen CHP reach current densities of 0.28 A/cm² and cost around \$30,000 – \$35,000 (entire system). With a cell area of approximately 7,100 cm², the specific cost of a SOFC CHP is around 4.20 – 4.90 \$/cm². Cost of the current system is 2.01 \$/cm² at more than 3 times higher current density or 0.87 \$/cm² at comparable current density. The specific cell cost (cell only) is 0.36 \$/cm² which is higher than some values found in literature (0.17 \$/cm²).⁶⁶ While this number appears to be in the right ballpark for large industrial scale systems, a cost sensitivity analysis is conducted and presented in a later section, due to the large uncertainty associated with SOC cost predictions. On the gas processing and compression side (including MEA process) costs amount to \$252,323,000, an increase of 136% compared to the steam cracker case as the molar gas flowrate increases by 158%. By far the largest cost driving factor is the refrigeration system contributing 29.3% to the TPC. With \$669,459,000, the cost more than doubled as all recycle gas has to pass through the refrigeration system prior to being returned to the OCM unit or burned in the furnace. Similarly, the cost of the cryogenic gas separation increases to \$145,553,000. The methanation section with its three gas phase reactors is small compared to the rest of the plant and costs \$11,936,000. Other plant units are 1) water treatment, 2) materials handling, 3) electrical and instrumentation, 4) site improvement, 5) structures and

foundations, and 6) miscellaneous equipment and expenses, which account for 1) \$6,839,000, 2) \$27,838,000, 3) \$93,935,000, 4) \$85,155,000, 5) \$107,959,000, and 6) \$72,808,000. A breakdown of the TPC can be found in **Figure 3-4**. To arrive at the total overnight capital preproduction cost, inventory capital cost, initial costs of catalysts, sorbents and chemicals, land, other owner’s expenses (such as project management, procurement and subcontracts, EPC warranty and EP fees) and financing costs area added as shown in **Table 3-10**. This leads to a total overnight capital expenditure of \$2,877,132,000.

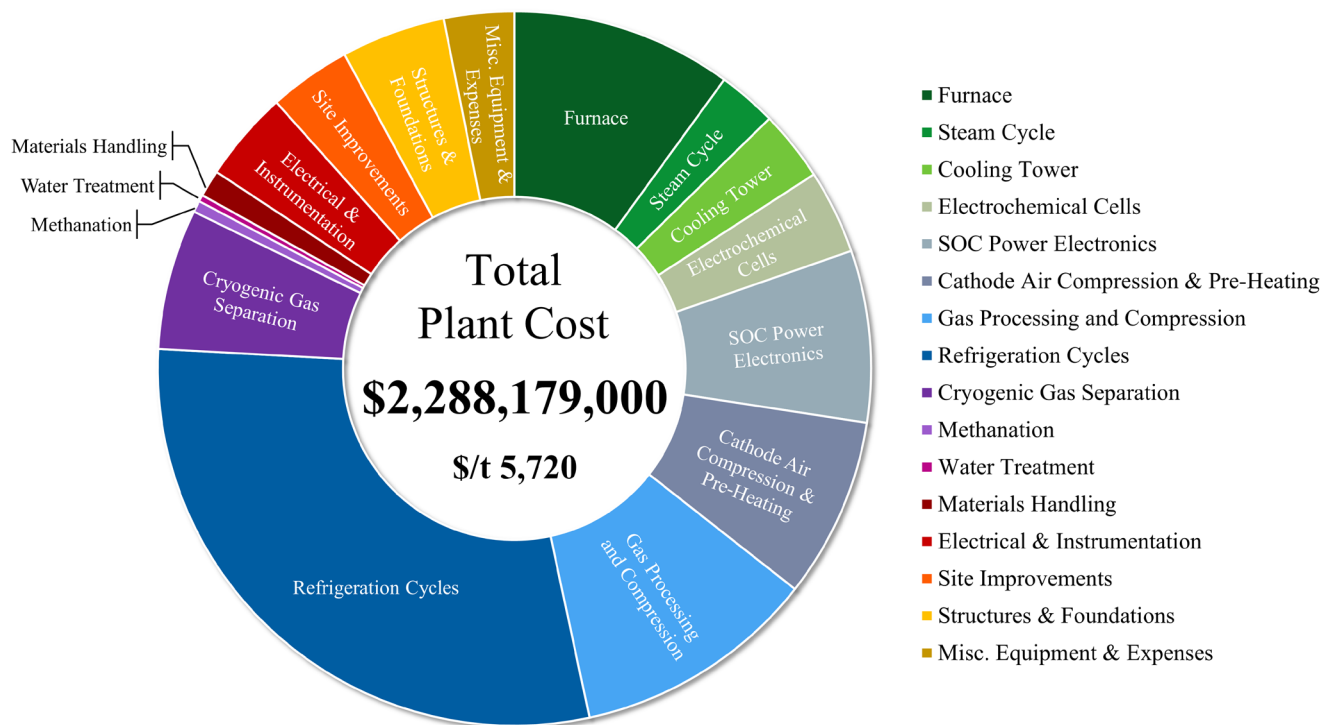


Figure 3-4: Breakdown of the OCM (air oxidant) total-plant-cost (TPC).

The annual fixed operating costs are \$102,637,000, which include labor (\$56,874,000), and tax and insurance (45,764,000). The operating labor is held constant between the steam cracker case and the OCM-A case, as the plant configurations are largely similar. Maintenance labor, however, is adjusted based upon individual equipment maintenance factors and reflected in the annual labor costs.

Annual variable operating costs are \$342,397,000. The annual feedstock cost in the OCM-A case, which uses natural gas, is \$110,026,000. This cost is very similar to the ethane feedstock cost in the steam cracker case; however, due to the electrochemical OCM process, the annual electricity bill increases from \$6,948,000 to \$178,373,000. Maintenance costs are \$32,311,000 per annum, a strong increase over the steam cracker case mainly because of high SOC replacement costs, which are over \$6,000,000 per year on a levelized basis. The methanation catalyst is assumed to be replaced every 4 years which results in an annualized expense of \$289,000 and replacement of the sulfur removal sorbent adds another \$1,632,000 per annum. In contrast the acetylene hydrogenation catalyst in the steam cracker case (which is no longer needed in the OCM plant) has only a levelized annual cost of \$74,000. Raw water expenses increase from \$1,623,000 (steam cracker) to \$4,588,000 (OCM-A). The most expensive running costs are MEA with \$7,403,000 and NaOH with \$7,148,000 (steep increases compared to the steam cracker due to higher CO₂ concentrations upstream of the cold box). This high usage of NaOH not only impacts the chemical costs but its disposal is also associated with a tipping fee. Total waste disposal costs account for \$628,000 per year. Key economic metrics for the OCM-A case are summarized in **Table 3-10**.

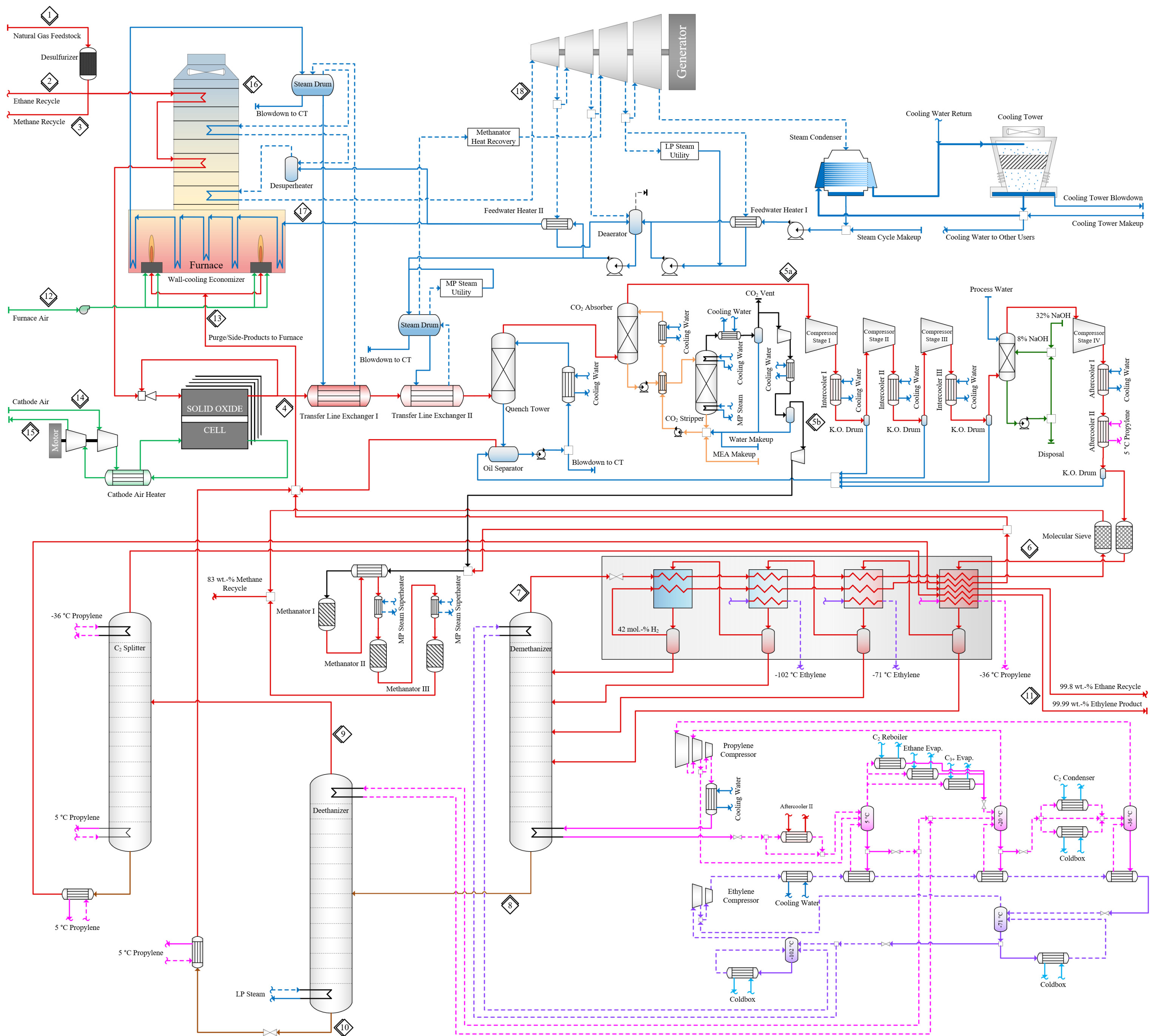


Figure 3-5: Simplified flowsheet of the electrochemical OCM plant with air as oxidant (OCM-A) for ethylene production.

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Table 3-9: OCM (Air Oxidant) Plant State-Point Stream Data

Stream Number	Unit	1	2	3	4	5a	5b	6	7	8	9
Temperature	°C	15	12	117	850	43	38	16	-97	6	-2
Pressure	bar	4.0	15.0	4.0	1.6	1.0	1.9	35.2	32.0	32.0	26.0
Mole Flowrate	kmol/h	4,471	4,305	3,929	15,306	12,840	116	11,608	2,661	5,982	5,933
Mass Flowrate	kg/h	77,475	129,509	64,417	331,659	277,177	5,011	253,773	42,463	177,443	175,172
Molar Vapor Fraction	–	1	1	1	1	1	1	1	1	0	1
Composition	mole-basis										
O ₂	–	0.00010	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
N ₂	–	0.01600	0.00000	0.03018	0.01242	0.01481	Trace	0.01638	0.01763	0.00000	0.00000
H ₂ O	–	0.00003	0.00000	0.06574	0.21073	0.08951	0.03536	0.00000	0.00000	0.00000	0.00000
H ₂	–	0.00000	0.00000	0.03384	0.08843	0.10540	0.00003	0.11659	0.04277	0.00000	0.00000
CO	–	0.00000	0.00000	0.01296	0.01205	0.01437	Trace	0.01589	0.01912	0.00000	0.00000
CO ₂	–	0.01000	0.00000	0.00463	0.02588	0.00031	0.96417	0.00000	0.00000	0.00000	0.00000
CH ₄	–	0.93087	0.00000	0.84840	0.25187	0.30022	0.00011	0.33180	0.91421	0.00003	0.00003
C ₂ H ₆	–	0.03200	0.99844	Trace	0.28538	0.34018	0.00016	0.37159	Trace	0.71943	0.72453
C ₂ H ₄	–	0.00000	0.00065	0.00424	0.10976	0.13083	0.00017	0.14362	0.00627	0.27254	0.27478
C ₃ H ₈	–	0.00700	0.00070	Trace	0.00196	0.00233	Trace	0.00244	0.00000	0.00473	0.00051
C ₃ H ₆	–	0.00000	0.00021	Trace	0.00035	0.00041	Trace	0.00044	0.00000	0.00085	0.00015
n-C ₄ H ₈	–	0.00400	Trace	Trace	0.00102	0.00122	Trace	0.00108	0.00000	0.00210	Trace
1-C ₄ H ₈	–	0.00000	Trace	Trace	0.00015	0.00018	Trace	0.00017	0.00000	0.00032	Trace
SO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Total	–	1	1	0.99999	1	0.99977	0.99999	1	1	1	1
Stream Number	Unit	10	11	12	13	14	15	16	17	18	
Temperature	°C	74	12	15	60	15	155	100	190	540	
Pressure	bar	26.0	18.3	1.0	2.0	1.0	1.0	0.9	128.5	121.7	
Mole Flowrate	kmol/h	49	1,628	20,263	1,641	404,866	402,983	21,645	19,698	19,647	
Mass Flowrate	kg/h	2,272	45,662	582,753	22,195	11,643,770	11,583,512	604,948	354,862	353,937	
Molar Vapor Fraction	–	0	1	1	1	1	1	1	0	1	
Composition	mole-basis										
O ₂	–	0.00000	0.00000	0.20824	0.00000	0.20824	0.20454	0.08804	0.00000	0.00000	
N ₂	–	0.00000	0.00000	0.78338	0.04359	0.78338	0.78704	0.73666	0.00000	0.00000	
H ₂ O	–	0.00000	0.00000	0.00838	0.02076	0.00838	0.00842	0.12393	1.00000	1.00000	
H ₂	–	0.00000	0.00000	0.00000	0.37733	0.00000	0.00000	0.00000	0.00000	0.00000	
CO	–	0.00000	0.00000	0.00000	0.04067	0.00000	0.00000	0.00000	0.00000	0.00000	
CO ₂	–	0.00000	0.00000	0.00000	0.00109	0.00000	0.00000	0.05127	0.00000	0.00000	
CH ₄	–	0.00000	0.00009	0.00000	0.43389	0.00000	0.00000	0.00000	0.00000	0.00000	
C ₂ H ₆	–	0.09808	0.00007	0.00000	0.03896	0.00000	0.00000	0.00000	0.00000	0.00000	
C ₂ H ₄	–	Trace	0.99984	0.00000	0.01375	0.00000	0.00000	0.00000	0.00000	0.00000	
C ₃ H ₈	–	0.51947	0.00000	0.00000	0.01640	0.00000	0.00000	0.00000	0.00000	0.00000	
C ₃ H ₆	–	0.08498	0.00000	0.00000	0.00266	0.00000	0.00000	0.00000	0.00000	0.00000	
n-C ₄ H ₈	–	0.25817	0.00000	0.00000	0.00951	0.00000	0.00000	0.00000	0.00000	0.00000	
1-C ₄ H ₈	–	0.03930	0.00000	0.00000	0.00139	0.00000	0.00000	0.00011	0.00000	0.00000	
SO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	
Total	–	0.99999	1	1	1	1	1	1	1	1	

The resulting 1st-year levelized costs of ethylene for this 400,000 MTPY ethylene plant is \$1,875.57 per metric tonne of ethylene. The overnight capital is responsible for 34.1% of the CoE, the variable operating costs for 50.7% and the fixed operating costs for 15.2%. A breakdown of the different cost driving factors of the CoE can be found in **Figure 3-10**. This CoE is about 2.1 times higher than the CoE of the steam cracker case and 1.5 times higher than the 2022 market price, the highest ethylene price in recent years. Major cost driving factor is electricity which has a share of 26.4% on the CoE in the OCM-A case. The high electricity consumption reflects the high overpotentials and illustrates the importance of reducing overpotentials of the OCM reaction. Second largest cost driving factor is natural gas (feedstock in OCM) with its cost of 305.63 \$/metric tonne of ethylene or 16.3%. Cost reduction on this front can be obtained by

improving the single pass yield to boost carbon yield, and thus, reduce the feedstock consumption. Moreover, with increased yields capital cost reductions can be expected as well. Especially since, the economies of scale for electrochemical plants are typically less dominant as for more traditional plant equipment. Also in this work, mass produced SOC modules are assumed, leading to smaller cost savings when moving to larger plant scales. On a 1,500,000 MTPY scale the OCM with air as oxidant reaches a CoE of \$1,570.51 per metric tonne of ethylene, a 16.3% reduction. A comparison of CoEs for a range of plant scales is provided in **Figure 3-11**.

Table 3-10: OCM (Air Oxidant) Plant Economics

Overnight Cost	Value	Unit
Total Plant Cost	2,288,179	\$ (thousands)
Preproduction Cost	85,876	\$ (thousands)
Inventory Capital Cost	14,936	\$ (thousands)
Initial Catalyst, Sorbent & Chemicals Cost	5,264	\$ (thousands)
Land	900	\$ (thousands)
Other Owners' Costs	420,196	\$ (thousands)
Financing Costs	61,781	\$ (thousands)
Fixed Operating Cost	Value	Unit
Annual Labor Cost	56,874	\$ (thousands)
Annual Tax and Insurance Cost	45,764	\$ (thousands)
Variable Operating Cost	Value	Unit
Annual Natural Gas Cost	110,026	\$ (thousands)
Annual Electricity Cost	178,373	\$ (thousands)
Annual Maintenance Materials Cost	32,311	\$ (thousands)
Annual Chemical, Catalyst & Disposal Costs	21,687	\$ (thousands)
Economic Performance Metrics	Value	Unit
Specific Ethylene Plant Cost	5,720	\$/metric tonne ethylene
1 st Year Levelized Cost of Ethylene	1,875.57	\$/metric tonne ethylene

3.3 Electrochemical OCM Plant with Steam as Oxidant

3.3.1 Technology Performance Analysis

In the electrochemical OCM plant with steam as oxidant (OCM-S), H₂ is co-produced. In this design, the cathode is supplied with a mixture of steam and H₂ (84/16 mol.-%) at 750 °C and 1.6 bar. In order to avoid overheating of the cell and limit the SOC off-gas to a temperature of 850 °C, a low steam utilization factor of 1.7% is necessary. To further reject heat, liquid economizer feed water is injected into the H₂ recycle after cooling/SOC inlet steam pre-heating. This is not only an effective measure to reject heat from the SOC but is also an energy efficient way of raising steam for the SOC. Furthermore, this design allows the steam side of the OCM to be controlled relatively independently allowing for more operational flexibility. However, steam concentration and the split fraction of H₂ going to the compression section has to be carefully controlled to keep the system in balance. The H₂ co-production in this plant is 60,240 MTPY (at 90% capacity) which is equivalent to 0.167 kg_{H₂}/kg_{Ethylene}. Natural gas consumption, NaOH and MEA use do not change in the OCM-S case when compared to the OCM-A case, since the anode-side with the OCM reaction and the downstream product processing remains identical. Water consumption on the other hand increases from 6,080,390 MTPY to 10,478,390 MTPY. While only about 535,000 MTPY are associated with the actual H₂ production, heat rejection in the H₂ recycle loop (to satisfy the thermal balance)

substantially increases water consumption in the cooling tower. The water consumption due to intercooling is relatively small and about two orders of magnitude smaller than the recycle loop heat rejection (labeled as “Vapor Condenser” in **Figure 3-6**). Heat rejection in this configuration increases due to the closed loop nature of the cathode side. In the previous design with air as oxidant, unutilized higher temperature air could simply be emitted into the environment without further cooling, and thus, does not present an additional duty for the cooling tower. The operating voltage in the OCM-S case is 2.48 V (vs. NHE). It is worth mentioning that this operating point implies a 16% reduction of the SOC’s heating potential, from 2.32 V (OCM-A) to 1.95 V (OCM-S). While the overpotentials in both cases are kept constant (steam activation energy is similar to O₂ activation energy as discussed in the OCM methodology section), the endothermic nature of the steam electrolysis reaction ($E_{Nemst} = 0.18$ V (vs. NHE); $E_{thermoneutral} = 0.57$ V (vs. NHE)) helps to reduce the cooling needs of the SOC. The resulting single pass cell efficiency is 22.9%. Since the overall reaction is now endothermic the efficiency becomes positive in this case. The overall plant efficiency increases from 40.47% in the OCM-A case to 52.71% (OCM-S), however, the NG to ethylene conversion efficiency remains constant at 58.90% since the anode-side or ethylene production-side is not affected by switching the oxygen supply from air to steam. A summary of the plant performance can be found in **Table 3-11**.

Table 3-11: OCM (Steam Oxidant) Plant Performance

Plant Design Capacity	Value	Unit
Ethylene Production Capacity	400,000	metric tonnes/year
Plant Capacity Factor	90	%
Actual Ethylene Production	360,000	metric tonnes/year
Actual Hydrogen Byproduct	60,240	metric tonnes/year
Consumables at 90% Capacity Factor	Value	Unit
Natural Gas	610,810	metric tonnes/year
Electricity	4,723,540	MWh/year
Raw Water Withdrawal	10,478,390	metric tonnes/year
NaOH Solution, 32%	8,890	metric tonnes/year
MEA	1,440	metric tonnes/year
Energy Metrics at Full Load Operation	Value	Unit
Natural Gas Feedstock Energy (LHV)	1,015,610	kW _e
Ethylene Product Energy (LHV)	598,180	kW _e
Hydrogen Product Energy (LHV)	252,990	kW _e
Electricity Consumption	599,130	kW _e
Cooling Tower Heat Rejection	731,290	kW _t
Efficiency Metrics	Value	Unit
NG to Ethylene Thermal Efficiency	58.90	%
Ethylene (incl. H ₂) Overall Thermal Efficiency	52.71	%

As expected, the electricity consumption in the OCM-S case increases and the annual electricity consumption is 4,723,540 MWh. The electricity generation in the steam cycle remains constant when switching from air oxidant to steam. Similarly, systems related to the ethylene-side of the plant, such as furnace air blower, induced draft fans, steam cycle feed water pumps, quench water circulation pumps, quench vent compressor, MEA removal, CO₂ compression, caustic recirculation pump, syngas compression, propylene refrigeration cycle, ethylene refrigeration cycle, and miscellaneous balance of plant, remain unchanged and have an identical power consumption as in the OCM-A case. The SOC power consumption increased by 54.7% to 499.665 kW_e. Along with the increased SOC power consumption inverter losses increase to 9,995 kW_e. The power needed to supply the steam and recycle the H₂ to the cathode is 36,660 kW_e compared to 100,065 kW_e for the cathode air system in the OCM-A case. However,

an additional 16,580 kW_e are needed in the OCM-S case for H₂ compression to a pressure of 50 bar. This compression power could be reduced if the SOC could operate with pressures differentials between anode and cathode, which might be possible with future metal supported cells. A list of all power generation systems and power consumers is provided in **Table 3-12**.

Table 3-12: OCM (Steam Oxidant) Plant Electric Power Consumption at Full Load Operation

Energy Output	Value	Unit
Steam Cycle	98,700	kW _e
Cold Box Expander	0	kW _e
Total Electricity Generation	98,700	kW_e
Auxiliary Load	Value	Unit
Solid Oxide Cell	499,665	kW _e
Inverter Loss	9,995	kW _e
Cathode Steam System	36,660	kW _e
Hydrogen Compression	16,580	kW _e
Furnace Air Blower	1,855	kW _e
Induced Draft Fan	3,040	kW _e
Steam Cycle Feedwater Pumps	2,565	kW _e
Quench Water Circulation Pump	245	kW _e
Quench Vent Compressor	100	kW _e
MEA CO ₂ Removal	120	kW _e
CO ₂ Compression	305	kW _e
Caustic Recirculation Pump	50	kW _e
Syngas Compression	48,700	kW _e
Cooling Water Circulation Pumps	4,815	kW _e
Cooling Tower Fans	3,560	kW _e
Propylene Refrigeration Cycle	44,515	kW _e
Ethylene Refrigeration Cycle	22,050	kW _e
Miscellaneous Balance of Plant	3,000	kW _e
Total Electric Load	697,825	kW_e
Net Electricity Usage	Value	Unit
Net Electricity Consumption	599,130	kW_e

The local CO₂ point source emissions of the OCM-S case are 480,996 MTPY which equates to 1.336 kg_{CO2}/kg_{Ethylene} (identical to the OCM-A case). Like in the OCM-A case, there are three different categories of CO₂ emissions: “capture ready” CO₂ from the MEA process, furnace emissions from the purge stream, and furnace emissions from higher hydrocarbon by-products. The distribution of CO₂ emissions is identical to the OCM-A case. Catalyst and sorbent disposal as well as liquid waste production remain unchanged. Only surface water discharge increases due to the increased cooling tower heat duty. Also, feedstock related upstream emissions are not impacted by switching the oxidant from air to steam. However, the strong increase in electricity demand, substantially increases grid related CO₂ emissions when considering today’s energy landscape in the US. Carbon dioxide emissions increased from 1,407,440 MTPY (OCM-A) to 1,823,285 MTPY, a 29.5% increase. Similarly, the specific electricity-related CO₂ emissions increase from 3.910 kg_{CO2}/kg_{Ethylene} to 5.065 kg_{CO2}/kg_{Ethylene}. The resulting overall plant emissions are 7.149 kg_{CO2}/kg_{Ethylene} in this scenario. It is important to realize that this way of carbon accounting assigns all CO₂ emissions to the ethylene product, and thus, no emissions are associated with the production of H₂. Since the H₂ is produced from steam and not from fossil resources, one can argue that this H₂ can be considered as green H₂; however, in reality this will be only completely true if renewable electricity is used in the electrochemical OCM process. Considering the ideal Nernst potential of the water

splitting reaction (at the encountered partial pressures and operating temperature of this scenario) at the average operating temperature of 800 °C, a voltage of 0.87 V is obtained. This is equivalent to a power consumption of 177,140 kW_e (simply based on the Nernst equation without considering overpotential losses). When comparing this power consumption to the difference in the SOC power consumption of the OCM-A and OCM-S case, 176,650 kW_e, it becomes apparent that multifunctional cells that can produce ethylene and H₂ form a synergistic system that allows the second reaction, in this case H₂ production, to proceed in an ideal manner without any losses (note that the ideal process in this scenario is contingent on comparable anode activation losses for O₂ and H₂O as previously discussed, in other cases small deviations from the ideal voltage might occur if differences in anode activation overpotentials exist). Using this ideal power consumption for the H₂ reaction, the specific electricity-related CO₂ emission on the ethylene-side can be reduced by 1.664 kg_{CO2}/kg_{Ethylene} to 3.401 kg_{CO2}/kg_{Ethylene}, which is lower than the specific electricity-related CO₂ emissions in the OCM-A case since the cathode steam supply system and H₂ compression require less power than the cathode air supply system in the OCM-A case. Hydrogen on the other hand would then have a specific CO₂ emission factor of 9.944 kg_{CO2}/kg_{H2}, which is similar to NG reforming (based on current grid emission factor) but could be substantially less in the future.⁶⁷ Assigning CO₂ emissions in a co-generation system is always challenging, especially fully understanding the contributions of overpotentials and if they should be entirely assigned to the ethylene side. More detailed life-cycle assessment (LCA) tools will be needed to provide more insights into this question; however, this is out of scope for this work. A summary of all emission values is provided in **Table 3-13**.

Table 3-13: OCM (Steam Oxidant) Plant Emissions

Point Source Emissions at 90% Capacity Factor	Value	Unit
Carbon Dioxide	480,996	metric tonnes/year
Specific CO ₂ Emission	1.336	kg _{CO2} /kg _{Ethylene}
Sulfur Oxides (as SO ₂)	0	kg/year
Specific SO ₂ Emission	0.000	ppm-wt. _{SO2} /kg _{Ethylene}
Catalyst and Sorbent Disposal	66	metric tonnes/year
Caustic Discharge (Disposal)	16,730	metric tonnes/year
Surface Water Discharge	2,658,792	metric tonnes/year
Indirect Carbon Dioxide Emissions at 90% Capacity Factor	Value	Unit
Electricity-related CO ₂ Emissions	1,823,285	metric tonnes/year
Specific Electricity-related CO ₂ Emissions	5.065	kg _{CO2} /kg _{Ethylene}
Ethane-related CO ₂ Emissions	0	metric tonnes/year
Specific Ethane-related CO ₂ Emissions	0.000	kg _{CO2} /kg _{Ethylene}
NG-related CO ₂ Emissions	269,475	metric tonnes/year
Specific NG-related CO ₂ Emissions	0.749	kg _{CO2} /kg _{Ethylene}

3.3.2 Economic Performance Analysis

The TPC of the plant with steam as oxidant and H₂ co-generation is \$2,407,051,000 and \$118,872,000 more expensive than the OCM-A plant. The resulting specific plant cost is 6,018 \$/metric tonne ethylene at a 400,000 MTPY plant scale. In general, most of the CAPEX of the major plant equipment of the OCM-S case is very similar to the OCM-A case. Differences can be seen in the cooling tower and water treatment, whose costs increased by 38.2% and 54.6%, due to the increased cooling load and water demand. Also, the cost of power electronics increases, which is related to the higher power demand. The cost of the SOC stacks; however, remains essentially constant since the operating voltage is adjusted to keep the current density constant. The cost for H₂ recirculation, pre-heating as well as compression and intercooling amount to a similar cost as the cathode air system in the OCM-A case. A breakdown of the TPC distribution by major category can be found in **Figure 3-7**.

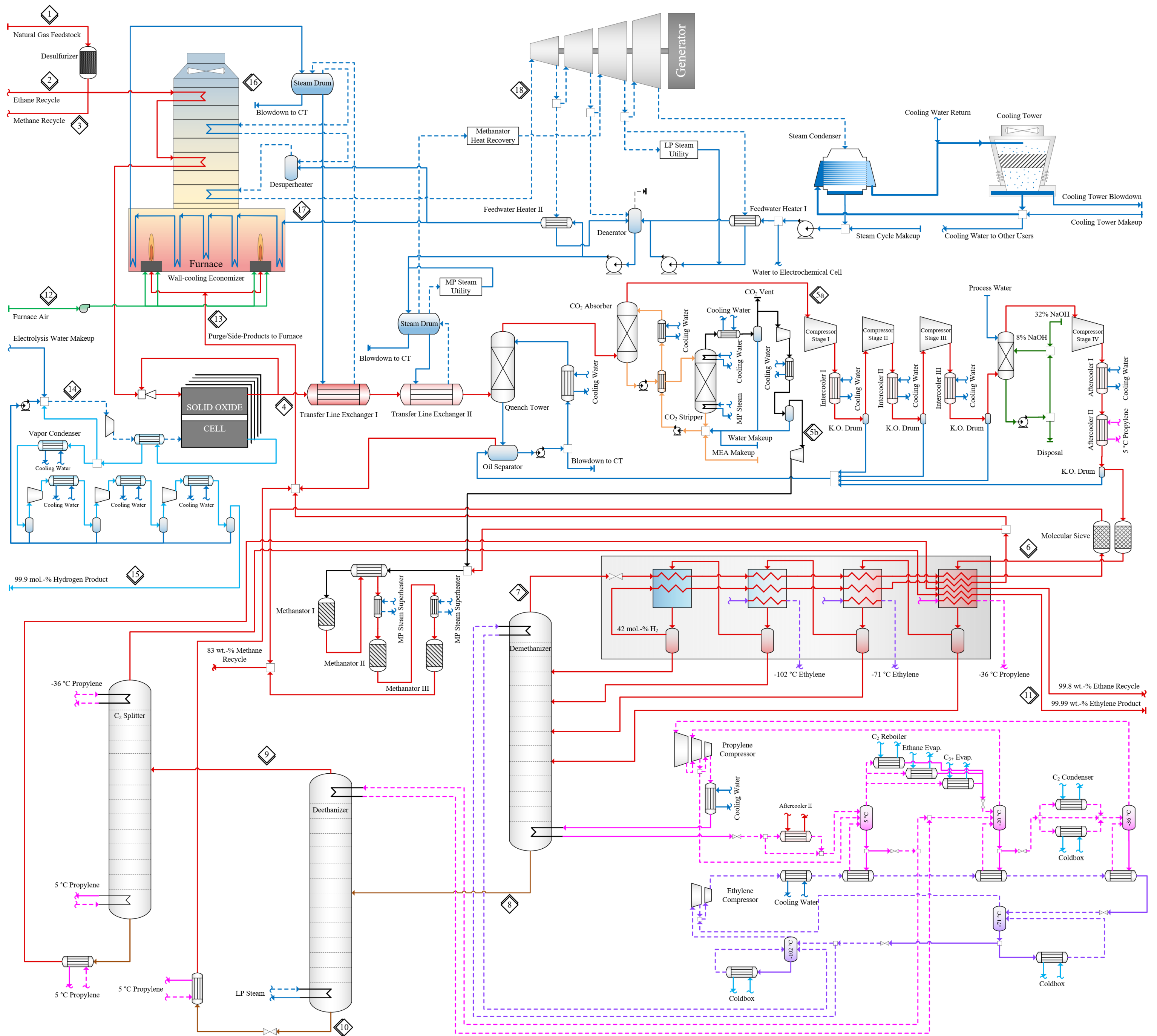


Figure 3-6: Simplified flowsheet of the electrochemical OCM plant with steam as oxidant (OCM-S) for ethylene production.

ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Table 3-14: OCM (Steam Oxidant) Plant State-Point Stream Data

Stream Number	Unit	1	2	3	4	5a	5b	6	7	8	9
Temperature	°C	15	12	117	850	43	38	16	-97	6	-2
Pressure	bar	4.0	15.0	4.0	1.6	1.0	1.9	35.2	32.0	32.0	26.0
Mole Flowrate	kmol/h	4,471	4,305	3,929	15,306	12,840	116	11,608	2,661	5,982	5,933
Mass Flowrate	kg/h	77,475	129,509	64,417	331,659	277,177	5,011	253,773	42,463	177,443	175,172
Molar Vapor Fraction	–	1	1	1	1	1	1	1	1	0	1
Composition	mole-basis										
O ₂	–	0.00010	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
N ₂	–	0.01600	0.00000	0.03018	0.01242	0.01481	Trace	0.01638	0.01763	0.00000	0.00000
H ₂ O	–	0.00003	0.00000	0.06574	0.21073	0.08951	0.03536	0.00000	0.00000	0.00000	0.00000
H ₂	–	0.00000	0.00000	0.03384	0.08843	0.10540	0.00003	0.11659	0.04277	0.00000	0.00000
CO	–	0.00000	0.00000	0.01296	0.01205	0.01437	Trace	0.01589	0.01912	0.00000	0.00000
CO ₂	–	0.01000	0.00000	0.00463	0.02588	0.00031	0.96417	0.00000	0.00000	0.00000	0.00000
CH ₄	–	0.93087	0.00000	0.84840	0.25187	0.30022	0.00011	0.33180	0.91421	0.00003	0.00003
C ₂ H ₆	–	0.03200	0.99844	Trace	0.28538	0.34018	0.00016	0.37159	Trace	0.71943	0.72453
C ₂ H ₄	–	0.00000	0.00065	0.00424	0.10976	0.13083	0.00017	0.14362	0.00627	0.27254	0.27478
C ₃ H ₈	–	0.00700	0.00070	Trace	0.00196	0.00233	Trace	0.00244	0.00000	0.00473	0.00051
C ₃ H ₆	–	0.00000	0.00021	Trace	0.00035	0.00041	Trace	0.00044	0.00000	0.00085	0.00015
n-C ₄ H ₈	–	0.00400	Trace	Trace	0.00102	0.00122	Trace	0.00108	0.00000	0.00210	Trace
1-C ₄ H ₈	–	0.00000	Trace	Trace	0.00015	0.00018	Trace	0.00017	0.00000	0.00032	Trace
SO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Total	–	1.00000	1.00000	0.99999	1.00000	0.99977	0.99999	1.00000	1.00000	1.00000	1.00000
Stream Number	Unit	10	11	12	13	14	15	16	17	18	
Temperature	°C	74	12	15	60	145	27	100	190	540	
Pressure	bar	26.0	18.3	1.0	2.0	1.5	50.0	0.9	128.5	121.7	
Mole Flowrate	kmol/h	49	1,628	20,263	1,641	262,726	3,769	21,645	19,698	19,646	
Mass Flowrate	kg/h	2,272	45,662	582,753	22,195	4,060,560	7,640	604,948	354,862	353,937	
Molar Vapor Fraction	–	0	1	1	1	1	1	1	0	1	
Composition	mole-basis										
O ₂	–	0.00000	0.00000	0.20824	0.00000	0.00000	0.00000	0.08804	0.00000	0.00000	
N ₂	–	0.00000	0.00000	0.78338	0.04359	0.00000	0.00000	0.73666	0.00000	0.00000	
H ₂ O	–	0.00000	0.00000	0.00838	0.02076	0.84001	0.00071	0.12393	1.00000	1.00000	
H ₂	–	0.00000	0.00000	0.00000	0.37733	0.15999	0.99929	0.00000	0.00000	0.00000	
CO	–	0.00000	0.00000	0.00000	0.04067	0.00000	0.00000	0.00000	0.00000	0.00000	
CO ₂	–	0.00000	0.00000	0.00000	0.00109	0.00000	0.00000	0.05127	0.00000	0.00000	
CH ₄	–	0.00000	0.00009	0.00000	0.43389	0.00000	0.00000	0.00000	0.00000	0.00000	
C ₂ H ₆	–	0.09808	0.00007	0.00000	0.03896	0.00000	0.00000	0.00000	0.00000	0.00000	
C ₂ H ₄	–	Trace	0.99984	0.00000	0.01375	0.00000	0.00000	0.00000	0.00000	0.00000	
C ₃ H ₈	–	0.51947	0.00000	0.00000	0.01640	0.00000	0.00000	0.00000	0.00000	0.00000	
C ₃ H ₆	–	0.08498	0.00000	0.00000	0.00266	0.00000	0.00000	0.00000	0.00000	0.00000	
n-C ₄ H ₈	–	0.25817	0.00000	0.00000	0.00951	0.00000	0.00000	0.00000	0.00000	0.00000	
1-C ₄ H ₈	–	0.03930	0.00000	0.00000	0.00139	0.00000	0.00000	0.00011	0.00000	0.00000	
SO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	
Total	–	0.99999	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	

The total overnight capital cost is \$3,026,827,000, whereby pre-production costs, inventory capital costs, initial catalyst and sorbent costs, land, other owner's expenses, and financing costs experience a small increase compared to the OCM-A case. Annual labor costs slightly increase compared to the OCM-A case due to an increase in maintenance labor (operating labor is held constant between the cases) and tax and insurance increase as it is a function of TPC.

The NG feedstock cost does not change between the OCM-A and OCM-S case. Small increases in annual operating costs are seen for maintenance materials due to additional equipment and in the chemical costs due to the increased raw water demand. Annual electricity costs increase by \$52,702,000 due to H₂ co-production but can be offset with the sales revenue of H₂, \$108,425,00. The sales price of H₂ is based on current fossil H₂ prices (1.80 \$/kg_{H2}) which are lower than renewably produced H₂ and more representative

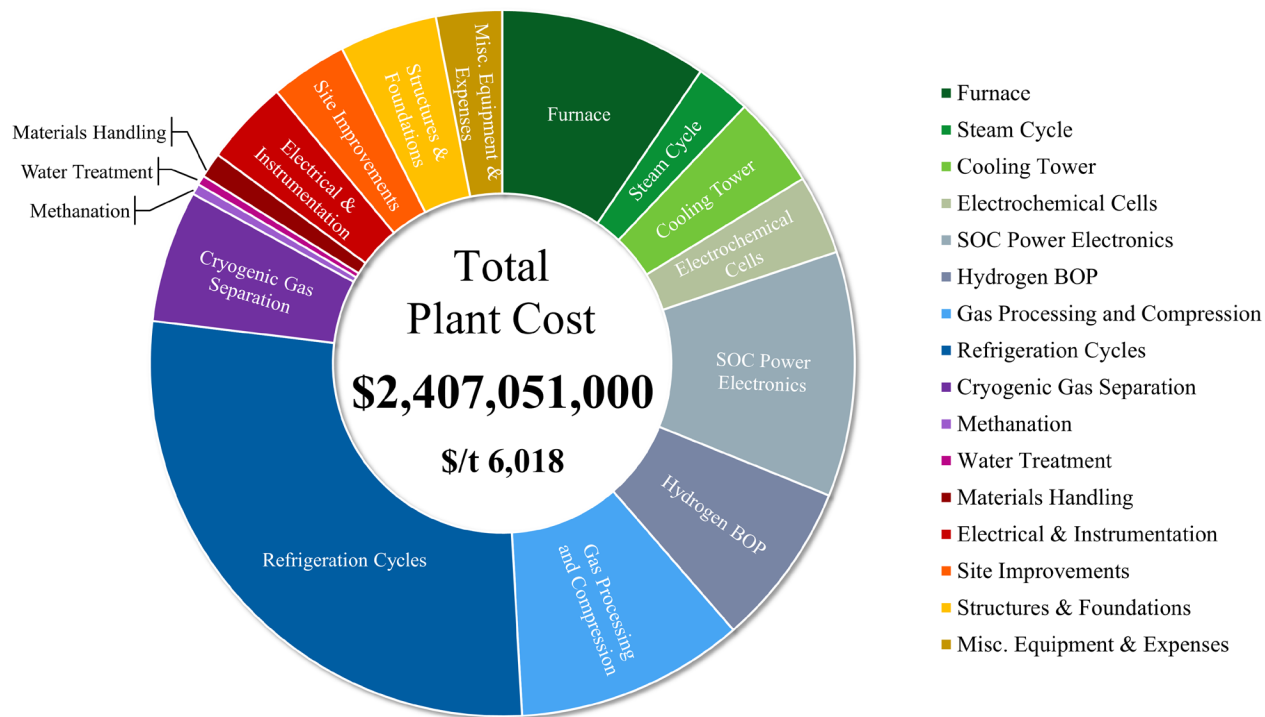


Figure 3-7: Breakdown of the OCM (steam oxidant) total-plant-cost (TPC).

for current market prices. If in the future large scale renewable H₂ becomes available at the US DOE target price of 1 \$/kg, the annual H₂ revenue in this scenario would fall to \$60,236,000 (it is important to note that DOE's low cost H₂ scenarios rely upon on significantly lower electricity prices which was not considered here). Without the H₂ sales revenue the CoE in the OCM-S case would be \$2,078.11 per metric tonne of ethylene; however, under current market conditions the sales revenue of H₂ can reduce the CoE by 301.18 \$/metric tonne of ethylene to \$1,776.93 per metric tonne of ethylene. The H₂ break-even price in the OCM-A case is at a H₂ sales price of 1.21 \$/kg_{H2} at using current electricity prices. A major cost driving factor for the cost of H₂ is the cost of electricity, and as cost of renewable hydrogen production drops with the help of lower electricity prices, also production cost savings in this case are expected. At a H₂ sales price of 1.00 \$/kg_{H2}, the break-even ethylene price of the OCM-A case can be reached if the current electricity price drops by 24.0% (considering cheaper electricity prices in both cases). The corresponding ethylene price is then \$1,756.39 per metric tonne of ethylene in both, the OCM-A and OCM-S cases. A summary of the economic results can be found in **Table 3-15** and a detailed breakdown of the various CoE cost driving factors is shown in **Figure 3-10** (note that the H₂ revenue is equally distributed between all cost driving factors leading to a cost reduction of 14.5% across all categories). The economies of scale behave very similarly to the OCM-A case and a CoE of \$1,473.00 per metric tonne of ethylene can be expected at a 1,500,000 MTPY scale, a 17.1% reduction. A comparison of the economies of scale is shown in **Figure 3-11**.

Table 3-15: OCM (Steam Oxidant) Plant Economics

Overnight Cost	Value	Unit
Total Plant Cost	2,407,051	\$ (thousands)
Preproduction Cost	90,459	\$ (thousands)
Inventory Capital Cost	16,137	\$ (thousands)
Initial Catalyst, Sorbent & Chemicals Cost	5,264	\$ (thousands)
Land	900	\$ (thousands)
Other Owners' Costs	442,026	\$ (thousands)
Financing Costs	64,990	\$ (thousands)
Fixed Operating Cost	Value	Unit
Annual Labor Cost	57,960	\$ (thousands)
Annual Tax and Insurance Cost	48,141	\$ (thousands)
Variable Operating Cost	Value	Unit
Annual Natural Gas Cost	110,026	\$ (thousands)
Annual Electricity Cost	231,075	\$ (thousands)
Annual Maintenance Materials Cost	33,764	\$ (thousands)
Annual Chemical, Catalyst & Disposal Costs	25,006	\$ (thousands)
Annual Hydrogen By-product Revenue	108,425	\$ (thousands)
Economic Performance Metrics	Value	Unit
Specific Ethylene Plant Cost	6,018	\$/metric tonne ethylene
1 st Year Levelized Cost of Ethylene	1,776.93	\$/metric tonne ethylene

3.4 Electrochemical OCM Plant with Carbon Dioxide Utilization via Methanation

3.4.1 Technology Performance Analysis

In the electrochemical OCM plant with CO₂ utilization (OCM-C), CO₂ is used as an additional carbon source to reduce the NG feedstock import. While the initial idea was to use CO₂ directly in the SOC to provide oxygen for the OCM reaction on the anode while producing CO on the cathode, this approach has been identified as problematic for three main reasons: I) there is no use for CO in an ethylene plant, II) CO methanation is more exothermic than CO₂ methanation and thermal management of the methanation reactors will be more problematic, and III) H₂ supply is the limiting factor for methanation in an ethylene plant (remember in the OCM-A case some CO₂ from the MEA unit is vented instead of methanized because of insufficient H₂).

Thus, instead of utilizing CO₂ in the SOC, CO₂ is utilized in the methanation section of the plant and the OCM unit in the OCM-C case operates in a similar fashion as in the OCM-S case (flowsheet is provided in **Figure 3-8** and corresponding state-point stream data in **Table 3-19**). By using steam as oxidant in the SOC, the produced H₂ can be used to maximize CO₂ utilization via methanation which means that the otherwise-vented CO₂ from the MEA unit plus a CO₂ feedstock stream can be methanized. However, even with this large supply of H₂, H₂ remains the limiting factor for CO₂ utilization setting the CO₂ utilization of this plant to 225,270 MTPY (at 90% capacity factor) at a 400,000 MTPY ethylene plant. With this additional carbon source, 116,480 MTPY of NG can be displaced. The electricity consumption slightly decreases despite the higher power consumption due to an increase in power generation, which will be discussed in more detail later. The water consumption increases due to a higher power generation in the steam cycle but also higher cooling demand of the ethylene-rich syngas quench and compressor intercooling related to a higher water content in the syngas, a side-product of the methanation reaction. Since the methanation reaction is an equilibrium reaction, also higher CO₂ concentrations are found in the syngas which increases the NaOH and MEA consumption. To minimize this increase of CO₂ in the syngas, a fourth

methanation stage is added to the design in the OCM-C case to better handle the temperature increase in the methanation reactors caused by the co-feeding of pure CO₂ and H₂ streams. The thermal NG-to-ethylene conversion efficiency increases to 72.78%; however, this metric is misleading for cases with CO₂ utilization as CO₂ is now an imported feedstock. The overall efficiency decreases from 52.71% in the OCM-S case to 42.16% in the OCM-C case, yet is still higher than in the OCM-A case with 40.47%. A summary of the results is provided in **Table 3-16**.

Table 3-16: OCM (CO₂ Utilization) Plant Performance

Plant Design Capacity	Value	Unit
Ethylene Production Capacity	400,000	metric tonnes/year
Plant Capacity Factor	90	%
Actual Ethylene Production	360,000	metric tonnes/year
Actual Carbon Dioxide Utilization	225,270	metric tonnes/year
Consumables at 90% Capacity Factor	Value	Unit
Natural Gas	494,330	metric tonnes/year
Carbon Dioxide	225,270	metric tonnes/year
Electricity	4,707,240	MWh/year
Raw Water Withdrawal	11,503,150	metric tonnes/year
NaOH Solution, 32%	10,070	metric tonnes/year
MEA	1,570	metric tonnes/year
Energy Metrics at Full Load Operation	Value	Unit
Natural Gas Feedstock Energy (LHV)	821,920	kW _c
Ethylene Product Energy (LHV)	598,180	kW _c
Electricity Consumption	597,060	kW _e
Cooling Tower Heat Rejection	806,960	kW _t
Efficiency Metrics	Value	Unit
NG to Ethylene Thermal Efficiency	72.78	%
Ethylene Overall Thermal Efficiency	42.16	%

Due to the exothermic nature of the methanation reaction, additional steam is raised in the methanation section of the OCM-C case as well as in the transfer line exchangers due to increased flow rates. This results in an 15.1% increase in power output of the steam cycle. On the auxiliary side, the SOC and power electronics consume slightly more power than in the OCM-S case, which is the result of a higher SOC water inlet concentration (anode), 9.0 mol.-% (OCM-S) versus 20.2 mol.-% (OCM-C), and leads to an increase in the Nernst voltage. Thus, to operate the cell at constant current density and overpotentials, the operating voltage is increased to 2.51 V (vs. NHE). Due to this concentration change on the anode, slight adjustments to the cathode recycle systems are necessary to satisfy the thermal cell constraints, which leads to an increase in the power consumption of the cathode steam system as well. Hydrogen compression power, however, is reduced as a H₂ supply pressure of 20 bar is sufficient for the methanation reactor. Furnace air blower, induced draft fan, steam cycle feedwater pumps, quench water circulation pump, quench vent compressor, MEA CO₂ removal, and caustic recirculation pump experience all a small increase in power consumption due to increased steam generation or higher CO₂ and water content in the ethylene-rich syngas. The power consumption of the CO₂ compression experiences a steep increase, which is a result of CO₂ utilization. In this scenario the “capture ready” CO₂ stream is fully utilized which now requires all the CO₂ to be compressed to 20 bar instead of venting part of the stream. Together with the increase in cooling demand, power consumption of cooling water circulation and cooling tower fans increases, which is mostly due to an increase in heat rejection from the steam cycle, syngas quench and water condensation during

syngas compression. An overview of the various power generation and auxiliary loads can be found in **Table 3-17**.

Table 3-17: OCM (CO₂ Utilization) Plant Electric Power Consumption at Full Load Operation

Energy Output	Value	Unit
Steam Cycle	113,620	kW _e
Cold Box Expander	0	kW _e
Total Electricity Generation	113,620	kW_e
Auxiliary Load	Value	Unit
Solid Oxide Cell	511,105	kW _e
Inverter Loss	10,220	kW _e
Cathode Steam System	39,740	kW _e
Hydrogen Compression	12,045	kW _e
Furnace Air Blower	1,950	kW _e
Induced Draft Fan	3,395	kW _e
Steam Cycle Feedwater Pumps	3,005	kW _e
Quench Water Circulation Pump	315	kW _e
Quench Vent Compressor	115	kW _e
MEA CO ₂ Removal	150	kW _e
CO ₂ Compression	1,290	kW _e
Caustic Recirculation Pump	55	kW _e
Syngas Compression	48,515	kW _e
Cooling Water Circulation Pumps	5,310	kW _e
Cooling Tower Fans	3,930	kW _e
Propylene Refrigeration Cycle	44,275	kW _e
Ethylene Refrigeration Cycle	22,265	kW _e
Miscellaneous Balance of Plant	3,000	kW _e
Total Electric Load	710,685	kW_e
Net Electricity Usage	Value	Unit
Net Electricity Consumption	597,060	kW_e

The local CO₂ point source emissions of the OCM-C plant are 398,442 MTPY, which is a 17.2% reduction over the OCM-S case. All CO₂ emissions in this scenario are from the furnace and the venting of the “capture ready” CO₂ steam has been eliminated. Electricity-related CO₂ emissions are 5.047 kg_{CO2}/kg_{Ethylene} and NG-related CO₂ emissions are 0.606 kg_{CO2}/kg_{Ethylene}. By using CO₂ as a feedstock over NG, related emissions could be reduced by 18.6%. On top of that, with the import and utilization of CO₂, over 100% of the NG-feedstock-related emissions could be offset. The overall plant emissions of the OCM-C case are 6.134 kg_{CO2}/kg_{Ethylene}, further highlighting that it is crucial for electrochemical systems to run on renewable electricity or even CO₂ utilization cannot bring the desired CO₂ emission reduction effect. With renewable electricity the CO₂ emissions would be 1.087 kg_{CO2}/kg_{Ethylene} and substantially lower than an ethane steam cracker using renewable electricity. The plant emission values are summarized in **Table 3-18**.

Table 3-18: OCM (CO₂ Utilization) Plant Emissions

Point Source Emissions at 90% Capacity Factor	Value	Unit
Carbon Dioxide	398,442	metric tonnes/year
Specific CO ₂ Emission	1.107	kg _{CO2} /kg _{Ethylene}
Sulfur Oxides (as SO ₂)	0	kg/year
Specific SO ₂ Emission	0.000	ppm-wt. _{SO2} /kg _{Ethylene}
Catalyst and Sorbent Disposal	58	metric tonnes/year
Caustic Discharge (Disposal)	18,777	metric tonnes/year
Surface Water Discharge	2,927,256	metric tonnes/year
Indirect Carbon Dioxide Emissions at 90% Capacity Factor	Value	Unit
Electricity-related CO ₂ Emissions	1,816,995	metric tonnes/year
Specific Electricity-related CO ₂ Emissions	5.047	kg _{CO2} /kg _{Ethylene}
Ethane-related CO ₂ Emissions	0	metric tonnes/year
Specific Ethane-related CO ₂ Emissions	0.000	kg _{CO2} /kg _{Ethylene}
NG-related CO ₂ Emissions	218,085	metric tonnes/year
Specific NG-related CO ₂ Emissions	0.606	kg _{CO2} /kg _{Ethylene}
CO ₂ Utilization-related CO ₂ Emission Reduction	225,273	metric tonnes/year
Specific CO ₂ Utilization-related CO ₂ Emission Reduction	0.626	kg _{CO2} /kg _{Ethylene}

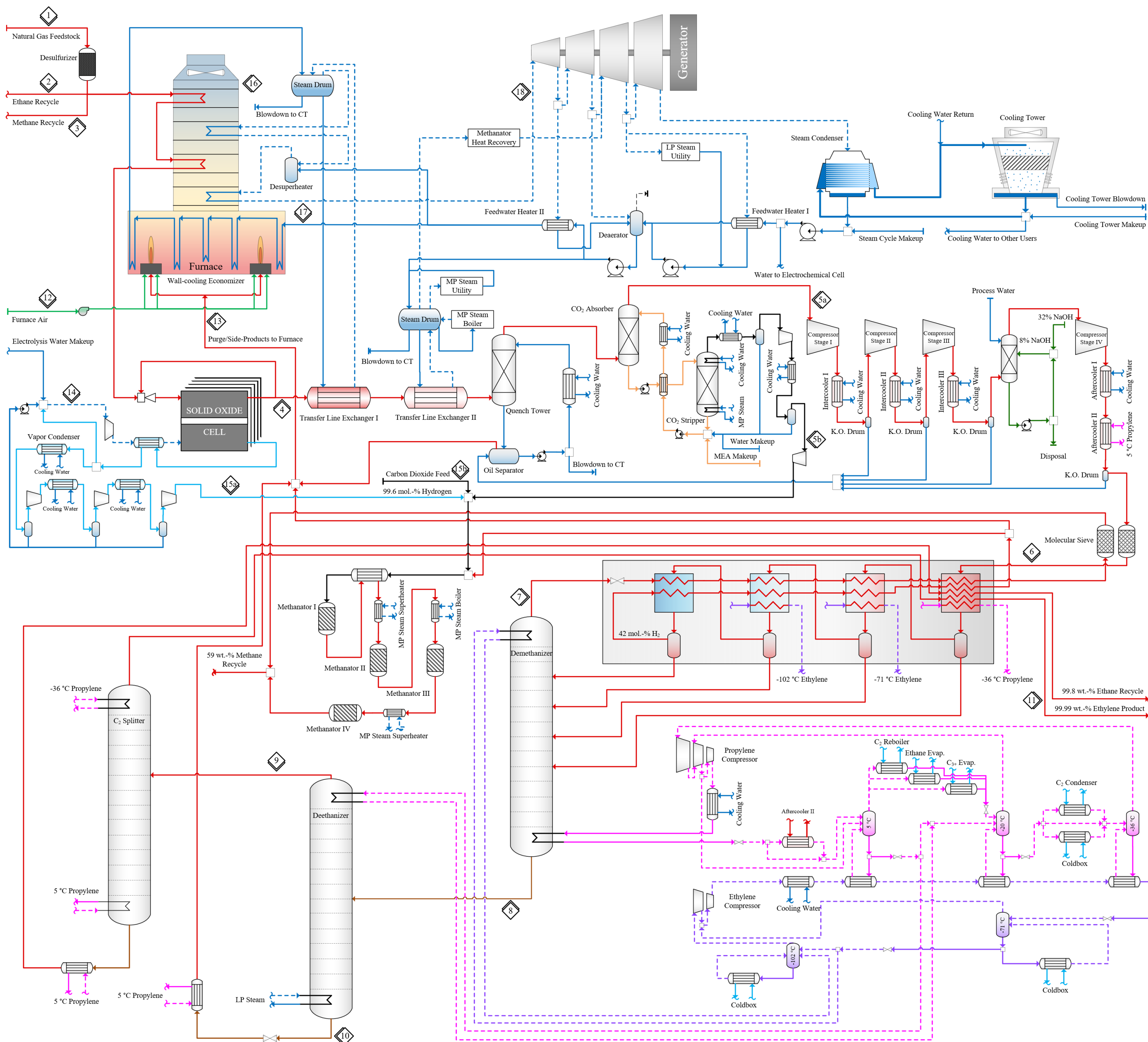


Figure 3-8: Simplified flowsheet of the electrochemical OCM plant with CO₂ utilization (OCM-C) for ethylene production.

Table 3-19: OCM (CO₂ Utilization) Plant State-Point Stream Data

Stream Number	Unit	1	2	3	4	5a	5b	6	7	8	9
Temperature	°C	15	12	213	850	43	8	16	-97	6	-2
Pressure	bar	4.0	15.0	4.0	1.6	1.0	1.9	35.2	32.0	32.0	26.0
Mole Flowrate	kmol/h	3,618	4,172	6,819	17,224	12,838	503	11,536	2,610	5,836	5,800
Mass Flowrate	kg/h	62,700	125,476	114,815	363,884	272,314	21,666	247,685	41,286	172,891	171,138
Molar Vapor Fraction	–	1	1	1	1	1	1	1	1	0	1
Composition	mole-basis										
O ₂	–	0.00010	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
N ₂	–	0.01600	0.00000	0.01229	0.00823	0.01104	Trace	0.01228	0.01292	0.00000	0.00000
H ₂ O	–	0.00003	0.00000	0.31454	0.29726	0.09507	0.03536	0.00000	0.00000	0.00000	0.00000
H ₂	–	0.00000	0.00000	0.03419	0.08615	0.11558	0.00003	0.12862	0.04531	0.00000	0.00000
CO	–	0.00000	0.00000	0.00623	0.00921	0.01236	Trace	0.01375	0.01619	0.00000	0.00000
CO ₂	–	0.01000	0.00000	0.01459	0.02864	0.00035	0.96418	0.00000	0.00000	0.00000	0.00000
CH ₄	–	0.93087	0.00000	0.61609	0.22492	0.30173	0.00010	0.33549	0.92017	0.00002	0.00002
C ₂ H ₆	–	0.03200	0.99834	Trace	0.24556	0.32944	0.00015	0.36201	Trace	0.71383	0.71816
C ₂ H ₄	–	0.00000	0.00096	0.00207	0.09755	0.13086	0.00017	0.14451	0.00540	0.27956	0.28132
C ₃ H ₈	–	0.00700	0.00053	Trace	0.00139	0.00187	Trace	0.00197	0.00000	0.00389	0.00038
C ₃ H ₆	–	0.00000	0.00017	Trace	0.00025	0.00033	Trace	0.00035	0.00000	0.00069	0.00012
n-C ₄ H ₈	–	0.00400	Trace	Trace	0.00073	0.00098	Trace	0.00088	0.00000	0.00174	Trace
1-C ₄ H ₈	–	0.00000	Trace	Trace	0.00011	0.00015	Trace	0.00014	0.00000	0.00027	Trace
SO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Total	–	1.00000	1.00000	1.00000	1.00000	0.99975	0.99999	1.00000	1.00000	1.00000	1.00000
Stream Number	Unit	10	11	12	13	14	15a	15b	16	17	18
Temperature	°C	82	12	15	60	194	144	15	124	190	540
Pressure	bar	26.0	18.3	1.0	2.0	1.5	20.0	20.0	0.9	128.5	121.7
Mole Flowrate	kmol/h	37	1,628	21,272	1,816	268,359	3,822	649	22,763	21,248	21,197
Mass Flowrate	kg/h	1,752	45,662	611,788	22,883	4,136,867	7,955	28,573	634,671	382,781	381,865
Molar Vapor Fraction	–	0	1	1	1	1	1	1	1	0	1
Composition	mole-basis										
O ₂	–	0.00000	0.00000	0.20824	0.00000	0.00000	0.00000	0.00000	0.08632	0.00000	0.00000
N ₂	–	0.00000	0.00000	0.78338	0.03188	0.00000	0.00000	0.00000	0.73463	0.00000	0.00000
H ₂ O	–	0.00000	0.00000	0.00838	0.02610	0.83750	0.00410	0.00000	0.12852	1.00000	1.00000
H ₂	–	0.00000	0.00000	0.00000	0.40313	0.16250	0.99590	0.00000	0.00000	0.00000	0.00000
CO	–	0.00000	0.00000	0.00000	0.03437	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
CO ₂	–	0.00000	0.00000	0.00000	0.00121	0.00000	0.00000	1.00000	0.05045	0.00000	0.00000
CH ₄	–	0.00000	0.00008	0.00000	0.43549	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
C ₂ H ₆	–	0.02742	0.00004	0.00000	0.03264	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
C ₂ H ₄	–	Trace	0.99988	0.00000	0.01327	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
C ₃ H ₈	–	0.56029	0.00000	0.00000	0.01200	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
C ₃ H ₆	–	0.09173	0.00000	0.00000	0.00195	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
n-C ₄ H ₈	–	0.27783	0.00000	0.00000	0.00695	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
1-C ₄ H ₈	–	0.04272	0.00000	0.00000	0.00102	0.00000	0.00000	0.00000	0.00008	0.00000	0.00000
SO ₂	–	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Total	–	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000

3.4.2 Economic Performance Analysis

The TPC of the plant with CO₂ utilization is \$2,477,769,000, and thus, \$70,718,000 more expensive than the OCM-S case. The specific plant cost is \$6,194 per metric tonne of ethylene at a 400,000 MTPY plant scale. The higher water mass flow rate in the OCM-C case, due to the methanation reaction, leads to more steam generation in the transfer line exchangers leading to more electricity generation but also higher capital costs in furnace, steam cycle, and cooling tower. The concentration change further impacts the SOC and power electronics, which experience a capital cost increase of 1.0%. The cost of the methanation unit increases from \$11,936,000 (OCM-S) to \$29,817,000 (OCM-C). Other plant areas, such as electrical and instrumentation, structures and foundation, site improvement, and miscellaneous expense, increase with

CO₂ utilization, while most of the remaining plant costs remain relatively constant compared to the OCM-S case. The only plant area where cost saving area achieved is the H₂ BOP equipment, whose cost is reduced from \$180,747,000 (OCM-S) to \$166,560,000 due to cost savings in the compression section related to the lower H₂ pressure requirement in the OCM-C case. The breakdown of the TPC is shown in **Figure 3-9**.

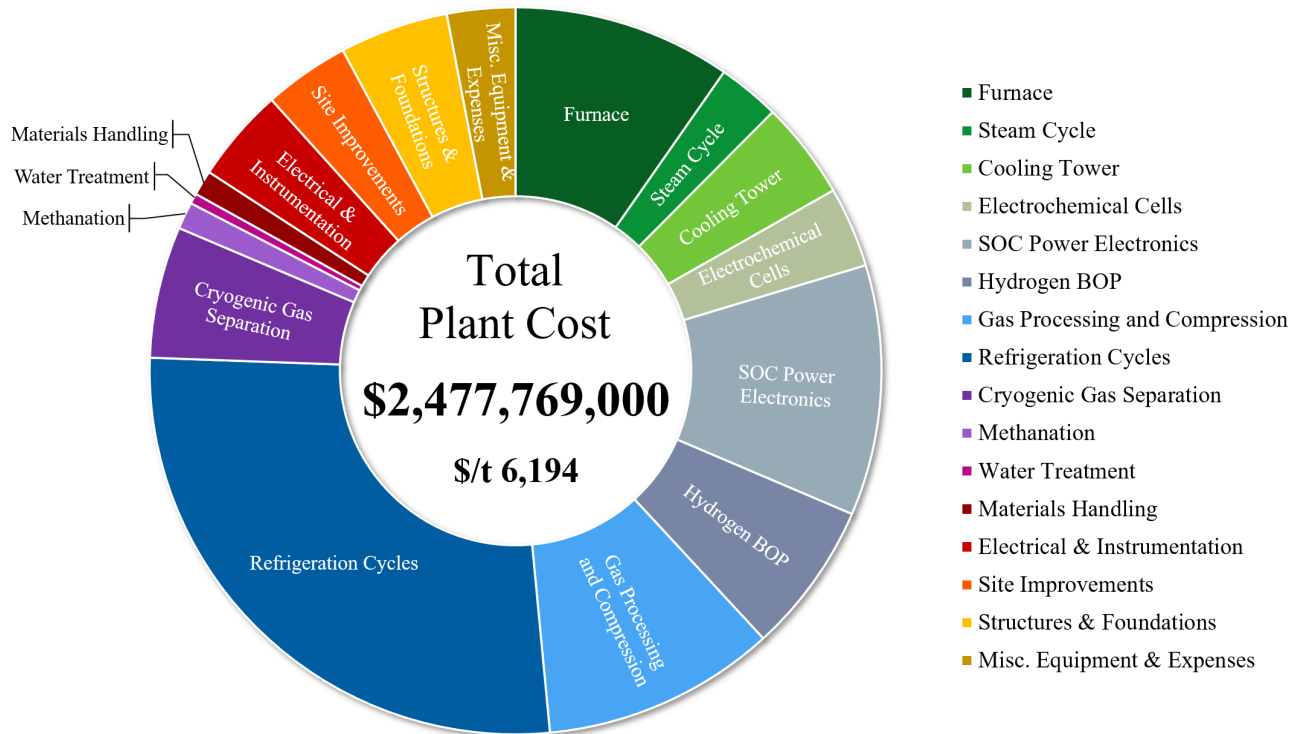


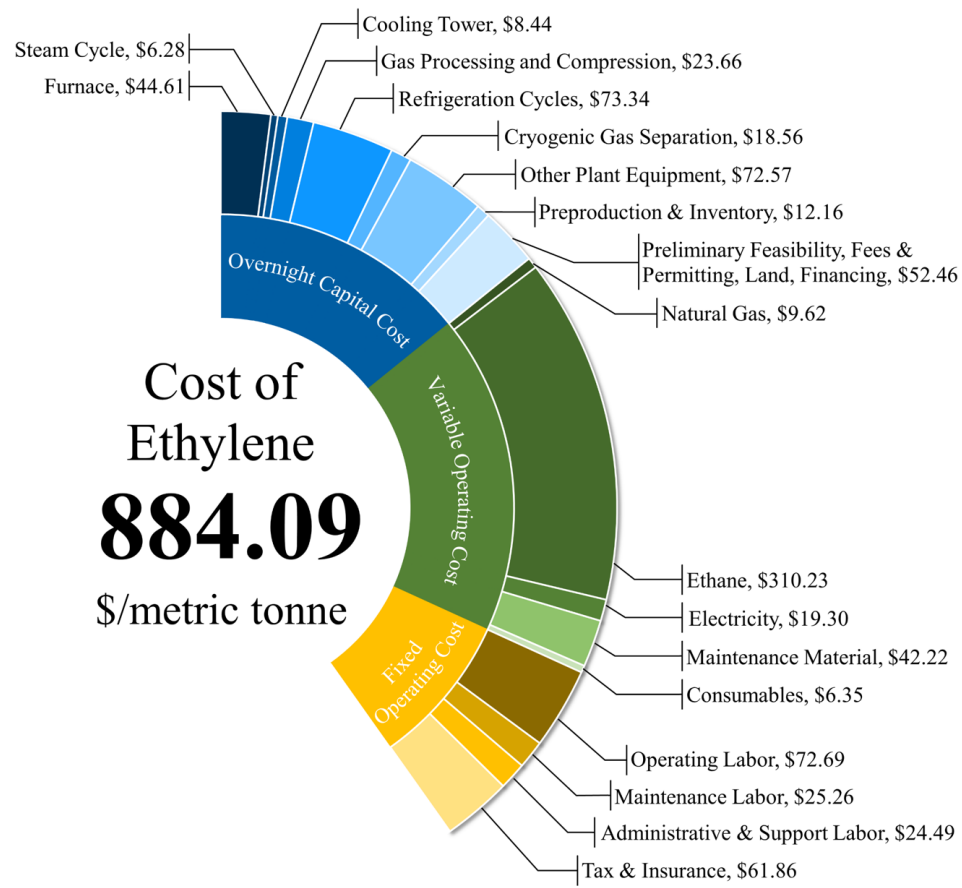
Figure 3-9: Breakdown of the OCM (CO₂ utilization) total-plant-cost (TPC).

The total overnight capital cost increases to \$3,115,339,000, which is primarily related to the increased TPC. Also, fixed operating costs slightly increase. The annual operating labor increases to \$58,411,000 per annum due to higher maintenance operating labor, and the annual tax and insurance costs increase to \$49,555,000 per year due to a higher TPC. Among the variable operating costs, higher catalyst demand in the methanation section leads to increased catalyst and disposal costs. On the feedstock-side, by replacing NG with CO₂ as feedstock, the annual NG cost is reduced by \$20,983,000; however, the CO₂ feedstock cost, at \$200 per metric tonne, increases the overall feedstock cost by \$24,072,000 per year. Yet, this is not the only cost penalty on the OCM-C case, it is important to understand that by utilizing CO₂, \$108,425,000 of H₂ by-product revenue are erased as well. The resulting CoE is \$2,175.49 per metric tonne of ethylene, which is the highest among the studied scenarios. Even as the cost of CO₂ approaches the DOE target of \$100 per metric tonne, the CoE remains relatively fix at \$2,112.80 per metric tonne of ethylene as the CO₂ feedstock cost is represents only 5.8% of the CoE. On top of the reduced CO₂ price of \$100 per metric tonne, a carbon utilization credit of \$536.73 per metric tonne of CO₂ would be needed to break even with the OCM-S case. A summary of the economic parameters is provided in **Table 3-20**. A detailed breakdown of the various cost driving factors is shown in **Figure 3-10** and the economies of scale are depicted in **Figure 3-11**.

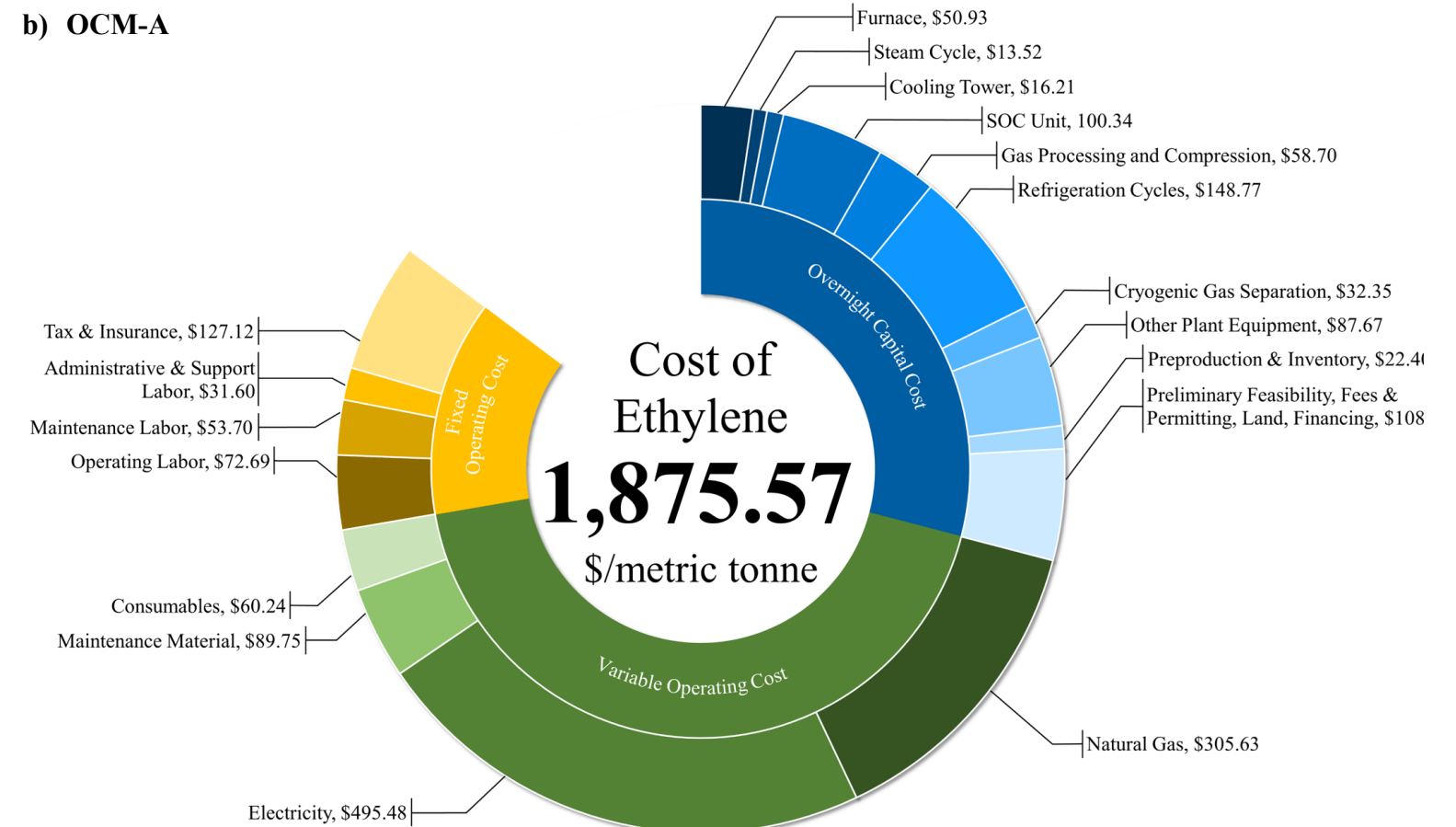
Table 3-20: OCM (CO₂ Utilization) Plant Economics

Overnight Cost	Value	Unit
Total Plant Cost	2,477,769	\$ (thousands)
Preproduction Cost	92,900	\$ (thousands)
Inventory Capital Cost	16,926	\$ (thousands)
Initial Catalyst, Sorbent & Chemicals Cost	4,932	\$ (thousands)
Land	900	\$ (thousands)
Other Owners' Costs	455,012	\$ (thousands)
Financing Costs	66,900	\$ (thousands)
Fixed Operating Cost	Value	Unit
Annual Labor Cost	58,411	\$ (thousands)
Annual Tax and Insurance Cost	49,555	\$ (thousands)
Variable Operating Cost	Value	Unit
Annual Natural Gas Cost	89,043	\$ (thousands)
Annual Carbon Dioxide Feedstock Cost	45,055	\$ (thousands)
Annual Electricity Cost	230,278	\$ (thousands)
Annual Maintenance Materials Cost	34,367	\$ (thousands)
Annual Chemical, Catalyst & Disposal Costs	27,239	\$ (thousands)
Annual Carbon Dioxide Utilization Credit	0	\$ (thousands)
Economic Performance Metrics	Value	Unit
Specific Ethylene Plant Cost	6,194	\$/metric tonne ethylene
1 st Year Levelized Cost of Electricity	2,175.49	\$/metric tonne ethylene

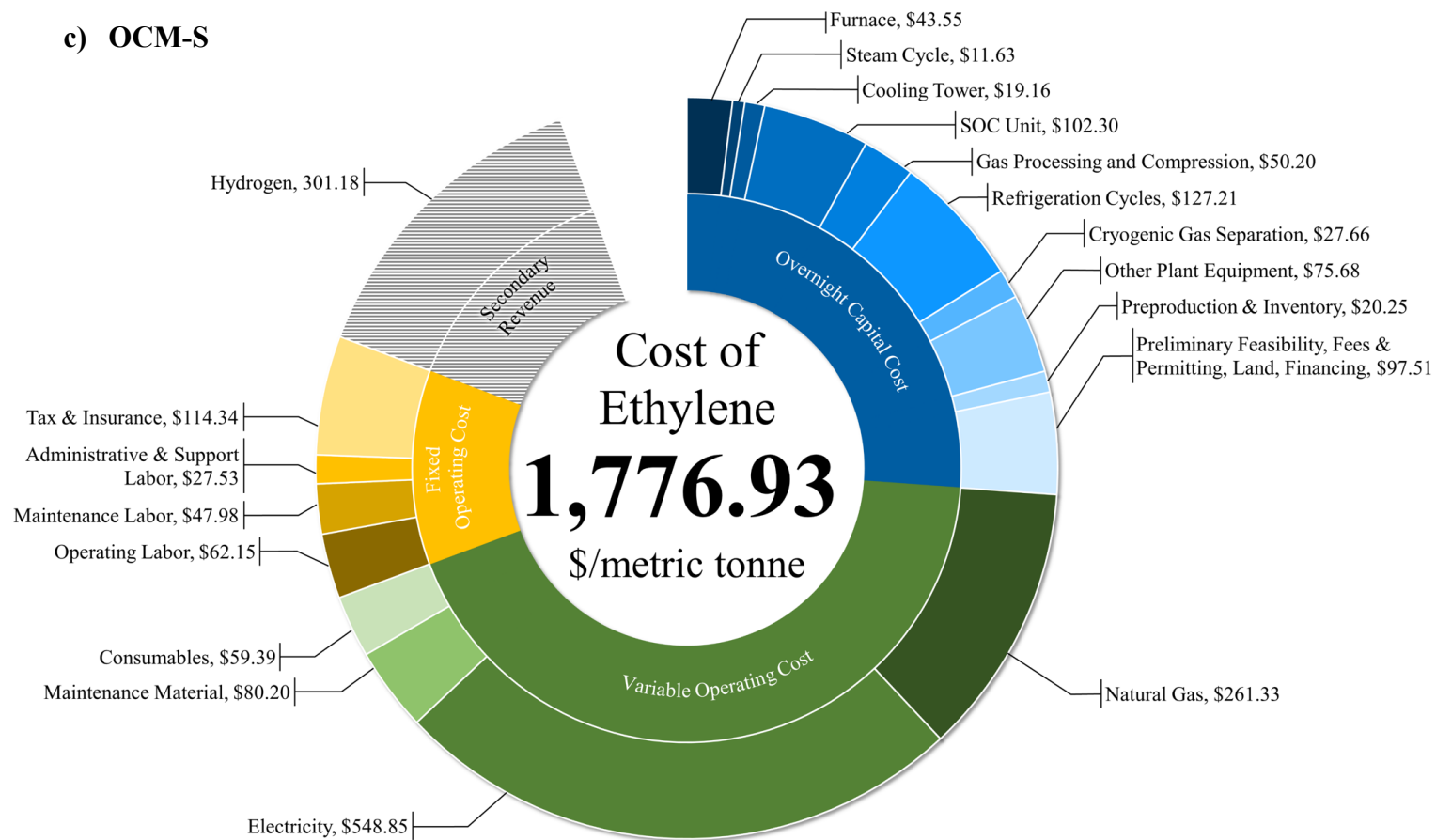
a) SOTA



b) OCM-A



c) OCM-S



d) OCM-C

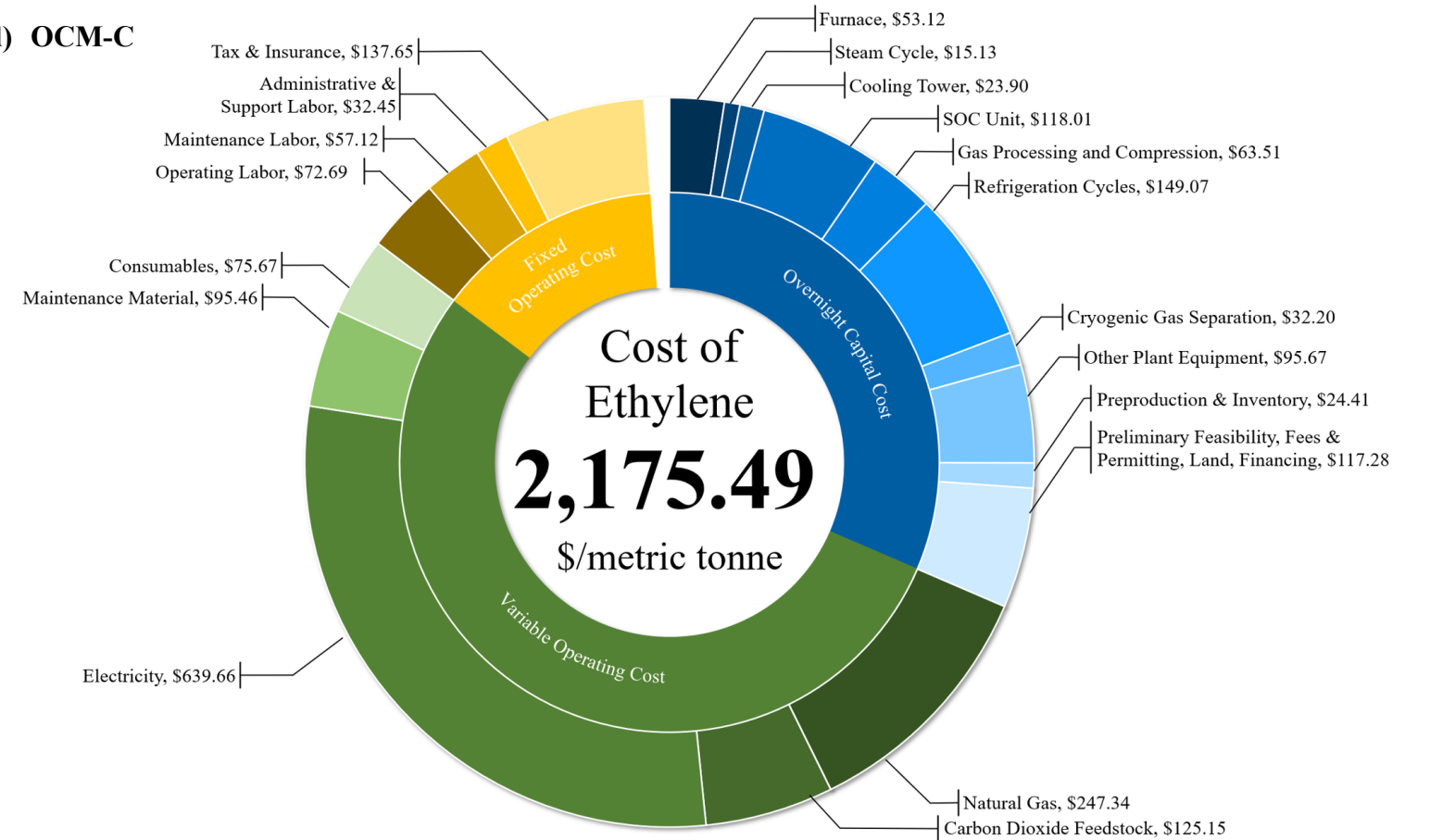


Figure 3-10: Cost of ethylene by scenario.

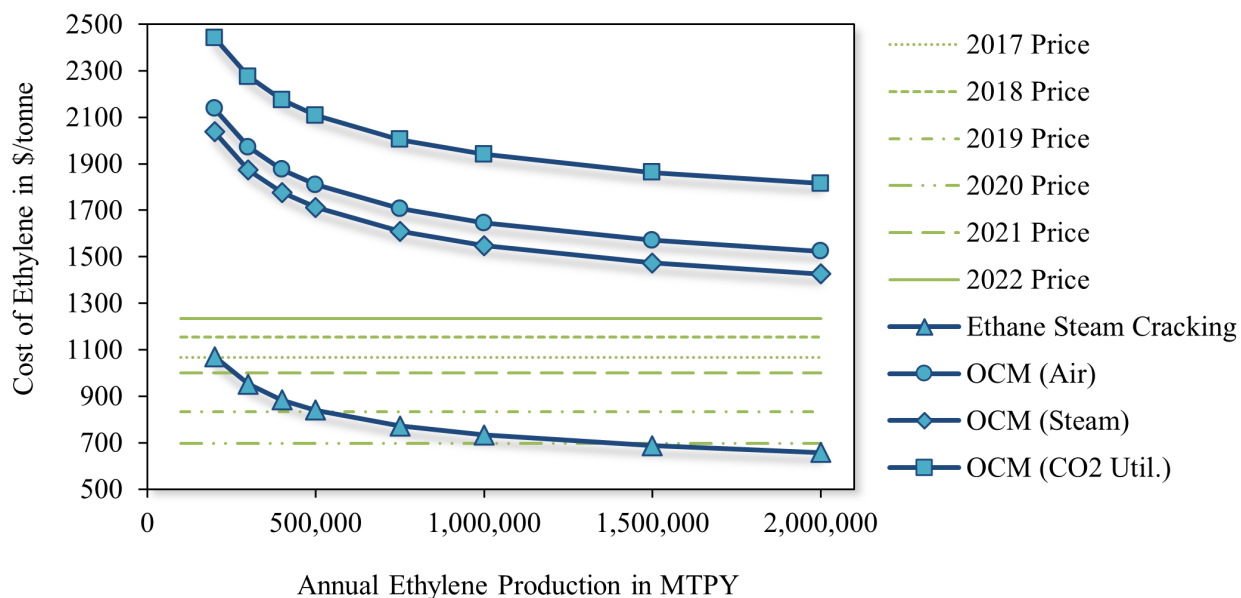


Figure 3-11: Economies of scale of the ethane steam cracker and OCM plants.

3.5 Sensitivity Analysis

In the following sensitivity analysis, the OCM-S case is further investigated to better understand cost driving factors. The OCM-S case has been selected for this analysis as it has shown to have the highest commercial potential among the studied scenarios. As electrochemical OCM is a relatively new area of research, current performance characteristics are low compared to some other electrochemical processes; thus, this sensitivity analysis will help to set performance targets that will allow this technology to become economically viable. First, in the sensitivity analysis the cost of the SOC cell stack and power electronics have been varied by $\pm 60\%$ to investigate their impact on the CoE. As seen in the TPC of the OCM-S case (**Figure 3-7**), the power electronics have a more dominant impact on the TPC compared to the cell stacks, which is not surprising given the fact that the OCM-S case has a power density that is about 10 times higher than commercial SOFC systems. The SOC operates at a current density of 0.9 A/cm^2 , which is substantially higher than current commercial SOFC systems (0.28 A/cm^2) and helps to reduce the cost of the SOC stacks as less cells/stacks are needed to facilitate the reaction. Due to this, variations in the costs of power electronics have a stronger impact on the CoE than variations in SOC cost, as illustrated in **Figure 3-12**. A SOC cost increase of 60%, increases the CoE by 0.8%, from \$1776.93 to \$1792.03 per metric tonne of ethylene. Similarly, a 60% reduction of the SOC cost results in a 0.8% CoE reduction to \$1761.77 per metric tonne of ethylene. With a 3.3% change in CoE per 60% change in cost-of-power electronics, the impact of cost reductions on the power electronics side are more than 3 times more effective. These effects are a result of CAPX and OPEX changes and it is important to understand that the SOC has a much higher levelized maintenance cost compared to the power electronics as the stacks need to be replaced after 10 years due to degradation. These higher maintenance costs of the SOC counteract some of the CAPX differences, otherwise the difference in CoE sensitivity between SOC and power electronics would be even greater.

This information is also important when looking at the current density and operating voltage. Increasing or decreasing the current density has a similar effect as changing the SOC cost; however, since the cell area doubles with halving the current density, this trend is now exponential. The CoE is relatively insensitive to the current density as current density only impacts the number of stacks needed, which is a relatively small

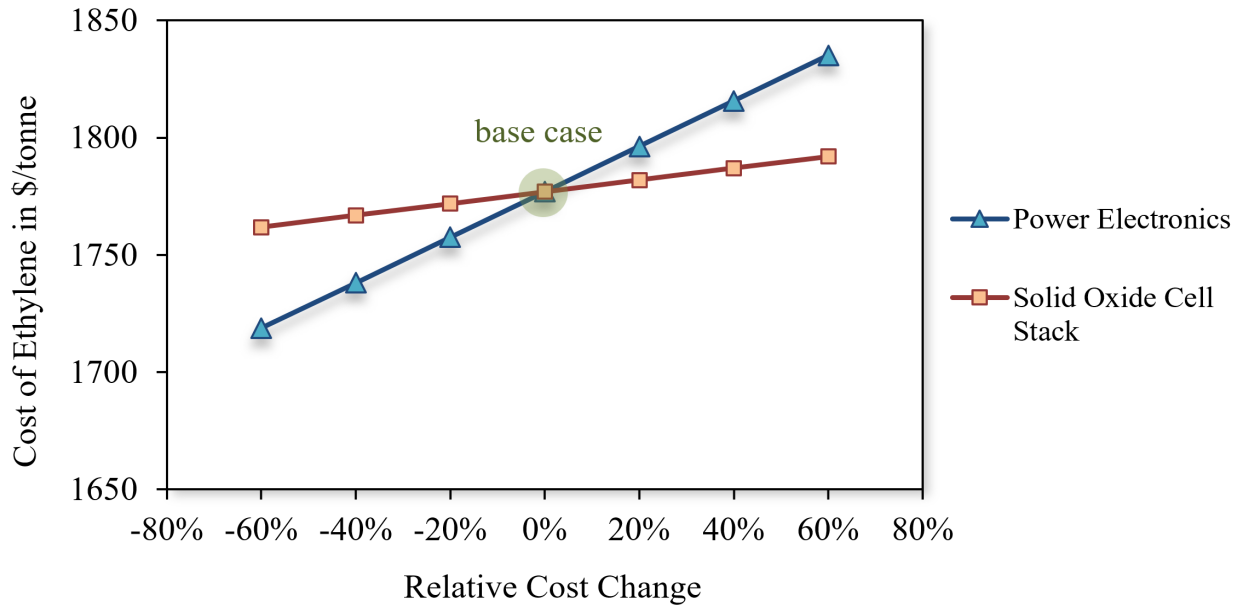


Figure 3-12: Impact of solid oxide cell cost and costs of power electronics upon the cost of ethylene.

portion of the overall cost (OCM cells operate at comparatively high current densities). Increasing the current density from 0.9 A/cm² to 1.5 A/cm² leads to a CoE reduction of only \$16.18 per metric tonne of ethylene. Reducing the current density to 0.3 A/cm² leads to a CoE increase of \$78.24 per metric tonne of ethylene. The results of the sensitivity analysis of the current density are shown in blue in **Figure 3-13** and values refer to the x-axis on the top of the graph. The green dot is the OCM-S base case previously discussed.

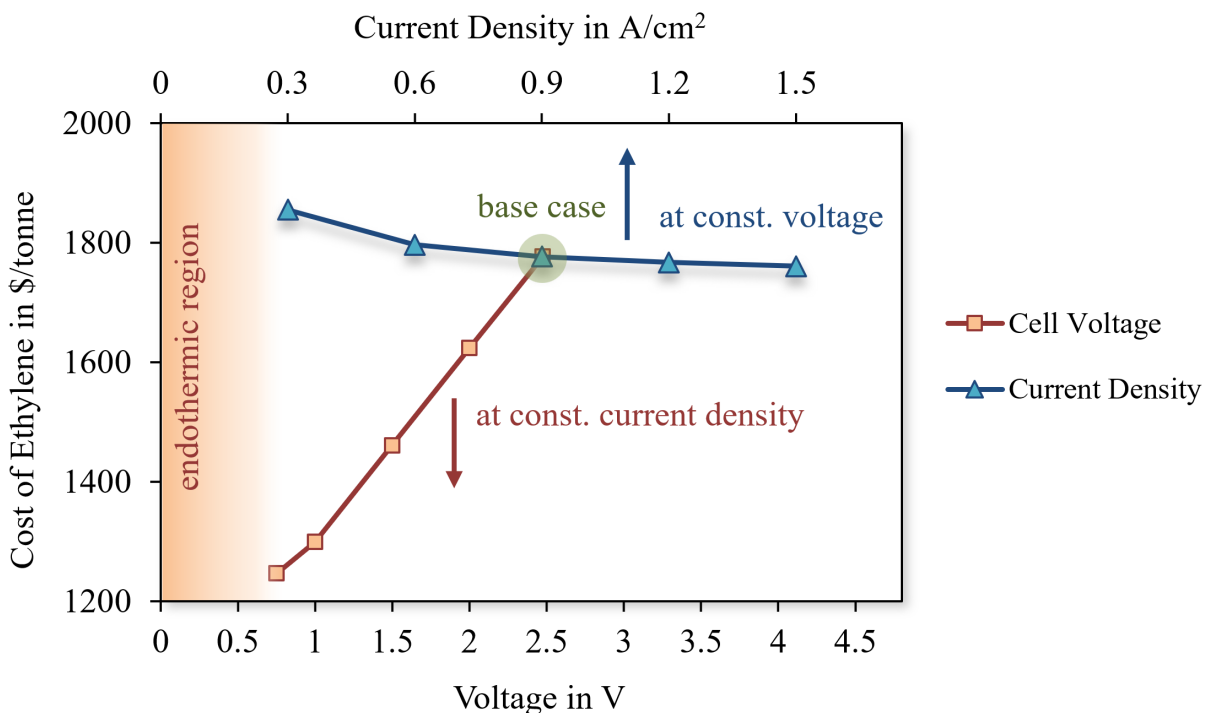


Figure 3-13: Impact of current density and operating voltage upon the cost of ethylene.

By reducing the operating voltage at constant current density, overpotentials/losses are reduced. This has primarily two effects: 1) reduce cost of power electronics and 2) reduce electricity consumption. If overpotentials – and thus operating voltage – can be reduced, substantial cost savings are achieved. Initially the CoE drops almost linearly at a rate of \$325.64/V and reaches a CoE of \$1299.63 per metric tonne of ethylene at an operating voltage of 1 V (vs. NHE). At this operating voltage the average overpotentials in the SOC are 0.87 V (a 1.59 V reduction over current state-of-the-art OCM cells with 2.46 V), which is still more than double as high as what current SOFCs can achieve. When moving to even lower voltages than 1 V (vs. NHE), the reaction conditions are approaching the endothermic region (0.57 V (vs. NHE), at 800 °C) and a change in slope is observed. At these conditions the cell operating temperature drops slightly and instead of liquid water makeup on the cathode side (for H₂ production) steam addition from the steam cycle is needed (SOC does not generate enough heat to raise steam in the cathode loop). This reduces the power generation in the steam cycle, which is further impacted by a reduced steam generation in the transfer line exchangers due to a lower SOC anode off-gas temperature. Thus, with the heat integration proposed in this study, 0.75 V (vs. NHE) represents the lower practical operating limit. However, this also means that there are potentially interesting system integration options with solar thermal or thermal energy storage solutions that could lead to substantial performance improvements thermodynamically and environmentally when operating the cell in the endothermic region. Just by improving the operating voltage, emission reductions of 2.981 kg_{CO2}/kg_{Ethylene} are possible.

For the single pass yield sensitivity study, the 0.75 V (vs. NHE) scenario has been chosen as base case. Increasing the single pass yield will substantially increase the heat generation inside the SOC, and thus, it has no practical value of studying single pass yield in scenarios that already suffer from extensive heat generation, e.g. cases that operate with high overpotentials. In the single pass yield scenarios the methane conversion rate of reactions (E 2-17) and (E 2-22) has been adjusted and the scenarios are referred to by the single pass yield of reaction (E 2-17), the OCM reaction. In the base case, the yields for reactions (E 2-17) and (E 2-22) are 23.0% and 9.0%, which corresponds to current state-of-the-art OCM cells. In a first step, yields are increased to 38.3%/15.0% and 53.6%/21.0% respectively before arriving at 69.0%/23.0% which corresponds to a total single pass CH₄ conversion of 85%. Changing the yields of reactions (E 2-17) and (E 2-22) also impacts the Faraday efficiency, which is presented in **Table 3-21**.

Table 3-21: Faraday Efficiency

Reaction	OCM-S Base Case	OCM-S 54% Yield	OCM-S 69% Yield
#1 CH ₄ → C ₂ H ₄	56.99%	74.38%	78.51%
#2 CH ₄ → C ₂ H ₆	13.63%	7.63%	6.26%
#3 CH ₄ → CO	12.39%	6.94%	5.69%
#4 CO → CO ₂	0.18%	0.04%	0.03%
#5 H ₂ → H ₂ O	1.03%	0.47%	0.39%
#6 C ₂ H ₆ → C ₂ H ₄	15.59%	10.40%	8.98%
#7 C ₃ H ₈ → C ₃ H ₆	0.12%	0.09%	0.09%
#8 C ₄ H ₁₀ → C ₄ H ₈	0.06%	0.05%	0.05%

Increasing the single pass yield can substantially decrease the CoE. Increasing the single pass yield from 23.0% to 69.0% decreases the CoE from 1,247.24 to \$789.95 per metric tonne of ethylene, as seen in **Figure 3-14**. This cost decrease is driven by a substantial CAPEX reduction as well as OPEX reduction. On the CAPEX side, a higher yield leads to less gas recirculation leading to a downscaling of the syngas compression section, refrigeration cycles and cryogenic gas separation. Cost savings in these units alone account for \$564,952,000. Also, the furnace, steam cycle and cooling water systems become substantially

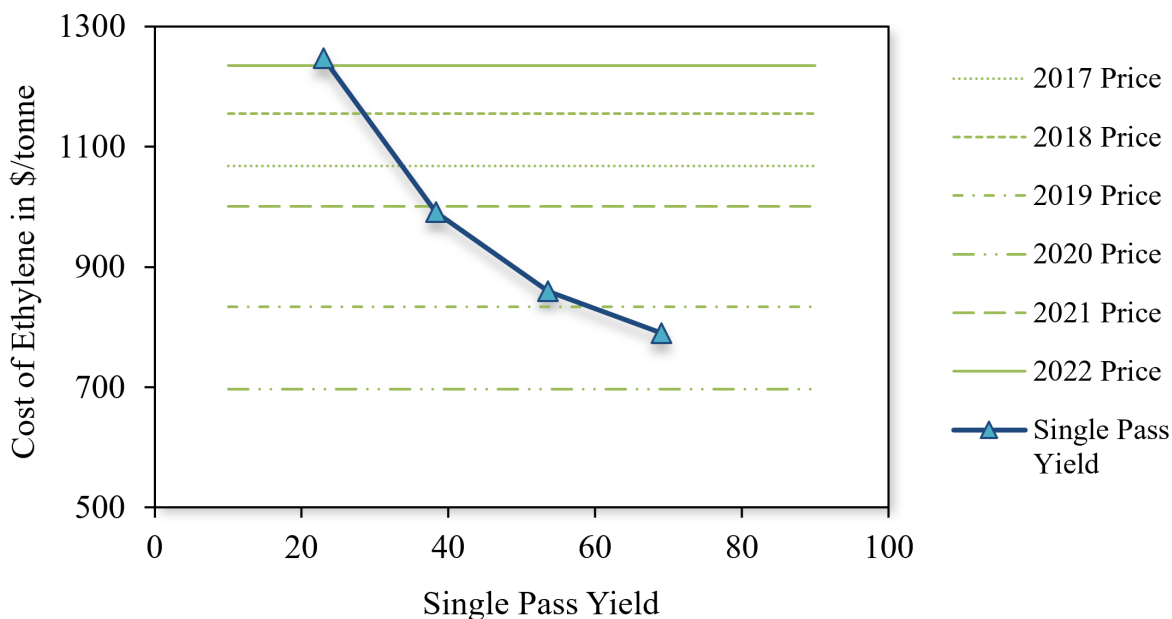


Figure 3-14: Impact of single pass yield upon the cost of ethylene.

cheaper if higher single pass yields are achieved as less purge gas needs to be burned. The equipment downsizing furthermore positively impacts the annual maintenance costs as well as power consumption, e.g. compression power. The higher Faraday efficiency helps to minimize by-products and reduces the annual fuel cost by \$21,599,000. This performance improvement results in an overall plant efficiency of 82.51%, which exceeds the efficiency of the ethylene steam cracker. Moreover, this performance increase positively impacts the plant emissions and on-site point source CO₂ emission are 0.459 kg_{CO2}/kg_{Ethylene}, a 12.4% decrease over the ethane steam cracker. Indirect CO₂ emissions are still higher than in the ethane steam cracker reference case and shows that decarbonizing the grid is of major importance for electrification of the petrochemical industry. A summary of CO₂ emissions is provided in **Table 3-22**. A breakdown of the CoE for this case is shown in **Figure 3-15**.

Table 3-22: OCM Y69 (Steam Oxidant) Plant Emissions

Point Source Emissions at 90% Capacity Factor	Value	Unit
Carbon Dioxide	165,382	metric tonnes/year
Specific CO ₂ Emission	0.459	kg _{CO2} /kg _{Ethylene}
Indirect Carbon Dioxide Emissions at 90% Capacity Factor	Value	Unit
Electricity-related CO ₂ Emissions	576,256	metric tonnes/year
Specific Electricity-related CO ₂ Emissions	1.601	kg _{CO2} /kg _{Ethylene}
Ethane-related CO ₂ Emissions	0	metric tonnes/year
Specific Ethane-related CO ₂ Emissions	0.000	kg _{CO2} /kg _{Ethylene}
NG-related CO ₂ Emissions	216,575	metric tonnes/year
Specific NG-related CO ₂ Emissions	0.602	kg _{CO2} /kg _{Ethylene}

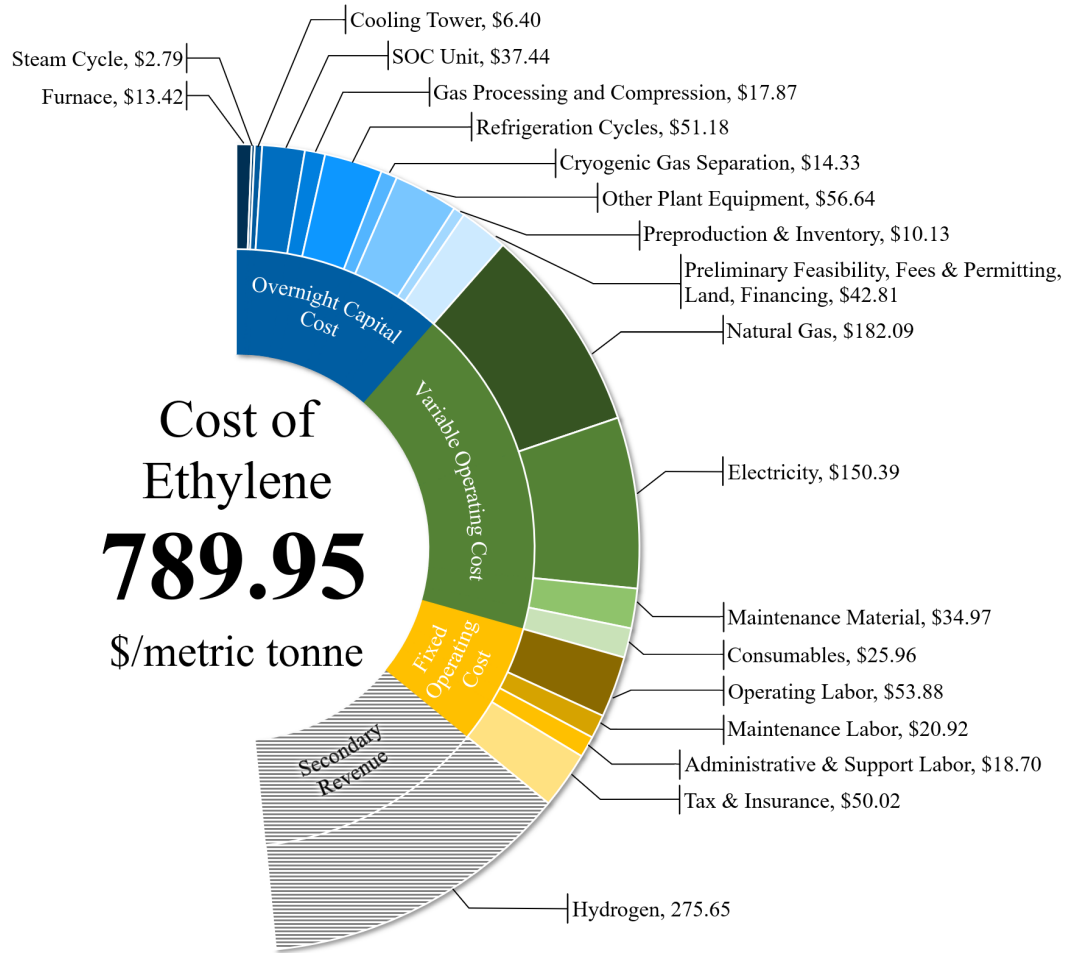


Figure 3-15: Cost of ethylene for the OCM-S case at a single pass yield of 69%.

4. Summary, Conclusions and Recommendations

4.1 Summary

In summary, a state-of-the-art ethane steam cracker plant for ethylene production has been analyzed and compared to ethylene plants that utilize electrochemical oxidative coupling of methane (OCM). In particular, three OCM scenarios have been investigated I) conventional OCM with air as oxidant (OCM-A) II) OCM with steam as oxidant and H₂ co-production (OCM-S), and III) OCM with steam as oxidant and CO₂ utilization via methanation (OCM-C). For the state-of-the-art ethane steam cracker plant the cost of ethylene (CoE) is \$884.09 per metric tonne of ethylene and CO₂ emissions are 0.524 kg_{CO2}/kg_{Ethylene} (direct) plus 1.078 kg_{CO2}/kg_{Ethylene} (indirect). While ethane steam crackers are an extremely mature technology, electrochemical OCM cells are considered early-stage technology. Current research focuses on increasing methane to ethylene conversion, current densities, as well as improved catalysts to reduce losses. Results show that current OCM cells are not yet economically competitive with the incumbent steam cracking route. The highest CoE is obtained in the OCM-C case. Producing the OCM feedstock (CH₄) onsite from CO₂ via methanation with H₂ from steam electrolysis, is substantially more expensive than fossil CH₄, resulting in a CoE of \$2175.49 per metric tonne of ethylene. The OCM-A case has a CoE of \$1875.57 per metric tonne of ethylene and the lowest CoE is achieved in the H₂ co-production scenario (OCM-S) with \$1776.93 per metric tonne of ethylene. Direct CO₂ emissions in the OCM cases increased by 111–155%, which is partly due to low single pass conversion rates requiring larger recycle loop purges as well as CO₂ produced by the overoxidation of the hydrocarbon feedstock and the burning of undesirable higher hydrocarbon byproducts. Indirect emissions increase by 332–439% mostly driven by the grid's electricity emission factor. This highlights the importance of using renewable electricity for electrochemical processes. Even CO₂ utilization cannot have a significant impact as long as grid emission factors are as high as they are today in the year 2024.

While current OCM cells, as expected, are not comparing favorably to the conventional ethane steam cracking process, once these cells reach performance metrics closer to current SOCs used in solid oxide fuel cells or electrolyzers, significant improvements in economics and emissions are observed. Improvements in current density are shown to only marginally impact the CoE; however, reductions of overpotentials and increased single pass conversion of methane to ethylene can bring the CoE down to \$789.95 per metric tonne of ethylene, which is lower than the SOTA ethane steam cracker plant. At the same time direct CO₂ emission drops to 0.459 kg_{CO2}/kg_{Ethylene}, a 12.4% decrease over the ethane steam cracker. Again, indirect emissions are closely tied to the grid emission factor, and as of today, indirect emissions of the improved OCM case remain high with 2.203 kg_{CO2}/kg_{Ethylene}. In a renewable grid this indirect emission factor would reduce to 0.602 kg_{CO2}/kg_{Ethylene}, a 44.2% reduction over the SOTA ethane steam cracker scenario. As long as the renewable power cost is below \$71.58 per MWh this scenario will be more economical than current SOTA ethane steam crackers.

4.2 Conclusions

MAIN CHALLENGES TO COMMERCIALIZATION ARE HIGH OVERPOTENTIALS AND LOW SINGLE PASS CONVERSION

Results show that the high overpotentials and low single pass conversion of methane to ethylene significantly hurt the economic performance of the OCM plants. By reducing overpotentials substantial savings in power electronics equipment and electricity costs can be achieved. Furthermore, lower overpotentials mean less cooling is needed. In the studied scenarios, cell cooling is not an issue once a cell operating voltage of 1.0–1.5 V (vs. NHE) is reached because of the large anode mass flow

due to low single pass conversion. Thus, once overpotentials have been reduced to operate the cell at about 1.0 V (vs. NHE), it is important to improve the single pass conversion in order to maintain the cell's operating temperature. Increasing the single pass conversion of methane to ethylene reduces the methane recycle which positively impacts the equipment size of the product separation equipment as well as electricity costs related to gas compression and refrigeration.

ELECTROCHEMICAL OCM HAS THE POTENTIAL TO BECOME MORE ECONOMICAL AND LOWER IN CO₂ EMISSIONS THAN CURRENT SOTA ETHANE STEAM CRACKING

Reducing cost and CO₂ emissions of OCM come hand in hand. Key for economical operation is the reduction of overpotentials to 0.55–0.87 V, which substantially reduces electricity consumption and indirect emissions from the grid. Additionally, the single pass yield of methane to ethylene should be around 54–69% to be economically competitive, which corresponds to a Faraday efficiency of 74.38–78.51%. Hitting these targets would allow OCM to be 11% cheaper and 12% lower in direct CO₂ emissions compared to current SOTA ethane steam cracking. However, in order to achieve comparable indirect CO₂ emissions it is crucial that the electricity emission factor is below 115 kgCO₂/MWh. If renewable biomethane is blended into the feed stream and renewable electricity is used, OCM has the potential to completely decarbonize ethylene production.

ELECTROCHEMICAL CELLS THAT CAN WITHSTAND ANODE-CATHODE PRESSURE DIFFERENTIALS COULD IMPROVE PLANT PERFORMANCE AND ECONOMICS

The analysis of the various OCM configurations has shown that improved system integration strategies would be possible if pressure differentials between the anode compartment and cathode compartment (across the membrane) were permissible. This is not only true for bifunctional cells, i.e. H₂ co-generation, where the substantial H₂ compression power could be reduced if the cathode was operated at higher pressure, but also in the air oxidant case (OCM-A) where large quantities of air need to be compressed to 1.6 bar – to match the required anode pressure of 1.6 bar – which increases power consumption and adds complexity. With electrochemical cells that tolerate pressure gradients across the anode and cathode compartments, H₂ generation can be shifted to higher pressures minimizing downstream H₂ compression (OCM-S case) or to lower cathode pressures – close to ambient pressure – in the OCM-A case to reduce air compression needs.

ELECTROCHEMICAL CELLS THAT CAN WITHSTAND HIGHER TEMPERATURE GRADIENTS COULD IMPROVE PLANT PERFORMANCE AND ECONOMICS

Commonly, temperature gradients in solid oxide cells are limited to 100 °C (inlet-outlet) to avoid cracking of the membrane due to thermal stress. Higher thermal gradients are desirable to reduce cooling requirements particularly in OCM scenarios where air is used as oxidant. Furthermore, larger thermal gradients would be beneficial for the integration of the hydrocarbon feedstock pre-heating system. To avoid cracking of the feedstock, the pre-heating temperature is limited to about 600 °C. Thus, allowing the feedstock to enter the SOC at that temperature and reach the required reaction temperature inside the SOC can be beneficial in limiting cracking side-reactions. Heating the feedstock to above 600 °C in an external heat exchanger poses a substantial risk that cracking reactions occur on the metallic pipe surfaces during the transport from an external heat exchanger to the SOC.

THE OVEROXIDATION OF HYDROCARBONS AT THE ANODE TO CO₂ IS PROBLEMATIC FOR THE DOWNSTREAM PRODUCT SEPARATION AND SHOULD BE MINIMIZED BY FINDING BETTER CATALYSTS

The production of CO₂ during OCM is problematic as separating CO₂ from the ethylene-rich product gas that is leaving the SOC unit is challenging (for comparison, ethane steam cracking only produces

trace amounts of CO₂). An additional MEA CO₂ absorption step is necessary to remove any CO₂ from the ethylene-rich syngas before the cryogenic gas separation, which increases CAPEX and OPEX. The separation of CO₂ from this mixture is particularly challenging as the vapor pressure curve of CO₂ lies in between ethane and ethylene which is problematic for the integration of cryogenic CO₂ separation into the existing cryogenic separation unit. Thus, it is judged that it is more effective to remove the CO₂ upstream of the gas compression section using a chemical solvent, which produces a “capture ready” CO₂ stream.

MAKING THE ELECTROCHEMICAL OCM CELL BIFUNCTIONAL BY SELECTING A VALUABLE REDUCTION REACTION, E.G. STEAM ELECTROLYSIS FOR CO-PRODUCTION OF H₂, ALLOWS THE SECOND REDUCTION REACTION TO PROCEED WITH MINIMAL LOSSES IMPROVING ECONOMICS

Since the activation energies of O₂ and H₂O on the cathode are of comparable magnitude, steam electrolysis on the cathode can proceed essentially loss-free at its ideal thermodynamic voltage. This approach substantially reduces OPEX and CAPEX of steam electrolysis leading to very low H₂ production costs. Furthermore, the additional revenue generated by the H₂ byproduct is shown to reduce the cost of ethylene.

USING AN ENDOTHERMIC REACTION ON THE CATHODE CAN REDUCE COOLING NEEDS

Cooling or heating needs depend on the thermoneutral voltage. If endothermic reactions like steam electrolysis or CO₂ reduction are used on the cathode, these reactions can serve as a heat sink that can help to protect the cell from overheating. If the overpotentials are low this characteristic can be used for advanced heat integration option e.g., with solar thermal, and increase efficiency.

USING CO₂ AS OXIDANT IN THE OCM CELL HAS NO PRACTICAL VALUE IN AN ETHYLENE PLANT AND USING CO₂ OVER H₂O COULD BE PROBLEMATIC WITH RESPECT TO CELL COOLING

Despite the fact that the reduction of CO₂ is very endothermic (lower cell heating potential than steam electrolysis) and could help with cell cooling, reducing CO₂ to CO at the cathode of the OCM cell is seen as of-little-value in the context of an ethylene plant. In an ethylene plant there is no practical use for CO and the methanation of CO to CH₄ using H₂ is less attractive than using CO₂ directly due to the very exothermic nature of the CO methanation reaction which would increase the complexity of a methanation unit (also note that there is not enough H₂ in the plant for CO methanation if CO₂ is used as oxidant in the OCM; thus, CO and H₂O would need to be co-electrolyzed which would further increase the complexity). Secondly, to thermally and stoichiometrically balance the SOC, a specific flow rate and inlet concentration (CO/CO₂ ratio) will be needed; consequently, a downstream CO/CO₂ separation process will be needed adding to CAPEX and OPEX (in comparison a mixture of H₂/H₂O is relatively easy to separate via condensation). If the ethylene plant were coupled with another plant that consumes CO, e.g. for sustainable methanol and carbonylation syntheses, direct reduction of CO₂ to CO at the cathode could be favorable.

WHEN MOVING TO LOW OVERPOTENTIALS AND HIGH SINGLE PASS CONVERSION ADDITIONAL SAVINGS CAN BE EXPECTED BY DEVELOPING A NEW HEAT INTEGRATION STRATEGY THAT BETTER FITS THESE OPERATING POINTS

When increasing the CH₄ conversion, the recycle purge stream is reduced, reducing the fuel for the furnace and making it more challenging to pre-heat the fuel and steam. As the steam generation continues to drop with increasing CH₄ single pass conversion, it becomes questionable for how long the steam cycle is of economic value and other heat integration options, e.g. where the OCM cell is

operated in an endothermic region using heat from the furnace, might become attractive. Also, with the decrease of H₂ in the syngas, the methanation section becomes less economical (H₂ is the limiting factor).

SOLID OXIDE OCM CELLS COULD BE NICELY COMPLEMENTED WITH PROTON CONDUCTING CERAMIC CELLS TO FACILITATE THE DEHYDROGENATION OF ETHANE IN A SEPARATE PROCESS UNIT

The OCM reaction produces many byproducts including substantial amounts of ethane. In the current configuration this ethane is recycled back to the OCM cell until it is eventually converted to ethylene via reaction (E 2-22). In this process, ethane is mixed with the incoming CH₄-rich feed stream and any unreacted ethane needs to go through the demethanizer, deethanizer and the C₂ splitter, in order to be separated again. By adding a proton conducting ceramic cell for the electrochemical dehydrogenation of ethane, the recycle to the OCM cell can be reduced as well as costs associated with gas compression and product separation. Additionally, this process would increase the H₂ production which can increase by-product revenue or can be used to reduce CO₂ emission via methanation (H₂ is the limiting factor for methanation). Thus, OCM and ethylene production in proton conducting cells should be viewed as complementing technologies, rather than competing technologies.

4.3 Recommendations

For the development of OCM cells it is recommended to focus research on reducing overpotentials even if that is at the expense of current density. The costs of power electronics are shown to be significantly higher than the cell costs in the case of OCM (this is expected when compared to current SOFCs since operating voltage and current density in OCM are significantly higher). The target for the overpotentials of the OCM reaction is an average value in the range of 0.55–0.87 V. At the lower range of these values, it is especially important to improve the single pass conversion of methane to ethylene to minimize sensible heat loss which can slow down reaction kinetic in the SOC. While this will increase thermal gradients, at these voltages cell cooling is not a concern anymore as the operating point is relatively close to the thermoneutral point. The single pass yield of methane to ethylene should be around 54–69% to be economically competitive, which corresponds to a Faraday efficiency of 74.38–78.51% in our cases.

Furthermore, it would be beneficial if the OCM could operate at lower temperatures of around 600–650 °C, which would simplify the heat integration and pre-heating of fuels with higher hydrocarbon contents, such as ethane and other C₂₊. More research is needed on a system level to better understand potential performance improvements that would come with an optimized heat integration strategy for advanced OCM cells. Also, the integration of proton conduction ceramic cells for the dehydrogenation of ethane could provide substantial performance improvements which should be explored in future research. With these improvements and the availability of renewable electricity OCM could lead to substantial cost benefits and reduced CO₂ emissions over current state-of-the-art ethane steam cracking.

5. References

1. AFPM. Ethylene: The “World’s Most Important Chemical”. <https://www.afpm.org/newsroom/blog/ethylene-worlds-most-important-chemical>.
2. Precedence Research. Ethylene Market. <https://www.precedenceresearch.com/ethylene-market>.
3. INEOS. PROJECT ONE. 1–10 <https://project-one.ineos.com/en/about-project-one/>.
4. Evans, M. R. Occidental Chemical Corporation - US EPA Permit Application Ethylene Plant San Patricio County - Update. (2014).
5. Climate Policy Watcher. Choice of emission factors Aaf. <https://www.climate-policy-watcher.org/emission-factors/choice-of-emission-factors-aaf.html> (2023).
6. Chang, J. US crackers will be fuelled by hydrogen to reduce carbon footprint. *ICIS* (2021).
7. Hu, H., Ding, D., Knighton, T., Wendt, D. & Boardman, R. Technoeconomic Analysis on an Electrochemical Nonoxidative Deprotonation Process for Ethylene Production from Ethane. *INL EXT 19 56936* (2019).
8. Liu, K. *et al.* Oxidative coupling of methane in solid oxide fuel cell tubular membrane reactor with high ethylene yield. *Catal. Commun.* **96**, 23–27 (2017).
9. Zhu, C. *et al.* Electrochemical conversion of methane to ethylene in a solid oxide electrolyzer. *Nat. Commun.* **10**, 1–8 (2019).
10. Hu, B., Rosner, F., Breunig, H. & Tucker, M. C. Electrochemical Conversion of Methane to Ethylene, Olefins, and Paraffins Using Metal-Supported Solid Oxide Fuel Cells, (in Review). *Int. J. Hydrogen Energy*.
11. Rosner, F., Tucker, M. C., Hu, B. & Breunig, H. Techno-Economic Analysis of Electrochemical Refineries Using Solid Oxide Cells for Oxidative Coupling of Methane. *ECS Meet. Abstr.* **MA2023-01**, 322–322 (2023).
12. U.S. Department of Energy/NETL. Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity. *NETL-PUB-22638* (2019).
13. U.S. Department of Energy/NETL. Quality Guidelines For Energy System Studies; Specification for Selected Feedstocks. *DOE/NETL-341/011812* (2012).
14. Rosner, F. Design and Thermo-Economic Analyses of Solid Oxide Fuel Cell-Gas Turbine Hybrid Systems with Water Recovery. *Diss. Univ. Calif. Irvine* (2021).
15. Energy Information Administration (EIA). How much carbon dioxide is produced per kilowatthour of U.S. electricity generation? <https://www.eia.gov/tools/faqs/faq.php?id=74&t=11#:~:text=In 2020%2C total U.S. electricity,CO2 emissions per kWh>.
16. Ecoinvent. *Version*. (2022).
17. U.S. Department of Energy/NETL. Cost and Performance Baseline for Fossil Energy Plants Volume 3a: Low Rank Coal to Electricity: IGCC Cases. *DOE/NETL-2010/1399* (2011).
18. Petrochemical. US ETHYLENE COMPLEX CONSTRUCTION COSTS DATA 2018 – 2020. *Downstr. Conf. Exhib. May 31-June 1, Galveston, Texas* (2018).
19. Woods, D. R. *Rules of Thumb in Engineering Practice*. (2007).

20. Cantley, M. F. THE SCALE OF ETHYLENE PLANTS: BACKGROUND AND ISSUES. *IIASA Work*. (1979).
21. Towler, G. & Sinnott, R. *Chemical Engineering Design: Principle, Practice and Economics of Plant and Process Design*. *Journal of Chemical Information and Modeling* vol. 53 (2013).
22. Garrett, D. E. *Chemical Engineering Economics*. (1989).
23. Love, D. Costs for ethylene projects in the U.S. on the rise: study | Petrochemical Update. *Reuters Events Downstr.* (2019).
24. Dang, V.-D. Separation of Methane from Hydrogen and Carbon Monoxide by an Absorption/Stripping Process. *Ind. Gas Sep.* 235–253 (2009) doi:10.1021/bk-1983-0223.ch012.
25. Chauvel, A., Fournier, G. & Raimbault, C. *Manual of Process Economic Evaluation*. (2003).
26. In house data based on correspondence with vendor. *contact Fabian Rosner*.
27. Ye, L., Duan, X. & Xie, K. Electrochemical Oxidative Dehydrogenation of Ethane to Ethylene in a Solid Oxide Electrolyzer. *Angew. Chemie* **60**, 21746–21750 (2021).
28. Farrell, B. L. & Linic, S. Oxidative coupling of methane over mixed oxide catalysts designed for solid oxide membrane reactors. *Catal. Sci. Technol.* **6**, 4370–4376 (2016).
29. Battelle Memorial Institute. Manufacturing Cost Analysis of 100 and 250 kW Fuel Cell Systems for Primary Power and Combined Heat and Power Applications. *DOE Contract No. DE-EE0005250* (2016).
30. Atsonios, K., Koumanakos, A., Panopoulos, K. D., Doukelis, A. & Kakaras, E. Techno-economic comparison of CO₂ capture technologies employed with natural gas derived GTCC. *Proc. ASME Turbo Expo* (2013) doi:10.1115/GT2013-95117.
31. Wikipedia. Shell Pennsylvania Petrochemicals Complex. https://en.wikipedia.org/wiki/Shell_Pennsylvania_Petrochemicals_Complex.
32. U.S. Department of Energy/NETL. Quality Guidelines For Energy System Studies; Cost Estimation Methodology for NETL Assessments of Power Plant Performance. *NETL-PUB-22580* (2019).
33. Westlake. Industry Pricing. <https://investors.westlake.com/industry-pricing/default.aspx>.
34. DiChristopher, T. Experts explain why green hydrogen costs have fallen and will keep falling. (2021).
35. NEWSWIRE, I. <https://isonewswire.com/2021/09/30/monthly-wholesale-electricity-prices-and-demand-in-new-england-august-2021/>. <https://isonewswire.com/2021/09/30/monthly-wholesale-electricity-prices-and-demand-in-new-england-august-2021/>.
36. U.S. Department of Energy/NETL. Cost and Performance Baseline for Fossil Energy Plants Volume 3b: Low Rank Coal to Electricity: Combustion Cases. *DOE/NETL-2011/1463* (2011).
37. Zaub. Detailed Import Data of Olemax 201. <https://www.zaub.com/import-olemax-201-hs-code.html>.
38. Rosner, F. Internal Data.
39. Rosner, F. *et al.* Process and Economic Data on the Thermo-Economic Analyses of IGCC Power Plants Employing Warm Gas CO₂ Separation Technology. *Data Br.* **27**, 104716 (2019).

40. LACSD. Liquid Waste Disposal. https://www.lacsd.org/wastewater/industrial_waste/liquid_waste_disposal/default.asp.
41. Froment, G. F., Van de Steene, B. O., Van Damme, P. S., Narayanan, S. & Goossens, A. G. Thermal Cracking of Ethane and Ethane-Propane Mixtures. *Ind. Eng. Chem. Process Des. Dev.* **15**, 495–504 (1976).
42. Thiruvenkataswamy, P. SAFETY AND TECHNO-ECONOMIC ANALYSIS OF ETHYLENE TECHNOLOGIES. *MS Thesis Texas A&M Univ.* (2015).
43. Karimzadeh, R., Godini, H. R. & Ghashghaee, M. Flowsheeting of steam cracking furnaces. *Chem. Eng. Res. Des.* **87**, 36–46 (2009).
44. U.S. Department of Energy/NETL. Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity. *DOE/NETL-2010/1397, Revis. 2a* (2013).
45. Borralho, F. J. O. Detailed Modelling and Optimisation of an Ethylene Plant Chemical Engineering Examination Committee. *Master Thesis Tech. Lisboa* (2013).
46. Sundaram, K. M. & Froment, G. F. Modeling of thermal cracking kinetics-I. Thermal cracking of ethane, propane and their mixtures. *Chem. Eng. Sci.* **32**, 601–608 (1977).
47. Emerson Process Management. Fisher Chemical Sourcebook. *www.Fisher.com* (2010).
48. Dehghani, O., Rahimpour, M. R. & Shariati, A. An experimental approach on industrial Pd-Ag supported α -Al₂O₃ catalyst used in acetylene hydrogenation process: Mechanism, kinetic and catalyst decay. *Processes* **7**, (2019).
49. Spallina, V. *et al.* Techno-economic assessment of different routes for olefins production through the oxidative coupling of methane (OCM): Advances in benchmark technologies. *Energy Convers. Manag.* **154**, 244–261 (2017).
50. García-Camprubí, M., Izquierdo, S. & Fueyo, N. Challenges in the electrochemical modelling of solid oxide fuel and electrolyser cells. *Renew. Sustain. Energy Rev.* **33**, 701–718 (2014).
51. Harun, N., Nittaya, T., Douglas, P. L., Croiset, E. & Ricardez-sandoval, L. A. Dynamic simulation of MEA absorption process for CO₂ capture from power plants. *Int. J. Greenh. Gas Control* **10**, 295–309 (2012).
52. Kao, Y. L., Lee, P. H., Tseng, Y. T., Chien, I. L. & Ward, J. D. Design, control and comparison of fixed-bed methanation reactor systems for the production of substitute natural gas. *J. Taiwan Inst. Chem. Eng.* **45**, 2346–2357 (2014).
53. Nguyen, T. T. M., Wissing, L. & Skjøth-Rasmussen, M. S. High temperature methanation: Catalyst considerations. *Catal. Today* **215**, 233–238 (2013).
54. Salladini, A., Agostini, E., Borgogna, A. & Iaquaniello, G. Waste feedstocks for sustainable chemicals and fuels. *Stud. Surf. Sci. Catal.* **179**, 193–213 (2019).
55. Choi, C. *et al.* Determination of Kinetic Parameters for CO₂ Methanation (Sabatier Reaction) over Ni/ZrO₂ at a Stoichiometric Feed-Gas Composition under Elevated Pressure. *Energy and Fuels* **35**, 20216–20223 (2021).
56. Hensley, J. C. Cooling Tower Fundamentals. *SPX Cool. Technol. Inc.* (2011) doi:10.1201/b11510-14.
57. Mafi, M., Naeynian, S. M. M. & Amidpour, M. Exergy analysis of multistage cascade low

- temperature refrigeration systems used in olefin plants. *Int. J. Refrig.* **32**, 279–294 (2009).
58. Fattouh, B. & Brown, C. US NGLs Production and Steam Cracker Substitution : What will the Spillover Effects be in Global Petrochemical Markets? *Oxford Inst. Energy Stud.* (2014).
 59. Ren, T., Patel, M. & Blok, K. Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes. *Energy* **31**, 425–451 (2006).
 60. Tham, M. T. DISTILLATION COLUMN DESIGN. *Costello*
<https://www.rccostello.com/distil/distildes.htm> (2016).
 61. Fábrega, F. M., Rossi, J. S. & D'Angelo, J. V. H. Exergetic analysis of the refrigeration system in ethylene and propylene production process. *Energy* **35**, 1224–1231 (2010).
 62. Vakkilainen, E. K. Steam Generation from Biomass: Construction and Design of Large Boilers. 57–86 (2016) doi:10.1016/b978-0-12-804389-9.00003-4.
 63. Ramesh, R. & van Goethem, M. W. M. High Efficiency Ethylene Cracking Furnaces. *25th Ethyl. Prod. Conf. San Antonio, USA.* (2013).
 64. Camarda, M. US ethane cracking margin turns negative.
<https://www.argusmedia.com/en/news/2345663-us-ethane-cracking-margin-turns-negative> (2022).
 65. Campanari, S., Mastropasqua, L., Gazzani, M., Chiesa, P. & Romano, M. C. Predicting the ultimate potential of natural gas SOFC power cycles with CO₂ capture – Part A: Methodology and reference cases. *J. Power Sources* **324**, 598–614 (2016).
 66. Siefert, N. S. & Litster, S. Exergy & economic analysis of biogas fueled solid oxide fuel cell systems. *J. Power Sources* **272**, 386–397 (2014).
 67. The Hydrogen Council. Hydrogen decarbonization pathways. 14 (2021).