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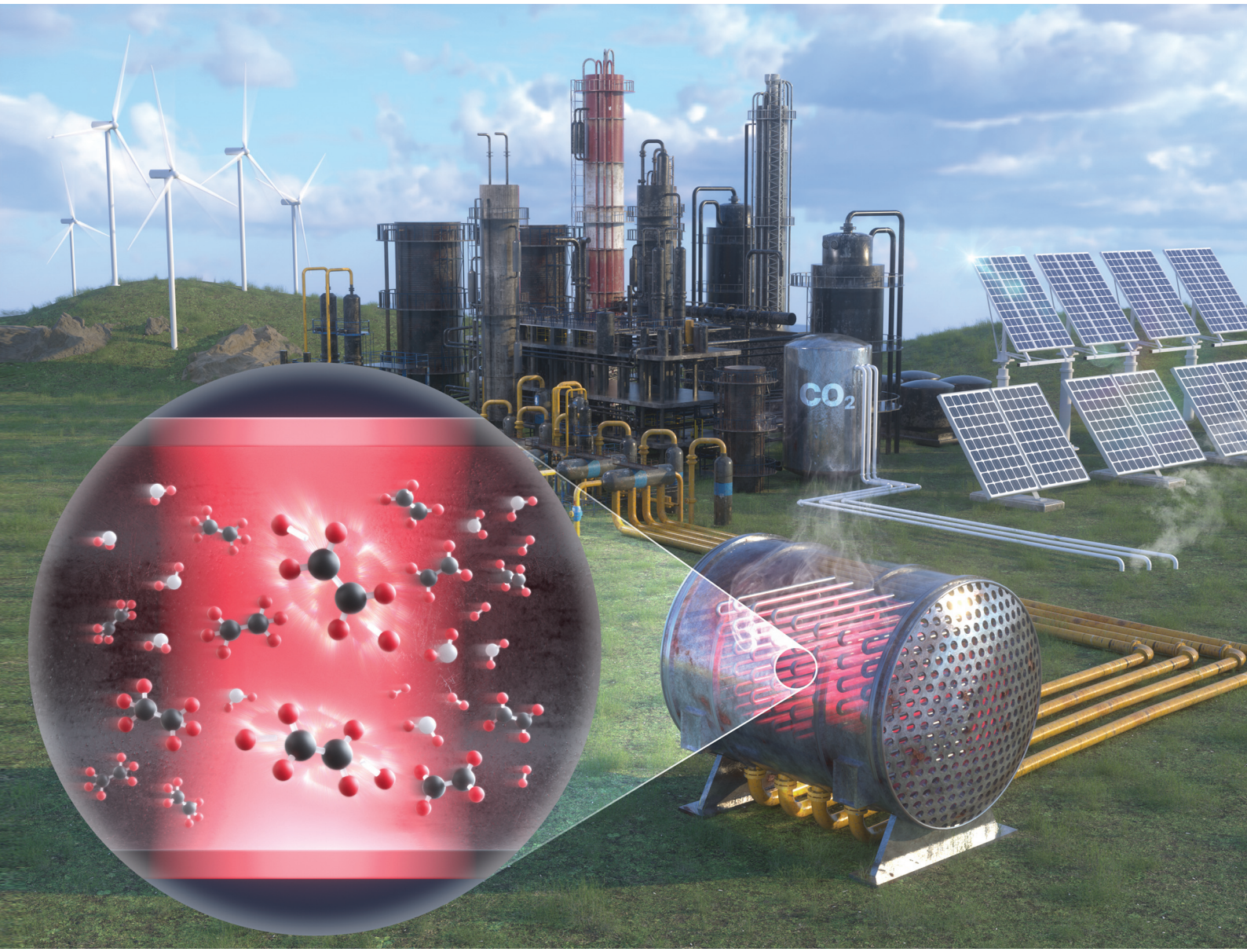

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Decarbonization approaches for ethylene production: comparative techno-economic and life-cycle analysis†

Woojae Shin, Bosong Lin, Haoxiang Lai, Gasim Ibrahim and Guiyan Zang *

Ethylene, a building block of the chemical industry, significantly contributes to global greenhouse gas (GHG) emissions, prompting interest in decarbonization approaches to align with recent carbon neutrality initiatives. This paper presents a comprehensive techno-economic analysis (TEA) and life cycle analysis (LCA) of GHG emissions, comparing conventional ethane-based ethylene plants with three decarbonization approaches. The study was conducted within the context of the U.S. average, with sensitivity analysis to identify key drivers affecting well-to-gate (WTG) GHG emissions and the levelized cost of ethylene (LCOE). The conventional plant exhibited a GHG emission of 869 $kgCO_2e$ per tonne-ethylene and a LCOE of $746 per tonne-ethylene. Substituting external natural gas fuels with grid or renewable electricity decreased the emissions to 806 and 717 $kgCO_2e$ per tonne-ethylene, respectively. The emissions of the grid-powered or renewable-powered electrically heated cracker that exports co-produced hydrogen to substitute conventional gray hydrogen were 1031 and −163 $kgCO_2e$ per tonne-ethylene, respectively. The application of CCS to purge gas showed 703 and 514 $kgCO_2e$ per tonne-ethylene emissions, respectively. The electric cracker showed lower emissions than the conventional plant below 380 $kgCO_2e$ per MW h electricity upstream, and at 60 $kgCO_2e$ per MW h, it achieved carbon neutrality. Regarding LCOE, when using a grid electricity source, no external natural gas, electric cracker, and adding CCS to purge gas showed $743, 833, and 771 per tonne-ethylene, respectively. When these plants adopt renewable electricity, their LCOEs will be $737, 746 and 757 per tonne-ethylene. Below $41.1 per MW h electricity price, the electric cracker had the lowest value among all cases. With hydrogen prices of $0.5–3.0 per kg-$H_2$, the electric cracker's LCOE ranged from −$45(cost)–128(saving) per tonne-ethylene compared to the conventional concept.

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Green foundation

1. This work provides comprehensive modeling results, techno-economic and life-cycle greenhouse gas emissions analysis of three decarbonization pathways for ethane-based ethylene production, advancing green chemistry by quantifying sustainability metrics with greenhouse gas emission reduction potential and cost impacts together.
2. We show that curtailing external natural gas use, electrifying steam crackers with hydrogen export, or applying carbon capture to purge gas significantly decreases well-to-gate greenhouse gas emissions while offering cost advantages under diverse U.S. regional and temporal scenarios, surpassing conventional steam crackers.
3. Future research will emphasize on-site renewable electricity integration, further exploration of low-carbon feedstocks, and flue gas CCS technology implementation to reduce environmental impacts and drive more sustainable ethylene production pathways.

1. Introduction

The chemical industry contributes significantly to global greenhouse gas (GHG) emissions, accounting for 19% of the industry sector.[1] Among various chemical products, ethylene stands out as the second-largest contributor to GHG emissions,[2,3] as it serves as a key building block in the petro-

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†Electronic supplementary information (ESI) available: Detailed process configuration (Fig. S1 and S12), allocation methodologies (Fig. S13–S16), stream information (Tables S1–S4), kinetic reaction (Table S5), equipment costs (Tables S6–S9), and financial assumption (Table S10). See DOI: https://doi.org/10.1039/d4gc04538f

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chemical processes and is used in the production of a wide array of products, such as polymers for synthetic rubber, ethanol, acetaldehyde, and other basic and intermediate chemical products.[3,4] Due to its diverse applications, approximately 225 million tonnes of ethylene are produced annually worldwide.[5] The ethylene market is predicted to experience a 63% growth from 2021 to 2030.[6] Ethylene is produced globally from feedstocks such as naphtha and natural gas (primarily ethane), with major producers including China, the United States, South Korea, Saudi Arabia, Iran, India, Japan, Germany, and Canada.[7]

Major ethylene production technologies are divided into two methods based on the accessibility and price of feedstock (naphtha and ethane) in the near region.[8] The first dominant process is the naphtha steam cracking process, which utilizes naphtha, a major co-product from crude oil refineries. Naphtha steam cracking is predominantly employed in regions such as China, Western Europe, Japan, and South Korea, where crude oil usage is high enough to produce a lot of co-products. Therefore, naphtha offers relative economic advantages. The second dominant is the ethane steam cracking process, which has gained prominence, particularly in the United States and the Middle East, due to their abundant accessibility of natural gas. This process has become increasingly favored in the U.S. with the advancement of shale gas production through hydraulic fracturing technology.[4]

Ethylene production processes, particularly those based on fossil fuels, are known to be energy and GHG emission-intensive. For the major reaction in steam cracking processes using hydrocarbons like naphtha and ethane, steam-diluted hydrocarbons undergo a high-temperature, very short-duration homogeneous pyrolysis reaction in the tubular reactor at approximately 800 °C to be converted into ethylene.[4,9] The cracker is usually externally heated in a furnace, and due to the high reactivity of the products, they are promptly quenched to inhibit their further reaction to other undesirable molecules.[4,9] Subsequently, ethylene and other byproducts, such as fuel gas and other heavy hydrocarbons are separated through multi-separation processes. Conventionally, internally recycled fuel gas and externally supplied natural gas are combusted for external heating of the furnace,[4,10] leading to direct on-site GHG emissions. Additionally, indirect GHGs could be counted for the electricity consumption of multiple compressors and chillers for gas mixture separation.

With ethylene accounting for a significant portion of global GHG emissions, discussions on more decarbonized ethylene production processes have been actively pursued. Among commercially available processes based on ethane and naphtha, ethane-based production processes exhibit higher ethylene yield (78 wt% for ethane-based and 34 wt% for naphtha-based)[9,11] and are less energy-intensive (16 GJ per tonne-ethylene for ethane-based and 23 GJ per tonne-ethylene for naphtha-based).[12] Consequently, it is known that the on-site CO_2 emission of ethane-based ethylene (0.4–1.6 $kgCO_2e$ per kg-ethylene[4,12–15]) is lower than that of naphtha-based ethylene (1.8–2.0 $kgCO_2e$ per kg-ethylene[13]). Moreover, these processes have already achieved over 90% thermal efficiency after decades of development,[8] indicating limited improvement potential for decarbonizing ethylene processes through optimization strategies such as enhancing the efficiency of traditional technologies. Instead, ethylene production processes with low-carbon feedstock or fuels such as biomass-based ethanol, renewable natural gas, renewable electricity as process fuels, and carbon capture and storage (CCS) technologies are being considered as primary approaches for feasible decarbonization strategies. These techniques offer retrofit-friendly or technology-ready solutions to reduce upstream GHG emissions from fossil-based feedstocks and fuels, grid electricity upstream, and on-site direct GHG emissions.[16–20] However, multidimensional analyses are required to assess these techniques' economic feasibility, ease of retrofit, extent of decarbonization, and suitability for different regions and circumstances.

Techno-economic analysis (TEA) is a critical method for analyzing the economics of industrial processes, and it is of significant importance at the decision-making stage. The levelized cost per unit mass of the product (also frequently expressed as the minimum-selling price), which makes the project's net present value zero, is one of the critical measures to compare different alternative processes across various chemical and energy sectors. The levelized cost of ethylene (LCOE) is an effective metric for ethylene production to compare the economic viability of alternatives.[19,21–23] The LCOE for the conventional steam cracker is predominantly influenced by the feedstock price among various capital and operating cost factors.[19,21–23] Boulamanti and Moya reported the LCOE of ethane-based steam crackers in various regions, including the EU.[22] The study demonstrated that the LCOE varied between €285–940 per tonne-ethylene depending on regional differences and showed the EU's LCOE of €748 per tonne-ethylene using a feedstock price of €612 per tonne-ethane. Chen *et al.* reported the LCOE in the context of U.S. ethane-based steam cracker assuming a feedstock price of $200 per tonne-ethane as $832 per tonne-ethylene.[21] Hu *et al.* reported an LCOE of $710 per tonne-ethylene, assuming the same feedstock price of $200 per tonne-ethane.[23] In addition to these TEA studies on conventional steam cracker technologies, TEA has also been conducted for low-carbon feedstock sources and emerging technologies. Nyhus *et al.* reported an LCOE ranging from €2800–5500 per tonne-ethylene for ethylene synthesized from zero-carbon feedstock sources (utilizing green hydrogen and direct air capture of CO_2) in the United Kingdom as a case study.[24] Chen *et al.* reported an LCOE of €790 per tonne-ethylene for an oxidative dehydrogenation of ethane.[21] Tiggeloven *et al.* focused on naphtha-based crackers and compared conventional steam crackers with electrified steam crackers utilizing grid electricity.[16] The results showed that the LCOE for the naphtha-based conventional plant was $660 per tonne-ethylene and indicated approximately $140 per tonne-ethylene higher costs for electrified steam crackers.[16] Also, the study demonstrated that using renewable energy and batteries resulted in a relatively higher LCOE of about $830–1120 per tonne-ethylene for an electrified steam cracker. Despite extensive study, there is limited comprehensive ana-

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lysis evaluating the economic performance of decarbonization approaches for ethane-based ethylene production.

Life Cycle Analysis (LCA) is the most well-known method for quantifying environmental impacts, especially GHG emissions, from the cradle to the final stage. The well-to-gate (WTG) scope encompasses entire upstream processes and plants, consisting of upstream emissions from feedstocks, process fuels, electricity, on-site emissions from the plant, and substitution effects due to co-product export. This system boundary for WTG GHG emissions is widely used in chemical manufacturing facilities,[15,25–28] including ethylene production processes. Previous studies have reported CO_2 direct emissions ranging from 0.4 to 1.6 $kgCO_2$ per kg-ethylene for conventional ethylene production processes.[4,12–15] The variance primarily stems from factors such as feedstocks (ethane or naphtha), whether internal tail gas (especially for hydrogen) recycling is incorporated, and whether co-product allocation is considered. Young *et al.* reported that the on-site CO_2 emission can achieve the lower end (0.407 $kgCO_2$ per kg-ethylene) when methane and hydrogen in the tail gas is recirculated and used as the heat source for the cracker;[15] it can increase to 0.65 $kgCO_2$ per kg-ethylene because of the use of additional makeup natural gas if hydrogen is considered a byproduct for sale. They reported WTG emission results of 1.053 and 1.304 $kgCO_2e$ per kg-ethylene for each case. Lee and Elgowainy provided an on-site CO_2 emission of ethane cracker of approximately 0.8 $kgCO_2e$ per kg-ethylene in case of selling all of the hydrogen from tail gas and supplementing its insufficient heat source with external natural gas.[26] Ghanta *et al.* pointed out that fossil fuel combustion for ethylene production processes, especially external natural gas combustion for cracker heating, is the most significant factor in GHG emissions. The process for the ethane-based ethylene (0.840 $kgCO_2e$ per kg-ethylene) is 26% less carbon-intensive than naphtha-based ethylene (1.135 $kgCO_2e$ per kg-ethylene).[14] Layritz *et al.* suggested that using renewable electricity to offset furnace input energy for naphtha cracking facilities could reduce the carbon footprint by 30% compared to conventional fossil fuel-based energy systems.[19] Additionally, the authors stated that further environmental benefits of up to 0.83 $kgCO_2e$ per kg-ethylene could be obtained by electrifying steam cracking processes and expanding the system to include residual purge gas (CH_4 and H_2), substituting fossil natural gas.[19] These previous studies have primarily focused on conventional processes using naphtha and ethane as feedstocks. Still, there is a significant lack of understanding regarding the GHG impact of the adoption of low-carbon technologies to ethane-based ethylene production.

While the previous studies compared ethylene production pathways using various feedstocks and technologies, no study has focused on comparing and analyzing the techno-economic and environmental feasibility of various decarbonization approaches applicable to ethylene production processes. To address this knowledge gap, we designed and compared three alternatives with the conventional ethane-based ethylene production: (1) no external natural gas importation by importing electricity, (2) adoption of an electrically heated steam cracker with additional external electricity importation and resultant hydrogen and residual gas exportation, and (3) CCS application to internal purge gas to reduce on-site CO_2 emission.

This study represents the first attempt to model, assess the technological-economic viability, and evaluate the GHG impact of decarbonization approaches applicable to ethane-based ethylene production processes simultaneously. Our study presents the techno-economic and GHG impact of various pathways of ethane supply sources (natural gas production regions) and associated grid electricity networks in the different areas of the United States, considering sensitivity analysis on emissions and prices of ethane, natural gas, and electricity.

2. Methodology and data

To evaluate the techno-economic feasibility and GHG emissions of the ethylene production pathways in this study, the mass and energy flows within the system boundary are first needed. For this purpose, we built four models using the process simulation software Aspen Plus V12. The resultant balances of mass and energy flows and scales of each component serve as the basis for TEA and LCA analyses.

This study compares four concepts of plants: one baseline conventional ethane cracker-based ethylene production plant and three decarbonization approaches for ethane cracker-based ethylene production plants. These options involve the heat source required by the ethane cracker and whether to apply CCS to the syngas within the process. The options were designated to analyze the impact of decarbonization approaches using clean sources and technologies, such as adopting electrically heated crackers using low carbonization of grid electricity, directly connecting to renewable electricity, avoiding fossil-originated heat source usage, or applying CCS. Three decarbonization approaches are as follows: (1) no external natural gas importation by importing electricity, (2) adoption of an electrically heated steam cracker with additional external electricity importation and resultant hydrogen and residual gas exportation, and (3) CCS application to internal purge gas. Each of the plants was designed to produce one million-tonnes per year of ethylene products, based on the projected average annual production of a new U.S. ethylene production plant until 2026, which is 0.94 million tonnes per year,[29] and the average annual production of existing 15 U.S. ethylene production plants is 0.97 million tonnes per year.[15] For more detailed configurations and mass and energy flows of each system design, please see Fig. S1–S12 and Tables S1–S4 in the ESI.†

2.1. Baseline ethane cracking-based ethylene production

Fig. 1 illustrates the process flow of the Baseline case of the ethylene production process based on conventional ethane cracking. The reaction and system modeling of the Baseline case was developed by referencing previous studies on ethylene cracking reaction mechanisms[30–34] and process modeling.[9,10,15,19,26,33–39] The SRK (Soave–Redlich–Kwong) is used for default property method for hydrocarbon processing applications, including ethane cracking, separation, and com-

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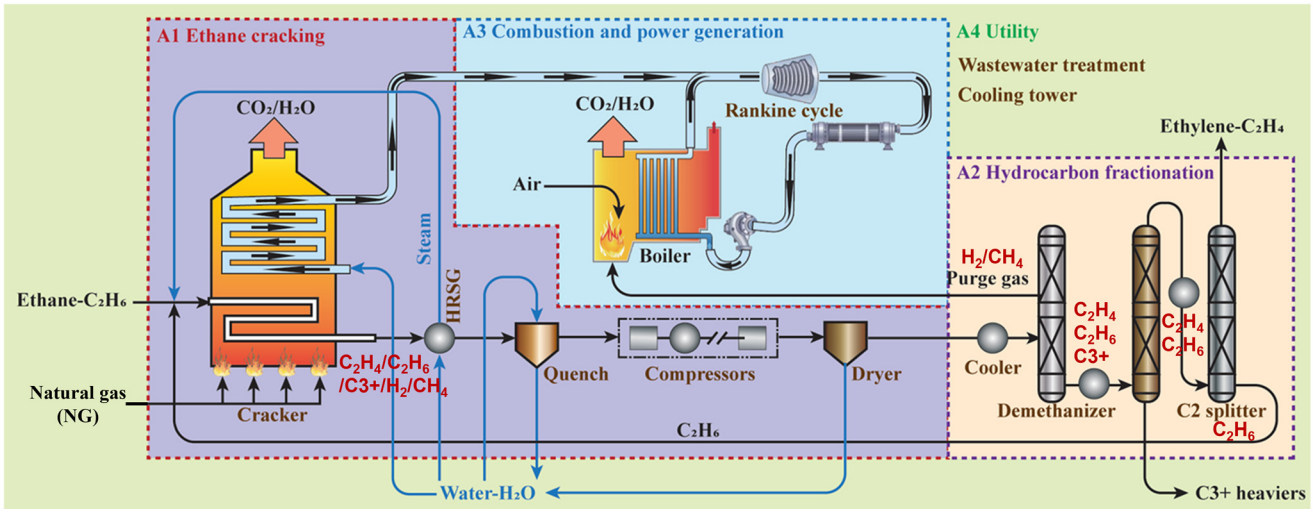

Fig. 1 Process configurations of Baseline case (conventional ethylene production based on ethane steam cracker).

bustion-related units. The Baseline model was validated based on previous process model results as shown in Table 1.

2.1.1. Baseline configuration. The process is divided into the following subsections:

- A1 ethane cracking: ethane feedstock is decomposed into ethylene and other molecules through a tubular flow reactor (Rplug reactor). For the ethane-to-ethylene reaction mechanism, 17 detailed kinetic reactions are used[30–34] as shown in Table S5, ESI.† Additionally, the steam-to-ethane ratio is set to 0.33 based on the maximum ethylene yield obtained at 0.3–0.35 (mass kg-H_2O per mass kg-ethane).[31] The heat required during ethane cracking is supplied by the combustion of imported natural gas and the combustion of purge gas which is separated from unit A2.

The mixture exiting the cracker is immediately cooled through a series of heat exchangers, quenching devices, a multi-stage compressor, and dryers, and then directed to the A2 unit. Simultaneously, water extracted from the produced syngas is treated in the wastewater treatment of the A4 unit.

- A2 hydrocarbon fractionation: after sufficient cooling through parallel splitters, coolers, and flash separators, hydrocarbon mixtures are de-methanized in the RadFrac device to separate methane and hydrogen through the upper stream, forming the purge gas. The bottom stream is then separated into ethane/ethylene mixture and liquid hydrogen carbon heavier than C_3 (denoted as C_{3+}) through multi-column distillation device (RadFrac). Finally, the C_2 mixture stream is separated into ethylene products through a C_2 splitter (RadFrac). Residual ethane is recycled after separating some impurity gases and as feedstock for the unit A1.

- A3 combustion and power generation: this unit aims for electricity generation through gas combustion to precisely offset the plant's electricity consumption. Purge gas and natural gas fuel are combusted in the boiler (RStoic), and the resultant heat extracted is transferred to the steam inside the Rankine cycle with a steam turbine with 88% isentropic efficiency. The extra natural gas on top of the purge gas is necessary to supply sufficient electricity for the compressor, pump, and chiller operation. Resultingly, the net electricity import and export for the plant is zero.

- A4 utility: this unit removes impurities from water obtained from unit A1 and supplies water stream to units A1, A2, and A3. The model predicts the power usage of the operating cooling tower. The proportion of this process to the overall electricity consumption is about 2.4%.

2.1.2. Model validation. The baseline Aspen model was validated with previous studies on similar ethane-based ethylene production processes.[9,12,15,26] Table 1 compares the usage of combustion heat energy per tonne of ethylene produced. This energy includes heat extracted from natural gas fuel supplied to the plant, which is used to offset combustion heat, and heat extracted from hydrogen and methane contained in the purge gas.

Table 1 Comparison of combustion energy use in ethylene production plant

Source	GJ per tonne-ethylene
This study	17.2
Argonne National Laboratory (Lee and Elgowainy (2018)[26], Young *et al.* (2020)[15])	17.7
Lawrence Berkeley National Laboratory (Worrell *et al.* (2000)[9])	19.4
Yao *et al.* (2015)[39]	17.1–21.3
Ren *et al.* (2006)[13]	17.0–21.0
U.S. Department of Energy (DoE) (Energetics (2000)[40])	13.0–25.0

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2.2. Alternative processes

Fig. 2 depicts the configuration of integrating decarbonization approaches into the ethane cracking-based ethylene production process set in this study with the Baseline case. Details of the alternative processes compared to the Baseline process are as follows:

2.2.1. No external NG case. This case is a system that does not import natural gas; instead, it increases the proportion of combustion of internally recycled purge gas to meet the cracker's heat requirements. However, eliminating external natural gas reduces electricity generation from the Rankin cycle. Therefore, extra electricity from the grid is required to drive the process. Also, this case does not require significant changes to the major components and streams within the process. Still, connection to the external power grid and detaching of the external natural gas supply chain are necessary for retrofitting.

2.2.2. Electrical heating case. This case uses an electrically heated ethane cracker that utilizes electricity as a heat source. The purge gas recycled from the A2 unit is not reused to generate electricity or combusted in cracker. Instead, the gas is purified and separated into hydrogen and other gas (primarily methane) products. Therefore, imported electricity is required

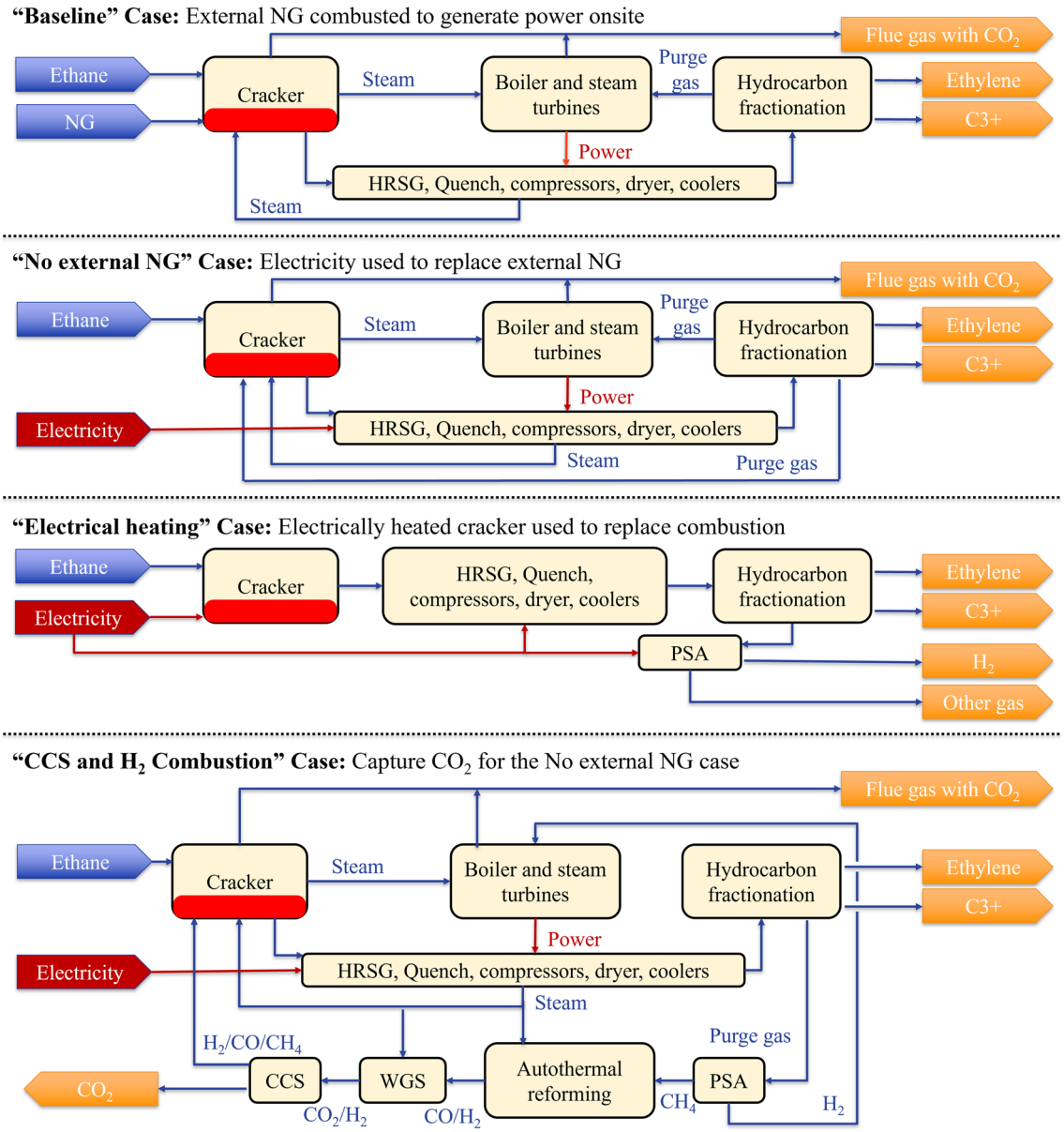

Fig. 2 Simplified process configurations of all cases. The units described in section 2.1.1. are different for the four cases. The A1 unit refer to cracker and heat recovery steam generator, quench, compressors, dryer, coolers, A2 unit refer to hydrocarbon fractionation, and A3 unit refer to boiler and steam turbines and PSA (electrical heating only), and PSA, ATR, WGS, CCS (CCS and H_2 combustion only). A4 unit is not expressed in this figure. For detail, please see Fig. S1–S12 and Tables S1–S4† for configuration and stream information.

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for operating components such as compressors, dryers, coolers, and the cracker. Consequently, there are no boiler and steam turbine systems, and the size of the cooling tower in the A4 unit is reduced. In purge gas, the major molecules are CH_4 and H_2, and they are both separated into H_2 products and other gases as sale products through pressure swing adsorption (PSA). The system concept aligns with the current demonstrative attempt of integrating renewable energy into an ethylene plant and producing hydrogen from internal syngas, which started operation in Germany in 2024.[41] The study assumes 100% efficiency for the electrically heated cracker, which is legitimate in that the electricity energy is fully converted into heat and subsequently transferred to the furnace.[42]

2.2.3. CCS and H_2 combustion case. This case integrates an auto-thermal reforming (ATR) and CCS process into the purge gas of the No external NG case. This system concept aligns with the current activity of decarbonized ethylene production approaches utilizing hydrogen production and reuse and CCS in Alberta, Canada.[43] This new plant aims to achieve net-zero scope 1 emissions by decarbonizing off-gas into hydrogen, which will be partially combusted in its cracker or supplied to nearby sustainable hydrogen consumers. The purge gas contains mostly hydrogen, methane, carbon monoxide, and CO_2. The combined system of PSA, ATR, water gas shift (WGS) reactor and CCS is designated for sequestrating carbon inside the purge gas and providing low-carbon fuel gas for cracker furnace and boiler. For the first step, after the purge gas is inputted to the A3 unit, the PSA device separates 85% of the hydrogen to feed the boiler. The remaining gas is pressurized and heated to 34 bar and 550 °C before inputting into the ATR facility. The ATR facility of the system consists of an air separation unit (ASU; note that the separated N_2 is considered as unsold byproduct), pre-reformer (RGibbs reactor[25]), auto-thermal reactor (REquil reactor[25]). In the reactors, the gas reacts with steam to produce hydrogen. Then, the high-temperature, high-pressure reformed gas passes through two consecutive WGS reactors to convert CO to H_2 to increase the yield of H_2 and simultaneously increase the amount of capturable CO_2. The gas after WGS with a CO_2 concentration of 19.3% is inputted into the Selexol CCS equipment, where 90.0% of the CO_2 is captured. During the capture process, CO_2 is absorbed using ethylene glycol at 30.8 bar and then released from four flash tanks at pressures of 13.8 bar, 3.4 bar, 1.0 bar, and 0.3 bar. Subsequently, these CO_2 gases are compressed, dried, and cooled before being exported from the plant to 153 bar and 43 °C. As a result, 77.6% of the carbon atoms contained in the purge gas are captured. The remaining gas has rich hydrogen (46.0 wt%) and CO (17.7 wt%), which are combusted and used as a heat source for the cracker.

2.3. LCA methodology

The LCA of ethylene production plants utilizing ethane, electricity, and natural gas is conducted for the WTG scope, which considers scope 1 (on-site direct GHG emissions), scope 2, and part of scope 3 (feedstock, fuel, and electricity's upstream GHG emission and emission credit from co-products displacement). In this study, the WTG life cycle GHG emissions are calculated using Argonne National Laboratory's The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model (GREET) 2021[44] to cover the entire fuel supply chain in analysis. The GHG emissions of CO_2, CH_4, and N_2O are assessed based on a functional unit of 1 metric ton of ethylene product, using the Intergovernmental Panel on Climate Change Fifth Assessment Report's Global Warming Potential (GWP)-100 year (CO_2: 1, CH_4: 30, N_2O: 265). The WTG analysis consists of three stages: (1) Upstream GHG emissions from feedstock (ethane) and process fuel (electricity and natural gas), (2) on-site combustion GHG emissions, (3) GHG emission credit from displaced co-products (hydrogen and other gases).

The first stage refers to emissions from the upstream processes of feedstock and fuel usage for the ethylene production plant. To calculate the upstream emissions of ethane and natural gas, references such as Zang *et al.*,[25] National Energy Technology Laboratory (NETL) study,[45] GREET 2021[44] were referenced. Initially, from the upstream processes of natural gas and ethane, CO_2, CH_4, and N_2O are emitted during NG production, gathering & boosting, processing, transmission, storage, pipeline transportation and distribution stages.[45] For the upstream CO_2 emissions from ethane and natural gas, the CO_2 emissions from GREET are utilized.[44] It is assumed that both ethane and natural gas originate 100% from shale basins. This assumption is based on the fact that almost all ethane in the U.S. originates from shale basins,[46] and ethane cracker plants that utilize natural gas as fuel are likely to receive natural gas from same sources with ethane. Additionally, the CH_4 emission of the first three upstream stages is based on basin-level specific data with a 95% confidence interval reported in the NETL study.[45] The basin-level data covers the entire upstream stages, but we utilized three major consecutive stages (production, gathering and boosting, and processing), which are common upstream stages for both ethane and natural gas supply chains.[45] The other CH_4 emissions after the processing stage and N_2O emissions from the entire stages are based on GREET.[44] The resultant total upstream GHG emissions for natural gas and ethane are presented in Table 2. Notably, the results from each basin are particularly influenced by the CH_4 emission rate in the upstream process, with a range of 0.29% to 2.50% (from production, gathering and boosting, and processing stages). The CH_4 emission rate includes non-combustion emission, which is also called CH_4 leakage, and combustion emission. 95% confidence range of the CH_4 emission rate is 0.36(P 2.5)–0.61(P 50.0)–0.96(P 97.5)%. By setting 0.61% CH_4 emission rate as a default, the default upstream GHG emissions used in the analysis are 8.21 $kgCO_2e$ per GJ-LHV (lower heating value (LHV) basis) for ethane and 12.21 $kgCO_2e$ per GJ-LHV for natural gas. The upstream GHG emissions for grid electricity are based on GREET,[44] at 439 $kgCO_2e$ per MW h. Table 2 also provides the upstream GHG emissions for each grid electricity network connected to the location of each basin[44] and estimated upstream GHG emissions for the same network in 2030 estimated by Zang *et al.*[25]

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Table 2 CH_4 emission rate and upstream GHG emission of ethane, natural gas, and grid electricity for each shale basin region

Shale basins	State	Shale gas production share [%]	CH_4 Emission rate from production, gathering & boosting, and processing stages [%]			Ethane upstream emission [$kgCO_2e$ per GJ]			Natural gas upstream emission [$kgCO_2e$ per GJ]			Grid electricity upstream emission [$kgCO_2e$ per MW h]	
			P2.5	Mean	P97.5	P2.5	Mean	P97.5	P2.5	Mean	P97.5	2019	2030
Anadarko	OK	4.65%	0.43%	0.68%	0.99%	6.99	8.66	10.75	10.95	12.68	14.82	491	177
Appalachian	PA	51.88%	0.29%	0.43%	0.61%	6.07	7.00	8.21	10.01	10.97	12.21	431	209
Arkla	LA	7.51%	0.39%	0.55%	0.78%	6.74	7.82	9.35	10.69	11.81	13.38	575	166
Arkoma	OK	1.61%	0.63%	0.95%	1.38%	8.32	10.47	13.36	12.32	14.54	17.51	491	177
East Texas	TX	2.33%	0.49%	0.79%	1.15%	7.42	9.38	11.84	11.39	13.41	15.95	590	152
Fort Worth Syncline	TX	3.22%	0.47%	0.81%	1.29%	7.29	9.56	12.77	11.27	13.60	16.90	590	152
Gulf Coast	TX	11.81%	0.54%	1.35%	2.50%	7.72	13.13	20.84	11.71	17.28	25.21	590	152
Permian	TX	9.48%	0.31%	0.50%	0.76%	6.19	7.48	9.20	10.12	11.45	13.22	590	152
South Oklahoma	OK	1.79%	0.37%	0.86%	1.53%	6.62	9.88	14.33	10.57	13.92	18.51	491	177
Strawn	TX	5.72%	0.36%	0.58%	0.88%	6.54	8.00	10.00	10.49	12.00	14.05	590	152
Total & weighted average	—	100.00%	0.36%	0.61%	0.96%	6.52	8.21	10.53	10.46	12.21	14.59	—	—

The second stage considers on-site GHG emissions from the ethylene production plant. On-site CO_2 emissions are calculated using the Aspen Plus model, while on-site CH_4 and N_2O emissions are further counted by considering the in-plant combustion energy and conventional boiler's emission factors.[44] Note that, the on-site emission does not include the captured CO_2.

In the third stage, GHG emission credits from the export of hydrogen and other gases (primarily methane), which are co-products of the Electrical heating case, are calculated. The hydrogen and other gases are assumed to replace hydrogen products from near central steam methane reforming (SMR) plants and the national average natural gas product, respectively. Consequently, the substituted emission credits of 78.98 $kgCO_2e$ per GJ-product for hydrogen and 12.40 $kgCO_2e$ per GJ-product for other gases are assumed.[44] The credits account well-to-gate emissions, explicitly excluding any emissions associated with subsequent stages, such as hydrogen transmission, distribution, and compression. Mass-based allocation is also applied for co-produced ethylene and C_{3+} products, considering the products are generally used as raw materials for other industries, not energy sources.

Comparison of life cycle GHG emission based on different allocation methodologies for co-products set in this study—the default methodology of 'substitution for hydrogen and mass-based allocation for C_{3+} product' and the alternative methodologies of (1) system expansion for all co-products, (2) mass allocation for all co-products, and (3) energy allocation for all co-products—is also analyzed. Table 3 summarizes the allocation factors for each methodology across all cases, while Fig. S13 to S16† provide a detailed comparison of the resulting emissions. Noted that, for the three cases without co-produced hydrogen, the allocation factors are relatively consistent across methodologies due to the comparable lower heating values (LHV) of ethylene (47.2 MJ kg^{-1}) and C_{3+} (45.0 MJ kg^{-1}). In contrast, the Electrical heating case exhibits a significantly lower allocation factor under energy-based allocation, attributed to the much higher LHV of hydrogen (120 MJ kg^{-1}). Moreover, the system expansion methodology demonstrates a high sensitivity to assumptions regarding substitution scenarios.

2.4. TEA methodology

The TEA for this study comprises the following steps. Initially, the total plant cost (TPC) is computed based on the aggregated installation cost from each component using the Aspen model's components and scale information and default cost data from various literature sources. Eqn (1) is used to calculate TPC.[25] Here, TPC_i is the plant cost for ith equipment, $C_{0,i}$ is the equipment cost provided by the reference, S_i is the scale of the equipment from the model, $S_{0,i}$ is the scale of the reference equipment, f is the scaling exponent, and F_{in} is the installation factor including other costs such as direct and indirect

Table 3 Allocation factors with different allocation methods for the four cases

Allocation methods	Baseline	No external NG	Electrical heating	CCS H_2 combustion
Mass allocation for C_{3+} and substitution for H_2 and other gas	87.9%	87.9%	87.9%	87.9%
System expansion for all co-products	N/A	N/A	N/A	N/A
Mass allocation for all co-products	87.9%	87.9%	75.6%	87.9%
LHV-based energy allocation for all co-products	88.4%	88.4%	69.4%	88.4%

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labor, project contingencies, contract services, and other supporting facilities.[25] For the calculated TPC, please refer to Tables S6–S9.†

$$\mathrm{TPC} = \sum \mathrm{TPC}_i = \sum C_{0,i} \times (S_i/S_{0,i})^f \times F_{\mathrm{in}} \quad (1)$$

Table 4 shows assumptions for calculating the total overnight cost (TOC) and fixed operating cost (FOC). Following this, leveraging the mass-energy balance derived from the model and price information, the variable operating cost (VOC) and revenue from co-product sales are calculated. Lastly, a H2A model[47] is modified to compute LCOE using its key default modeling assumptions and discounted cash flow methodology.

For the capital cost of components, research from the National Renewable Energy Laboratory,[48–50] NETL,[51,52] and the Pacific Northwest National Laboratory[53] is utilized. From these, we calculate the equipment's installation cost, and the resulting TPC outcomes and details including referenced installation cost factors and scaling exponent are provided in ESI Tables S6–S9.† Table 4 summarizes the economic parameters and assumption required for calculating TOC, FOC, VOC, and revenue of co-products sales. For more detailed financial assumption, please refer to ESI Table S10.† The prices of ethane and natural gas are assumed to be \$10 and \$5.275 per mmbtu-LHV, respectively, based on the average of historical industrial prices data over the past decade,[54–56] considering their high volatility. The price of grid electricity is set to \$70 per MW h, reflecting the 2019 national average industrial price according to the U.S. Energy Information Agency (EIA).[58] For calculating co-product sales revenue, the C_{3+} is assumed to have the same price as butane (\$443 per tonne-C_{3+}),[59] which is a historical average. The price of hydrogen (\$1.15 per kgH_2) is based on the average of the 2030 refinery's end-use willingness to pay, as estimated by the U.S. DoE.[60]

3. Results

3.1. Mass and energy balance

Table 5 presents the mass and energy balances for the four cases producing 1 million tonnes of ethylene annually: a Baseline case, and three cases with decarbonization approaches applied. In all cases, the same amount of ethane is inputted, with only the Baseline case utilizing natural gas as the fuel. Consequently, external power input becomes necessary for the three decarbonization approaches. The No external NG case requires 0.23 kW h per kg-ethylene more than the Baseline case. The CCS and H_2 combustion case, requiring more power due to power consumption for the PSA and ASU facility operation, uses approximately 0.26 kW h per kg-ethylene more than the No external NG case. Additionally, for the electrically heated cracker case, significantly more power (2.86 kW h per kg-ethylene) is consumed compared to the No external NG case. Moreover, in the Electrical heating case where purge gas from the hydrocarbon fractionation process is not reused as a heat source but purified and exported, hydrogen (65.1 kg per tonne-ethylene) and other gases (119.5 kg per tonne-ethylene) are co-produced. It is noted that other gases majorly consist of methane (83.3% CH_4, 9.6% H_2, 6.7% C_2H_4, weight basis). Furthermore, as depicted in Fig. 3, on-site GHG emissions are in order of amount of fossil fuels combustion (Baseline, No external NG, CCS and H_2 combustion, and

Table 4 Economic input parameter and assumption

Parameter	Values
Parameters to calculate TOC[57]	
TPC	Estimated based on scaling (see ESI Tables S6–S9†)
Site Preparation Cost (SPC)	2.0% of TPC
Engineering and Design Cost (EDC)	10.0% of TPC
Land Cost (LC1)	\$500 000
Other Owner's Costs (OOC)	15% of TPC
TOC	TPC + SPC + EDC + LC1 + OOC
Parameters to calculate FOC per year[24,47]	
Labor Cost (LC2)	Plant staff: 64, burdened labor cost: \$50 per man-h
General and Administrative Cost (GAC)	20% of LC2
Property Tax and Insurance Cost (PTIC)	2% of TPC
Material Cost (MC)	3% of TPC
FOC	LC2 + GAC + PTIC + MC
Parameters to calculate VOC	
Ethane price (\$ per mmbtu-LHV)	10[54,55]
Natural gas price (\$ per mmbtu-LHV)	5[56]
Grid electricity price (\$ per MW h)	70[58]
Parameters to calculate co-product revenue per year	
C_{3+} price (\$ per tonne)	443 [59]
Hydrogen price (\$ per mmbtu-LHV)	10[60]
Other gas price	Same with natural gas price

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Table 5 Mass and energy balance of the four ethylene production cases

		Unit	1 Baseline	2 No external NG	3 Electrical heating	4 CCS and H_2 combustion
Input	Ethane (C_2H_6)	kg h^{-1}	151 182	151 182	151 182	151 182
	Electricity	MW	0	26	353	56
	NG (CH_4)	kg h^{-1}	5920	0	0	0
Output	Ethylene (C_2H_4)	kg h^{-1}	114 335	114 335	114 335	114 335
	C_{3+}	kg h^{-1}	15 738	15 738	15 738	15 738
	H_2	kg h^{-1}	0	0	7448	0
	Other gas	kg h^{-1}	0	0	13 659	0
On-site	GHG emissions	kgCO_2e per h	50 505	34 265	0	7880
	Combustion energy	MJ h^{-1}	1 173 780	452 559	0	0
Efficiencies	Thermal efficiency	% of LHV	82.96	85.27	93.15	84.02
	Thermal efficiency (electricity adjusted)	% of LHV	82.96	83.64	75.92	80.70
	Carbon conversion	% of input C	93.04	93.04	93.04	93.04

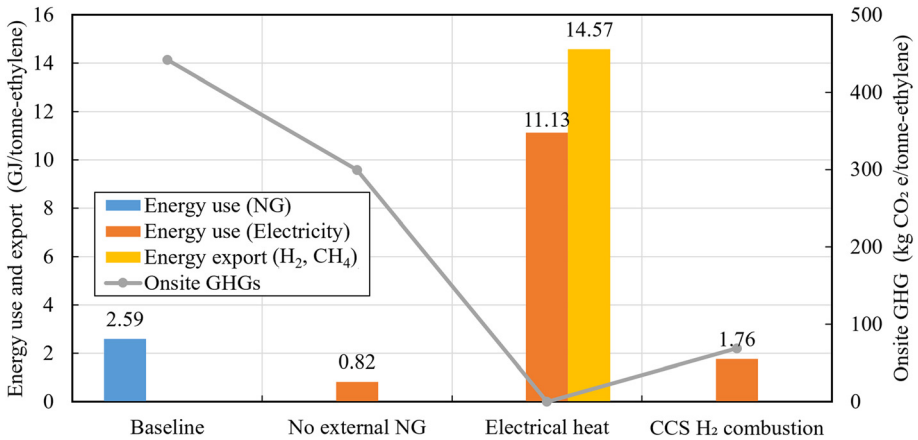

Fig. 3 Energy use, energy export, and on-site GHG emission for the four ethylene production cases.

Electrical heating cases emitting 442, 300, 69, 0 kgCO_2e per tonne-ethylene, respectively, before allocation to the ethylene product). Additionally, thermal energy efficiency (η_{th}) and carbon conversion efficiency (η_c) are calculated using eqn (2) and (3).

$$\eta_{th} = \frac{LHV_{C_2H_4} + LHV_{C_{3+}} + LHV_{H_2} + LHV_{Other\,gas}}{LHV_{C_2H_6} + LHV_{NG} + P_e} \quad (2)$$

$$\eta_c = \frac{\text{carbon in Ethylene} + \text{carbon in } C_{3+}}{\text{carbon in Ethane}} \quad (3)$$

For the equations, each input and output's LHV flow amount, electricity consumption (P_e), and the amount of carbon atoms contained in ethylene feedstock and products are inputted. When calculating P_e in eqn (2), a conversion factor of 3.6 MJ kW^{-1} h^{-1} is used as a default and the resultant efficiency is denoted as 'Thermal efficiency'. However, in some cases, the power generation by utilizing the waste heat recovery system for syngas from feedstock or flue gases, and by utilizing boiler and steam turbine system are both included. As a result, comparing processes that produce electricity with the processes that import electricity may not be fair from the perspective of difference between power generation efficiency and power-to-heat efficiency, which is almost 100%. To assess fairly, primary energy equivalent can be considered.[61] Therefore, considering the typical efficiency of power plants (conservatively 40%), a conversion factor of 9.0 MJ kW^{-1} h^{-1} (ref. 61) is used for P_e calculation to display electricity-adjusted thermal efficiency simultaneously. Results indicated that thermal efficiency of all cases exhibit efficiency of over 80%, with the Electrical heating case having the highest at 93.15%. The reason for this is that it does not reflect the energy efficiency of the waste heat recovery system inside the plant, but it reflects the high efficiency of electricity usage since the plant's internal energy requirements are entirely met with imported electricity. This is confirmed by the Electrical heating case in Fig. 3 having export energy greater than use energy compared to other cases. Therefore, when comparing

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electricity-adjusted thermal efficiency, the Baseline case and No external NG case exhibit the highest efficiency, while the Electrical heating case shows a high thermal efficiency drop. For the CCS and H_2 combustion case, it has lower electricity-adjusted thermal efficiency than the Baseline case and No external NG case because the plant utilizes the electricity-intensive ASU and PSA units.

3.2. LCA results

3.2.1. WTG GHG emissions of four cases. The life cycle GHG analysis has been conducted on the scope of WTG for the four ethylene production cases. Fig. 4 presents the WTG GHG emissions breakdown into detailed emission stages as described in section 2.3. The results are depicted in two different scenarios based on the electricity sources. The Baseline case showed 869 $kgCO_2e$ per tonne-ethylene, a result notably akin to the findings of Ghanta *et al.*,[14] which reported 840 $kgCO_2e$ per tonne-ethylene. Also, the on-site emission is 389 $kgCO_2e$ per tonne-ethylene, which is similar to 407 $kgCO_2e$ per ton-ethylene reported by Young *et al.*[15] Ethane upstream emissions remain constant across all four cases at 454 $kgCO_2e$ per tonne-ethylene. Moreover, natural gas upstream emissions are only exclusive to the Baseline case, with a negligible value (upstream 30 $kgCO_2e$ per tonne-ethylene) due to minimal usage. Since the Baseline case involves no electricity import, it is not relevant to the electricity sources scenarios. The No external NG case demonstrates approximately 63 $kgCO_2e$ per tonne-ethylene lower emissions compared to the Baseline case, attributed to the mitigation of natural gas originated on-site GHG emissions (113 $kgCO_2e$ per tonne-ethylene) resulting from the recycling of fuel gas, when grid electricity is supplied by U.S. current grid. However, this inevitably leads to a reduction in on-site power generation capacity and consequently increases the import of electricity. The case exhibiting the highest WTG emissions is the Electrical heating case, primarily due to its electricity-intensive nature, utilizing U.S. average grid electricity at 439 $kgCO_2e$ per MW h, which is similar with electricity from natural gas combined cycle (492 $kgCO_2e$ per MW h (ref. 44). Consequently, electricity upstream emission in the Electrical heating case was 1194 $kgCO_2e$ per tonne-ethylene. The substitution credits from H_2 and other gases are calculated at −543 and −74 $kgCO_2e$ per tonne-ethylene, respectively, assuming the substitution of hydrogen from a central NG-based SMR plant and the average natural gas in the United States. The smallest WTG emission in using grid electricity scenario is observed in the "CCS and H_2 combustion" case, owing to the utilization of CCS implemented purge gas. However, despite capturing 90.0% of CO_2 in the stream injected into Selexol unit (after WGS), the capture ratio of carbon atoms remains at only 77.5%, as other carbon (CO, CH_4, *etc.*) are not captured. Moreover, additional power consumption is incurred for operating ASU and CCS facilities. Consequently, although the CCS and H_2 combustion case exhibits a 77% (203 $kgCO_2e$ per tonne-ethylene) reduction in on-site GHG emissions compared to the No external NG case, there is a 114% (101 $kgCO_2e$ per tonne-ethylene) increase in electricity upstream emissions, resulting in a net reduction of WTG GHG emissions by 12.8% (102 $kgCO_2e$ per tonne-ethylene). If three decarbonized cases use renewable electricity such as wind, water, or solar-power, electricity upstream emissions are becoming zero when excluding embodied emissions. The effects are significant in the cases with higher electricity consumption. For example, Electrical heating case showed −163 $kgCO_2e$ per tonne-ethylene of WTG GHG emission. This significant negative value is based on the assumption that while the plant's power source is clean, the substituted hydrogen is assumed to be gray hydrogen (NG SMR-based). This assumption may apply to certain plants with similar circumstances, but it does not represent a decarbonized future where ethylene plants are expected to use renewable energy, and the nearby hydrogen producers produce clean, blue or green hydrogen. If substituting blue or green

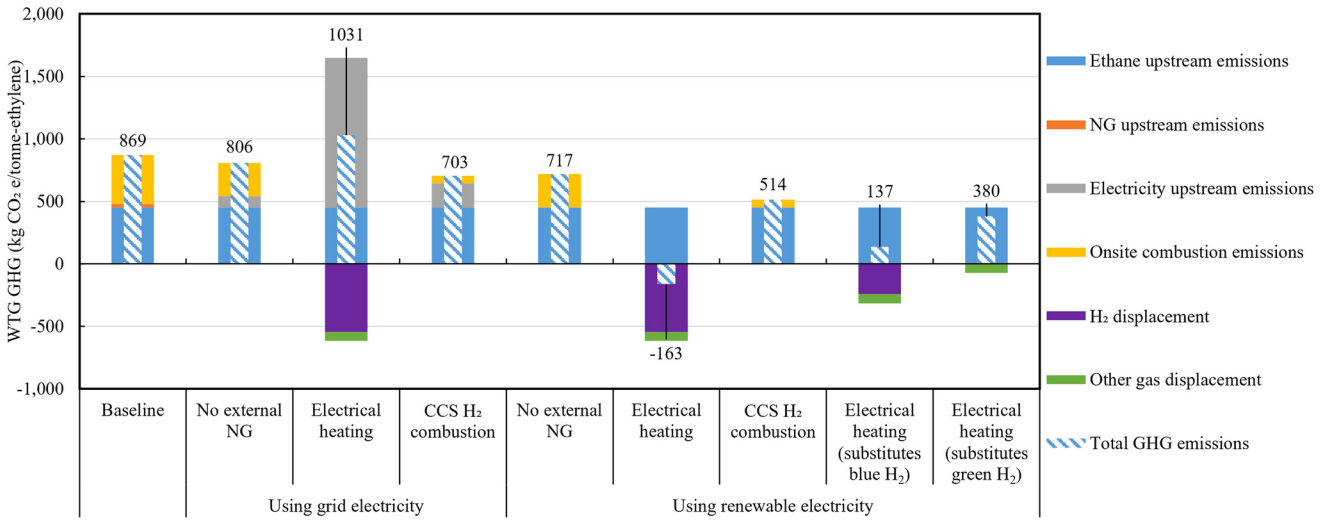

Fig. 4 WTG GHG emission breakdown for the four ethylene production cases.

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hydrogen is assumed, the WTG GHG emission results are 137 and 380 $kgCO_2e$ per tonne-ethylene, respectively.

As shown above, the WTG GHG emission results are affected by the GHG assumptions for ethane, NG, electricity, and substituted hydrogen. Consequently, the sensitivity analysis results are comprehensively provided as follows:

3.2.2. Sensitivity analysis on CH_4 emission rate and NG upstream emission. For all cases in Fig. 4, WTG GHG emissions originate from ethane and natural gas upstream emissions are over 44%. These upstream emissions, particularly during the fuel production process, are significantly influenced by methane leakage (vent and fugitive emissions). Therefore, in this study, we calculate the WTG GHG emission results due to the CH_4 emission rate variation of the process at the production site of ethane feedstock and natural gas fuel sourced from shale gas basin. Accordingly, the results of varying CH_4 emission rates are illustrated in Fig. 5. It is noted that the CH_4 emission rate is defined as aggregated value of both non-combustion CH_4 emissions (also called CH_4 leakage, including vent and fugitive emissions) and combustion CH_4 emissions. Please refer to section 2.3 and Table 2 for regional variation and range of the U.S. shale basins' CH_4 emission rate. As the CH_4 emission rate increases from 0.1% to 2.5%, the upstream emission of ethane and NG rise from 8.69 to 25.2 and from 4.79 to 20.86 $kgCO_2e$ per GJ, respectively. These results in an increase of WTG emissions by 888 $kgCO_2e$ per tonne-ethylene across all three decarbonization approaches, where ethane and natural gas usage are constant, resulting in parallel slopes in the graph. In the Baseline case where only natural gas is used as the energy input, the increase due to the increase of CH_4 emission rate is 923 $kgCO_2e$ per tonne-ethylene. Therefore, the Baseline case is more sensitive to upstream CH_4 emission rate variance compared to cases without NG fuel, but there is no reversal of WTG GHG emission trends across the 0–2.5% leakage range for all cases.

While natural gas is predominantly fossil fuel-based, it could also originate from renewable natural gas (RNG) sources such as animal waste. Applying a marginal approach to RNG produced from waste sources (subtracting avoided emissions in the counterfactual scenario from the fuel use scenario) can result in negative upstream GHG emission values.[44,62,63] Fig. 6 illustrates the WTG GHG emissions for ethylene production

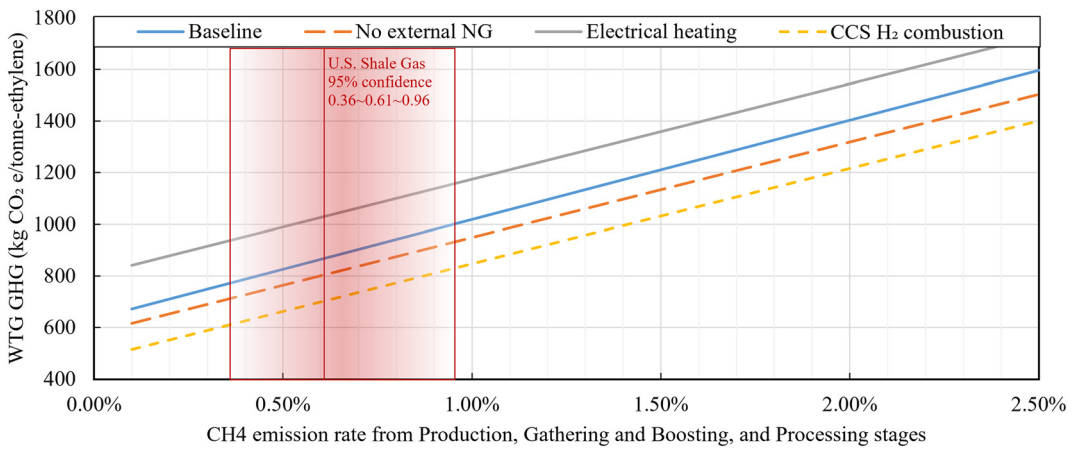

Fig. 5 Impact of CH_4 emission rate on WTG GHG emissions of ethylene production. CH_4 emission rate is varied on three upstream stages (production, gathering and boosting, and processing). 95% confidence range of U.S. shale gas mix is 0.36% (P2.5)—0.61% (mean)—0.96% (P97.5).

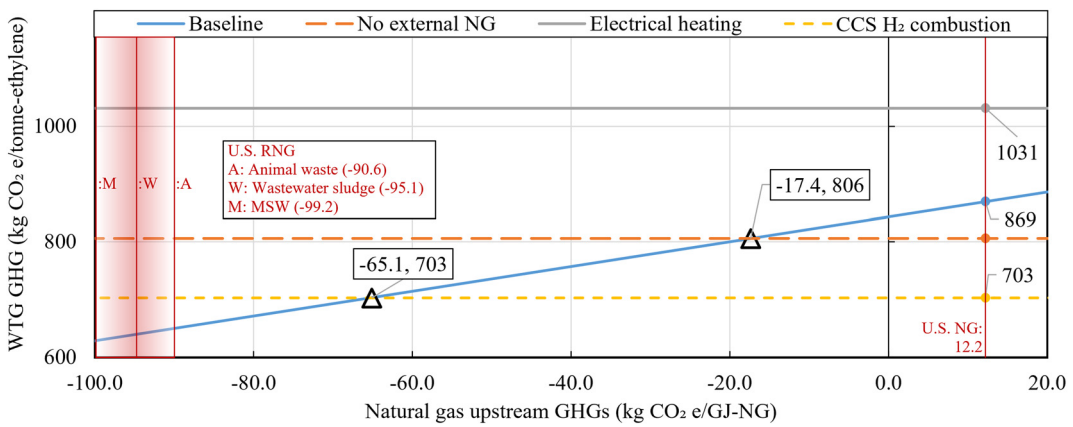

Fig. 6 Impact of NG upstream GHG emission on WTG GHG emission of ethylene production.

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cases varying NG upstream GHG emission, to show the effects of RNG with negative upstream emissions used as fuel. The default fossil-based natural gas upstream emission applied in this study, based on GREET 2021, is 12.2 $kgCO_2e$ per GJ-NG, while RNG upstream emissions from animal waste, wastewater sludge, and municipal solid waste are −90.6, −95.1, and −99.2 $kgCO_2e$ per GJ-NG, respectively.[44] The Baseline case, using natural gas as the input, fluctuates with NG upstream emission variations, while other cases remain unchanged. Specifically, when NG upstream emissions become −17.4 and −65.1 $kgCO_2e$ per GJ-NG, reversals occur with the No external NG case and CCS and H_2 combustion case, respectively. Therefore, in scenarios where approximately 70% or more of the natural gas is derived from biowaste sources, the Baseline case exhibits the lowest GHG emissions, amounting to 703 $kgCO_2e$ per tonne-ethylene. This represents a reduction of 166 $kgCO_2e$ per tonne-ethylene compared to the case utilizing 100% fossil-based natural gas.

3.2.3. Sensitivity analysis on upstream emission of electricity. Fig. 7 illustrates the impact of upstream GHG emissions of electricity on the four ethylene production cases. The impact is greater for the case with greater inputted electricity amount per unit ethylene production. The case with the highest power consumption, the Electrical heating case, intersects with Baseline, No external NG, and CCS and H_2 combustion cases at 380, 350, and 296 $kgCO_2e$ per MW h, respectively. All the intersections are lower than the 2019 U.S. grid electricity mix's upstream emission, 439 $kgCO_2e$ per MW h, and between the current and 2030 Grid estimation. In other words, the Electrical heating case may be more advantageous from a GHG emission perspective when the electricity upstream emission is lower than these intersect values. Currently, these intersection of upstream emissions does not fall within the range of upstream emissions from the grid power network where the shale basin is located. However, the Electrical heating case will become more prominent in light of the near-future grid electricity decarbonization approaches, considering U.S. 2030 and U.S. 2050 plans.[64] Additionally, when upstream electricity emissions are below 60 $kgCO_2e$ per MW h, the Electrical heating case has WTG GHG emissions of less than 0. This implies that if approximately 305 MW of renewable energy were applied to an electrically heated cracker-based ethylene production plant with 1 million-tonnes per year, WTG GHG emission would become zero. Note that GHG credit from H_2 displacement is assumed to be identical, as the H_2 produced by the ethylene plant is assumed to substitute nearby NG SMR-based gray hydrogen. Considering that the U.S. ethylene production was approximately 40 million tonnes per year in 2020,[65] utilizing about 12.2 GW of renewable energy and transitioning plant to electrically heated cracker and substituting natural-gas based gray hydrogen by exportation of purified internal purge gas would make the U.S. ethylene production process carbon neutral.

3.2.4. Sensitivity analysis on substitution effect of hydrogen. Fig. 8 illustrates the impact of GHG emissions of substituted hydrogen on the four cases. Excluding the remaining three cases without co-produced hydrogen, only the Electrical heating case exhibits sensitivity to the substitution effect of hydrogen. The Electrical heating case is depicted with five lines corresponding to scenarios of electricity upstream emissions at 600, 439(default), 300, 200 and 0 $kgCO_2e$ per MW h. Each line intersects with the Baseline case at hydrogen GHG emissions of 166, 103, 48 and 8 $kgCO_2e$ per GJ, respectively, while the other line for renewable electricity (0 $kgCO_2e$ per MW h) does not intersect. The GHG emissions of representative hydrogen pathways (NG SMR, NG Autothermal reforming (ATR) + CCS, Biomass gasification, electrolysis using wind/solar or nuclear-based electricity), shown in red on the figure, are based on well-to-gate scope results from GREET 2021 and 2023 (specifically for ATR + CCS). As the GHG emission value of substituted hydrogen increases, the WTG GHG emission of ethylene decreases. When substituting NG SMR-based gray hydrogen, the WTG GHG emissions are lower than those of the Baseline case at an electricity upstream emission of 379 $kgCO_2e$ per MW h or less. For NG ATR + CCS-based blue hydrogen, the WTG GHG emissions are lower than those of

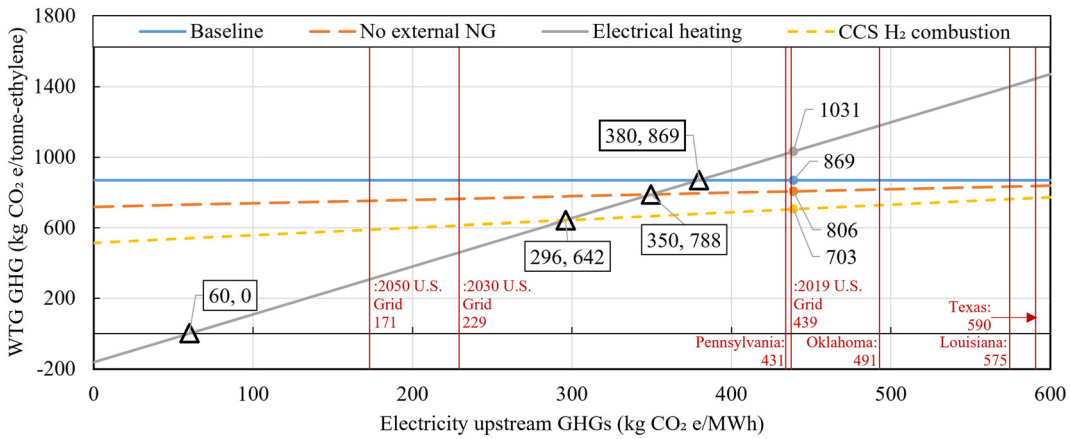

Fig. 7 Impact of electricity upstream GHG emission on WTG GHG emission of ethylene production.

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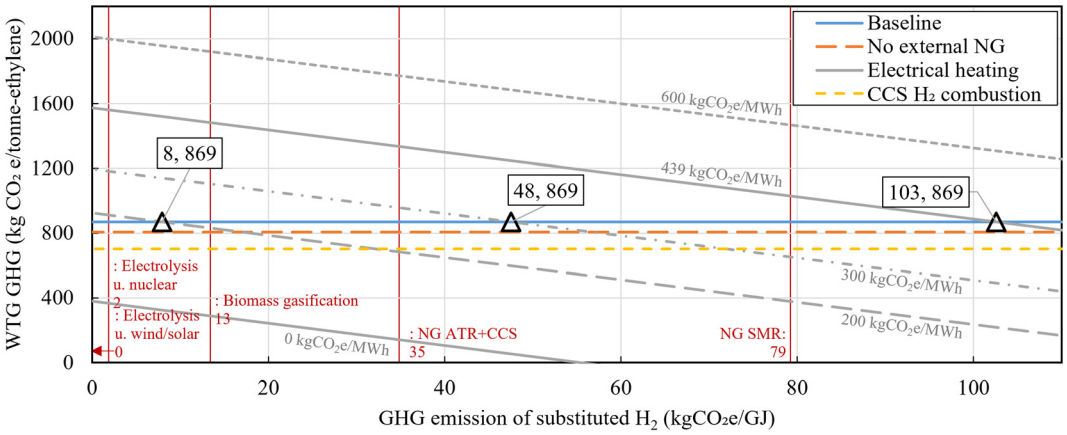

Fig. 8 Impact of GHG emission of substituted H_2 on WTG GHG emission of ethylene production.

the Baseline case at an electricity upstream emission of 269 $kgCO_2e$ per MW h or less. When substituting green hydrogen, the WTG GHG emissions are lower than those of the Baseline case at an electricity upstream emission of 180 $kgCO_2e$ per MW h or less. Current typical ethylene production plants rarely use renewable energy, and most hydrogen production in the market is still gray hydrogen. Therefore, the WTG GHG emission of 1031 $kgCO_2e$ per tonne-ethylene, based on the current grid electricity upstream GHG emission (439 $kgCO_2e$ per MW h) and the assumption of NG SMR-based gray hydrogen substitution, is more representative of the "current" situation. However, it is more likely in the future that the ethylene production plant will use more decarbonized grid electricity or directly introduce renewable power generation units, in which case the production pathway for the hydrogen distributed around the plant will rely on cleaner hydrogen such as blue or green hydrogen pathways. Consequently, the WTG GHG emissions of 137 and 380 $kgCO_2e$ per tonne-ethylene, based on the renewable electricity upstream GHG emission (0 $kgCO_2e$ per MW h) and assumptions of blue or green hydrogen substitution, respectively, are more representative of "future" scenarios. This implies that if the power source utilized by ethylene production plants is decarbonized, regardless of the decarbonization status of the surrounding hydrogen production market, ethylene production plants employing Electrical heating technology will be superior in terms of GHG emissions.

3.3. TEA results

3.3.1. LCOE of four cases. The TEA analysis was conducted based on the financial and economic assumptions listed in Table 4. Fig. 9 presents the results by categorizing the installed cost of each component that constitutes TPC (see ESI Tables S6–S9†). These results are expressed as TPC per daily ethylene production capacity of the facility. For all cases, the ethane cracker represents the largest portion, which amounts to $135

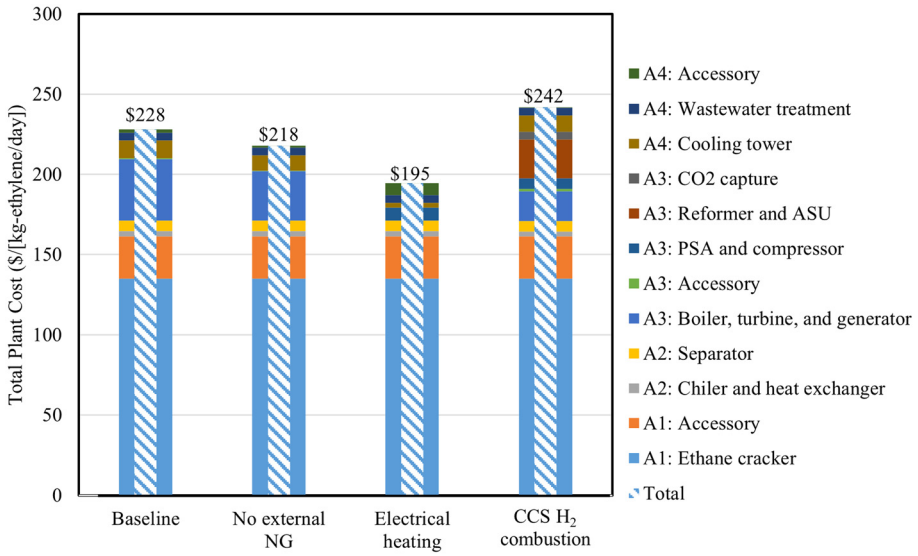

Fig. 9 Total plant cost of four ethylene production cases.

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per kg-ethylene per day. Additionally, the TPC of the Electrical heating case is the lowest at \$195 per kg-ethylene per day. This is primarily due to the reduction in costs by \$38 per kg-ethylene per day compared to the Baseline, attributed to the absence of boiler and power generation equipment, and relevant small size of cooling tower within the plant. It is worth noting that despite the Electrical heating case having lower TPC compared to the other cases, its variable operating cost is the highest due to significant energy input as discussed below. Moreover, the CCS and H_2 combustion case has the highest TPC value of \$242 per kg-ethylene per day. The main contributors to this TPC difference are the Reformer and ASU, CO_2 capture, PSA and compressor, costing \$24, \$5, and \$7 per kg-ethylene per day, respectively, with ASU being the largest contributor. The cost associated with CO_2 capture units appears relatively lower than other factors, mainly because it captures syngas (with high CO_2 concentration) rather than typical flue gas (with low CO_2 concentration). For reference, the CO_2 concentration in the captured gas after WGS is 19.3 vol%. The TPC value for the No external NG case is \$10 per kg-ethylene per day lower than the Baseline case. This primarily due to the \$7 per kg-ethylene per day lower cost in Boiler, turbine, and generator (\$31 per kg-ethylene per day). This reduction is mainly attributed to the decrease in the size of required combustion and power generation equipment as internal combustion energy decreases with the additional use of external electricity. For the same reason, the duty of cooling tower is lower, resulting in lower costs.

According to the assumptions in Table 4, TOC is calculated based on the estimated TPC values, and VOC, FOC, and revenue from co-products sales are calculated. Discounted cash flow analysis is performed, and the LCOE is calculated where the net present value achieves zero. Fig. 10 presents the results of the LCOE analysis for the four ethylene production cases. The results are depicted in two different scenarios based on the electricity sources. Our LCOE results for the Baseline case (\$746 per tonne-ethylene) are consistent with those reported by Hu *et al.*,[23] \$710 per tonne-ethylene, under similar feedstock price assumptions. Since the Baseline case involves no electricity import, it is not relevant to the electricity sources scenarios. Baseline case and grid electricity using scenario results show the impact of capital cost on aggregated LCOE value for all cases ranges from 8.2% to 10.4%, significantly smaller than the impact of VOC due to ethane feedstock usage, which ranges from 77.7% to 87.2%. Fixed operating costs contribute between 6.9% and 9.0% for all cases. Additionally, revenue from C_{3+} sales contribute approximately −8% to the net LCOE results for all cases. Note that the negative value indicates that sales revenue negatively impacts the levelized cost. All LCOE results except for Electrical heating case with hydrogen sold at a high price fall within the range of the minimum and maximum global ethylene sales prices from 2017 to 2022.[66]

In grid electricity using scenario, contrary to the minimal TPC in the Electrical heating case, the LCOE is the highest. This is because the increase in costs due to external electricity usage dominates the contribution of capital costs reduction. Approximately 28.2% (\$235 per tonne-ethylene) of the cost in this case is from electricity usage. Purge gas purification and external sales revenue (other credits) account for almost half of the cost increase due to external electricity imports, at \$111.6 per tonne-ethylene. This suggests that internal purge gas recycling is a more effective strategy than purge gas purification and sales and external electricity importation strategy. In the same scenario, the LCOE of the CCS and H_2 combustion case is approximately \$28 per tonne-ethylene higher than that of the No external NG case. This is primarily influenced by the increase in LCOE due to increased electricity usage, at \$20 per tonne-ethylene, while the capital cost's contribution increased by \$7 per tonne-ethylene. This is mainly due to the increase in capital costs related to ATR, ASU, WGS, and CO_2 capture. On the other hand, this modification achieves a reduction of

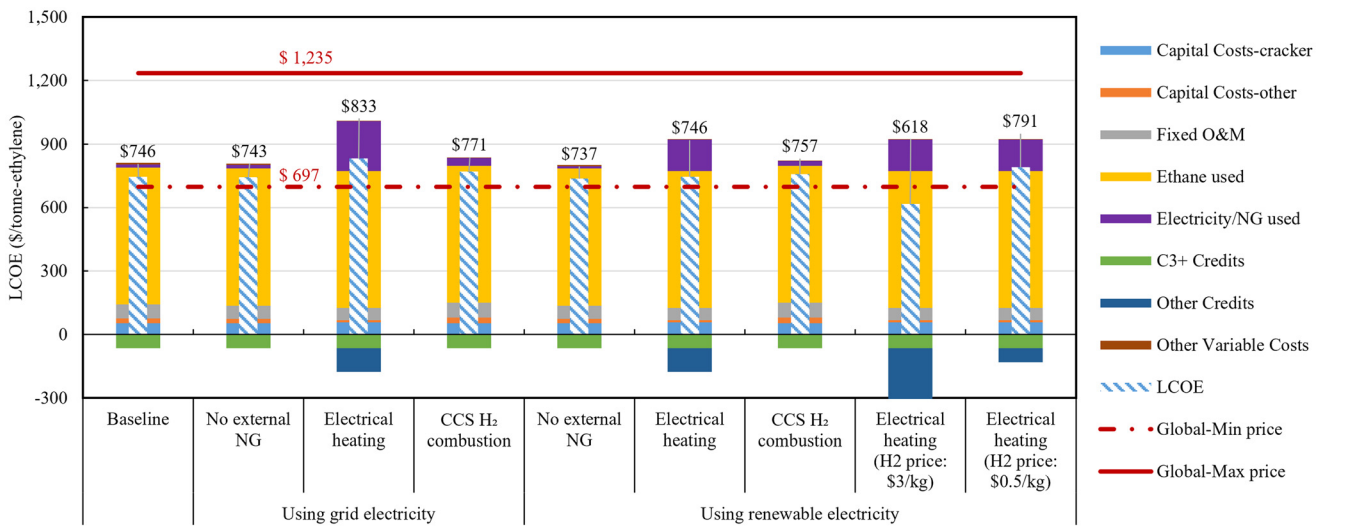

Fig. 10 LCOE of four ethylene production processes. Global minimum and maximum price of ethylene are both expressed in the figure.

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103 kgCO_2e per tonne-ethylene in WTG GHG emissions. Based on these differences, compared to the No external NG case, the calculated CO_2 avoidance cost of the CCS and H_2 combustion case is \$266 per tonCO_2e.

In the renewable electricity scenario, the only difference from the grid scenario is the cost difference due to electricity use. Additionally, in the last two cases with different hydrogen prices, there is a difference in revenue due to hydrogen selling credits. The renewable electricity assumed in this study is based on the median levelized cost of electricity for a 100 MW-scale solar PV plant in the U.S., calculated by the International Energy Agency and the OECD Nuclear Energy Agency (NEA),[67] at \$44 per MW h. Additionally, the median power generation cost for U.S. wind onshore plants (>1 MW) is \$39 per MW h, and for NG-based combined cycle gas turbine power plant, it is \$45 per MW h, all showing similar range. Note that since electricity production costs, not prices, are used, this assumes that renewable electricity power generation modules are directly operated and managed within the ethylene production plants or accessed at near-cost prices. The grid electricity price is assumed to be \$70 per MW h, so directly producing or accessing solar-based renewable electricity at cost levels (\$44 per MW h) can reduce electricity usage costs by 37%. This reflects the situation in the U.S. where renewable energy is already competitively priced compared to fossil fuel or nuclear-based power. Consequently, the three decarbonized cases using renewable electricity show similar or lower ethylene production costs compared to the baseline case. The No external NG case had already shown cost parity with grid electricity usage instead of NG import, but with the additional cost reduction from using renewable electricity, it achieved \$9 per tonne-ethylene savings compared to the Baseline case. Additionally, the Electrical heating case could result in a cost of \$45 per tonne-ethylene to savings of \$128 per tonne-ethylene compared to the Baseline case, depending on the hydrogen sale price (\$0.5–3.0 per kg), respectively.

Fig. 11 shows the CO_2 avoidance cost results based on the Baseline case, calculated using life cycle GHG emissions (Fig. 4) and LCOE (Fig. 10). Each case is clustered by different colors according to three hydrogen sale prices. The results showed that excluding the Electrical heating case, which export hydrogen, the two cases have same CO_2 avoidance cost regardless of hydrogen price. A negative CO_2 avoidance value indicates superiority in both cost and emissions, as both the LCOE cost, and WTG GHG emissions decrease from the Baseline case. All No External cases show negative CO_2 avoidance costs, indicating superiority over conventional plants in both cost and emissions. In contrast, the Electrical heating cases substituting gray hydrogen using grid electricity yields a negative CO_2 avoidance value in the low hydrogen price range due to increases in both the LCOE and WTG GHG emissions, indicating inferiority on both fronts, and thus it was not depicted in the figure. The Electrical heating cases show negative avoidance costs at hydrogen prices above \$1.2 per kg-H_2, and positive avoidance costs at lower hydrogen prices.

As shown above, the LCOE results are affected by the price and cost assumptions for NG, electricity, and selling hydrogen. Consequently, the sensitivity analysis results are comprehensively provided as follows:

3.3.2. Sensitivity analysis on natural gas price. The four cases utilize ethane as the only feedstock, and since the ethane input per unit of ethylene production is consistent across all cases, there is no relative variability due to ethane prices. However, the Baseline case, only process reliant on natural gas input, is influenced by natural gas prices. According to the US EIA, the US natural gas industrial prices fluctuated between 2.4 to \$9.1 per GJ^{-1} over the recent five years.[56] In Fig. 12, the sensitivity of LCOE due to changes of natural gas price is shown. As the natural gas price increases from \$2.4 per GJ to \$9.1 per GJ, the LCOE of the Baseline case shifts from \$739 per tonne-ethylene to \$758 per tonne-ethylene. It is noteworthy that below \$4.1 per GJ, a range that

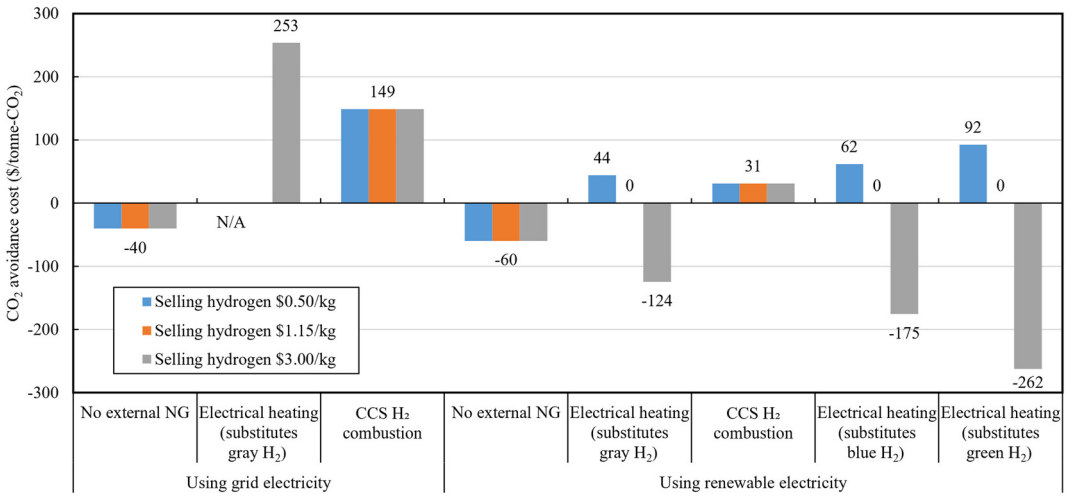

Fig. 11 CO_2 avoidance cost results based on the Baseline case.

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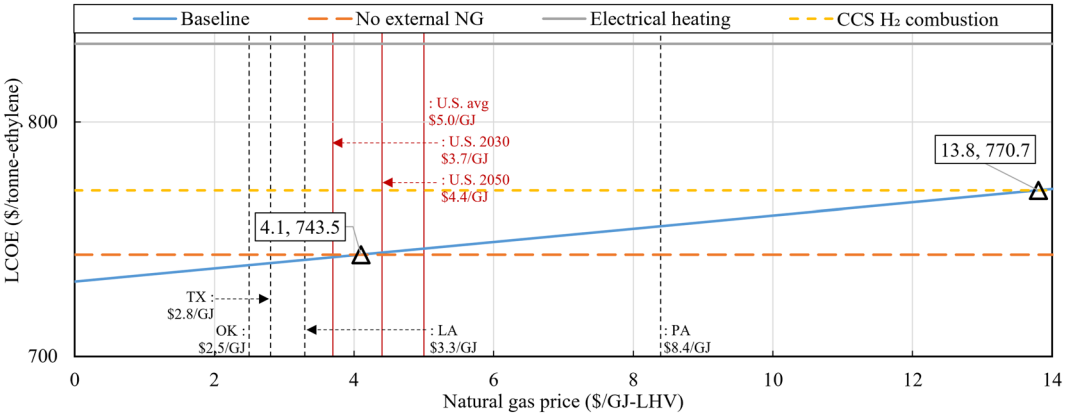

Fig. 12 Impact of natural gas price on LCOE of ethylene production.

includes the projected U.S. natural gas prices[64] for 2030 and 2050, the Baseline case is most advantageous, while above this threshold, the No external NG case becomes the most favorable. This indicates that in regions where natural gas prices are advantageous compared to electricity prices, the Baseline case holds an advantage. Furthermore, from natural gas prices exceeding $13.8 per GJ, the CCS and H_2 combustion case becomes more favorable than the Baseline case.

3.3.3. Sensitivity analysis on electricity price. The sensitivity of LCOE due to changes of electricity price or production cost of electricity is illustrated in Fig. 13. According to the EIA, the monthly average industrial electricity prices in the mainland of United States varied from $62 per MW h (Washington) to $180 per MW h (Rhode Island) in 2022.[58] As electricity prices rise from $62 to $180 per MW h, the LCOE increases from $741, $806, and $766 per tonne-ethylene to $771, $1203, and $829 per tonne-ethylene for the No external NG, Electrical heating, and CCS and H_2 combustion cases, respectively. The intersection points of these cases with the Baseline case occur at $27.8 per MW h, $44.0 per MW h, and $73.6 per MW h. Additionally, the levelized cost of electricity for various power sources in the U.S. (solar, wind, CCGT, geothermal, hydropower, nuclear, and coal power plants), calculated by the IEA and OECD NEA,[67] is also shown in the figure. These power generation costs are depicted considering scenarios where the ethylene production process directly integrates renewable power plants or imports electricity at comparable prices. In the range of $0 to $41.1 per MW h, the Electrical heating case exhibits the lowest LCOE. In the range of $41.1 to $73.6 per MW h, the No external NG case shows the lowest LCOE. Beyond this range, the Baseline case becomes the most advantageous. In conclusion, a case benefiting from lower electricity price or cost is that with higher electricity usage. This implies that if electricity prices fall along with the spread of renewable electricity in the future, or if ethylene plants directly introduce already inexpensive renewable power plants, the potential that Electrical heating case become the most advantageous will increase in terms of LCOE and WTG GHG emission.

3.3.4. Sensitivity analysis on hydrogen price. The sensitivity of LCOE due to changes of hydrogen selling price is shown in Fig. 14. Excluding the three cases that have no co-produced hydrogen, only the Electrical heating case exhibits sensitivity to the substitution effect of hydrogen. The Electrical heating case is depicted with two lines based on the electricity

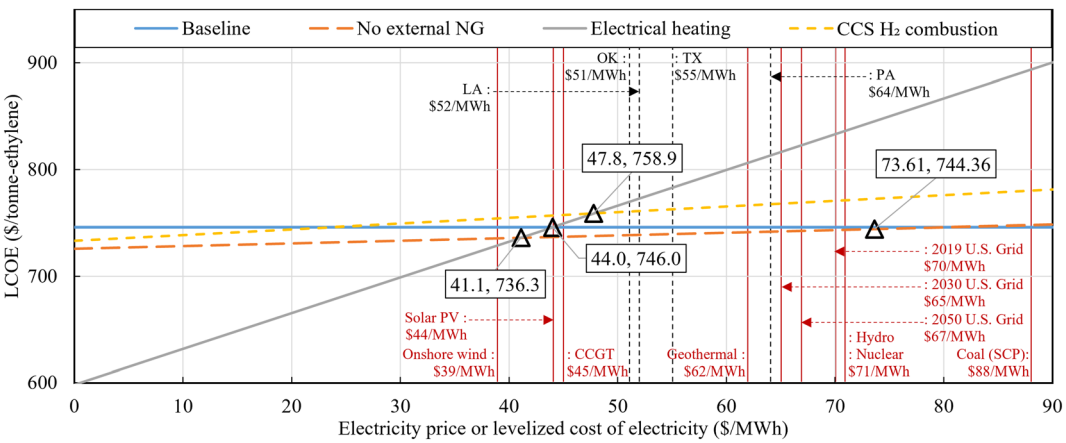

Fig. 13 Impact of electricity price on LCOE of ethylene production.

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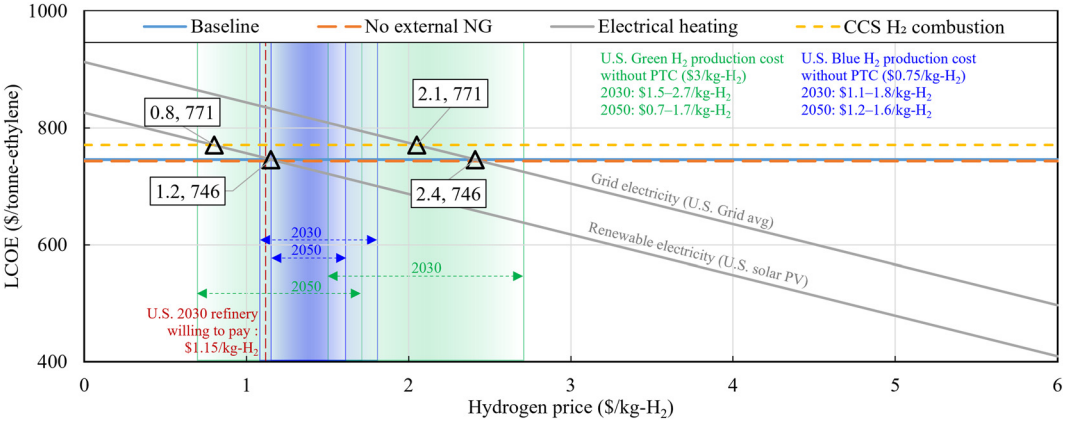

Fig. 14 Impact of hydrogen price on LCOE of ethylene production.

source scenarios: grid electricity and renewable electricity (U.S. solar PV). Each line intersects with the Baseline case at hydrogen prices of \$2.4 and \$1.2 per kg-H_2, respectively. The graph also shows the default hydrogen price defined in this study as \$1.15 per kg-H_2 (red line) and the projected production costs of U.S. blue and green hydrogen for 2030 and 2050[60] (blue and green shaded areas, respectively). As the hydrogen price increases, the LCOE of the electrical ethylene plant decreases due to additional revenue from the plant. The price of hydrogen varies significantly depending on supply and demand conditions, the type of production pathways, and the supply chain (including infrastructure and charging stations). However, given that the long-term hydrogen prices are targeted to be lower, ethylene production plants that sell hydrogen externally can generally be expected to see hydrogen sale revenues decline over time (note that, the lifespan of the plant set in this study is 40 years, encompassing 2030 and 2050). Furthermore, ethylene production plants based on Electrical heating will exhibit different economic viability compared to the conventional methods, depending on the hydrogen selling price. Specifically, the break-even hydrogen price is estimated to be \$1.2 per kg-H_2 when using renewable electricity and \$2.4 per kg-H_2 when using grid electricity, which aligns closely with the projected future hydrogen costs in the United States. Notably, when using renewable electricity, the hydrogen price that achieves economic parity with conventional plants corresponds to the lower bound of the projected 2050 blue hydrogen production costs. Therefore, this renewable option presents a lower price risk for future profitability.

Policy-driven decarbonization pathways and economic support policies for ethylene production processes and by-products (C_{3+}, hydrogen and methane), which may be introduced in the coming decades, can significantly influence the profitability of these approaches. Particularly, considering the attractive CO_2 avoidance cost of the three ethylene decarbonization approaches, carbon credits could be considered to mitigate long-term price risks. Also, if the U.S. Inflation Reduction Act 45V clean hydrogen credit is applied to operators simultaneously producing and supplying both ethylene and hydrogen, a tax credit of \$0.6–3.0 per kg-H_2 can be granted depending on the hydrogen Tier (which translates to a \$42–208 per tonne-ethylene LCOE reduction for the Electrical heating case). It is noteworthy that the Electrical heating case, one of the potential by-product hydrogen production system, includes a more complex variety of products and related sub-systems compared to blue and green hydrogen. Consequently, a market impact analysis and a consequential GHG reduction assessment in expanded system boundary are necessary to determine the inclusion of these processes under clean hydrogen title. This decision will heavily rely on the LCA approach[68] that will be determined in the future.

3.4. Regional variance analysis

The single parameter sensitivity analysis above demonstrates the impact of CH_4 emission rates, upstream emissions, and prices of NG, electricity, and substituted hydrogen on LCA and TEA results. However, uncertainties in these factors typically occur simultaneously in real-world scenarios and exhibit significant regional variability. To address this, this section analyzes scenarios where ethylene plants are located near various shale basins in the U.S. Each region assumes different upstream emissions and prices as detailed in Table 2 and below Table 6. The analysis encompasses both 2019 and 2030, with variations in electricity prices, upstream emissions, NG prices, and upstream emissions of substituted hydrogen applied for each year. For 2019, it is assumed that the co-produced hydrogen substitutes nearby gray hydrogen, while for 2030, substitutions are assumed to align with the U.S. roadmap:[69] 50% gray hydrogen, 25% blue hydrogen, and 25% green hydrogen.

Fig. 15(a) illustrates the WTG GHG emissions of the four ethylene production processes for 2019 and 2030. In 2019, due to relatively high upstream emissions from grid electricity, the Electrical heating case exhibits the highest WTG GHG emissions across all regions. Among these, the Appalachian shale basin shows the lowest emissions, attributed to its low CH_4 emission rate on production, gathering & boosting, and processing stages and low upstream emissions from electricity in

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Table 6 Prices of natural gas, and grid electricity for each shale basin region (2019[56,58] and 2030[25])

Shale basins	State	Shale gas production share [%]	Electricity price [$ per MW h]		Industrial NG price [$ per GJ]	
			2019	2030	2019	2030
Anadarko	OK	4.65%	50.7	52.6	2.37	2.77
Appalachian	PA	51.88%	64.1	55.5	8.07	3.81
Arkla	LA	7.51%	52.3	52.6	3.19	2.77
Arkoma	OK	1.61%	50.7	52.6	2.37	2.77
East Texas	TX	2.33%	54.5	52.6	2.73	2.77
Fort Worth Syncline	TX	3.22%	54.5	52.6	2.73	2.77
Gulf Coast	TX	11.81%	54.5	52.6	2.73	2.77
Permian	TX	9.48%	54.5	52.6	2.73	2.77
South Oklahoma	OK	1.79%	50.7	52.6	2.37	2.77
Strawn	TX	5.72%	54.5	52.6	2.73	2.77
Total & weighted average		100.00%	59.0	54.1	5.51	3.31

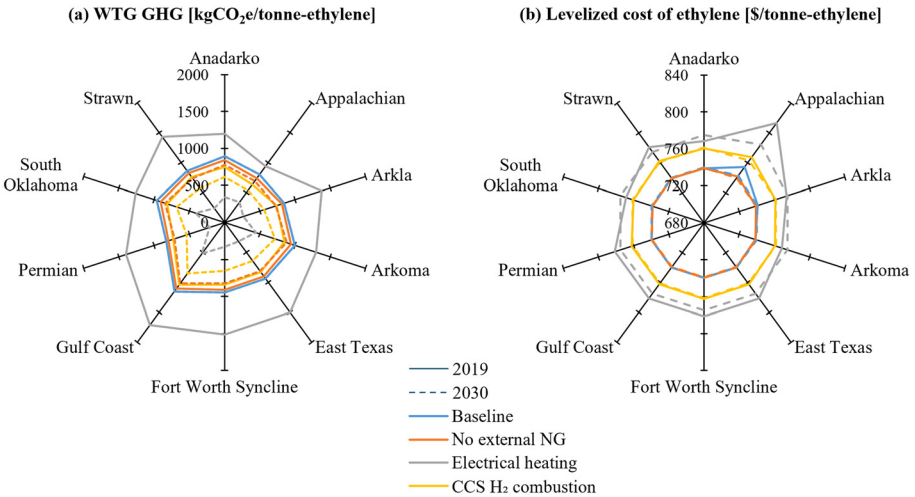

Fig. 15 Regional variance of (a) WTG GHG emission and (b) LCOE of the four cases for shale basins in U.S.

the Pennsylvania. Across all regions, the CCS H_2 combustion case exhibits the lowest emissions, reaffirming the reduction achieved through on-site emissions mitigation. In contrast, by 2030, the Electrical heating case demonstrates the lowest WTG GHG emissions in all regions, driven by the low carbonization of grid electricity projected for 2030. Consequently, the Baseline case shows the highest WTG GHG emissions across all regions, indicating that the three decarbonization strategies will serve as more robust tools for emissions reduction in the future compared to current conditions.

Fig. 15(b) shows the LCOE results for the four cases in 2019 and 2030. Across all regions, in both years, the Electrical heating case exhibits the highest cost, followed by the CCS H_2 combustion case, highlighting the continuing economic sensitivity of electricity-intensive processes to electricity prices. And across all regions, the No external NG and Baseline cases show almost identical LCOE values. The Appalachian shale basin emerges as the region with the highest LCOE due to its high current and future electricity and natural gas prices. Unlike the WTG GHG results, LCOE results display relatively low regional variability. This is because the most significant cost component—ethane feedstock price—is assumed to be constant across regions. As ethane prices typically fluctuate between NG and propane prices,[55] incorporating NG price variability into feedstock ethane prices could make LCOE outcomes more sensitive to regional NG price differences. However, ethane price fluctuations do not alter the relative rankings among the four cases within individual regions, since they consume same amount of feedstock for unit product.

Taking a holistic view of WTG GHG emissions and LCOE, these findings suggest that, as the grid electricity continues to decarbonize, electrification of ethane crackers and the adoption of CCS technologies offer the greatest potential for cutting GHG emissions. However, given the projected high production costs, strategic policy measures—such as targeted subsidies for production or investment—could prove essential in accelerating the broad deployment of these cleaner technologies.

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4. Conclusion

This study provides comprehensive TEA and LCA results for various decarbonization approaches in ethane steam cracker-based ethylene production processes. The Baseline case is a conventional ethane-based ethylene production process (with a capacity of 1 million tonnes per year) and three decarbonization approaches are as follows: (1) no external natural gas importation by importing electricity, (2) adoption of an electrically heated steam cracker with additional external electricity importation and resultant hydrogen and residual gas exportation, and (3) CCS application to internal purge gas. The study presents a comparative analysis of life cycle GHG emissions and LCOE, validating the results for the conventional case through comparison with previous research and providing novel insights into the decarbonization potential of the three unique cases examined. In addition, sensitivity analysis is conducted considering upstream GHG emissions of feedstock and fuel and CH_4 emission rates from natural gas, as well as natural gas and electricity prices.

For LCA, to assume upstream GHG emissions in the context of U.S. average, the emission values 8.213 $kgCO_2e$ per GJ for ethane, 12.211 $kgCO_2e$ per GJ for natural gas, are 439 $kgCO_2e$ per MW h for grid electricity are used. Across all cases, ethane's upstream GHG emissions accounted for nearly 50% of the WTG GHG emissions. The conventional plant exhibited a WTG GHG emission of 869 $kgCO_2e$ per tonne-ethylene, which align closely with previous studies' results. Furthermore, the strategy of grid electricity importation to remove external natural gas usage has lower WTG GHG emissions of 806 $kgCO_2e$ per tonne-ethylene. When this strategy is combined with the utilization of renewable electricity, the emissions further reduced to 717 $kgCO_2e$ per tonne-ethylene. Electrically heated cracker plant showed 1031 $kgCO_2e$ per tonne-ethylene of emission. GHG credits obtained by purifying and selling hydrogen and purge gas (616 $kgCO_2e$ per tonne-ethylene) were smaller than the increase in grid electricity's upstream emissions (1106 $kgCO_2e$ per tonne-ethylene) resulting from the deficiency of fuel gas recycling. However, when this strategy is combined with the adoption of renewable electricity, the result is −163 $kgCO_2e$ per tonne-ethylene, which assumes the substitution of NG SMR-based gray hydrogen. When substituting NG ATR + CCS-based blue hydrogen and green hydrogen, the results are 137 and 380 $kgCO_2e$ per tonne-ethylene, respectively. The CCS application to purge gas case resulted in the lowest emissions of 703 $kgCO_2e$ per tonne-ethylene among all cases in grid electricity using cases due to the reduction of on-site emission. When this strategy is combined with the adoption of renewable electricity, the emissions further decreased to 514 $kgCO_2$ per tonne-ethylene. In the case of substituting nearby gray hydrogen with co-produced hydrogen, the electrically heated case showed lower emissions than the conventional case when the upstream GHG emissions of electricity were below 380 $kgCO_2e$ per MW h. In the same substitution assumption, with upstream electricity emissions at 60 $kgCO_2e$ per MW h, the electrically heated cracker plant can achieve carbon neutrality. This implies that achieving carbon neutrality for all U.S. ethylene production processes using electrified steam crackers, approximately 12.2 GW of renewable electricity would be required.

For TEA, to assume fuel prices in the context of U.S. average, industrial grid electricity was priced at $70 per MW h and natural gas at $5 per GJ. Results showed that, when using grid electricity as electricity source, electrically heated cracker and adding CCS to purge gas case showed $833 and $771 per tonne-ethylene, respectively, both higher than conventional case's LCOE of $746 per tonne-ethylene, which also align closely with previous studies' results. For the no external natural gas case exhibited the lowest LCOE of $743 per tonne-ethylene. When these plants introduce renewable power generation modules on-site or import electricity at a near-cost price of $44 per MW h, the LCOEs of the above three decarbonization cases were $746, $757, and $737 per tonne of ethylene, respectively. Below $41.1 per MW h of electricity price, the electrically heated cracker case proved advantage compared to all other cases. Between $41.1 and $73.6 per MW h, the case with substituting external gas to external electricity had the lowest LCOE, while above $73.6 per MW h, the conventional plant had the lowest LCOE. Additionally, the price of natural gas did not significantly influence the trends, except for the conventional case. In the range of natural gas prices below $4.1 per GJ, the conventional case was the most feasible, whereas above this threshold, the no external natural gas case demonstrated the highest advantage. Another highly sensitive factor was the price of hydrogen sold, which only showed sensitivity in the electrically heated cracker case where hydrogen export exists. Notably, in the scenario utilizing renewable electricity, as the price of hydrogen varied from $0.5 to $3.0 per kg-$H_2$, the LCOE ranged from a cost of $45 per tonne-ethylene to savings of $128 per tonne-ethylene compared to the base conventional concept.

In order to capture variations across regions and address real-world uncertainties, a regional variance analysis was conducted. This analysis spans all U.S. shale gas basins and presents both current and future WTG GHG emissions as well as LCOE estimates.

This study holds a distinctive advantage in quantitatively comparing traditional ethylene production processes with promising decarbonization approaches. Our future work will focus on considering emerging decarbonization strategies or potentially robust ones not addressed in this study, such as oxidative coupling of methane technology and integration of flue gas CCS technology with ethylene production processes.

Author contributions

Woojae Shin: writing – original draft, investigation, formal analysis, writing – review & editing. Bosong Lin: investigation, writing – review & editing. Haoxiang Lai: investigation, formal analysis, writing – review & editing. Gasim Ibrahim: investigation, writing – review & editing. Guiyan Zang: conceptualiz-

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ation, methodology, investigation, formal analysis, writing – review & editing, supervision.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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