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Life Cycle Assessment of plasma-assisted methane to ethylene process

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Preface

I would like to take the opportunity to thank everyone who contributed to completing this master's thesis. Firstly, I would like to show my appreciation and gratitude towards prof. dr. ir. Georgios D. Stefanidis for his help through the whole project, for providing an interesting thesis topic and giving me the opportunity to conduct a life cycle assessment. My sincere gratitude goes to my daily supervisor ir. Evangelos Delikonstantis. His advice and guidance were of essential importance throughout the entire year and without him this thesis would not have been possible. He devoted hours of his time to assist me and assured a successful thesis in the end. Special thanks go to Minbo Yang who helped me familiarize with the topic of LCA, gave me critical feedback and really made my thesis accelerate already from the start. Many thanks go to my friends, family and fellow master students who supported me in any way possible and I would love to thank my parents who gave me the opportunity to study in Leuven and supported me emotionally and financially.

Finally, I would like to add that working on this topic helped me understand the importance of LCA in comparing environmental performances of various processes and identify places for improvement. It made me realize that LCA is a very powerful assessment tool to capture the global environmental impact of processes and can aid in decision making and developing new policies.

Hereby I would like to close one chapter and open another one that will hopefully be as interesting and rewarding as the years I studied at KU Leuven.

Michael Augustinus

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Abstract

Switching to reactors that drive on electricity could be a reasonable step towards decarbonisation of the chemical industry when the energy mix continues to become greener. From this point of view, plasma-assisted ethylene production is a promising alternative to conventional steam cracking processes that result in considerable quantities of greenhouse gasses. This thesis presents an estimation of the carbon footprint of the plasma-assisted ethylene production process, defining the most polluting steps and comparing with three alternative and/or upcoming ethylene production processes based on steam cracking of shale gas and two pathways for manufacturing ethylene from biomass, based on corn grain and corn stover. Therefore, material and energy streams are calculated within the boundary limits of the investigated systems. On this basis, a life cycle analysis is conducted to systematically compare the environmental impact of the different processes. An estimation of the eco-burden is done using the EcoInvent database to compute greenhouse gas emissions and global warming potential based on the life cycle inventory.

An in-depth comparison is made between the different ethylene production pathways. It is observed that the two-step process has a better performance in terms of life cycle greenhouse gas emissions than the one-step plasma process. Both plasma processes consume a considerable amount of electrical power resulting in substantial GHG emissions when taking electricity from the grid. The environmental impact analysis shows that the largest contribution comes from the NPD-reactor power demand which is therefore the most polluting unit. By applying renewable energy the life cycle emissions of the plasma processes can be reduced by up to 88%. The best performance is found for the hybrid plasma process integrated with wind energy and when the purge stream is used as co-product resulting in a total of 0,8 kg CO_2-eq/$kg_{ethylene}$. In this case, the plasma process has a lower carbon footprint than conventional ethylene production: 1,1 kg CO_2-eq/$kg_{ethylene}$ for naphtha and 1,7 kg CO_2-eq/$kg_{ethylene}$ for shale gas as feedstock. Plasma-assisted ethylene production is therefore a promising technology in combination with green energy and is considered an encouraging solution to valorising methane-rich waste gas streams, where conventional ethylene production cannot be applied, thus contributing to a reduction in global GHG emissions.

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Nomenclature

BECCS	Bioenergy with carbon capture and storage
BTU	British thermal unit(s)
CAPEX	Capital expenditure
CIS	Commonwealth of Independent States
CO_2-eq	Carbon dioxide equivalent
CTUh	Comparative toxic unit for human
DDGS	Distiller's dried grains with solubles
EIA	U.S. Energy Information Administration
EPA	U.S. Environmental Protection Agency
fU	Functional unit
GHG	Greenhouse gas
GREET	Greenhouse gases, Regulated Emissions and Energy use in Transportation
GWP	Global warming potential
HHV	Higher heating value
HP/MP/LP	High/medium/low pressure
HV	High voltage
ISO	International Standardization Organization
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LHV	lower heating value
MEA	Monoethanolamine
MJ	Megajoule(s)
MMBTU	Million British Thermal Unit
MMSCFD	Million metric standard cubic feet per day
NGL	Natural gas liquid
PE	Polyethylene
PGC	Potential Gas Committee
PSA	Pressure swing adsorption
TEG	Triethylene glycol
XTO	Subsidiary of ExxonMobil

1 Objective and approach

Conventional ethylene production processes (e.g. naphtha steam cracking) result in substantial greenhouse gas emissions coming from fuel combustion to acquire elevated temperatures inside cracking furnaces. Switching to reactors that drive on electricity could be a major step towards CO_2-neutral production of ethylene when the electricity mix continues to become greener. From this point of view, plasma reactors are considered a promising step towards reducing the carbon footprint of the ethylene industry.

The aim of this thesis is to estimate the carbon footprint of plasma-assisted ethylene production, defining the most polluting steps within this process and compare with alternative or upcoming ethylene production processes: ethylene from thermal cracking of shale gas and producing ethylene from biomass. This is done through the approach of life cycle assessment (LCA). Therefore, material and energy streams are calculated. An estimation of the eco-burden is done using the EcoInvent database to compute greenhouse gas emissions and global warming potential.

For this study, shale gas production and manufacturing of ethylene are considered in the U.S. Originally it was intended to do the study for Europe, but due to environmental concerns shale gas extraction is currently not executed or to a much lesser extent applied in the EU. However, ongoing tests in the UK and Poland might change things in the future. Due to the low shale gas price in the U.S., the margins are large enough that shale gas could be shipped from North-America to Europe. This allows ethylene manufacturers outside the U.S. to take advantage of the local low ethane prices. [1] However, long-distance sea transport would lead to a bigger environmental burden related to transportation in comparison with the process itself. This could lead to misinterpretation of the LCA study as the main objective is to compare different ethylene production processes. For this reason, feedstock production and processing together with final ethylene production are considered in the United States.

2 Introduction

2.1 Natural gas: origin, reserves and exploration

Natural gas originates from plant and animal remains that decayed and accumulated into thick layers millions of years ago. Under heavy layers of sediment, the material is compressed and this increasing pressure and heat converted the organic material into oil, coal and natural gas. Most of the natural gas that rises towards the surface encounters impermeable geological formations called sedimentary basins. These sedimentary basins can trap enormous reservoirs of natural gas. Besides basins, sedimentary rock like shale formations can contain a considerable amount of shale gas. The development of hydraulic fracking for these formations has led to a substantial increase in the availability of natural gas during the last decade. [2, 3]

When mentioning gas and oil reservoirs, two terms 'reserves' and 'resources' must be distinguished. A volume of gas or oil is described as a reserve if it is economically recoverable using existing technologies. Resource is a term used if the reservoir is known and documented but the existing technology does not allow to commercially extract the accumulation. [4]

In 2017, global natural gas reserves were proved to 193,5 trillion m^3. At the global production level of 2017 this is sufficient to meet another 52 years. The Middle East and CIS (Commonwealth of Independent States) hold the largest proved reserves. Figure 2.1 gives the reserves to production (R/P) ratios for natural gas per region in 2017. [5]

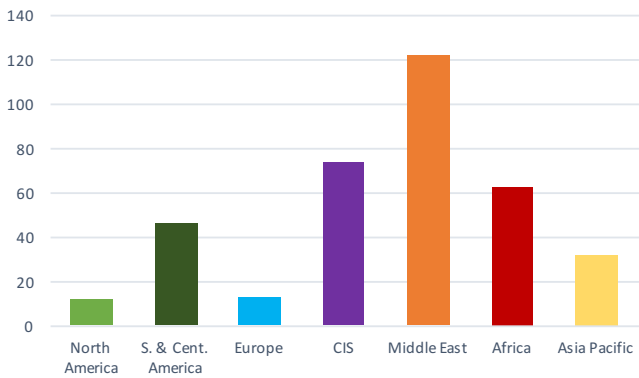

Figure 2.1: *Natural gas reserves to production (R/P) ratio by region in 2017 [5]*

The composition of raw natural gas typically consists of 70-90% methane; 0-20% ethane, propane and butane; 0-8% carbon dioxide; 0-5% nitrogen; 0-5% hydrogen sulphide and trace amounts of oxygen, argon, helium, neon and xenon. [6] When the natural gas is near to pure methane it is considered as 'dry'. In the presence of other hydrocarbons, the natural gas is called 'wet'. Once extracted from the underground, the gas is refined and impurities like water and hydrogen sulphide are removed. The clean gas can then be transported via a network of pipelines. [6]

The Potential Gas Committee (PGC) estimated that the United States possess more than 76 trillion m^3 of natural gas supply of which 40% is extractable shale gas. This reserve translates into another 50 years of production at current rates of consumption. [7] Note that the BP Statistical Review of World Energy (Figure 2.1) predicts another 12 years of natural gas reserves following current production for North America. However, one should keep in mind that the U.S. total natural gas proved reserves have more than doubled from 2007 to 2017 and this trend is still expected to extend further. [8] The sharp growth in shale gas production in the last decade has allowed the U.S. to reduce its gas import and become a net exporter of liquefied petroleum gas (LPG). [7] As depicted in Figure 2.2, the largest contributor to growth in U.S. natural gas production comes from the continued development of shale gas and gas associated with tight oil plays. According to projections, both will together account for more than 65% of the total U.S. production by 2040. [9]

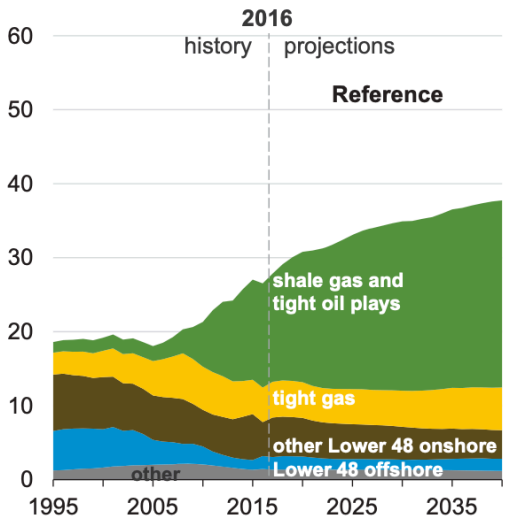

Figure 2.2: *Dry natural gas production by type (trillion cubic feet) [9]*

Like in natural gas, methane (CH_4) is the dominant component in shale gas, typically being around 75-90% of the total. The other components consist of varying amounts of NGL's (Natural Gas Liquids) like ethane, propane and butanes as well as acid gases like CO_2 and H_2S and small amounts of N_2, He and H_2O. The major product from shale gas processing is sales gas which contains mostly CH_4. Sales gas must meet very strict quality standards and is transported by pipeline systems. To avoid potential freezing problems in cryogenic environments (e.g. demethanizer) H_2O and CO_2 should be removed. To remove these undesired components together with H_2S, N_2 and heavy hydrocarbons, four gas treatment steps are employed. These include acid gas removal, sulphur recovery, dehydration and finally nitrogen rejection. [7]

Fugitive methane emissions associated with shale gas production are of recent concern because they may result in high greenhouse gas emissions. Osborn et al. concluded that methane concentrations have increased in ground water wells adjacent to drilling sites. [10] An additional concern related to shale gas production is the considerable water usage linked to hydraulic fracturing and horizontal drilling. Shale gas production is known to consume noticeably more water than conventional natural gas. [11, 12, 13]

2.2 Ethylene: importance and production

The successful application of advanced extraction technologies resulted during recent years in a sharp increase of shale gas production in the United States providing low cost NGLs for the chemical industry. Accordingly, the manufacturing of ethylene from shale gas-based feedstocks instead of from naphtha is of thriving interest. [12] Most of the shale gas formations in the U.S. are rich in ethane and 99% of ethane derived from NGLs is nowadays used as the primary feedstock to produce ethylene. [7]

Ethylene gives rise to a very large number of products and is therefore the second most used commodity chemical after ammonia. [14] It can be used as a monomer that through polymerization gives polyethylene, a polymer that has many uses in plastic bottles, wire coating and packaging film. [15] Besides, it is also a very important building block for the preparation of various chemicals like ethylene oxide (precursor of polyols that can be further converted to polyurethanes), ethylene dichloride (precursor for vinyl chloride) and ethylbenzene (precursor for styrene). Figure 2.3 shows the demand profile of the main end products. [16]

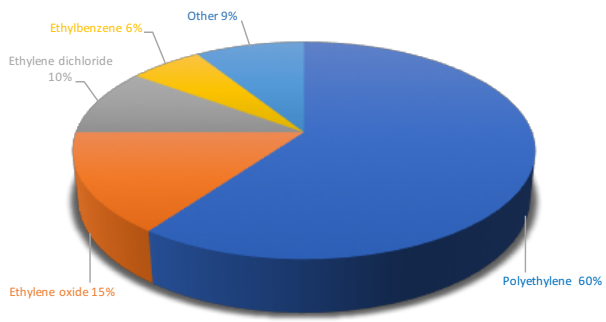

Figure 2.3: *Demand of ethylene for major end products [16]*

Ethylene is commercially produced from natural gas and petroleum. In Europe and Asia naphtha cracking is the primary way to produce ethylene. In the US however ethane from natural gas is increasingly cracked for its production. [15, 17] In steam cracking, hydrocarbons in the presence of steam are broken down to light organic molecules. To break the carbon-carbon bonds a high energy input is required and therefore this process is typically conducted in cracking furnaces operating at elevated temperatures between 700 - 900 °C. Depending on the feedstock, the energy consumption for the production of 1 kg of ethylene ranges from 15000 to 27000 kJ/kg. [18] Steam cracking has become the state of the art method for producing light alkenes like ethylene, propylene and butadiene. The feedstock that is thermally cracked in the pyrolysis furnaces

usually consists of naphtha, LPG or ethane and to a lesser extent propane and butane. The yield of ethylene is about 35% for naphtha as a feedstock and 80% for ethane. [19, 20] To prevent side reactions from occurring the residence time inside the cracking furnace is kept very short being less than 0,5 seconds. In addition to further avoid pyrolysis the cracked gas is immediately quenched in a quench oil tower. Steam is used to dilute the mixture, decreasing the partial pressure and in this way increase the conversion. Besides steam being inert, it reduces fouling formation by reacting with the coke deposited inside the furnace. [18]

2.3 Alternative routes for ethylene manufacturing

Steam cracking is very energy intensive and therefore leads to significant amounts of greenhouse gases coming from fuel combustion. Approximately 10% of the CO_2-emissions from chemical industry come from ethylene production. [14] Besides, a lot of waste heat must be discharged using cooling water systems which consume considerable quantities of water. Fugitive methane emissions associated with shale gas production may result in high greenhouse gas emissions. In addition, shale gas production comes with considerable water usage linked to hydraulic fracturing and horizontal drilling. [11, 12, 13] Because of increasing environmental concerns it is interesting to look for alternative production processes to manufacture ethylene. In this section two promising routes are described: non-oxidative methane reforming and producing ethylene from biomass. The first process uses the same feedstock, namely shale gas, but applies plasma to convert the methane fraction into ethylene. In the second upcoming technology, ethylene is manufactured from biomass which is considered to decrease the dependency on fossil fuels and leads to less greenhouse gas emissions.

2.3.1 Non-oxidative methane coupling

The industrial importance of methane as source for energy and chemicals will increase significantly within the next few decades due to the excessive proven natural gas reserves and lower cost. [21] Technological improvements in hydraulic fracking have greatly increased the supply for methane resulting in a noticeable price drop. [22, 23] Therefore, it is interesting to look for alternative systems that are able to valorise methane to liquid fuels or chemicals. Processes that can convert methane into ethylene are highly desired due to the high market price of ethylene. [24] Two routes for direct coupling of methane to ethylene have currently been investigated being oxidative and non-oxidative coupling. In oxidative methane coupling high temperatures (700 - 1000 °C) are required in the presence of metal oxide catalysts and high purity oxygen. Due to the low single-pass yield and formation of byproducts an intensive downstream purification is needed and has so far limited the industrial potential. [21]

Non-oxidative processes, in particular non-thermal plasma, allow methane coupling to added-value products at low temperatures improving the process safety and energy efficiency. [24] This is achieved in a nanosecond pulsed discharge (NPD) reactor with a feed consisting of an equimolar mixture of methane and hydrogen. In the plasma zone, electrons are accelerated due to the presence of a strong magnetic or electric field. The high-energy electrons generate ions, excited species and radicals through collisions with the molecules and transmitting part of their

energy. After initial radical formation, the reaction mechanism prevails by radical recombination forming stable molecules. The reactor configuration (i.e. the potential, pulse frequency, discharge gap, catalyst, …) is optimized in such way to generate ethylene as the main product. The unreacted methane and hydrogen are being recycled to the reactor. [25, 24] In comparison to thermal cracking, plasma-assisted methane coupling involves much lower temperatures. [26]

Two designs have been developed: a hybrid system (two-step process) which makes use of a catalyst and operates at 1 bar and the second design consisting of a gas phase system (one-step process) which operates at 5 bar. In the hybrid system, acetylene is the main product coming out of the plasma reactor. The second step is to hydrogenate the obtained acetylene on a palladium based catalyst to form ethylene in the post-plasma zone. The overall ethylene yield amounts around 26% per pass and the energy consumption is reported close to 1600 kJ/mol ethylene being the lowest energy cost reported for plasma-assisted methane to ethylene processes so far. [27] In the second design, the reactor is operated at 5 bar and no additional catalytic step is required because ethylene is the main product formed in the plasma zone. The advantage of this configuration is that no catalyst is needed, however it involves a higher operating cost. In the one-step process an ethylene yield of nearly 20% is achieved, so far the highest yield accomplished with plasma technology. [24] Figure 2.4 shows the reaction mechanism for the one-step and two-step process.

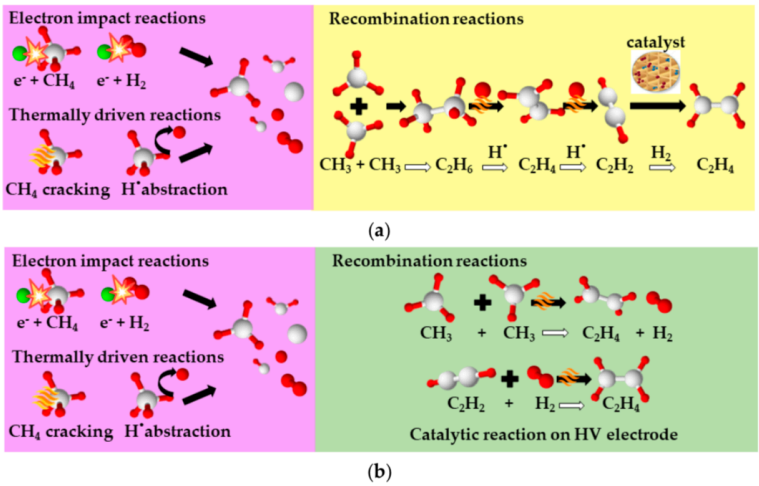

Figure 2.4: *Reaction mechanism for (a) hybrid process and (b) gas phase process [28]*

Combustion of fossil fuels is prevented in plasma-assisted methane coupling because electricity instead of heat is used to start the reforming reactions. However, this goes at the expense of a high electricity consumption. Electric power consumption is the main economic factor of plasma-assisted ethylene manufacturing processes. At present, ethylene production from plasma-assisted methane coupling is not economically viable considering the current electricity prices. If electricity prices drop below 35 and 23 USD/MWh, the hybrid system and gas phase system respectively become breakeven and will result in a positive profit margin. Thus, with expected reductions in electricity price plasma processes might become practicable in the future. [28]

Plasma-assisted methane coupling might provide an encouraging solution to the valorisation of waste gas streams that are rich in methane wherefore conventional ethylene production cannot

be applied and instead are flared. Valorising waste gas is an appealing approach to reduce the greenhouse gas emissions coming from flaring which is considered an important environmental concern. [29, 30, 31] Elvidge et al. [32] estimate that 90% of global gas flaring occurs at oil extraction sites where natural gas from underground reservoirs flows up to the surface due to change in pressure. Despite efforts to capture it, technical and economic constraints result in burning of approximately 140 billion m^3 of natural gas every year producing more than 300 million tons of CO_2. [32] Plasma reactor modules show great potential for these applications since they provide rapid start-up and shut down and require small space. [33]

2.3.2 Biomass as feedstock for ethylene production

Today, most of the ethylene production comes from petroleum derivatives. During the last decades however, there is an increasing interest in using biomass as an alternative and renewable feedstock. The first bio-ethylene plants were built in Brazil and India and at present they account for about 0,5% of the global ethylene capacity. The biopolymer market is growing rapidly and several large production plants are under construction or planned in China. The largest plant in Brazil is already in operation and can produce op to 200 kton/yr of bio-ethylene to be used for downstream products like biobased polyethylene. [34]

Bio-ethylene is produced by catalytic dehydration of bio-ethanol. Bio-ethanol is a liquid biofuel of which the United States and Brazil account respectively 63% and 24% of the global production. [34] In the US mainly corn is used as a feedstock while Brazil adopts mostly sugarcane. Recent studies propose the use of lignocellulosic biomass coming from agricultural and forest residuals to produce bio-ethylene. [34] The advantage is that this feedstock does not compete with food production, requires less water and no or less arable land is needed. However, at present no commercial bio-ethanol plants on lignocellulosic material are operational because the conversion into ethanol is more challenging due to the complicated chemical structure. Recent estimates state that bio-ethylene can reduce GHG emissions from cradle-to-factory by more than 40% and significantly reduce the environmental impact in comparison to petrochemical ethylene. [34] Besides the reduction in lifetime greenhouse gas emissions, acquiring ethylene from biomass also reduces the dependence of the chemical industry on fossil feedstocks. [34]

The cost of bio-ethylene is dependent on the price and availability of local biomass feedstock and most of time is still higher than petroleum based ethylene. For Brazil and India, the cost of bio-ethylene is estimated to be close to petrochemical based ethylene. The price gap with petrochemical ethylene and the availability of biomass are the most important factors in determining to what extent bio-ethylene can replace conventional ethylene. The production cost of ethylene from sugarcane in Brazil and India is estimated around 1,200 USD/ton ethylene. In the US where bio-ethylene production is based on corn and in Europe on sugar beets higher costs are estimated around 2,000 USD/ton and 2,600 USD/ton respectively. The market price of petrochemical ethylene is substantially lower ranging from 600 - 1,300 USD/ton with a global average of 1,100 USD/ton in 2013. [34]

Bio-ethanol production processes are well developed and currently two production routes are followed. One is by fermentation of sucrose rich feedstock like sugarcane, the other way is by hydrolysing starchy biomass like corn which is followed by fermentation. [19] Sucrose rich biomass like sugarcane, sugar beet and sweet sorghum is easy to break down and can directly be fermented into ethanol using yeast. Brazil is the leading country in the production of bio-ethanol from sugarcane. In more temperate regions, mainly Europe, sugar beet is grown. Starchy biomass like wheat and corn contains cellulose polysaccharides that first have to be depolymerized into glucose before fermentation. Most starch-based ethanol from corn is produced in the US. 1st generation bioethanol is produced from these sources where the sugars are relatively easy to obtain. 1st generation bioethanol plants for the production of bio-ethylene are already present although they are not functioning without government subsidiaries. Ethanol production from lignocellulosic biomass can be done in five steps consisting of pretreatment, hydrolysis, fermentation and distillation. However, pretreatment of lignocellulosic biomass is viewed as one of the most expensive processing steps within its conversion to fermentable sugars. [34, 19, 35] Lignocellulosic biomass (e.g. wood, grass, straw) forms the largest potential for bio-ethanol production because it is largely available at low cost. Besides it has attractive yields on low-quality land and has a low environmental impact. The process in converting lignocellulosic feedstock to 2nd generation bio-ethanol is however more challenging and expensive. Lignocellulosic materials have three main components including cellulose, hemicellulose and lignin and because of the complicated structure the hydrolysis of these components is more difficult in comparison to starch. Cellulose and hemicellulose are polysaccharides that can be hydrolysed into sugars and then fermented to bio-ethanol. The lignin fraction is resistant to chemical and biological degradation and cannot be used to produce bioethanol. Generally, softwoods contain more lignin than hardwoods. [34, 19, 35]

In this study corn stover is used as source of lignocellulosic biomass. However, it should be noted that taking away all stover after harvest results in increased soil erosion and runoff. It is therefore recommended to keep at least 30% of the soil surface covered with residues. With the removal of stover, carbon and other nutrients that the stover contains are also removed which affects subsequent crop production and results in higher fertiliser usage. [36]

Figure 2.5 gives a summarizing scheme of the different production methods for ethanol described earlier.

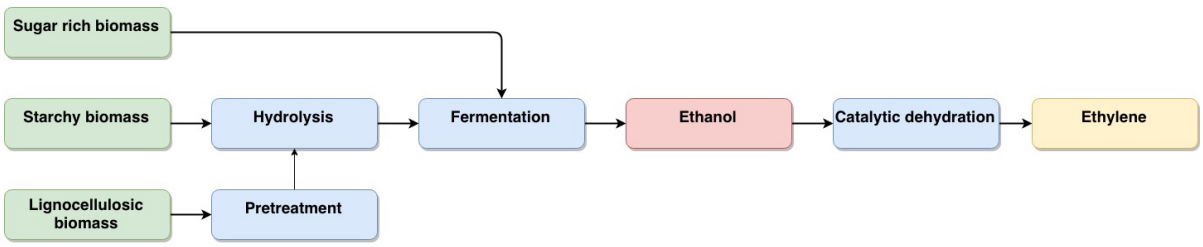

Figure 2.5: *Different production routes for bio-ethylene*

Bio-ethanol is converted into bio-ethylene using an alumina-based catalyst. To produce 1 tonne of bio-ethylene approximately 1,75 ton of ethanol (hydrated) is required. At present, the

production capacity is near 375 kton per year of which more than 50% is adopted to produce polymers like bio-PE. The remainder is being used for the manufacturing of ethylene glycol. [19]

Haro et al. [37] showed that ethylene from Brazilian ethanol is cost-competitive at current market prices. When Bioenergy with Carbon Capture and Storage (BECCS) is considered these results would be greatly enhanced and the process would be profitable. The BECCS concept holds that storage of CO_2 with a renewable origin allows selling the amount of sequestered CO_2 through CO_2-credits leading to extra revenues from emissions trading. [37] It should be mentioned that producing ethylene from biomass comes at a significant land use, 0,47 ha/ton for corn and 0,19 ha/ton for lignocellulosic biomass. [34]

2.4 Life cycle assessment

With the growing awareness for the environment and sustainability, decision makers and managers are looking at products and services from cradle to grave. Investigating resource exploitation, manufacturing operations, usage and final disposal. Out of the need for an environmental impact assessment tool came Life Cycle Assessment which developed into a standardized method. A Life Cycle Assessment (LCA) captures the global environmental impact of a process, product or human activity and provides an accurate presentation of potential environmental trade-offs. It involves acquisition of raw materials, production processes, usage and waste management. [38]

As standardized by the International Standardization Organization (ISO), present LCA method consists of four interrelated phases: [38]

1. Defining the goal and outlook of the study, including selection of a functional unit.
2. Compile a Life Cycle Inventory (LCI) containing all relevant material and energy inputs and releases to the environment. In this step, all needed data on e.g. energy, water, materials consumption and environmental releases like wastewater, waste disposal and direct emissions to the air are collected and organised.
3. Conducting a Life Cycle Impact Assessment (LCIA), associated with the identified inputs and releases, to evaluate the environmental impacts. This stage consists of translating the LCI data into final results using the correct emission factors for each impact category.
4. Interpretation of results and decision making.

The quality of the data used in an LCA is of significant importance, with the results from the LCA being only as accurate as the input data. Besides, the lack of publically available data makes LCA a very time-consuming and costly procedure. [39]

Life cycle assessments are generally applied to compare the environmental performance of similar objects and processes, to identify places for improvement, reduce negative effects or develop new policies. To assess the impact of the system under investigation different impact categories exist. Commonly used impact categories consist of climate change or global warming (kg CO_2-eq),

acidification (kg SO_2-eq), eutrophication (PO_4-eq), land use (m^2) and eco-toxicity or human-toxicity (CTUh). [40] For this study it is chosen to express the results in terms of global warming.

2.5 Greenhouse effect

Greenhouse gasses increase the radiation absorption of the atmosphere within the infrared (IR) window of approximately 10 to 15 µm. This increases the average temperature of the troposphere and life on earth would only be possible by the natural greenhouse effect leading to an average surface temperature of 15 °C instead of -18 °C without it. [40] The most common greenhouse gasses include: carbon dioxide (CO_2), water (H_2O), methane (CH_4), nitrous oxide (N_2O), ozone (O_3) and synthetic and halogenated chemicals (CF_4, SF_6, NF_3). [40]

To weigh the different greenhouse gasses against each other a relative scale of the impact is necessary. This is done using global warming potential (GWP). GWP indicates the mass of CO_2 which has the same impact as the emission of 1kg of another greenhouse gas during a period of 100 years (GWP_{100}). For LCA's a time horizon of 100 years is mostly taken, but GWP_{20} and GWP_{500} also can be found. In most LCA studies CO_2 is the most important contributor to the overall GWP/fU. The term carbon footprint is also often used for global warming potential. [40]

The total GWP is calculated using equation (1):

$$\mathrm{GWP} = \sum_i (m_i \cdot GWP_i) \tag{1}$$

With m_i being the load of the respective substance i per functional unit (fU).

Table 2.1 gives the lifetime and GWP_{100} (time horizon of 100 years) values of various greenhouse gasses.

Table 2.1: *Atmospheric lifetime and GWP of various greenhouse gasses [40]*

Chemical substance	**Lifetime in the troposphere (year)**	**GWP_{100} (kg CO_2-eq/kg_{GHG})**
Carbon dioxide (CO_2)	Determined according to the Berne C-cycle*	1
Methane (CH_4)	12	25
Nitrous oxide (N_2O)	120	298
Sulphur hexafluoride (SF_6)	3200	22800
Nitrogen trifluoride (NF_3)	740	17200
Tetrafluoride methane (CF_4)	50000	7390
Hexafluoroethane(C_2F_6)	10000	12200
Sulfur hexafluoride (SF_6)	3200	22800
CFC-12 (CCl_2F_2)	100	10200
HCFC-22 ($CHClF_2$)	12	1760

*The average tropospheric residence time of CO_2 depends on various sources and sinks and thus cannot be described by a single value.

3 Process description

3.1 Ethylene from thermal cracking of shale gas

3.1.1 Shale gas extraction

An essential large shale formation is the Marcellus Shale, underlying the states of New York, Pennsylvania, West Virginia and Ohio. The overall gas reserves are estimated to be more than 42 trillion m^3, with technically extractable reserves estimated at 4 trillion m^3 by the Energy Information Administration in 2012. [41] Moreover, the Marcellus Shale plane is located close to pipelines and large natural gas markets in the north-eastern part of the U.S. [41]

Air rig drilling is most applied to drill vertically to a few hundred metres above the shale formation. To prevent soil from collapsing into the hole, steel casing is inserted along the entire vertical section of the drilling hole. Cement is used to fill up the space between the casings to isolate the well from the surrounding environment to prevent contamination of drinking water supplies or migration of natural gas to the surface. The horizontal holes are drilled by a directional drilling rig. The lateral drillings vary in length from 400 m to over 3000 m and are also cased with steel and cemented. [41] Figure 3.1 gives a schematic overview of shale gas extraction.

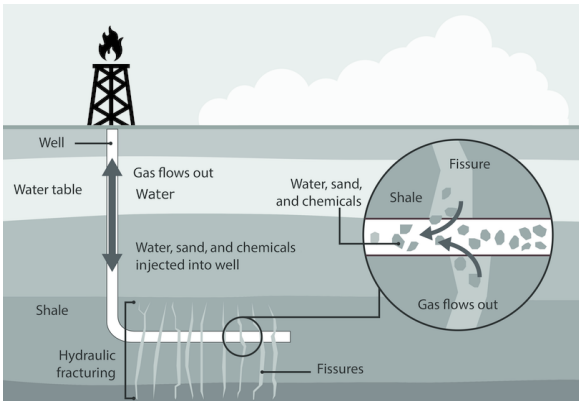

Figure 3.1: *Shale gas extraction [45]*

Targeted explosive charges cause perforation in the casing creating a channel extending in the shale formation. [42] Next, the hydraulic fracturing process utilizes water mixed with sand and chemicals at high pressure to fracture the shale formation and increase permeability. This allows the gas to flow from the fractured area to the borehole and surface. The total water consumption varies between 8000 m^3 and 14000 m^3 per well depending on the local geology and the length of

the lateral holes. [41, 43] The mean usage for water and sand lie around 12000 m^3 and 1800 tons for 2011 - 2012. The water can come from local streams, groundwater or large rivers and is transported via trucks or pipelines. In 2011-2012, 30% of water was assumed to be trucked and 70% brought by pipelines. [41] Conscientious management of wastewater is crucial to minimize environmental impact. In 2011, a production average of 108 million m^3 of natural gas was calculated. [41] After extraction, the raw shale gas is transported by pipelines to nearby gas processing plants. [44]

3.1.2 Shale gas processing and thermal cracking

You et al. used shale gas from the Marcellus shale play in their LCA simulation because the shale gas produced in this region is of great interest for ethylene manufacturing due to the high ethane fraction as can be seen in Table 3.1. [44]

Table 3.1: *Composition of raw Marcellus shale gas [44]*

Component	Concentration (mol%)
N_2	0,70
CO_2	0,14
CH_4	75,66
C_2H_6	14,46
C_3H_8	5,16
i-C_4H_{10}	0,74
n-C_4-H_{10}	1,47
i-C_5H_{12}	0,48
n-C_5H_{12}	0,40
C_6H_{14}	0,80

Figure 3.2 shows the process flowsheet for manufacturing ethylene from ethane-rich shale gas. First raw shale gas is pressurized to obtain downstream operating conditions. Afterwards, from the pressurized gas the acid components are removed in an acid gas removal unit. [44] The sour gas is sent to a sulphur recovery unit to convert H_2S to elemental sulphur using the Claus process. [7] This unit operation is not shown in Figure 3.2 because the H_2S content is considered lower than the threshold limit (differs for each shale gas well). From the sweet gas, the water content is reduced in a dehydration unit. This is done to prevent corrosion and hydrate formation in the following cryogenic separation unit in which the natural gas liquids (NGLs) are recovered. [13] The resulting methane gas is compressed and sent out via pipelines. The mixture of NGLs is further fractionated into ethane, propane, butane and natural gasoline in NGL fractionation equipment. [44, 7]

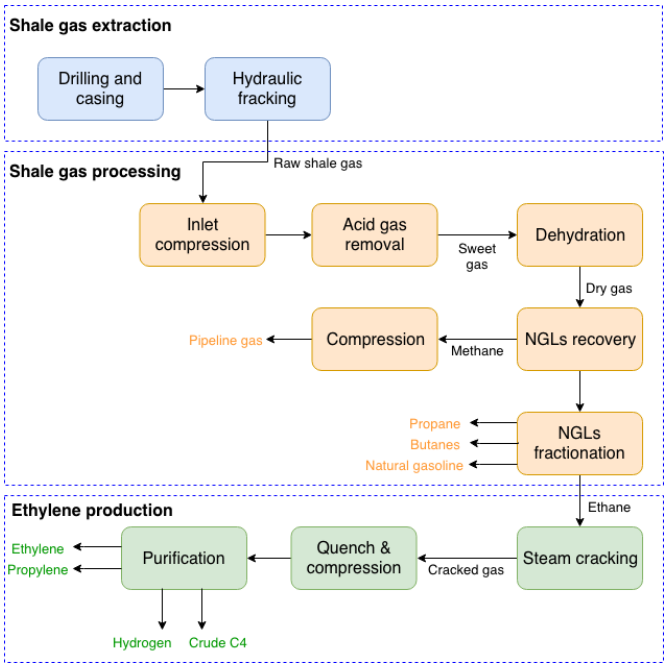

Figure 3.2: *Overview of ethylene manufacturing from thermal cracking of shale gas [44]*

Afterwards the ethane, coming from several distributed shale gas processing sites, is transported by trucks to a cracking plant. Here, the ethane derived from shale gas processing is cracked in cracking furnaces. The cracking gas is quenched, pressurized and in a final ethylene purification section the gas is separated into ethylene, ethane, hydrogen and other products. [44] In the remaining of this section each unit described above is explained in further detail.

To meet downstream operating conditions the raw shale gas is first pressurized by two compressors, each followed by intercooling to control the temperature. As depicted in Table 3.1, the extracted shale gas contains CO_2 which can cause corrosion and solid formation. [13, 46] Therefore, the carbon dioxide is removed in an absorption unit based on monoethanolamine (MEA). MEA is nonselective and can effectively react with both H_2S and CO_2. [44] The raw shale gas enters from the bottom and contacts with the MEA solution coming from the top. Afterwards, the loaded MEA solution from the bottom of the absorber is sent to a stripper where the carbon dioxide is stripped off. The regenerated MEA solution is then pumped back to the absorption column. After absorption, the CO_2 concentration is decreased to less than 50 ppm. [12, 47] By contacting with an amine solution the sweet gas is saturated with water. For the following cryogenic separator, this water should be removed to avoid hydrate formation. Removal of water is done in a dehydration unit based on triethylene glycol (TEG). [44] The sweet gas comes in at the bottom of the contactor and leaves as dry gas at the top. The rich glycol is then sent to a regenerator for recovery of the TEG. The lean glycol stream coming from the bottom of the regenerator is purified further in a stripper unit. The regenerated TEG is then mixed with makeup TEG and pumped back to the contactor for reuse. [44]

The NGLs are recovered using a cryogenic separation unit. Before entering the demethanizer the dry shale gas is first cooled in a series of heat exchangers and preseparated by using two-phase separators. The gas product from the last separator is sent through an expander which reduces its temperature lower than -90 °C. [44] In the demethanizer methane-rich gas is obtained from

the top of the column while NGLs are recovered from the bottom. The methane stream is used as a coolant in the previous heat exchangers. To pipe it as sales gas the excess nitrogen is rejected using a cryogenic process. The mixture of NGLs is consequently fed into a de-ethanizer, depropanizer and debutanizer to separate the mixture into ethane, propane, butanes and natural gasoline. [44]

The ethane fraction is fed into the cracking furnaces with addition of steam at a mass-based ratio of 1:0.4. This mixture is preheated to about 700 °C in the convection section of the furnace where it exchanges heat with the hot off gases coming from burning of fuel. [44] Afterwards, in the radiant section the ethane is thermally cracked into ethylene, hydrogen, methane and other components. The cracking gas is sent to a transfer-line exchanger to produce high pressure (HP) steam which is next superheated in the convection section of the cracking furnace. Power for all compressors is provided by using steam turbines driving on the HP steam. The cracking gas is sent to a heat exchanger for additional heat recovery and then to a quench water tower reducing the temperature to 40 °C. [44] Afterwards, the cracking gas is pressurized to 37 bar by five compressors with intercooling to control the temperature lower than 100 °C and avoid polymerization of ethylene. In a caustic tower before the fourth compression stage, the acid components of the cracking gas are removed using sodium hydroxide. Remains of water are removed in a molecular sieve dryer. [44]

The cracking gas is precooled in consecutive heat exchangers and preseparated using two separators. All liquid products coming from these separators are fed to a demethanizer to remove methane. The methane-free liquid product is separated into a C_2, C_3 and C_4 mixture using a de-ethanizer and a depropanizer. The C_2 mixture is then sent through a hydrogenation reactor where acetylene is converted into ethylene. This stream is fed to a C_2 splitter where polymer grade ethylene with a purity of 99,9% is drawn from an intermediate tray. [44] From the top of the splitter an ethylene-rich stream is obtained. The bottom of the C_2 splitter is fed to the cracking furnaces. In the C_3 splitter polymer grade propylene with 99,5% purity is obtained from the top. [44] The remaining bottom products and methane rich products are consumed as fuel for the cracking furnaces. [44]

3.2 Ethylene production through plasma-assisted methane coupling

Plasma-assisted non-oxidative methane coupling is an alternative route to obtain ethylene from natural gas. The process consists of a plasma zone where methane is converted. Two designs have been developed and simulated with Aspen Plus: A hybrid system (two-step process) which makes use of a catalyst and operates at 1 bar and a gas phase system (one-step process) which operates at 5 bar. A general process block scheme is given in Figure 3.3.

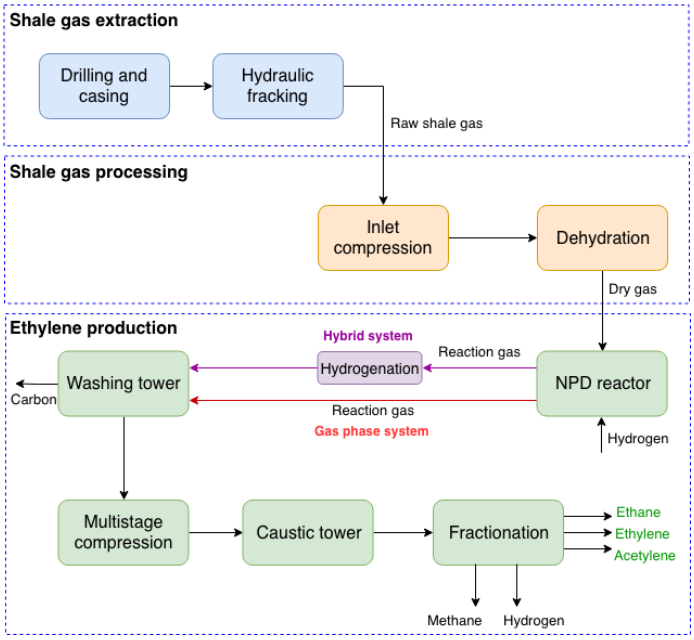

Figure 3.3: *Overview of plasma-assisted ethylene manufacturing*

The feedstock used for this process is considered shale gas. Therefore, in comparison to the thermal cracking pathway for producing ethylene only the process differs while the feedstock remains the same. For more details on shale gas extraction the author refers to part 3.1.1, since this step remains the same as in the thermal cracking pathway. After extraction, the raw shale gas is pressurized to obtain downstream operating conditions. From the pressurized gas the moisture content is reduced in a dehydration unit. This is done to prevent hydrate formation and corrosion in the downstream cryogenic separation units. [44] Water is absorbed by contacting the raw shale gas with a stream of triethylene glycol (TEG). In a subsequent stripping column the water is stripped from the rich TEG. The recycled TEG is then sent back to the absorber. [28] In comparison to thermal cracking, no gas sweetening is applied because the operation of plasma reactors is robust in the presence of CO_2. [28] The dehydrated shale gas can directly be fed to the NPD reactor. As was shown by Delikonstantis et al [28], ethane and CO_2 that are still present in the feed stream do not affect the NPD reactor performance.

In the plasma reactor, a high voltage is applied to generate a strong electric field in which the free electrons are accelerated. On collision with plasma components ionization, dissociation and excitation reactions occur. [26, 25] When two radicals combine, they form stable molecules. The reactor configuration (i.e. the potential) is optimized in such way to generate ethylene as the

main product. The unreacted methane and hydrogen are being recycled to the reactor. [26] In the hybrid system (operated at atmospheric pressure), acetylene is the main product coming out of the plasma reactor. The second step, right after the plasma zone, is to hydrogenate the obtained acetylene on a palladium based catalyst to form ethylene. [26, 27] In the gas phase design the reactor is operated at 5 bar and no catalyst is required because ethylene is the main product formed in the plasma zone. When operating at high pressure the HV copper-based electrode acts as catalyst in the hydrogenation reaction of acetylene to ethylene. Besides, at elevated pressure the direct coupling of methane to ethylene is promoted. [28] The advantage of this configuration is that no subsequent catalytic step is needed, however it involves a higher operating cost. [26, 24] Over time, the ethylene yield decreases due to coke deposition on the reactor electrodes and decoking is periodically applied. [28]

The reactor outlet consists of several components which need to be separated in further downstream processes. Pure carbon is first removed by washing the mixture with liquid water. The washing tower contains packing material used to distribute the washing water and create a large contacting area with the process gas. The reactor outlet comes in from the bottom of the tower while water is fed at the top. Afterwards, the carbon-free stream is compressed in multiple stages to reach the desired pressure for downstream operations (e.g. cryogenic distillation). After each compression step intercooling is applied to prevent high temperatures (<120°C) and thus ethylene polymerization which could lead to product losses and increased equipment fouling. The one-step process requires three multistage compression steps to go from 5 to 31 bar. [28] For the hybrid system, to compress the stream from 1 to 31 bar, five compressors, four intercoolers and four flash drums are used. Water is condensed in the compression and intercooling stages and therefore removed in flash drums placed after each compression step. [26, 28]

Subsequently, carbon dioxide together with entrained water from the washing tower are removed in a caustic tower. In this unit, an aqueous solution of sodium hydroxide is contacted with the product stream. Carbon dioxide is absorbed and afterwards converted to sodium carbonate (Na_2CO_3) and sodium formate (HCOONa). Water and carbon dioxide removal is applied to prevent hydrate and ice formation in the upcoming cryogenic distillation units. Dehydration is typically conducted after the compression stage since higher pressures allow operating with smaller volumes of absorbent. [18] The absorption unit removes more than 99% of the water present in the product stream. The dry gas is then sent through a heat exchanger with liquid methane as coolant to meet cryogenic conditions. In a series of distillation columns, the product stream is then separated into its remaining compounds e.g. hydrogen, methane, ethane, ethylene and acetylene. The first cryogenic distillation column serves to remove hydrogen and methane both of which are partly recycled back to the NPD reactor. [26] The amount of hydrogen recovered is sufficient to satisfy the feed demand due to hydrogen being produced in the reactor itself. Therefore, added value is created by selling the excess hydrogen. Part of the hydrogen present in the overhead stream is obtained as side product using a pressure swing adsorption unit (PSA). The bottom stream of the demethanizer column contains the C_{2+} fraction which is sent to a second distillation tower. From the top of this distillation column an enriched ethylene stream is obtained, while ethane is extracted from the bottom. The ethylene-rich top stream is then sent to a third and final distillation unit. In the final distillation unit, ethylene with a

purity of 99,96% (following the market requirements) is obtained. Since the boiling points of ethane and ethylene are close, separating both components results in high operating costs.

To reduce the external utility demand, heat integration was incorporated by Delikonstantis et al [28]. For the gas phase system a reduction of 75% hot utility demand and 51% cold utility demand is achieved. After heat integration, for the hybrid system, no external heat input is required (100% saving) and a reduction of 56% in cold utility is obtained. [28]

3.3 Manufacturing ethylene from biomass

The production of bio-ethylene starts with producing ethanol from biomass followed by catalytic dehydration into ethylene. Two potential sources of biomass for ethanol production are considered in this study, namely corn grain and corn stover.

3.3.1 Ethanol production

a) Ethanol from starchy biomass: corn grain

In this part focus lies on the production of bioethanol from corn grain. In section 3.3.2 the conversion of bioethanol to ethylene is covered. Figure 3.4 gives a general block diagram for the production of ethylene from corn grain.

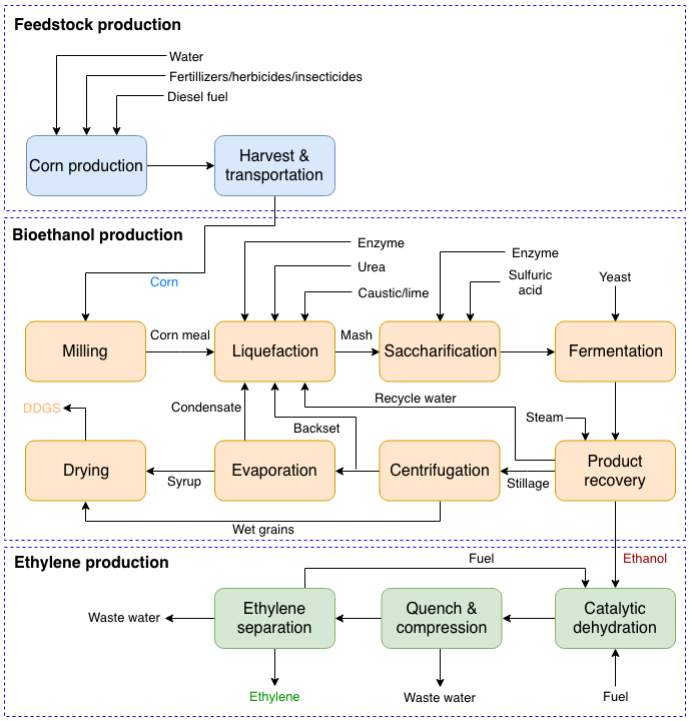

Figure 3.4: *Overview of ethylene manufacturing from corn grain [44]*

First, the corn is conveyed to a grain cleaning unit and afterwards milled to fine meal using milling equipment. In a liquefaction unit, the corn meal is mixed together with water and alpha-amylase. To provide suitable acidity and calcium for the alpha-amylase also caustic and lime are

added. [44] Alpha-amylase is an enzyme that hydrolyses polysaccharides like starch yielding glucose and maltose. Like most enzymes, it has an optimal temperature and pH at which the catalytic activity is maximum. Urea is added to supply nitrogen for the downstream yeast fermentation. From the corn starch, maltose and other higher oligomers are produced using alpha-amylase. The obtained mash is then sent to a saccharification unit where glucoamylase and sulfuric acid are added to obtain sugars. The resulting mash is cooled and fed to four continuous fermenters in series. [44] During the fermentation ethanol and carbon dioxide are produced. Following the fermentation comes a product recovery unit in which bioethanol is obtained by distillation, scrubbing and dehydration. The stillage from the product recovery is fed to a centrifugation unit. A fraction of the thin stillage obtained in the centrifugation unit is recycled back to the liquefaction section and the remaining syrup is concentrated in an evaporation unit. The wet grains obtained in the centrifugation unit and the concentrated syrup from the evaporator are dried and sold as distiller's dried grains with solubles (DDGS) which finds applications as fodder for livestock. [44, 48]

b) Ethanol from lignocellulosic biomass: corn stover

In this part focus lies on the production of bioethanol from corn stover. In section 3.3.2 the subsequent conversion of bioethanol to ethylene is covered. In Figure 3.5 a general overview of manufacturing ethylene from corn stover is depicted.

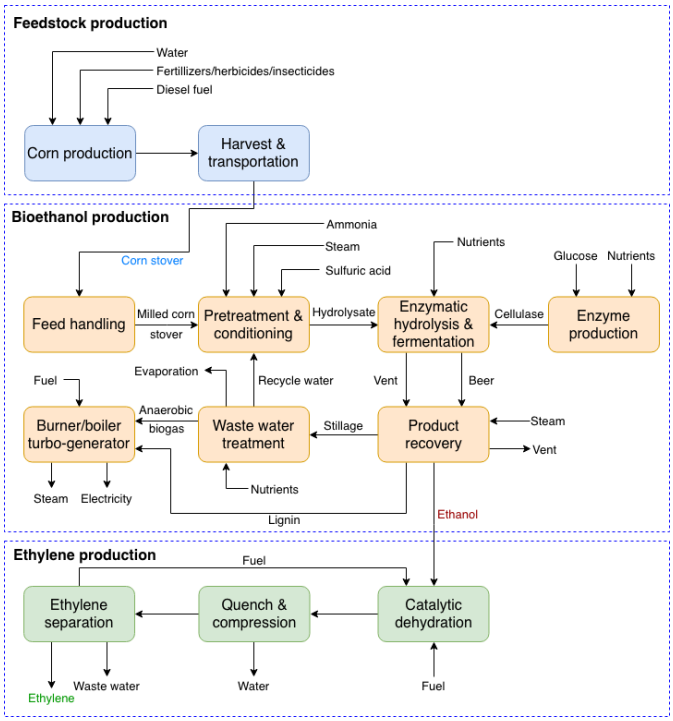

Figure 3.5: *Overview of manufacturing ethylene from corn stover [44]*

In a first step the corn stover is delivered to a feed handling unit that consists of uploading, weighing, milling and conveying. Next, the corn stover is pretreated with dilute sulfuric acid to release hemicellulose sugars and partly break down the biomass. Afterwards ammonia is added to adjust the acidity of the slurry so it becomes suitable for enzymatic hydrolysis. In the

subsequent unit, cellulase enzyme is added for saccharification of the cellulose chains into glucose. [44, 49] The obtained mash is then fermented into bioethanol. The enzyme production unit uses glucose as the main carbon source and is considered on-site. In the recovery section, bioethanol, water and residual solids are separated using distillation and solid-liquid separation. Wastewater that is generated during the whole production is gathered and treatment by anaerobic and aerobic digestion is applied. The solids obtained from the recovery section and the obtained biogas from the wastewater treatment unit are combusted to obtain high pressure (HP) steam used to produce electricity and satisfy the process heat demand. [44]

Ethanol produced at various distributed bioethanol plants is transported by trucks to a central ethylene production plant. [44] To obtain polymer grade ethylene, bioethanol derived from the corn stover and corn grain is catalytically dehydrated into ethylene, water and other co-products. The reactor effluent is quenched and pressurized and finally is sent to a purification unit. This part is discussed into more detail in section 3.3.2.

3.3.2 Catalytic dehydration of ethanol

Ethanol dehydration is an endothermic reaction requiring 1,6 $MJ/kg_{ethylene}$. [50] At 300 – 500 °C the highest selectivity towards ethylene is achieved (Eq. 2). At lower temperatures, the reaction shifts towards diethyl ether while higher temperatures favour the production of acetaldehyde. [19]

$$C_2H_5OH \xrightarrow{Cat} C_2H_4 + H_2O \tag{2}$$

The dehydration takes place in the vapor phase in an adiabatic fixed-bed reactor containing a series of packed beds with catalyst. The heat necessary for the reaction is provided by an inert heat-carrying fluid while furnaces are intermediately used to reheat the feed stream for the next reactor. Between each stage, make-up streams of ethanol are added to keep the steam to ethanol weight proportion in the right range. [19, 50, 51] The inlet temperature lies between 450 – 500 °C and the feed is pressurized to 4.5 bar. Overall, four consecutive adiabatic reactors are used in this process. The output of the last reactor has a temperature higher than 370 °C and is used for steam production in a steam generator. The produced steam is adopted to evaporate the ethanol feed. After the steam generator, the temperature of the reaction stream is around 144 °C. Because this stream still has a high heating capacity it is therefore used to preheat the ethanol feed after which the temperature of the reaction mixture falls to 90 °C. [19] Through the use of steam, coke formation is lowered and catalyst is regenerated merely between 6 to 12 months. The overall conversion amounts higher than 99% with an ethylene selectivity of 97 - 99%. [19]

The dehydration reaction is acid-catalyzed. Oxide catalysts including activated alumina-based catalysts are currently applied in industrial plants. These catalysts tend to be very stable and the purity of the produced ethylene is high. However low ethanol concentration needs higher temperatures and lower space velocity resulting in higher energy consumption. [19, 51] Syndol

catalysts in the form of spherical pellets, with main components of Al_2O_3-MgO/SiO_2, are used in this process. [19, 52]

To produce polyethylene, a very high purity is required since impurities have negative consequences on the polymerization reaction. Therefore, different purification operations follow the reactor. The outlet stream is first cooled and subsequently a quench tower eliminates formed water and condensable polar molecules including small amounts of acetic acid, non-reacted ethanol and acetaldehyde. Here cold water of 40 °C is sprayed from the top of the column to condense and remove the water vapor from the ethylene. Carbon dioxide is removed in a scrubbing tower by washing with sodium hydroxide. Afterwards the stream is compressed and sent through a drying bed with molecular sieves to obtain ethylene with a purity higher than 99%. To produce polymer-grade ethylene the stream is fractionated in a cryogenic distillation column to eliminate the remaining contaminants. Prior to distillation, the stream passes an expansion valve reducing the pressure to about 20 bar and dropping the temperature to 30 °C. [19] Two distillation columns are used, the first distillation tower removes the heavy impurities from the ethylene stream, i.e. ethane, propylene and butadiene. The second cryogenic column removes the light impurities like hydrogen and methane. [19]

A simulation by Mohsenzadeh et al. was done for a production of 180 kton/yr and a pure ethanol (95 wt%) stream was used as a feed. [19] This feed stream represents the ideal case obtained from an ethanol factory with starch as feed. In addition, the impact of impurities of the bioethanol feed on the quality of the produced ethylene was investigated. Different streams were studied including lignocellulosic ethanol containing additional impurities like furfural, acetone and acetic acid. From these studies, it was concluded that the impurities in the ethanol feed do not have significant effect on the ethylene quality. [19] Figure 3.6 gives a summarizing block scheme of the ethanol dehydration step.

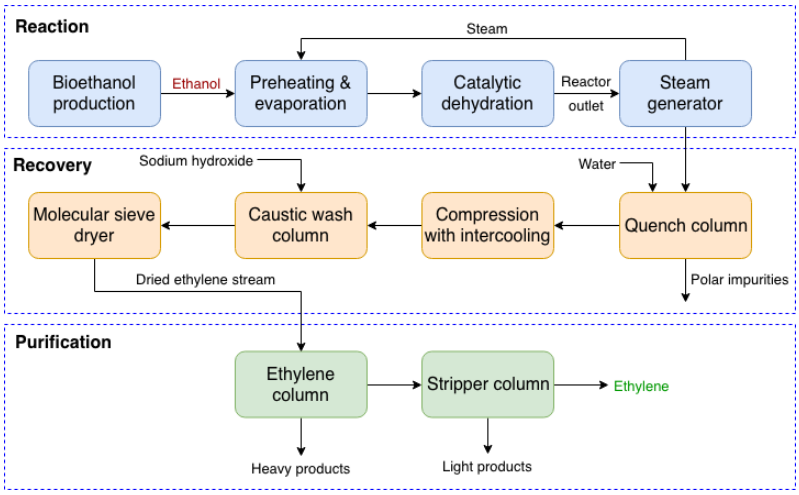

Figure 3.6: *Ethylene manufacturing through ethanol dehydration [19]*

4 Environmental analysis

4.1 Functional unit and system boundaries

A crucial step in LCA is defining the correct functional unit (fU) since choosing the wrong functional unit could lead to wrong conclusions. For a lot of systems the functional unit is simply the unit for the calculation. Examples are: per kg, per year, per km, per piece, per MJ, … [53] The functional unit that is used for this life cycle assessment is defined as 1 kg of ethylene produced at the plant gate. In this study, the impact category considered for the environmental performance is related to GHG emissions.

System boundaries determine which parts are included in the system and which are left out. The specification of these boundaries is one of the most important steps in an LCA study. [40] For this LCA a cradle to gate approach is studied because the use and end of life aspects can differ significantly per final product manufactured from ethylene. Figure 4.1 shows the system boundaries of the five different ethylene manufacturing pathways. This life cycle assessment considers for the production of ethylene through thermal cracking of shale gas: shale gas extraction and transportation, shale gas processing, ethane transportation and ethylene manufacturing. For the manufacturing of ethylene from corn stover and grain this LCA encompasses: crop production, corn or grain transportation, production of ethanol, ethanol transportation and ethylene manufacturing. In terms of manufacturing ethylene from shale gas through plasma-assisted methane coupling this study considers: shale gas extraction and transportation, shale gas processing, methane transportation and ethylene production.

Novel technologies to produce ethylene need to be viable from a technical and economic point of view as well as from an environmental one. Therefore, in the following, the life cycle environmental impacts of manufacturing ethylene are systematically analysed and compared for the thermal cracking based pathway, both biomass pathways (corn grain, corn stover) and the plasma based routes. For ethylene production through plasma assisted methane reforming the process designs are modelled in Aspen Plus V10 from which the corresponding mass and energy balances on each unit are determined. For the corn stover, corn grain and thermal cracking pathways the mass and energy balances are extracted from existing literature. To calculate GHG emissions, data and emission factors are mainly collected from the EcoInvent database [54] and the Argonne GREET Model. [55] The assessment is limited to CO_2, CH_4 and N_2O and the emissions are translated in terms of CO_2-equivalents. In all five pathways, multiple side products are produced for which the mass and energy streams together with the associated emissions should be allocated. This way the individual contributions to environmental burden of each product are proportionally reflected. The most common methods for allocation are the mass

based allocation and the economic value based allocation. For this study it is chosen to allocate the environmental impacts using both mass and economic value based method. Mass based allocation is most reliable since economic values can change drastically over time. Nevertheless, economic value-based allocation is still applied. The reason therefore lies in the fact that in the corn stover pathway electricity is generated as a 'byproduct' for which the mass based allocation method is less applicable. It should be noted that greenhouse gas emissions related to the construction of production plants, pipeline systems etc. are not taken into account.

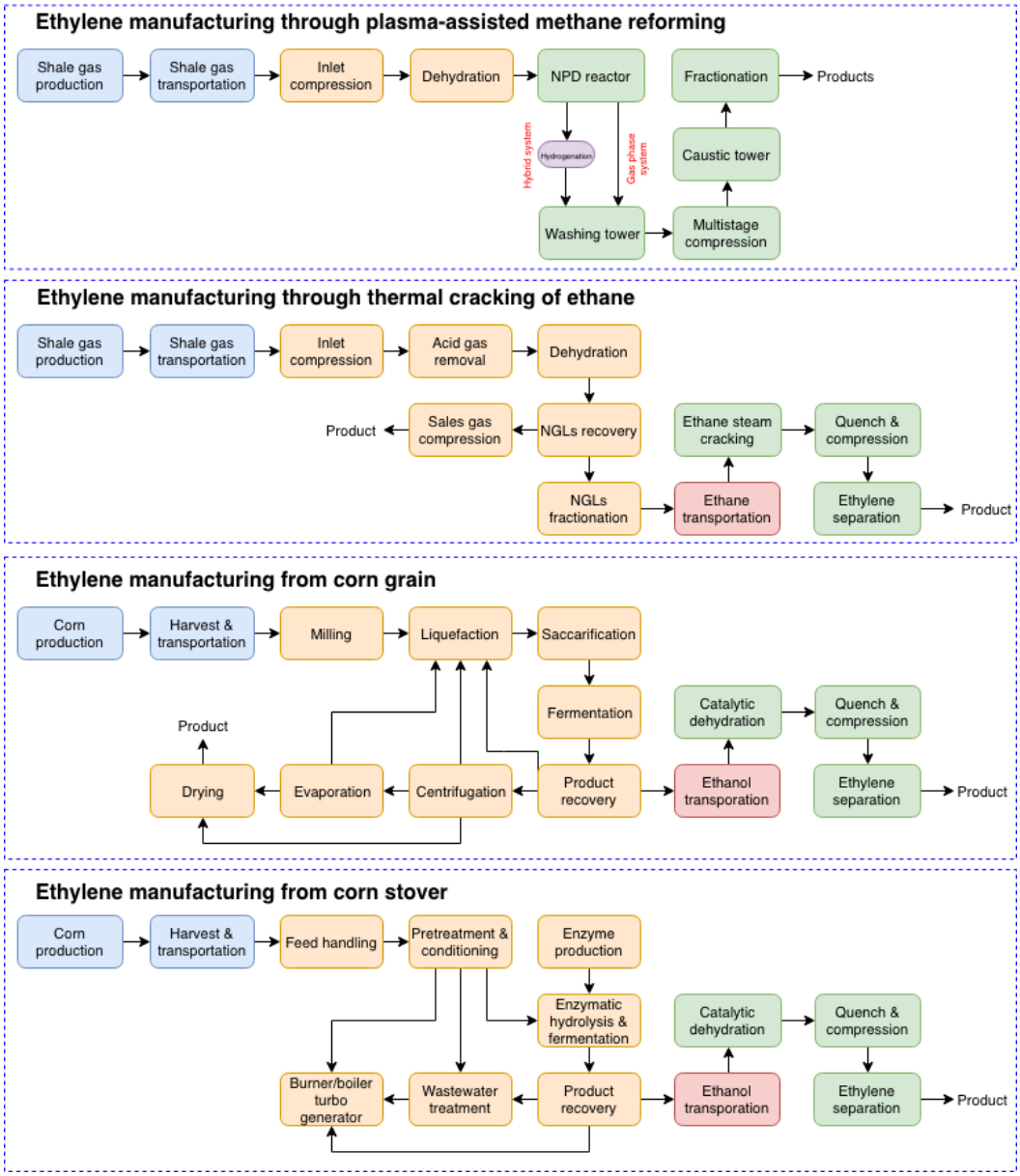

Figure 4.1: *System boundaries of investigated ethylene manufacturing pathways [44]*

4.2 Ethylene from thermal cracking of shale gas

4.2.1 Emissions from shale gas extraction

The environmental impact of the thermal cracking pathway is analysed using the LCA approach. First, life cycle greenhouse gas emissions were calculated for extraction of shale gas. Table A2 in the appendix shows detailed LCI data on GHG emissions generated at the stage of shale gas extraction. This information was gathered from Laurenzi et al. [42]

In the extraction phase the largest contributions to global warming are coming from wastewater transport, casing manufacture, drilling, hydraulic fracturing, completion flowback, gathering compressor losses, pneumatic devices and injection pumps, compressor engines, venting from liquids unloading and road transport for well maintenance. When all contributions are added together shale gas extraction results in 8,80 kg CO_2-eq/GJ on basis of higher heating value (HHV).

4.2.2 Emissions from shale gas processing and thermal cracking

To meet the required ethylene production rate of 1000 kton/yr, 7890 million m^3 of raw shale gas is processed. [44] It is considered the case of five distributed shale gas processing plants that provide ethane to a centralized cracking plant. The life cycle inventory is conducted based on the mass and energy balances. Table 4.1 contains the mass and energy balances within the system boundaries and corresponding GHG emissions for processing of shale gas and subsequent cracking of the obtained ethane fraction. The data is on the basis of 1 kg of ethylene produced and is constructed with information extracted from You et al. [44]

Table 4.1: *Mass and energy balances and related GHG emissions of shale gas processing and thermal cracking of ethane [44]*

	Mass & Energy requirements per kg ethylene	**GHG emissions (kg CO_2-eq/$kg_{ethylene}$)**	
		Mass allocation	**Economic value allocation**
Shale gas processing			
Input			
Raw shale gas (m^3)	7,89	see extraction phase	
MEA (g)	0,28	$1{,}0 \times 10^{-4}$	$1{,}0 \times 10^{-4}$
TEG (g)	0,05	$2{,}0 \times 10^{-5}$	$2{,}0 \times 10^{-5}$
Output			
Sales gas (m^3)	6,6	/	/
Ethane (kg)	1,28	/	/
Ethane (m^3)	$3{,}4 \times 10^{-4}$	/	/
Propane (m^3)	$1{,}7 \times 10^{-4}$	/	/
Butanes (m^3)	$7{,}0 \times 10^{-4}$	/	/
Natural gasoline (m^3)	$5{,}0 \times 10^{-4}$	/	/
Direct CO_2 emissions (kg)	0,02	$4{,}0 \times 10^{-3}$	$3{,}0 \times 10^{-3}$

Utilities			
Power (kW)	1,17	0,09	0,07
HP steam (MJ)	0,04	(generated on-site)	
MP steam (MJ)	2,04	0,01	0,01
LP steam (MJ)	2,05	0,01	0,01
Makeup water (kg)	1,51	$5{,}0 \times 10^{-4}$	$7{,}0 \times 10^{-3}$
Cooling water (MJ)	8,26	/	/
Total		**0,11**	**0,09**
Thermal cracking			
Input			
Ethane (kg)	1,28	/	/
NaOH (g)	0,45	$1{,}0 \times 10^{-3}$	$1{,}0 \times 10^{-3}$
Output			
Ethylene (kg)	1,00	/	/
Propylene (kg)	0,01	/	/
Crude C_4 (kg)	0,10	/	/
Hydrogen (kg)	0,10	/	/
Direct CO_2 emissions (kg)	0,94	0,78	0,84
Utilities			
Natural gas (m^3)	0,6	0,23	0,25
Power (kW)	0,69	(generated on-site)	
Makeup water (kg)	9,99	0,01	0,02
Cooling water (MJ)	10,94	/	/
Total		**1,02**	**1,11**

As can be seen from Table 4.1, byproducts coming from the shale gas processing consist of sales gas, propane, butanes and natural gasoline. Due to the production of byproducts the greenhouse gas emissions relevant to ethylene production should only be allocated to ethane which is further used in the subsequent cracking step to obtain ethylene. Mass-based and economic-value based allocation are the most common allocation methods. Since economic values can change rapidly and to ensure long term validity of this work it is decided to do a mass based allocation. However, the mass-based allocation method cannot fully be used due to the generation of electricity in the bioethanol production step of the corn stover to ethylene pathway. Therefore, in this LCA, the economic-value based allocation method is also used. The economic values of the different products were extracted from the supporting information accompanying You et al. [12, 44] and are depicted in Table 4.2 and 4.3 together with the mass allocation.

Table 4.2: *Mass and economic allocation for shale gas processing*

Product	Economic value ($/MMBTU)	Economic value ($/kg$_{ethylene}$)	Mass (kg/kg$_{ethylene}$)
Sales gas	3,1	0,68	4,47
Ethane	3,3	0,21	1,28
Propane	6,68	0,24	0,74
Butanes	7,37	0,15	0,40
Natural gasoline	9,2	0,19	0,42
	Allocation factor:	**0,14**	**0,18**

Table 4.3: *Mass and economic allocation for thermal cracking*

Product	**Economic value ($/kg)**	**Economic value ($/kg$_{ethylene}$)**	**Mass (kg/kg$_{ethylene}$)**
Ethylene	1,2	1,20	1,00
Propylene	1,4	0,02	0,01
Crude C_4	0,9	0,09	0,10
Hydrogen	0,31	0,03	0,10
	Allocation factor:	**0,90**	**0,83**

From Table 4.2 a mass allocation factor of 0,18 and economic allocation factor of 0,14 is obtained. In what follows only the mass allocation method is explained in detail. For the economic value-based allocation method, the approach is identical but gives different end results which will be compared and discussed. Following the mass allocation method, it is concluded that about 18% of the total emissions coming from shale gas processing are allocated towards ethane. In the subsequent steam cracking section, on mass basis, 83% of the total GHG emissions are allocated to ethylene as can be seen from Table 4.3.

After allocation, the resulting GHG emissions per kg of ethylene produced coming from shale gas extraction are 0,53 kg CO_2-eq/kg$_{ethylene}$. In the shale gas processing stage the largest contributors to greenhouse gas emissions are combustion of natural gas by compressor engines, power consumption and low and medium pressure (LP, MP) steam generation. After allocating the GHG emissions to ethane, the processing step results in emissions of approximately 0,11 kg CO_2-eq/kg$_{ethylene}$. The GHG emissions related to the cracking stage are mostly coming from production and burning of natural gas resulting in a total amount of 1,02 kg CO_2-eq/kg$_{ethylene}$ after allocating to ethylene. Byproducts obtained in the cracking step consist of propylene, crude C_4 and hydrogen. Emission factors used to calculate GHG emissions were extracted from EcoInvent [54], Idemat [56] and You et al. [44] These are summarized in the appendix in Table A1.

The ethylene production step is the major contributor to GHG emissions which has a share of more than 61% of the total greenhouse gas emissions. The shale gas extraction step results in about 32% while shale gas processing has the smallest contribution of approximately 6% of the total emissions. Transportation leads to considerably less emissions taking up only 1% of the total. The net GHG emissions are about 1,68 kg CO_2-eq/kg. As comparison, the cumulative GHG emissions related to steam cracking of naphtha are 1,14 kg CO_2-eq/kg$_{ethylene}$. [57] Figure 4.2 presents the total life cycle GHG emissions of manufacturing ethylene through thermal cracking of ethane from shale gas for both mass and economic allocation.

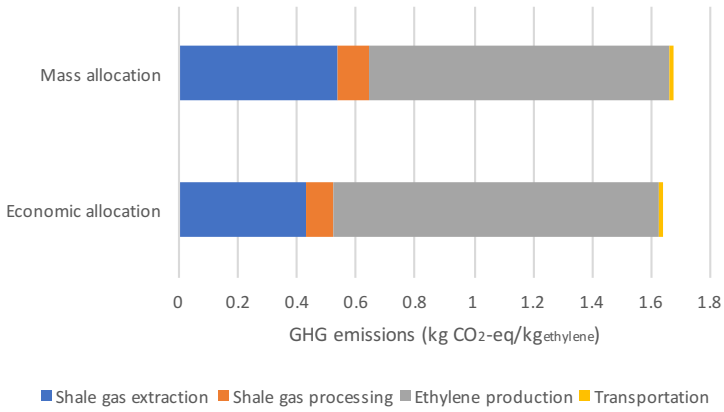

Figure 4.2: *Life cycle GHG emissions of ethylene from thermal cracking of shale gas*

From Figure 4.2 it is observed that mass allocation results in slightly higher net GHG emissions than the economic allocation method. The values obtained from economic allocation are in close range to the ones obtained by You et al. [44] who also applied economic value-based allocation. The minor differences can be explained by using more recent emission factors and updated economic values of each product.

4.3 Manufacturing ethylene from biomass

4.3.1 Corn stover pathway

To meet the given ethylene production rate (1000 kton/yr), the corn stover pathway consumes 816,2 ton/h of corn stover. [44] It is considered the case of five distributed bioethanol plants that provide ethanol to a centralized dehydration plant. First, life cycle GHG emissions were calculated for feedstock production which account for about 0,63 kg CO_2-eq/$kg_{ethylene}$ following the mass allocation method. Feedstock production involves energy intensive H_2 production for the synthesis of ammonia fertilizer. The main process for H_2 production is steam reforming of CH_4 which involves considerable CO_2 emissions. [57] In the subsequent step, corn stover is converted into bioethanol. The largest contributions to GHG emissions in this section come from the production of ammonia, corn steep liquor, glucose and sodium hydroxide. The solids obtained from the recovery section and the obtained biogas from the wastewater treatment unit are combusted to produce high pressure (HP) steam used to generate electricity and satisfy the process heat demand. As denoted in the previous section, it is therefore more feasible to apply economic value-based allocation. For consistency, the results will be presented using mass based allocation and afterwards the final results are compared to the economic allocation method. After allocating the emissions to ethanol the resulting GHG emissions for the ethanol production step are around 0,99 kg CO_2-eq/$kg_{ethylene}$.

Finally, ethanol is dehydrated to ethylene. In this process no co-products are formed, thus the emissions can be calculated directly without allocation. Greenhouse gas emissions come to a large extent from production and combustion of natural gas as well as power generation since dehydration of ethanol is highly endothermic (input of 1,6 MJ/$kg_{ethylene}$). [50, 57] Besides the

endothermicity of the dehydration reaction, also separating water from ethanol is an energy intensive process. The ethylene production step results in approximately 0,50 kg CO_2-eq/$kg_{ethylene}$ manufactured. Table 4.4 presents the mass and energy balances within the system boundaries for the ethanol production step and the subsequent ethylene manufacturing stage and greenhouse gas emissions for mass and economic allocation.

Table 4.4: *Mass and energy balances and related GHG emissions of ethylene production from corn stover [44]*

	Mass & Energy requirements per kg ethylene	**GHG emissions (kg CO_2-eq/$kg_{ethylene}$)**	
		Mass allocation	**Economic allocation**
Ethanol production			
Input			
Corn stover (kg)	6,53	/	/
Sulfuric acid, 93% (kg)	0,16	0,02	0,02
Ammonia (kg)	0,09	0,19	0,18
Corn steep liquor (kg)	0,10	0,16	0,14
Diammonium phosphate (kg)	0,01	0,01	0,01
Glucose (kg)	0,19	0,13	0,12
Host nutrients (kg)	5,28	0,01	$4{,}0 \times 10^{-3}$
Sulfur dioxide (kg)	1,29	$1{,}0 \times 10^{-3}$	$1{,}0 \times 10^{-3}$
NaOH (kg)	0,18	0,41	0,38
Boiler chemicals (kg)	$2{,}0 \times 10^{-5}$	$1{,}0 \times 10^{-4}$	$1{,}0 \times 10^{-4}$
Lime (kg)	0,07	0,05	0,05
Cooling tower chemicals (kg)	$1{,}9 \times 10^{-4}$	$3{,}0 \times 10^{-4}$	$2{,}0 \times 10^{-4}$
Output			
Ethanol (kg)	1,71	/	/
Electricity (kW)	1,07	/	/
Utilities			
Makeup water (kg)	11,53	0,02	0,02
Total		**0,99**	**0,92**
Ethylene production			
Input			
Ethanol (kg)	1,71	/	/
NaOH (kg)	$4{,}5 \times 10^{-3}$	0,01	0,01
Output			
Ethylene (kg)	1,00	/	/
Direct CO_2 emissions (kg)	0,30	0,30	0,30
Utilities			
Natural gas (m^3)	0,30	0,08	0,08
Power (kW)	0,23	0,10	0,10
Makeup water (kg)	3,26	0,01	0,01
Cooling water (MJ)	3,70	/	/
Total		**0,50**	**0,50**

The net life cycle GHG emissions for ethylene production from corn stover result in -0,97 kg CO_2-eq/$kg_{ethylene}$. This negative value is the result of sequestration of carbon dioxide. Unlike the previous manufacturing pathway for ethylene, corn stover and corn grain sequester carbon in their biomass. Following You et al [44]: 1 mol of ethylene sequesters 2 mol of carbon. Expressed in 1 kg of ethylene the mass of sequestered carbon equals $\frac{2\ \text{mol} \cdot 44\ \text{kg}\ CO_2\text{–eq/mol}}{1\ \text{mol} \cdot 28\ \text{kg/mol}} = 3{,}1$ kg CO_2-eq/kg.

Figure 4.3 gives the life cycle GHG emissions of ethylene production from corn stover for both mass and economic allocation. Following mass allocation, in manufacturing ethylene from corn stover the feedstock production accounts for 29% of the total GHG emissions. The production of ethanol contributes 47% of the total emissions while the ethylene production stage results in 23% of the total. Transportation takes up only about 1% of the GHG emissions. The values obtained for the economic allocation accord with the ones calculated by You et al. [44] For calculating the above percentages sequestration of carbon dioxide was excluded.

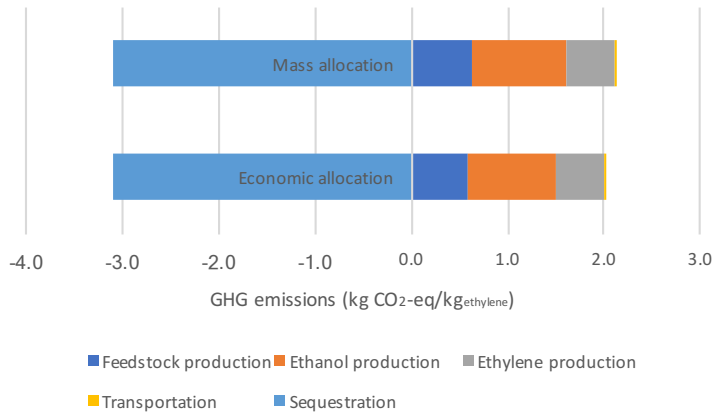

Figure 4.3: *Life cycle GHG emissions of ethylene production from corn stover*

Emission factors used to calculate GHG emissions were extracted from EcoInvent [54], Idemat [56] and You et al. [44] For corn steep liquor, glucose, diammonium phosphate and potassium phosphate the emission factors were calculated with data extracted from GREET 2018 [55] and the corresponding calculation method is included in the appendix in Table A7. Calculation of the economic allocation factor is depicted in Table 4.5. About 93% of the total emissions from the ethanol production step are allocated towards ethanol using economic allocation. In the mass allocation method 100% of the emissions is allocated to ethanol production since no other byproducts are produced. All emission factors used for the corn stover pathway can be found in Table A1 of the appendix.

Table 4.5: *Mass and economic allocation for ethanol production from corn stover*

Product	Economic value ($/kg, $/kWh)	Economic value ($/$kg_{ethylene}$)
Ethanol:	0,54	0,92
Electricity:	0,07	0,08
	Allocation factor:	**0,93**

4.3.2 Corn grain pathway

The corn grain pathway consumes 669,9 ton/h of corn grain to meet an ethylene production rate of 1000 kton/yr. [44] Corn grain is converted in five distributed bioethanol production plants that provide feedstock to a centralized ethanol dehydration plant. Using the mass based allocation method the GHG emissions for corn grain production were calculated to about 0,66 kg CO_2-eq/$kg_{ethylene}$. Table 4.6 shows the mass and energy balances together with the corresponding GHG emissions for the ethanol and ethylene production stages.

Table 4.6: *Mass and energy balances and related GHG emissions for ethylene manufacturing from corn grain [44]*

	Mass & Energy requirements per kg ethylene	**GHG emissions (kg CO_2-eq/$kg_{ethylene}$)**	
		Mass allocation	**Economic allocation**
Ethanol production			
Input			
Corn grain (kg)	5,36	/	/
NaOH (kg)	0,03	0,03	0,05
Alpha-amylase (kg)	$3{,}7 \times 10^{-2}$	$2{,}0 \times 10^{-3}$	$3{,}0 \times 10^{-3}$
Glucoamylase (kg)	$5{,}0 \times 10^{-3}$	0,01	0,02
Sulfuric acid (kg)	0,01	$1{,}0 \times 10^{-3}$	$1{,}0 \times 10^{-3}$
Lime (kg)	$6{,}0 \times 10^{-3}$	$2{,}0 \times 10^{-3}$	$3{,}0 \times 10^{-3}$
Urea (kg)	0,01	0,02	0,03
Yeast (kg)	$1{,}0 \times 10^{-3}$	$1{,}0 \times 10^{-3}$	$2{,}0 \times 10^{-3}$
Output			
Ethanol (kg)	1,71	/	/
DDGS (kg)	1,77	/	/
Utilities			
Power (kW)	0,46	0,09	0,14
Natural gas (m^3)	0,60	0,59	0,89
Makeup water (kg)	11,38	0,01	0,01
Cooling water (kg)	49,39	0,04	0,06
Total		**0,80**	**1,22**
Ethylene production			
Input			
Ethanol (kg)	1,71	/	/
NaOH (kg)	$4{,}5 \times 10^{-3}$	0,01	0,01
Output			
Ethylene (kg)	1,00	/	/
Direct CO_2 emissions (kg)	0,30	0,30	0,30
Utilities			
Natural gas (m^3)	0,17	0,08	0,08
Power (kW)	0,23	0,10	0,10
Makeup water (kg)	3,26	0,01	0,01
Cooling water (MJ)	3,70	/	/
Total		**0,50**	**0,50**

Emissions from the ethanol production stage are for 49% allocated to ethanol, the remaining part is allocated to DDGS, a co-product in the ethanol production step. In Table 4.7 the allocation method is depicted.

Table 4.7: *Mass and economic allocation for ethanol production in the corn grain pathway*

Product	Economic value ($/kg)	Economic value ($/kg$_{ethylene}$)	Mass (kg/kg$_{ethylene}$)
Ethanol	0,54	0,92	1,71
DDGS	0,18	0,32	1,77
	Allocation factor:	**0,74**	**0,49**

The largest contributors to GHG emissions in the ethanol production step consist of power generation, natural gas production and combustion, sodium hydroxide production and producing cooling water. Bioethanol production from corn grain results in 0,80 kg CO_2-eq/kg$_{ethylene}$ manufactured using mass allocation. Ethylene production results in 0,50 kg CO_2-eq/kg$_{ethylene}$ to which natural gas production and combustion together with power generation contribute for more than 96%. The net GHG emissions including the amount of sequestered carbon are around -1,09 kg CO_2-eq/kg for mass based allocation. The emission factors for alpha-amylase, glucoamylase and yeast were calculated using data from GREET 2018 [55] and are included in the appendix in Table A11. The remaining emission factors were extracted from EcoInvent [54], Idemat [56] and You et al. [44] and can be found in Table A1.

The life cycle GHG emissions for each step in the manufacturing of ethylene from corn grain are depicted in Figure 4.4. The major contributor to GHG emissions is the ethanol production section which contributes over 40% of the total greenhouse gas emissions. The feedstock production step results into about 33% while ethylene production has the smallest contribution of approximately 25% of the total emissions. Transportation causes less significant GHG emissions occupying less than 3% of the total. Similar to corn stover, these percentages are calculated excluding the sequestered renewable carbon. The values obtained for economic allocation accord closely with the calculations by You et al. [44]

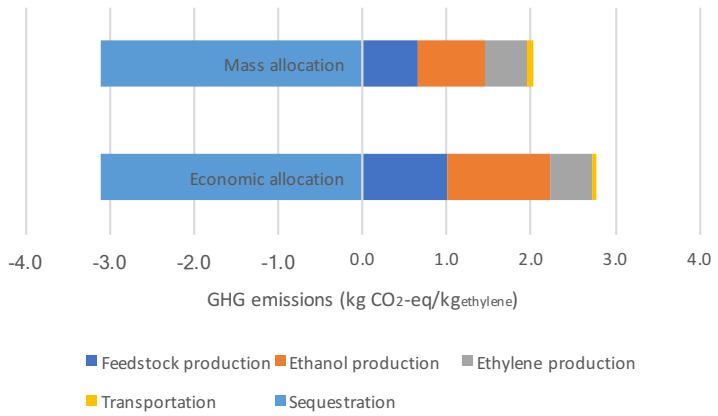

Figure 4.4: *Life cycle GHG emissions of ethylene production from corn grain*

4.4 Ethylene from plasma-assisted methane coupling

4.4.1 Gas phase system

The gas phase system operates at elevated pressure (5 bar) in which ethylene is the major product. First mass and energy balances (shown in Table 4.8) were set up within the system boundaries. It should be noted that the output of the shale gas processing section and the input to the ethylene production section match closely but are not completely identical. This is because the two systems were simulated separately in Aspen Plus V10.

Table 4.8: *Mass and energy balances and related GHG emissions for plasma-assisted ethylene production (gas phase system, total purge stream combustion)*

	Mass & Energy requirements per kg ethylene	**GHG emissions (kg CO_2-eq/$kg_{ethylene}$)**	
		Mass allocation	**Economic allocation**
Shale gas processing			
Input			
Carbon dioxide (kg)	0,19	/	/
Methane (kg)	1,81	/	/
Ethane (kg)	0,64	/	/
Water (kg)	0,08	/	/
TEG (kg)	0,13	Recycled	Recycled
Output			
Carbon dioxide (kg)	0,19	/	/
Methane (kg)	1,81	/	/
Ethane (kg)	0,64	/	/
Water (kg)	0,01	/	/
Utilities			
Power (kW)	0,08	0,02	0,03
Hot utility (kW)	0,06	Generated by flaring	Generated by flaring
Total		**0,02**	**0,03**
Ethylene production			
Input			
Carbon dioxide (kg)	0,18	/	/
Methane (kg)	1,95	/	/
Ethane (kg)	0,64	/	/
Water (kg)	23,39	0,02	0,03
NaOH (kg)	0,29	0,40	0,56
Output			
Ethylene (kg)	1,00	/	/
Hydrogen (PSA) (kg)	0,27	/	/
Ethane (96% purity; de-ethanizer) (kg)	0,33	/	/
Ethane (84% purity; purifier) (kg)	0,09	/	/
Direct CO_2 emissions (kg)	0,73	0,44	0,61
Utilities			
Power (kWh)	28,10	7,10	9,87

Hot utility (MJ)	4,20	Generated by flaring	Generated by flaring
Total		**7,94**	**11,05**

To stay consistent and by means of comparing all results it is also decided for this pathway to allocate all emissions based on both mass and economic value. The allocation method is depicted in Table 4.9. In conclusion, 60% of the life cycle emissions are allocated to ethylene following mass based allocation. It should be noted that the sodium carbonate and sodium formate coming from the caustic tower are not taken into account in the allocation method for the plasma processes. This mixture could be considered as a byproduct, however since the salts are present in small amounts and diluted in water, reclaiming would require an intensive separation. The cost of this separation is expected to be substantially higher than the profit of the salt sales.

Table 4.9: *Mass and economic allocation for plasma-assisted ethylene manufacturing (gas phase system, total purge stream combustion)*

Product	**Economic value ($/kg)**	**Economic value ($/kg$_{ethylene}$)**	**Mass (kg/kg$_{ethylene}$)**
Hydrogen	0,31	0,08	0,27
Ethylene	1,20	1,20	1,00
Ethane	0,39	0,15	0,39
	Allocation factor:	**0,83**	**0,60**

The total greenhouse gas emissions of the gas phase system amount about 8,24 kg CO_2-eq/kg$_{ethylene}$ following mass based allocation. The emissions for each step in this production pathway are depicted in Figure 4.5. 3% of the total emissions are related to the extraction processes involved to obtain raw shale gas. Both transportation and shale gas processing (i.e. dehydration) account for less than 1%. The largest contribution to the total emissions is coming from the ethylene production stage i.e. NPD-reactor and downstream operations. This step involves more than 96% of the life cycle GHG emissions. More than 67% of the GHGs emitted at the ethylene production stage are coming from the NPD-reactor power consumption. The remaining emissions come from compression steps (20%), including the compression of cooling methane and work recovered in the expansion steps. To reduce power consumption in the compression steps it is possible to couple the expansion turbine shaft to the compressor to win some work. This resulted in a reduction in GHG emissions of about 0,45 kg CO_2-eq/kg$_{ethylene}$. The remaining emissions coming from the ethylene production stage are related to water production for the washing column, producing sodium hydroxide for the caustic tower and emissions directly coming from flaring the purge stream. In fact, flaring results in more than 5% of the total emissions. In Table 4.8 the emissions related to flaring to provide hot utility are summed up under the CO_2 emissions tab in the output section.

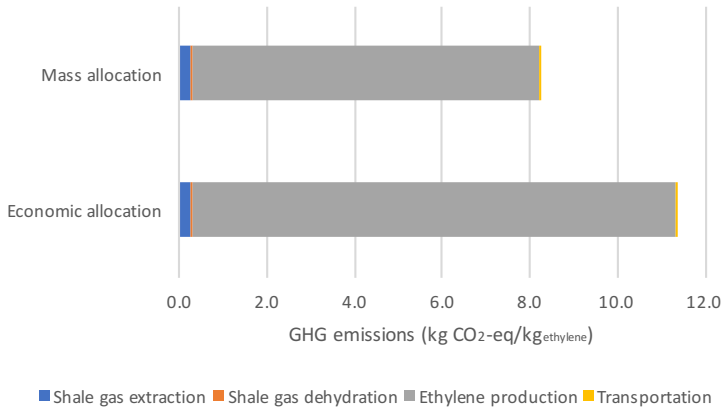

Figure 4.5: *Life cycle GHG emissions of plasma-assisted ethylene production (gas phase system, total purge stream combustion)*

After heat integration, the gas phase system still requires a hot utility of 4,2 MJ/$kg_{ethylene}$. To satisfy this demand, the heat of combustion obtained by flaring the purge stream can be utilised. Burning the purge results in a heat release of 21 MJ/$kg_{ethylene}$. This is more than enough to satisfy the heat demand and thus the excess heat can be either discarded or exchanged to an external user. In the previously discussed case, in which the excess heat is discarded to the environment, all emissions related to combustion of the purge stream are allocated to the ethylene manufacturer.

Now the case for which an external user can utilize the excess purge is discussed. The purge is then partially considered as a byproduct to which emissions will be located. The allocation method, based on mass and economic values of the different products, is given in Table 4.10. The fraction allocated towards ethylene is in this case lower than in the case without purge stream combustion, resulting in 52% and 82% of the total GHG emissions for mass and economic allocation respectively.

Table 4.10: *Mass and economic allocation for plasma-assisted ethylene manufacturing (gas phase system, partial purge stream combustion)*

Product	**Economic value ($/kg)**	**Economic value ($/$kg_{ethylene}$)**	**Mass (kg/$kg_{ethylene}$)**
Hydrogen	0,31	0,08	0,27
Ethylene	1,20	1,20	1,00
Ethane	0,39	0,15	0,39
Purge	0,12	0,03	0,25
	Allocation factor:	**0,82**	**0,52**

For the case of partial purge stream combustion, the mass and energy balances stay the same as for the total purge stream combustion case. However, due to the lower allocation factor towards ethylene, the related GHG emissions will be reduced as depicted in Table 4.11.

Table 4.11: *Mass and energy balances and related GHG emissions for plasma-assisted ethylene production (gas phase system, partial purge stream combustion)*

	Mass & Energy requirements per kg ethylene	**GHG emissions (kg CO_2-eq/$kg_{ethylene}$)**	
		Mass allocation	**Economic allocation**
Shale gas processing			
Input			
Carbon dioxide (kg)	0,19	/	/
Methane (kg)	1,81	/	/
Ethane (kg)	0,64	/	/
Water (kg)	0,08	/	/
TEG (kg)	0,13	Recycled	Recycled
Output			
Carbon dioxide (kg)	0,19	/	/
Methane (kg)	1,81	/	/
Ethane (kg)	0,64	/	/
Water (kg)	0,01	/	/
Utilities			
Power (kW)	0,08	0,02	0,03
Hot utility (kW)	0,06	Generated by flaring	Generated by flaring
Total		**0,02**	**0,03**
Ethylene production			
Input			
Carbon dioxide (kg)	0,18	/	/
Methane (kg)	1,95	/	/
Ethane (kg)	0,64	/	/
Water (kg)	23,39	0,02	0,03
NaOH (kg)	0,29	0,35	0,55
Output			
Ethylene (kg)	1,00	/	/
Hydrogen (PSA) (kg)	0,27	/	/
Ethane (96% purity; de-ethanizer) (kg)	0,33	/	/
Ethane (84% purity; purifier) (kg)	0,09	/	/
Direct CO_2 emissions (kg)	0,14	0,08	0,12
Utilities			
Power (kWh)	28,10	6,18	9,68
Hot utility (MJ)	4,20	Generated by flaring	Generated by flaring
Total		**6,62**	**10,35**

After partially allocating the purge stream the life cycle GHG emissions are 6,91 kg CO_2-eq/$kg_{ethylene}$ for the mass allocation method as presented in Figure 4.6. This is a reduction of more than 16% compared to the case of total purge stream combustion. Following mass allocation, 4% of the total emissions are related to the extraction of shale gas. The largest contribution comes from the ethylene production step, resulting in more than 96% of the total. As was the case for the total purge stream combustion, most of the emissions are related to power

consumption, i.e. NPD-reactor and compression, accounting for 89% of the life cycle GHG emissions.

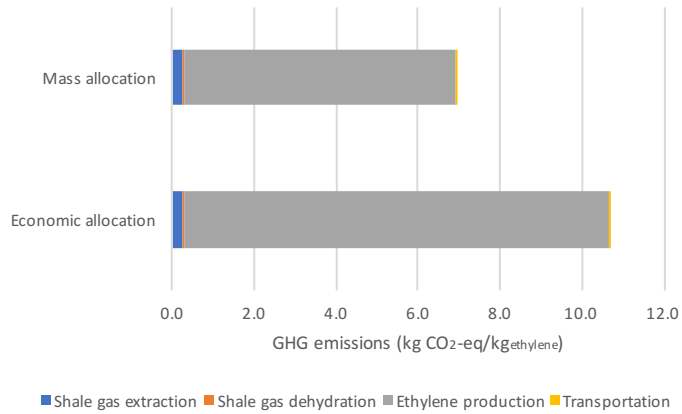

Figure 4.6: *Life cycle GHG emissions of plasma-assisted ethylene production (gas phase system, partial purge stream combustion)*

4.4.2 Hybrid system

The hybrid system operates at atmospheric pressure in which acetylene is the main product coming from the reactor. In the post-plasma zone a hydrogenation catalyst based on palladium is placed to subsequently hydrogenate the acetylene to ethylene. The hydrogen required in the catalytic step is obtained by cracking methane in the plasma reactor. Table 4.12 contains the mass and energy balances within the system boundaries. It should again be noted that the minor differences between the shale gas processing output and input to the ethylene production section are because the two processes are simulated separately.

Table 4.12: *Mass and energy balances and related GHG emissions for plasma-assisted ethylene production (hybrid system, total purge stream combustion)*

	Mass & Energy requirements per kg ethylene	**GHG emissions ($kg\ CO_2$-eq/$kg_{ethylene}$)**	
		Mass allocation	**Economic allocation**
Shale gas processing			
Input			
Carbon dioxide (kg)	0,15	/	/
Methane (kg)	1,47	/	/
Ethane (kg)	0,52	/	/
Water (kg)	0,06	/	/
TEG (kg)	0,11	Recycled	Recycled
Output			
Carbon dioxide (kg)	0,15	/	/
Methane (kg)	1,47	/	/
Ethane (kg)	0,52	/	/
Water (kg)	0,00	/	/

Utilities			
Power (kWh)	0,06	0,02	0,02
Hot utility (MJ)	0,05	Available through heat integration	
Total		**0,02**	**0,02**
Ethylene production			
Input			
Carbon dioxide (kg)	0,15	/	/
Methane (kg)	1,44	/	/
Ethane (kg)	0,52	/	/
Water (kg)	91,71	0,11	0,14
NaOH (kg)	0,24	0,37	0,47
Hydrogenation catalyst (kg)	$7{,}8 \times 10^{-5}$	0,03	0,04
Output			
Ethylene (kg)	1,00	/	/
Hydrogen (PSA) (kg)	0,15	/	/
Ethane (96% purity; de-ethanizer) (kg)	0,25	/	/
Ethane (84% purity; purifier) (kg)	0,09	/	/
Direct CO_2 emissions (kg)	0,60	0,41	0,52
Utilities			
Power (kWh)	23,24	6,58	8,46
Hot utility (MJ)	0,17	Available through heat integration	
Total		**7,48**	**9,61**

Likewise, mass and economic-value based allocation is used and shown in Table 4.13. 67% of the emissions are allocated towards ethylene. The remaining emissions are allocated to hydrogen, obtained after the pressure swing adsorption unit and ethane which is obtained as bottom product of the de-ethanizer (96% purity) and from the purifier bottom (84% purity).

Table 4.13: *Mass and economic allocation for plasma-assisted ethylene manufacturing (hybrid system, total purge stream combustion)*

Product	Economic value ($/kg)	Economic value ($/kg$_{ethylene}$)	Mass (kg/kg$_{ethylene}$)
Hydrogen	0,31	0,05	0,15
Ethylene	1,20	1,20	1,04
Ethane	0,39	0,13	0,35
Acetylene	0,65	0,01	0,02
	Allocation factor:	**0,86**	**0,67**

Compared to the gas phase system, the hybrid system makes use of a hydrogenation catalyst placed in de post-plasma zone. Table 4.14 gives the mass and energy inputs required to produce the catalyst. Data is extracted from Agarski et al. [58] With an expected lifetime of 3 years the catalyst is being consumed at a rate of 7,8E-05 kg catalyst/kg ethylene. The largest contribution to GHG emissions related to catalyst processing is coming from power consumption (81%). Mining and extraction of primary palladium results in about 16% of the total emissions.

Table 4.14: *Mass and energy balances for hydrogenation catalyst production [58]*

	Mass & Energy requirements per kg ethylene	GHG emissions (kg CO_2-eq/$kg_{ethylene}$)	
		Mass allocation	**Economic allocation**
Catalyst formation			
Input			
Palladium (kg)	$1x10^{-6}$	$5,1x10^{-3}$	$6,5x10^{-3}$
Hydrochloric acid (kg)	$1x10^{-6}$	$1x10^{-6}$	$1x10^{-6}$
Deionised water (kg)	0,07	$1,0x10^{-4}$	$1,0x10^{-4}$
Hydrogen (liquid) (kg)	$7,3x10^{-4}$	$1,0x10^{-3}$	$1,3x10^{-3}$
Aluminium oxide (kg)	$4,1x10^{-4}$	$1,0x10^{-3}$	$1,0x10^{-4}$
Output			
Hydrogenation catalyst (kg)	$5,8x10^{-5}$	/	
Utilities			
Power (kW)	0,09	0,03	0,03
Total		**0,03**	**0,04**

The life cycle emissions for the hybrid system are about 7,72 kg CO_2-eq/$kg_{ethylene}$ following mass based allocation. Figure 4.7 presents the GHG emissions for each production step. About 3% of the total emissions are coming from shale gas extraction. Shale gas dehydration and transportation have a negligible contribution to the total emissions. The remaining 97% is allocated to the ethylene production step, mainly coming from electrical power consumption. The NPD-reactor is responsible for more than 65% of the greenhouse gas emissions coming from the ethylene production section. The remainder is linked to the multistage compression, refrigerant generation (together 21%) and emissions coming from producing water for the washing column, sodium hydroxide for the caustic tower and direct emissions by flaring (14%). Some work was recovered by coupling the expansion and compression steps, resulting in a reduction of about 0,53 kg CO_2-eq/$kg_{ethylene}$. Direct CO_2 emissions are coming from flaring the purge, giving rise to 0,60 kg CO_2-eq/$kg_{ethylene}$.

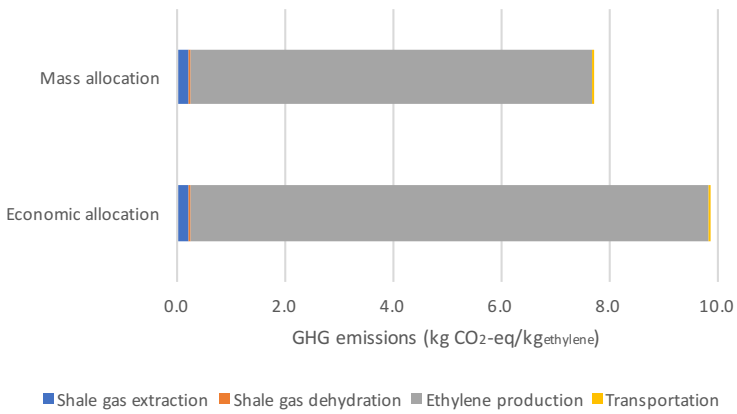

Figure 4.7: *Life cycle GHG emissions of plasma-assisted ethylene production (hybrid system, total purge stream combustion)*

In practice the purge stream is usually completely combusted. In the worst case scenario all emissions due to burning are therefore charged to the ethylene manufacturer. In some cases, an external user could be interested in using the purge stream further e.g. burning to provide process heat. In this case it is considered that the ethylene manufacturer does not combust the purge stream, instead the purge is sold as a byproduct to the customer, thus changing the allocation factors. Table 4.15 shows the updated allocation factors for the case the purge stream is not combusted.

Table 4.15: *Mass and economic allocation for plasma-assisted ethylene manufacturing (hybrid system, no purge stream combustion)*

Product	Economic value ($/kg)	Economic value ($/kg$_{ethylene}$)	Mass (kg/kg$_{ethylene}$)
Hydrogen	0,31	0,05	0,15
Ethylene	1,20	1,20	1,00
Ethane	0,39	0,13	0,35
Acetylene	0,65	0,01	0,01
Purge stream	0,10	0,03	0,26
	Allocation factor:	**0,85**	**0,57**

Due to a change in allocation factor also the resulting GHG emissions will differ despite that the mass and energy balances stay identical apart from the direct CO_2-emissions related to combustion. The results are summarized in Table 4.16.

Table 4.16: *Mass and energy balances and related GHG emissions for plasma-assisted ethylene production (hybrid system, no purge stream combustion)*

	Mass & Energy requirements per kg ethylene	GHG emissions (kg CO_2-eq/kg$_{ethylene}$)	
		Mass allocation	**Economic allocation**
Shale gas processing			
Input			
Carbon dioxide (kg)	0,15	/	/
Methane (kg)	1,47	/	/
Ethane (kg)	0,52	/	/
Water (kg)	0,06	/	/
TEG (kg)	0,11	Recycled	Recycled
Output			
Carbon dioxide (kg)	0,15	/	/
Methane (kg)	1,47	/	/
Ethane (kg)	0,52	/	/
Water (kg)	0,00	/	/
Utilities			
Power (kWh)	0,06	0,02	0,02
Hot utility (MJ)	0,05	Available through heat integration	
Total		**0,02**	**0,02**

Ethylene production			
Input			
Carbon dioxide (kg)	0,15	/	/
Methane (kg)	1,44	/	/
Ethane (kg)	0,52	/	/
Water (kg)	91,71	0,09	0,13
NaOH (kg)	0,24	0,31	0,46
Hydrogenation catalyst (kg)	$7{,}8 \times 10^{-5}$	0,03	0,04
Output			
Ethylene (kg)	1,00	/	/
Hydrogen (PSA) (kg)	0,15	/	/
Ethane (96% purity; de-ethanizer) (kg)	0,25	/	/
Ethane (84% purity; purifier) (kg)	0,09	/	/
Direct CO_2 emissions (kg)	0,00	0,00	0,00
Utilities			
Power (kWh)	23,24	5,55	8,28
Hot utility (MJ)	0,17	Available through heat integration	
Total		**5,96**	**8,90**

The net GHG emissions in the case of no purge stream flaring are 6,20 kg CO_2-eq/$kg_{ethylene}$ following mass allocation. This equals a reduction of almost 25% compared to the case of total purge stream combustion due to the substantial lower mass allocation factor and by avoiding direct CO_2 emissions from flaring. More detailed breakdown of the emissions coming from each stage are depicted in Figure 4.8.

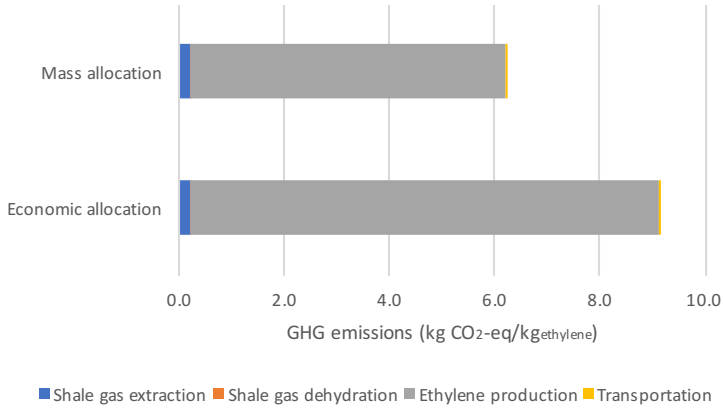

Figure 4.8: *Life cycle GHG emissions of plasma-assisted ethylene production (hybrid system, no purge stream combustion)*

5 Discussion

5.1 Comparison of environmental performance

In this section, a comparison is made between the different ethylene production pathways in terms of greenhouse gas emissions. Figure 5.1 shows the total GHG emissions related to the production of ethylene through steam cracking of naphtha (a) steam cracking of shale gas (b), corn stover pathway (c), corn grain pathway (d), gas phase plasma process (e) and hybrid plasma process (f).

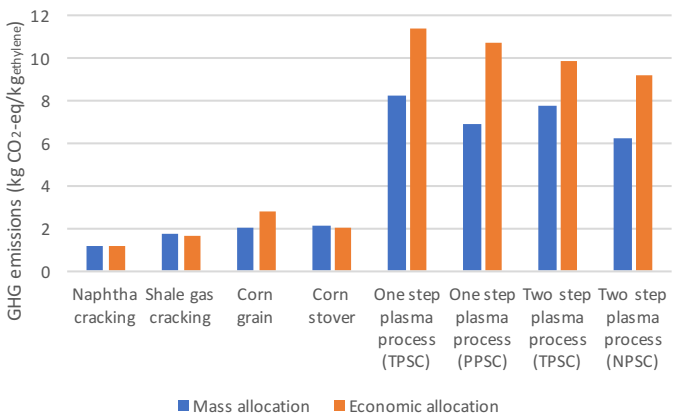

Figure 5.1: *Life cycle GHG emissions of the investigated ethylene production pathways Total (T), Partial (P) or No (N) Purge Stream Combustion (PSC)*

Steam cracking of naphtha is currently the state of the art technology to produce ethylene in Europe and the Middle-East. From Figure 5.1 it can be observed that naphtha steam cracking produces the least amount of GHG emissions, resulting in 1,13 or 1,17 kg CO_2-eq/$kg_{ethylene}$ on respectively mass or economic basis. [12] The thermal cracking of shale gas based pathway results in a total of 1,68 kg CO_2-eq/$kg_{ethylene}$ using mass allocation. As discussed in section 4, the largest addition comes from the thermal cracking step in which ethane is cracked to ethylene. Steam cracking is a very energy intensive process and requires high operating temperatures in cracking furnaces for which a large quantity of fuel is burned, producing considerable amounts of CO_2-emissions. The biobased pathways have a net negative amount of CO_2-eq emitted, -0,97 and -1,09 kg CO_2-eq/$kg_{ethylene}$ for respectively corn stover and corn grain, indicating that CO_2 is being captured and sequestered into the feedstock. Despite capturing CO_2, greenhouse gasses are emitted during the feedstock production, transportation and at the ethanol and ethylene production step. Without taking sequestration into account the corn stover pathway to produce

ethylene results in 2,13 kg CO_2-eq/$kg_{ethylene}$ whereas the corn grain route emits a total of 2,01 kg CO_2-eq/$kg_{ethylene}$. Both processes to convert biomass into ethylene result in between 1,20 to 1,27 times more GHG emissions than thermal cracking of shale gas. To a large extent these additional emissions are related to the ethanol production stage in which biomass is converted to ethanol. For corn stover, which is a lignocellulosic biomass, this process requires harsh pretreatment conditions (i.e. sulfuric acid, ammonia, sodium hydroxide) to break down hemicellulose and cellulose chains. Besides the previously mentioned chemicals, the remainder of the GHG emissions in the ethanol production step are coming from producing corn steep liquor (CSL), glucose and lime needed for enzyme production required for hydrolysis. Producing ethanol out of corn grain is easier since this type of biomass is made up from starch which can be broken down by adding alpha-amylase and glucoamylase. In the corn grain pathway, the major GHG emissions in the ethanol production step are coming from combustion of natural gas to provide process heat. Whereas in the corn stover pathway the otherwise not used lignin fraction is burned, allowing electricity to be produced on site. In comparison to corn stover, the ethanol production step for corn grain results in 19% less GHG emissions using mass allocation. In the economic allocation, electricity is seen as co-product in the corn stover pathway and thus lowering the allocation factor from 100% in mass allocation to 92,5% in economic allocation. This explains the small reduction from mass to economic allocation for corn stover.

From all pathways and for both allocation methods, the plasma-assisted ethylene production routes result in the highest greenhouse gas emissions. In both cases the highest contribution to the total GHG emissions is coming from the ethylene production stage (more than 95%) as presented in Figure 5.2 (mass allocation).

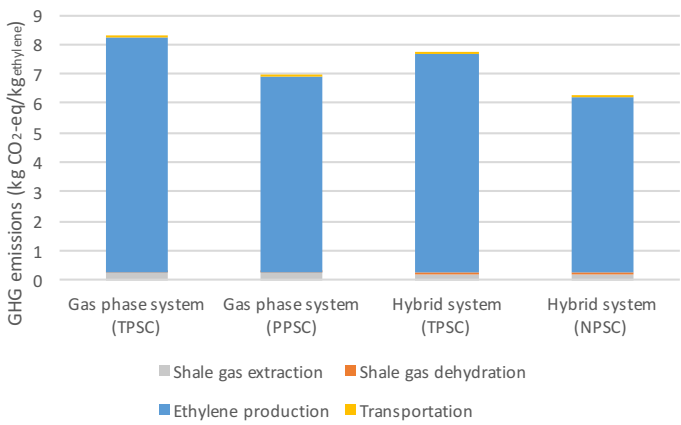

Figure 5.2: *Carbon footprint breakdown of plasma-assisted ethylene production Total (T), Partial (P) or No (N) Purge Stream Combustion (PSC)*

This step includes the NPD-reactor, multistage compression and cryogenic distillation which consume a considerable amount of electrical power. Therefore, emissions generated in this step are mostly coming from the production of electricity. From the mass based allocation, the gas phase system results in a total of 8,24 kg CO_2-eq/$kg_{ethylene}$ when the purge stream is completely burned and 6,91 kg CO_2-eq/$kg_{ethylene}$ in the case of partial purge stream flaring. The hybrid system performs slightly better, resulting in a total of 7,72 kg CO_2-eq/$kg_{ethylene}$ in the case of total purge stream combustion and 6,20 kg CO_2-eq/$kg_{ethylene}$ when the purge stream is not combusted.

Since more than 95% of the life cycle GHG emissions of the plasma processes are related to the ethylene production step it is important to know how the emissions are distributed within this stage. Figure 5.3 shows the breakdown of the GHG emissions of this step. It can be confirmed that electricity production plays a significant role in the total life cycle GHG emissions. Besides, flaring the purge also has a considerable share in the carbon footprint related to this stage.

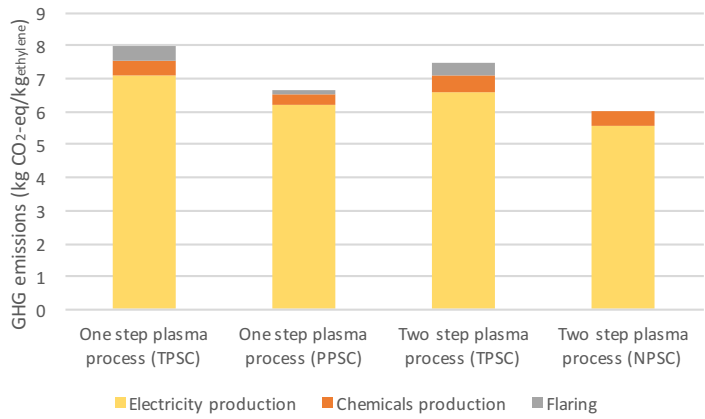

Figure 5.3: *Breakdown of GHG emissions from the ethylene production step Total (T), Partial (P) or No (N) Purge Stream Combustion (PSC)*

In the one-step process (gas phase system), all reactions occur in the gas phase. Therefore, problems related to catalyst deactivation and poisoning due to carbon or other impurities present in the shale gas and the accompanying regeneration are avoided in contrary to the two-step process (hybrid system). [28] The hybrid system obtains a higher ethylene yield per single pass (7% higher) than the gas phase process. Thus, the amount to be recycled will be lower for the hybrid system and this involves a higher volume to be handled in the downstream purification section. [28] However, since the ethylene yield is higher for the hybrid system, 21% less electricity is required per amount of ethylene produced. [28] Consequently, this translates into a lower carbon footprint for the hybrid system. The hybrid system involves an additional catalytic step, however due to the long lifetime and high activity of the catalyst the resulting CO_2-emissions of 0,03 kg CO_2-eq/$kg_{ethylene}$ are almost negligible. Figure 5.4 gives an overview of the power consumption for each pathway.

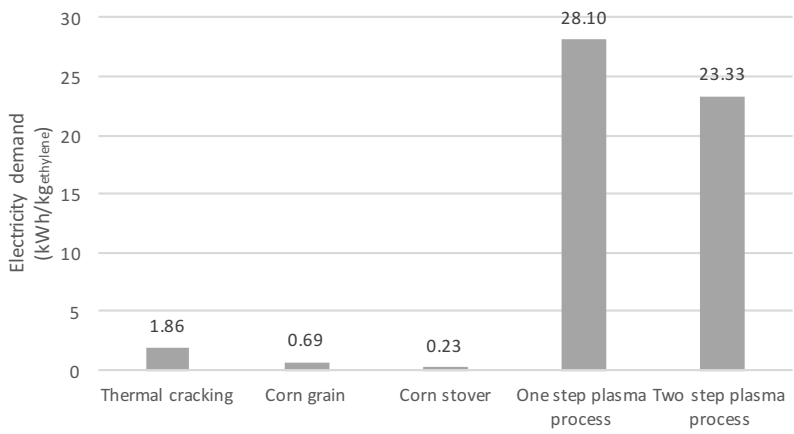

Figure 5.4: *Electricity demand of the investigated pathways for ethylene manufacturing*

From Figure 5.4 it is observed that the plasma processes for ethylene production consume considerably more power than thermal cracking and the biobased routes. In both plasma processes the NPD-reactor contributes the most to the total electricity demand. The 2017 U.S. energy mix consists of the following energy sources and their respective share of the total: natural gas (31,7%), coal (30,1%), petroleum (0,5%), nuclear (20%) and renewables (17,1%). Renewable energy sources can further be subdivided into hydropower (7,5%), wind (6,3%), biomass (1,6%) and solar (1,3%). [8] Producing energy thus emits GHGs coming from burning of fossil fuels, mostly based on natural gas and coal and to a lesser extent petroleum. Since GHG emissions related to electricity production form the biggest fraction of the total emissions for the plasma processes, it is interesting to look at different energy sources and how this affects the life cycle emissions (see Figure 5.5). Therefore, emission factors for wind and photovoltaic energy were extracted from Koffi et al. [59] and Amponsah et al. [60] respectively. In the previous calculations, the U.S. grid electricity mix of 2017 was used. If all electricity would be coming from green sources, e.g. wind and solar energy, the total emissions could be reduced by up to 84% and 87% for the gas phase system, resulting in 1,31 and 0,87 kg CO_2-eq/$kg_{ethylene}$ respectively for total and partial purge stream flaring. In case of the hybrid system, a reduction of 83% and 87% of the life cycle GHG emissions can be achieved. This brings about 1,27 and 0,76 kg CO_2-eq/$kg_{ethylene}$ accordingly for total or no purge stream combustion. Therefore, integration of plasma-assisted ethylene production with renewable energy sources is required to achieve a sustainable electrified process.

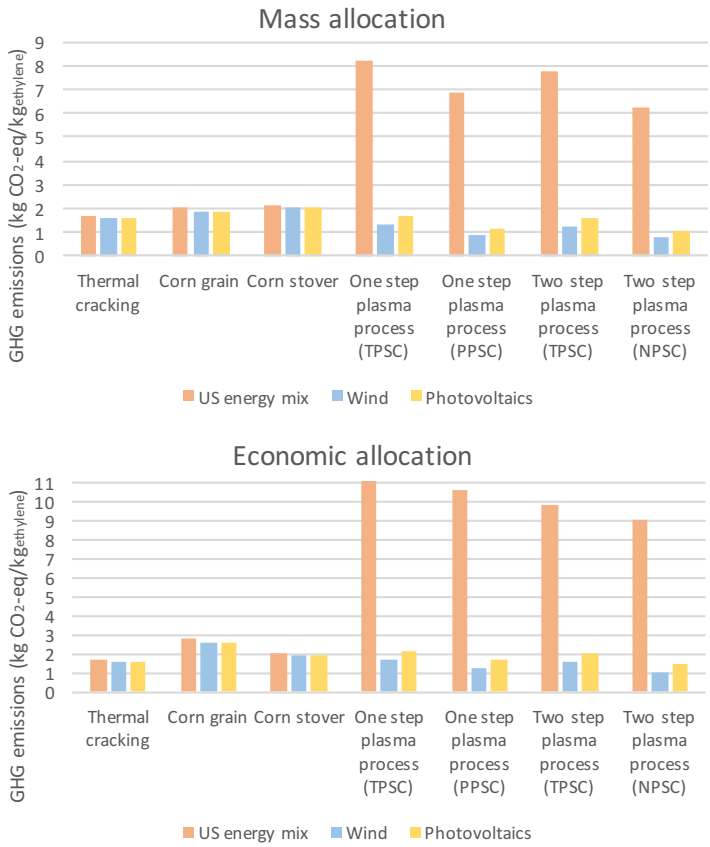

Figure 5.5: *Life cycle GHG emissions for various energy sources Total (T), Partial (P) or No (N) Purge Stream Combustion (PSC)*

From Figure 5.5 it can as well be seen that for the thermal cracking, corn grain and corn stover pathway a reduction (up to 9%) in total GHG emissions is achieved by changing to renewable energy sources. Energy coming from wind turbines in comparison to photovoltaic panels allows the largest reduction in GHG emissions due to wind energy having a lower emission factor. It should be mentioned that if all electricity would be coming from low-cost and renewable sources the conventional ethylene production processes (i.e. steam cracking) would switch from natural gas combustion to electrically driven heat generation inside cracking furnaces and thus also avoid greenhouse gas emissions related to fuel combustion.

Applying wind energy seems to reduce the carbon footprint the most for the plasma processes. Therefore, it is decided to investigate the greenhouse gas emissions coming from the ethylene production stage when electricity is provided by wind turbines. These results are presented in Figure 5.6. It can be concluded that emissions related to electricity production have significantly lowered compared to Figure 5.3 which represents the case of electricity from the grid. For the cases where the purge stream is combusted the largest contributions to the carbon footprint are coming from chemicals production and purge stream flaring. Emissions from chemicals production are mainly related to sodium hydroxide production that is required for the caustic tower and are for the gas phase and hybrid plasma process more or less the same.

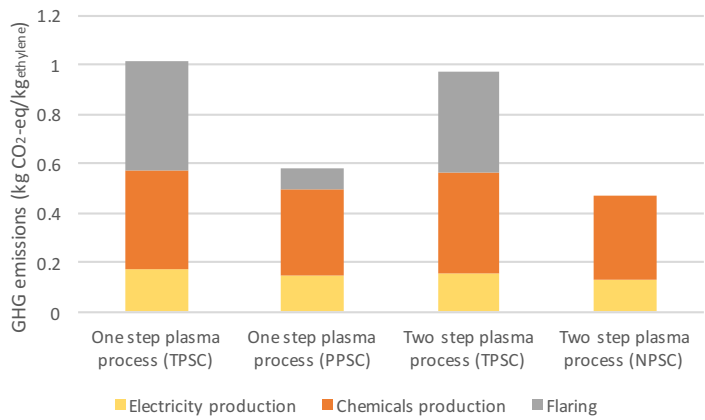

Figure 5.6: *Breakdown of GHG emissions from ethylene production step using wind energy Total (T), Partial (P) or No (N) Purge Stream Combustion (PSC)*

5.2 General comparison

So far, a comparison was made in terms of greenhouse gas emissions. In this section the five different ethylene production pathways are compared with four additional performance classes: water consumption, chemicals consumption, electricity demand and breakeven ethylene price. Corn farms and shale gas reservoirs are for the most part geographically distributed and to supply the ethane or ethanol demand on economic scales, an ethylene production site is mostly provided with feedstock from various suppliers. [13, 61, 62] For the thermal cracking pathway and both biobased pathways (corn grain and corn stover), it is considered the case of 5 distributed shale gas processing/bioethanol plants with a yearly production capacity of 1000 kton following the study of You et al. [44]

Figure 5.7 presents the performance of each pathway for the five investigated impact categories. Corresponding data can be found in Table A27 in the appendix. The results are presented on a relative scale ranging from 0 to 5, where 5 equals the value of the worst performer in that particular category. GHG emissions are without sequestration to make a comparison between the different production processes possible and are presented on mass allocation basis. Each category is now discussed.

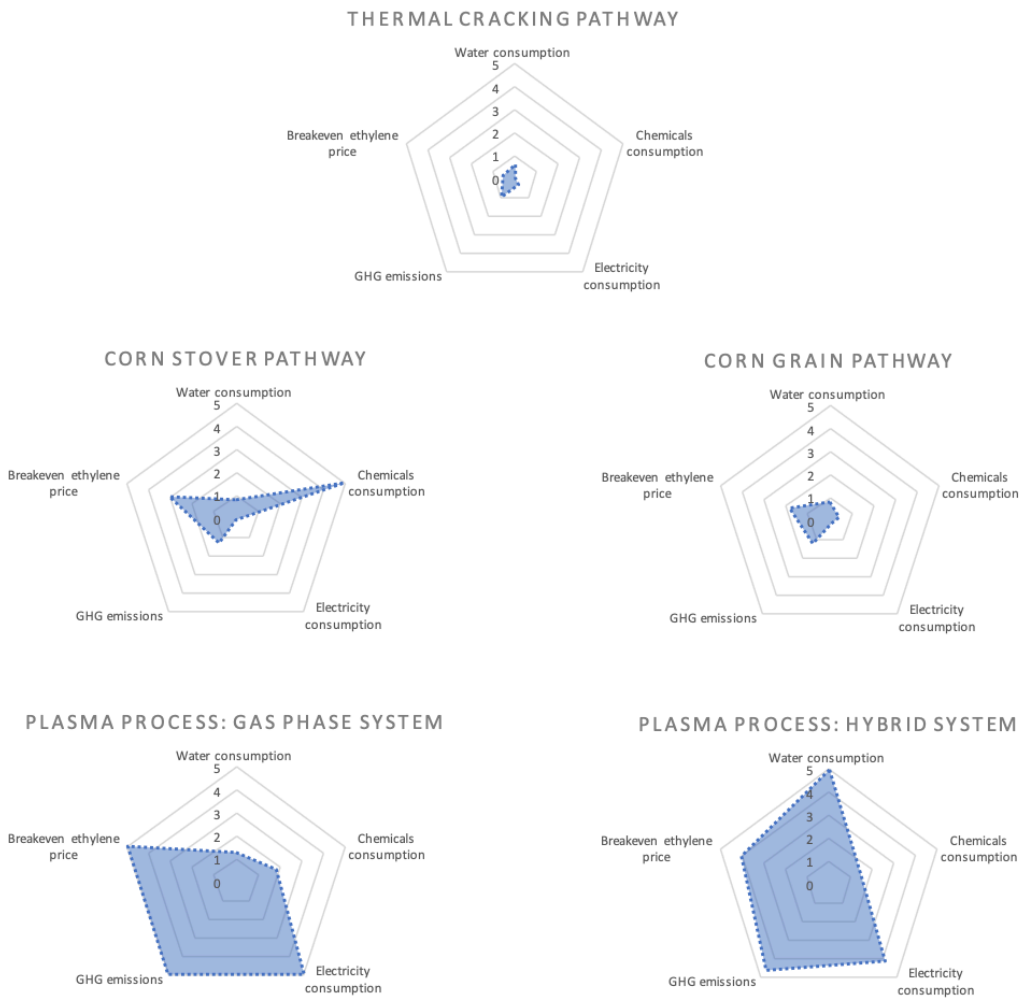

Figure 5.7: *Plasma process (current design) performance for different impact categories*

Figure 5.8 shows the water consumption for feedstock production, processing and final ethylene production for the different pathways. It can be concluded that both biobased routes require the largest amount of water. To produce 1 kg of ethylene a water input of 1200 kg is needed for corn production. [63] It should be noted that water applied for hydraulic fracking in the thermal cracking pathway is considered to be recycled.

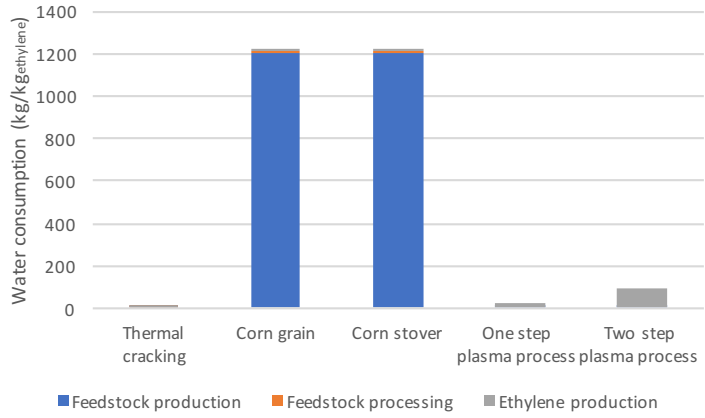

Figure 5.8: *Life cycle water consumption of the investigated ethylene production pathways*

Figure 5.9 contains the water consumption without feedstock production to make a comparison between the production processes feasible.

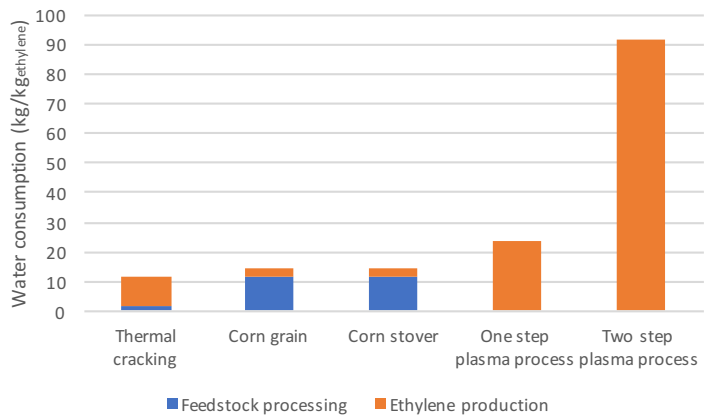

Figure 5.9: *Water consumption related to feedstock processing and ethylene production*

For the plasma process there is a remarkable difference in water consumption between the gas phase system and the hybrid system (Figure 5.7 and Figure 5.9). The two-step process has a 3,9 times higher water consumption than the one-step plasma process. The reason why the hybrid system consumes a larger amount of water is that this system operates at five times lower pressure than the gas phase system (1 bar vs 5 bar). This lower pressure decreases the performance of the washing tower, which is used to remove solid carbon from the NPD-reactor outlet, and thus increases water consuming at this stage. By applying additional separation techniques the solid carbon can be separated from the wastewater such that it can be recycled and reused and thus significantly lowering the water demand. Burning the purge stream does produce water as byproduct. However, this water does not necessarily precipitate in the same

region as the process water was restrained from and thus does not compensate the total water consumption. The other pathways (thermal cracking, corn stover and corn grain) consume considerably less water than both plasma processes. The current design of the hybrid process requires between 6,2 and 8,0 times more water than the biobased and thermal cracking pathways. For the gas phase system this factor lies between 1,6 and 2,0. However, when the waste water from the washing tower is completely recycled the water consumption can be drastically reduced as shown in Figure 5.10. In this case the water consumption is only 1,05 and 0,85 kg/$kg_{ethylene}$ coming mainly from the caustic tower in the form of sodium hydroxide solution.

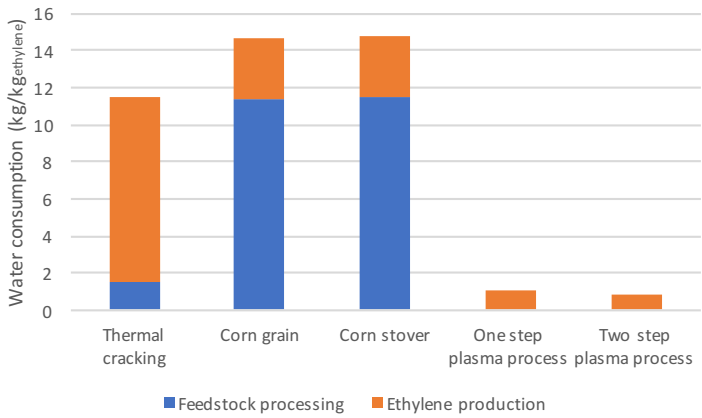

Figure 5.10: *Water consumption considering recycling the washing water*

Figure 5.11 encompasses the total amount of chemicals required to produce 1kg of ethylene for each pathway. From Figure 5.11, it can be concluded that the corn stover pathway involves the largest chemicals consumption. As discussed in section 5.1, this is mainly coming from sulfuric acid, ammonia, sodium hydroxide, corn steep liquor, host nutrients, sulfur dioxide, glucose, lime and cooling tower chemicals (hydrogen peroxide) required in the bioethanol production step. The hybrid and gas phase plasma process consume respectively 70% and 64% less chemicals. For both processes this mainly consists of sodium hydroxide used in the caustic tower to remove carbon dioxide. The corn grain and thermal cracking pathway use considerably less chemicals, resulting in respectively 9% and less than 1% of the amount required in the corn stover pathway. Chemicals required in the corn grain pathway consist of sodium hydroxide, alpha-amylase, glucoamylase, sulfuric acid, lime and urea, but are needed to a much lesser extent to produce ethylene than in the corn stover case. In the thermal cracking pathway monoethanolamine (MEA) is applied for carbon dioxide removal from the raw shale gas. Afterwards the rich MEA solution is regenerated in a stripping column. Triethylene glycol (TEG) is used for dehydration of the sweet gas and recovered by stripping. Sodium hydroxide is utilized to remove the acid components from the cracked gas. Due to insignificant sodium hydroxide consumption and MEA and TEG being regenerated, the thermal cracking pathway has the best performance in this impact category, consuming only 0,0008 kg chemicals/$kg_{ethylene}$.

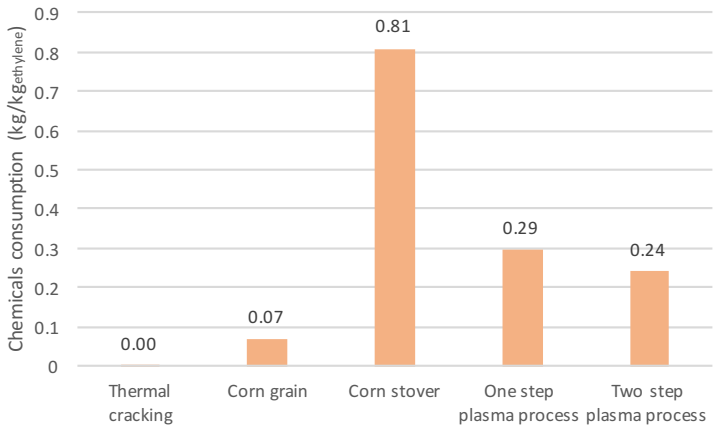

Figure 5.11: *Total chemicals consumption for each pathway*

From You et al. [44] the breakeven ethylene prices were extracted for the three comparative pathways. For the hybrid and gas phase plasma processes the breakeven ethylene prices were computed from the supplementary information of Delikonstantis et al. [28] The gas phase system has a profit margin of zero for an ethylene production cost of around 2806 USD/ton (for an electricity price of 100 USD/MWh). Together with a raw material cost of 546 USD/ton, this results in a breakeven price of 3352 USD/ton ethylene. The yearly production capacity of the gas phase system is 0,72 kton, assuming the operating time to be 8000 h/yr at a production rate of 90 kg/h of ethylene. In case of the hybrid system the profit margin is zero at an ethylene production cost of 2324 USD/ton (electricity price 100 USD/MWh) and together with a raw material cost of 383 USD/ton results in a breakeven price of 2707 USD/ton ethylene. The hybrid system has a production capacity of 0,87 kton/yr, operating for 8000 h/yr and with a production rate of 109 kg/h.

The economic performance of the different ethylene manufacturing routes are set side by side in terms of breakeven ethylene price. The breakeven ethylene prices for each pathway are summarized in Figure 5.12. The highest breakeven ethylene price is found for the gas phase plasma process, resulting in 3352 USD/ton. While the current ethylene sell price is around 1200 USD/ton ethylene, this process currently results in a negative profit margin. The hybrid plasma process performs better with a breakeven price of 2707 USD/ton ethylene. These breakeven prices are between 1,6 and 9,6 times larger than the breakeven ethylene price for the thermal cracking pathway, the corn grain and stover routes for producing ethylene. The high breakeven prices for both plasma processes are mainly due to the substantial power consumption. Delikonstantis et al [28] showed that the hybrid and gas phase system become profitable at an electricity price of 35 and 23 MWh respectively. The corn stover pathway results in a breakeven ethylene price of around 2030 USD/ton. For the corn grain pathway the resulting breakeven ethylene price is around 1250 USD/ton, being close to the current ethylene price of 1200 USD/ton. The reason that the breakeven ethylene price for corn stover is higher than for corn grain is to be found in the fact that corn stover is a lignocellulosic biomass which requires more severe pretreatment and thus a more complex processing than converting corn grain. From all ethylene production routes considered in this study only the thermal cracking pathway results in a positive profit margin with a breakeven price of 350 USD/ton ethylene. Thus, producing

ethylene through thermal cracking of shale gas on large scales gives a lower breakeven price than the current market price of ethylene and results in a cost-effective process. The economics of this state-of-the-art and highly optimized technology can be hardly challenged. The large-scale implementation of alternative ethylene production processes is therefore mostly threatened by their lack of economic viability. [64]

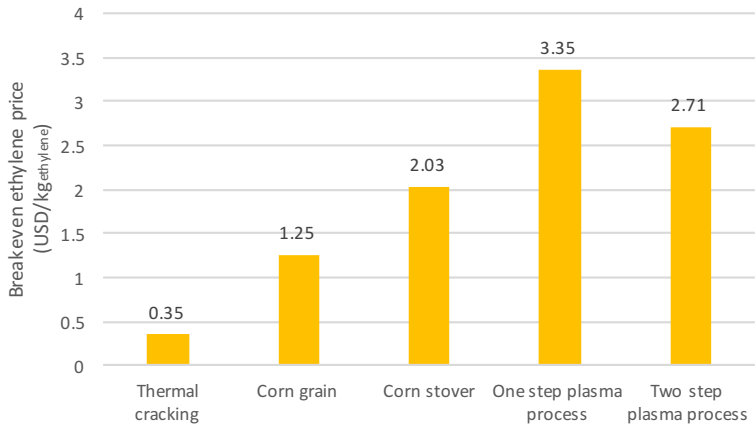

Figure 5.12: *Breakeven ethylene price for the different ethylene production pathways*

You et al. [44] showed that manufacturing ethylene from corn stover results in notably higher total capital investment costs than producing ethylene from corn grain (by 207 - 224%) and from thermal cracking of shale gas (by 83 - 186%). The high capital cost is related to the bioethanol production step because of large investments needed in pretreatment, enzymatic hydrolysis, enzyme production, fermentation and wastewater treatment facilities. Considering a production capacity of 1000 kton/yr, the thermal cracking pathway has a total capital cost of 1,692 billion USD consisting of: shale gas gathering pipelines (18%), 5 distributed shale gas processing plants (27%), centralized cracking plant (55%). Manufacturing ethylene (1000 kton/yr) from corn stover results in a total capital cost of 4,375 billion USD of which 96% is related to the 5 distributed bioethanol plants and the remainder to a centralized dehydration plant (4%). The corn grain pathway has an investment cost of 1,385 billion USD for an ethylene manufacturing capacity of 1000 kton/yr. 89% of the capital cost comes from ethanol production plants and the ethanol dehydration plant contributes 11% of the total. Spallina et al. [65] performed a techno-economic assessment for various ethylene production routes in which the overnight capital cost of a conventional naphtha steam cracking plant was estimated to about 2,534 billion USD. This is more than 49% higher than the capital cost of the investigated ethane (shale gas) steam cracker. To a large extent these additional costs can be related to the cold section where more unit operations are required to separate the reactor effluent in case of naphtha as feedstock (i.e. depropanizer, propane/propylene separation, debutanizer, etc.).

Albani G. [26] performed a CAPEX study for both the gas phase and hybrid plasma process with a production capacity of respectively 0,72 kton/yr and 0,87 kton/yr. Extrapolating these results to a 1000 kton/yr capacity results in a capital investment of 1,227 billion USD for the gas phase plasma process and 1,129 billion USD for the hybrid system. In this study [26], the biggest contribution to the investment cost is coming from the adsorption tower (51,5%). The remainder is related to compressors (23,3%), distillation columns (14,8%), heat exchangers

(6,8%), pumps (2,5%) and washing tower (1,1%). In the hybrid system, the breakdown of the CAPEX is made as follows: adsorption tower (48,3%), compressors (27,3%), distillation columns (13,5%), heat exchangers (9,7%) and washing tower (1,2%). It should be noted that in the current design the adsorption tower is replaced by a caustic tower and an extra distillation unit is added to obtain an ethylene stream following the market requirements. A comparison of the capital costs is presented in Figure 5.13.

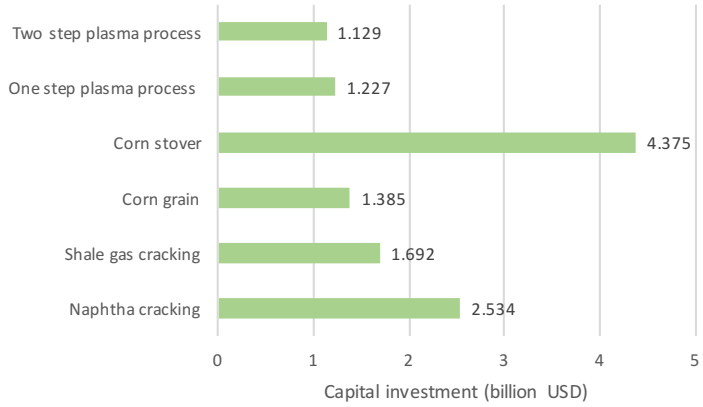

Figure 5.13: *CAPEX of investigated ethylene production processes*

Overall, the gas phase plasma process has the highest score in three out of the five performance categories: GHG emissions, electricity consumption and breakeven ethylene price. Compared to the gas phase system, the hybrid plasma process performs slightly better in these categories. However, from all processes, the hybrid system has the largest water consumption. The corn stover pathway results in the largest chemicals consumption while the thermal cracking of shale gas performs the best in this category with the least amount of external chemicals required. Besides, the corn stover pathway has the smallest electrical power consumption due to electricity being generated at the ethanol production stage. The thermal cracking pathway has the best performance in four out of five impact categories being GHG emissions, water consumption, chemicals consumption and breakeven ethylene price. These results are summarized in Figure 5.7 and represent the current design and mode of operation of the plasma-assisted process. However, as mentioned earlier, the water consumption can drastically be reduced by recycling the washing water and the carbon footprint can greatly be mitigated by applying renewable energy (i.e. wind turbines). Therefore, it is decided to compare the best-case scenario with the other ethylene production processes. These results are presented in Figure 5.14. The same relative scale is used as in Figure 5.7, with the value of 5 corresponding to the worst performer of that particular category.

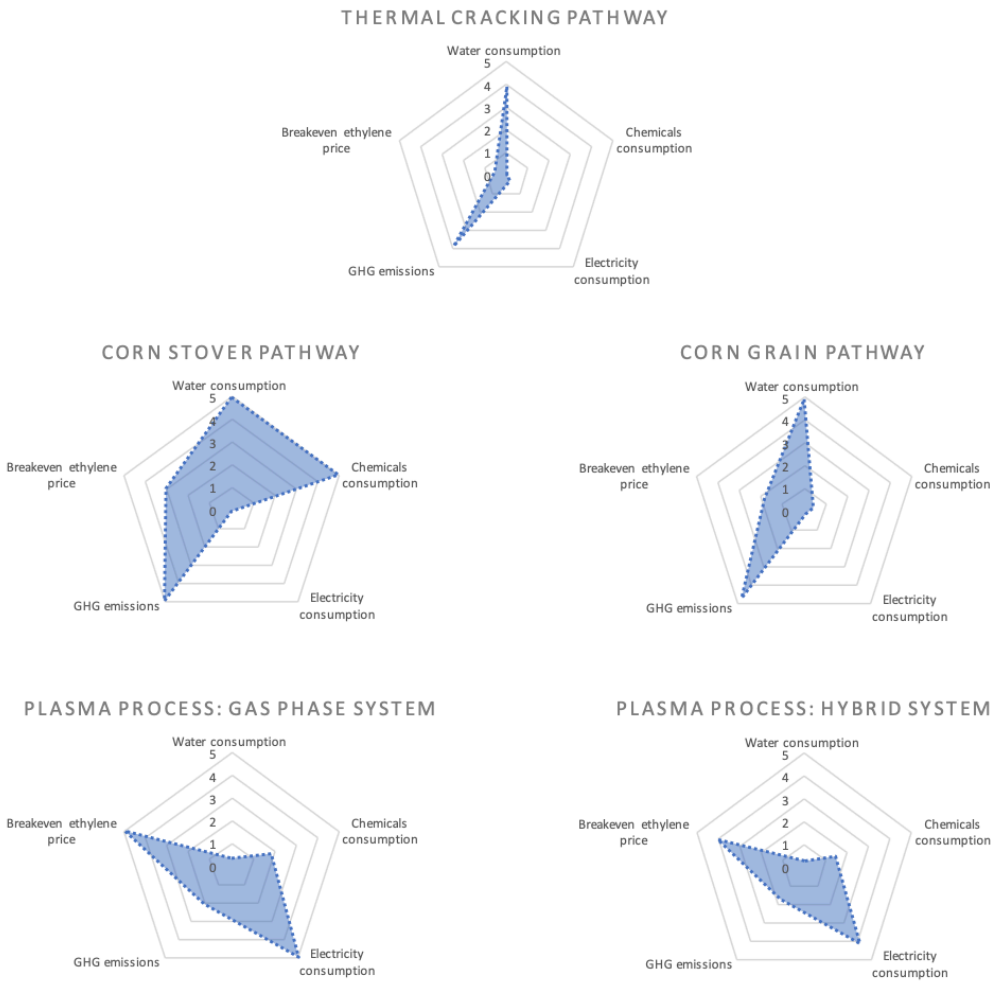

Figure 5.14: *Plasma process (best-case scenario) performance for different impact categories*

From Figure 5.14 it is observed that the best-case scenario for both plasma processes result in the lowest water consumption of all investigated pathways. In this case, water usage only comes in the form of aqueous sodium hydroxide solution used in the caustic tower for which the hybrid system now has a lower consumption per kg of ethylene than the gas phase system. Considering life cycle greenhouse gas emissions without carbon sequestration, both plasma processes result in the lowest carbon footprint compared to ethylene from thermal cracking of shale gas and ethylene from corn grain and corn stover. For the other categories, the conclusions have not changed. It can be concluded that the hybrid plasma system still performs slightly better in all five categories and thus has a lower environmental and economic impact than the gas phase system.

5.3 Sensitivity and uncertainty analysis

A sensitivity analysis was conducted to investigate the impact of altering economic parameters on the environmental performance of ethylene production. Since one of the allocation methods is based on economic values, the total greenhouse gas emissions are influenced by changes to the economic values of the products. Figure 5.15 presents the shift in total greenhouse gas emissions when product prices deviate with 10% of their present values.

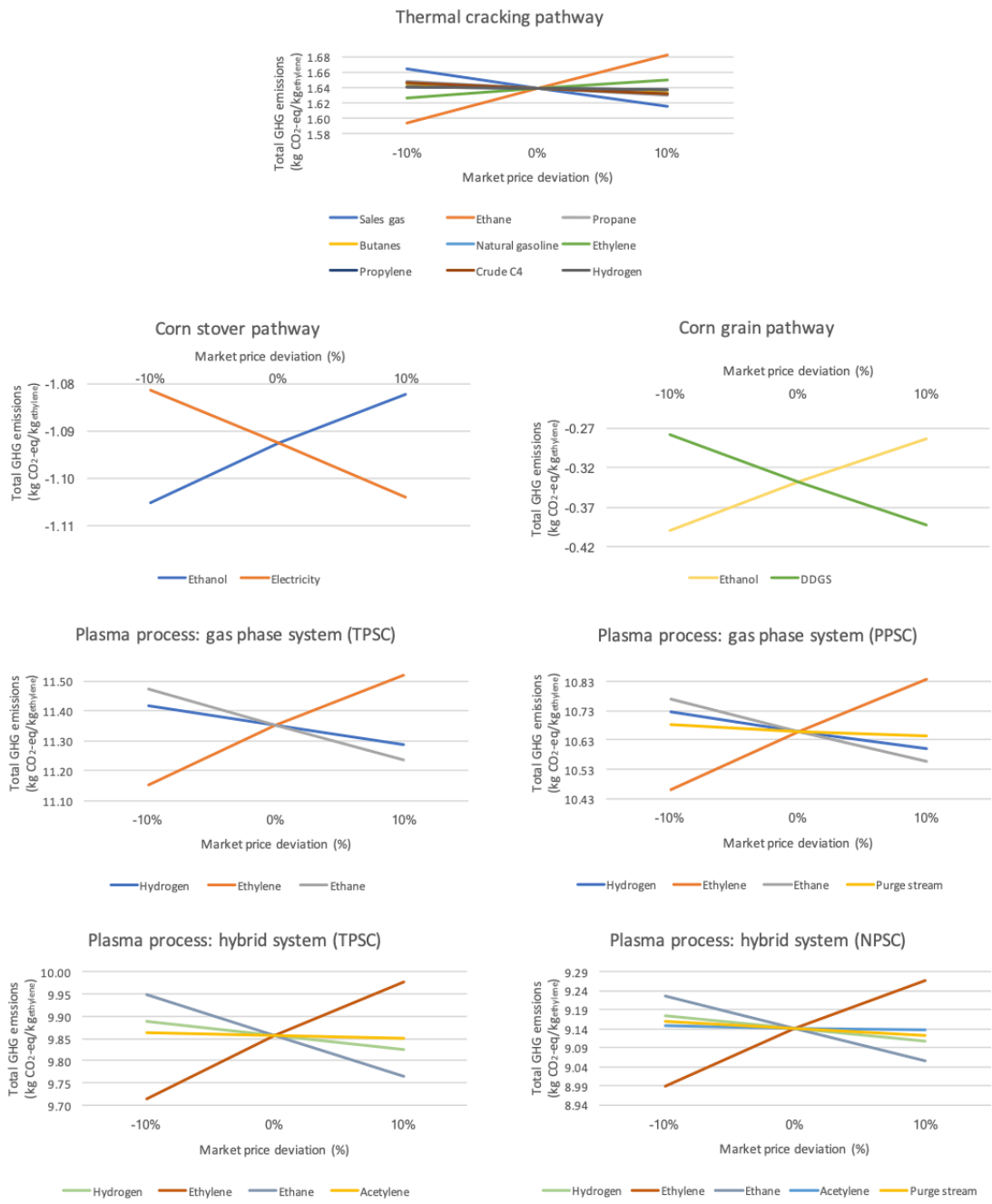

Figure 5.15: *Results of the sensitivity analysis for carbon footprint with varying market price Total (T), Partial (P) or No (N) Purge Stream Combustion (PSC)*

From Figure 5.15 it can be observed that for the thermal cracking pathway the main factors influencing the total GHG emissions are the ethane and ethylene price (highest slope). For both parameters the slopes are positive, indicating that an increase in the market price will result in a larger amount of CO_2 allocated towards ethylene production. Note that for the other products there is a reversed effect, since they are byproducts in contrary to ethane which acts as an intermediate product. Natural gasoline, Crude C_4 and propylene have little effect. Figure 5.15 also illustrates the sensitivity results for the corn stover pathway. Here, an increase in ethanol price and a decrease in electricity price will result in higher GHG emissions allocated towards ethylene production. For the corn grain pathway a positive correlation is found for the ethanol price, while the price of dried distillers grains and solids (DDGS) is negatively correlated to the total GHG emissions. The main factors influencing net GHG emissions for the gas phase plasma process are the ethylene and ethane price. Both an increase in ethylene price as well as a decrease in ethane and/or hydrogen market price will result in higher total GHG emissions. A negative correlation is found for the purge stream as co-product to which emissions are allocated when not completely burned. For the hybrid system similar trends can be found for varying hydrogen, ethylene and ethane market prices compared to the gas phase system. In addition, this pathway shows the sensitivity results for varying the acetylene market price. A negative slope indicates that an increase in acetylene market price reduces the total GHG emissions allocated towards ethylene. The effect is however not substantial due to the small negative slope because acetylene is only a minor byproduct. Under the investigated price changes, the corn stover and corn grain pathways still give the best performance in terms of total GHG emissions related to ethylene production.

The approach that was followed so far in this study uses average values of process parameters like ethylene yield, electricity price, emissions factors, etc. The life cycle GHG emissions that are obtained give an indication about the average value but do not consider deviations related to reactor performance and emission factors. The value of an emission factor is namely related to the geographical location. Therefore, Delikonstantis et al. [33] performed a Monte Carlo simulation for the plasma processes that takes into account all possible values that the process parameters and emission factors can take. The ethylene yield is varied by approximately 25% from the average yield, knowing that the highest experimental ethylene yield was found at 30% above the average. By using ethylene yield-performance parameter correlations the values of all the process parameters are recalculated. From the simulation, a confidence interval is determined that quantifies the uncertainty related to the life cycle greenhouse gas emissions. The uncertainty analysis is presented in Figure 5.16.

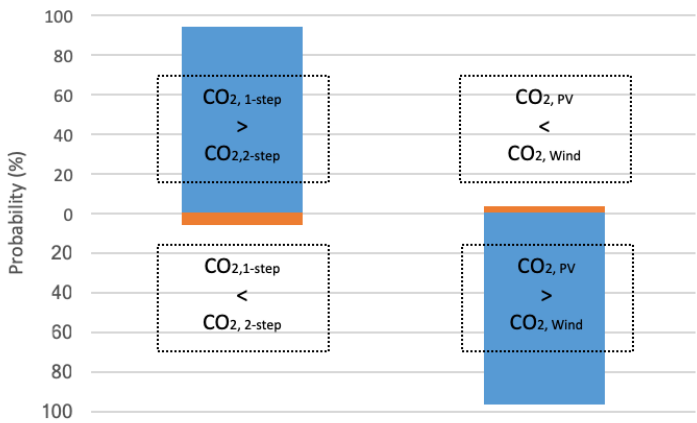

Figure 5.16: *Results of the uncertainty analysis for process alternative (one-step plasma process vs two-step plasma process) and electricity source (wind energy vs photovoltaic energy)*

With a confidence interval of 93,5% it is highly probable that the life cycle GHG emissions of the hybrid system are lower than the gas phase plasma process. For the best-case scenario of the two-step plasma process (no purge stream combustion and wind energy) an uncertainty analysis was performed on the deviation of the total carbon footprint and was found to be maximum ±0.43 kg CO_2-eq/$kg_{ethylene}$. Besides carbon footprint, it was decided to conduct an uncertainty analysis for the electricity source. A confidence interval of 96,7% is obtained for which it is highly probable that the CO_2-emissions from photovoltaic panels are found to be higher than in the case of wind turbines. [33]

6 Conclusions

The primary goal of this study was to evaluate greenhouse gas emissions over the life cycle of five different ethylene production pathways: thermal cracking, corn stover, corn grain, gas phase plasma process and hybrid plasma process. The corn stover and corn grain pathway show the best performance in environmental impact from the viewpoint of GHG emissions. For corn stover and corn grain the total GHG emissions are respectively -1,0 and -1,1 kg CO_2-eq/$kg_{ethylene}$ indicating that a net amount of CO_2 is sequestered. For mass and economic based allocation the highest greenhouse gas emissions are found for the plasma processes. In the worst-case scenario (total purge stream combustion) the total emissions are 8,2 and 7,7 kg CO_2-eq/$kg_{ethylene}$ for respectively the one-step and two-step process when applying mass allocation. When the purge stream is partially combusted (one-step) or not combusted (two-step) the life cycle emissions are 6,9 and 6,2 kg CO_2-eq/$kg_{ethylene}$ accordingly for the gas phase system and hybrid system. These emissions are between 3,7 and 4,9 times higher than the life cycle emissions coming from steam cracking of shale gas and between 5,5 and 7,3 times higher in the case of naphtha steam cracking. The largest contributor to the GHG emissions of both plasma processes comes from power consumption (up to 90% of the total emissions) of which the largest part is related to the NPD-reactor (up to 79% of the total power consumption) and thus being the most polluting step within the full process. Besides the NPD-reactor, flaring the purge stream results in substantial greenhouse gas emissions contributing for 5% and 14% of the total emissions for the one-step and two-step process respectively. An uncertainty analysis was performed and concluded that with a probability of 93,5% the hybrid system results in a lower carbon footprint than the gas phase system. Due to the high energy demand, it was investigated how the total emissions are altered by applying renewable energy sources. A maximum reduction of up to 87% is achieved using wind energy for the gas phase system resulting in 1,3 and 0,9 kg CO_2-eq/$kg_{ethylene}$ accordingly for the case of total and partial purge stream flaring. For the hybrid system a decrease of maximum 88% of the life cycle GHG emissions can be achieved resulting in 1,3 and 0,8 kg CO_2-eq/$kg_{ethylene}$ for respectively the case of total and no purge stream combustion. When using wind turbines as energy source and partially or not combust the purge stream the carbon footprint of both plasma processes are lower than conventional naphtha steam cracking (1,1 kg CO_2-eq/$kg_{ethylene}$) and shale gas steam cracking (1,7 kg CO_2-eq/$kg_{ethylene}$).

In addition to global warming, importance was given to determine water consumption during the life cycle associated with feedstock processing and subsequent ethylene production. Without taking water consumption for feedstock production into account and based on the current design, the plasma processes require between 1,5 and 8 times more water than the biobased and thermal cracking pathways. When comparing the hybrid and gas phase plasma process it can be

concluded that the two-step process has a 3,9 times higher water consumption than the one-step plasma process. This major difference is related to the decreased performance of the washing tower which operates at lower pressure in case of the hybrid system. However, the water consumption can be significantly lowered (up to 99%) by applying an additional separation step such that the washing water can be recycled and reused. In that case both plasma processes result in the lowest water consumption of all pathways investigated in this study.

Comparing all ethylene manufacturing pathways in terms of chemicals consumption. It can be concluded that the corn stover pathway consumes the largest amount of external chemicals mainly due to the harsh conditions required for pretreatment in the ethanol production stage. The two-step and one-step plasma process consume respectively 70% and 64% less chemicals. The best performances are found for the corn grain and thermal cracking pathway which use considerably less chemicals and result respectively in only 9% and less than 1% of the amount required in the corn stover pathway.

Finally, the economic performance of the different ethylene production pathways are compared in terms of breakeven ethylene price. The gas phase plasma process results in the highest breakeven ethylene price of 3352 USD/ton, while the hybrid system performs better with a breakeven price of 2707 USD/ton ethylene. At the moment of writing, the ethylene market price fluctuates around 1200 USD/ton and thus both processes have a negative profit margin. The plasma processes are less competitive having a breakeven price that is between 1,6 and 9,5 times higher than the thermal cracking pathway and both biobased routes. The plasma processes can become profitable at lower electricity price since the high breakeven prices are for the most part due to the high power demand. Only the thermal cracking pathway currently results in a positive profit margin with a breakeven price of 350 USD/ton ethylene.

The latter conclusion is that the high electricity requirement of plasma-assisted methane coupling results in an increased carbon footprint when providing electricity from the grid. Therefore, integration of plasma-assisted ethylene production with renewable energy sources is required to achieve a sustainable electrified process. It can be concluded that the plasma processes result in a lower carbon footprint than conventional ethylene manufacturing when the purge stream is further used as byproduct and by applying electricity from wind turbines. Considering the current energy mix and not taking carbon sequestration into account, ethylene is at present being produced through the least polluting processes (i.e. naphtha and shale gas steam cracking). However, plasma-assisted methane coupling has economic and environmental potential for valorisation of methane-rich waste gas streams that are otherwise flared and thus reducing global GHG emissions.

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8 Appendix

Table A1: *Emission factors used to compute global warming potential*

Alpha-amylase (kg CO_2-eq/kg)	1,21	GREET 2018
Ammonia (kg CO_2-eq/kg)	2,09	EcoInvent v3.3
Ammonium sulfate (kg CO_2-eq/kg)	2,24	EcoInvent v3.3
Ammonium sulfate (kg CO_2-eq/kg)	2,24	EcoInvent v3.3
Boiler chemicals (kg CO_2-eq/kg)	3,06	EcoInvent v3.3 (Sodium phosphate)
Calcium chloride (kg CO_2-eq/kg)	0,99	EcoInvent v3.3
Calcium chloride (kg CO_2-eq/kg)	0,99	EcoInvent v3.3
CO_2 emissions (kg CO_2-eq/kg)	1	
CO_2 emissions (kg CO_2-eq/t)	1000	
Cooling tower chemicals (hydrogen peroxide) (kg CO_2-eq/kg)	1,39	EcoInvent v3.3
Corn grain (kg CO_2-eq/kg)	0,25	You et al. [44]
Corn steep liquor (kg CO_2-eq/kg)	1,50	GREET 2018
Corn stover (kg CO_2-eq/kg)	0,10	You et al. [44]
Deionised water (kg CO_2-eq/kg)	0,0016	EcoInvent v3.3
Diammonium phosphate (kg CO_2-eq/kg)	1,09	GREET 2018
Ethanol (kg CO_2-eq/kg)	1,27	Idemat 2015
Glucoamylase (kg CO_2-eq/kg)	5,51	GREET 2018
Glucose (kg CO_2-eq/kg)	0,70	GREET 2018
Host nutrients (kg CO_2-eq/kg)	0,0045	Appendix
HP steam (kg CO_2-eq/MJ)	0,024	EcoInvent v3.3
Hydrochloric acid (kg CO_2-eq/kg)	1,71	EcoInvent v3.3
Hydroelectric energy (kg CO_2-eq/kWh)	0,006	Koffi et al. [59]
Hydrogen (liquid) (kg CO_2-eq/kg)	2,13	EcoInvent v3.3
Lime (kg CO_2-eq/kg)	0,74	Idemat 2015
LP steam (kg CO_2-eq/MJ)	0,024	EcoInvent v3.3
Magnesium sulfate (kg CO_2-eq/kg)	0,48	EcoInvent v3.3
Magnesium sulfate (kg CO_2-eq/kg)	0,48	EcoInvent v3.3
Makeup water (kg CO_2-eq/t)	1,74	You et al. [44]
MEA (kg CO_2-eq/kg)	2,76	EcoInvent v3.3
MP steam (kg CO_2-eq/MJ)	0,024	EcoInvent v3.3
NaOH (kg CO_2-eq/kg)	2,29	EcoInvent v3.3
Natural gas (kg CO_2-eq/MMBTU)	15,19	You et al. [44] Including production and combustion
Natural gasoline (kg CO_2-eq/MJ)	0,056	RVO
Palladium (primary) (kg CO_2-eq/kg)	5199,27	Idemat2015
Photovoltaic energy (kg CO_2-eq/kWh)	0,030	Amponsah et al. [60]
Potassium phosphate (kg CO_2-eq/kg)	0,04	GREET 2018
Potassium phosphate (kg CO_2-eq/kg)	0,042	GREET 2018
Power (kg CO_2-eq/kWh)	0,42	You et al. [44]
Power (kg CO_2-eq/MJ)	0,17	EcoInvent v3.3
Raw shale gas (kg CO_2-eq/GJ (HHV basis)	8,8	You et al. [44]
Sulfur dioxide (kg CO_2-eq/kg)	0,49	EcoInvent v3.3
Sulfuric acid, 93% (kg CO_2-eq/kg)	0,11	Idemat 2015
TEG ((kg CO_2-eq/kg)	1,97	EcoInvent v3.3
Urea (kg CO_2-eq/kg)	3,61	EcoInvent v3.3
Wind energy (kg CO_2-eq/kWh)	0,010	Koffi et al. [59]
Yeast (kg CO_2-eq/kg)	2,35	GREET 2018

8.1 Life cycle inventory

8.1.1 Ethylene production through thermal cracking of shale gas

Table A2: *GHG emissions related to shale gas extraction [42]*

Process	GHG emissions (kg CO_2-eq/GJ)
Pad construction and production	
Casing manufacture	0,32
Cement manufacture	0,06
Completion flowback: methane (XTO)	0,05
Completion flowback: carbon dioxide (XTO)	0,24
Diesel (well to refinery)	0,02
Drilling (XTO)	0,19
Field separation equipment losses (EPA)	0,08
Gathering compressor losses (EPA)	0,31
Gathering system compressors: Engine exhaust (EPA)	1,07
Gathering system compressors: Engine exhaust (XTO)	3,52
Hydraulic fracturing (XTO)	0,15
Pneumatic devices & Chemical injection pumps (EPA)	1,74
Production blowdowns (EPA)	0,03
Road transportation for well maintenance (XTO)	0,42
Sand transport (road)	0,02
Sand transport (train)	0,08
Slickwater additive manufacture	0,01
Venting from liquids unloading (XTO)	0,29
Wastewater transport	0,20
Total	**8,80**

Translating raw shale gas input to GHG emissions related to shale gas extraction:

835,50 MMSCFD	*MMSCFD: million standard cubic feet gas per day*
= 34,81 MMSCFH	*MMSCFH: million standard cubic feet gas per hour*
= 0,00028 MMSCF/$kg_{ethylene}$	*For a production of 125 tons ethylene/h*
= 0,0000079 Mm^3	*SCF to m^3*
= 7,889 m^3	*Raw shale gas has a heating value of 43,9 MJ/m^3 [66]*
= 346,20 MJ	*Emission factor: 8,8 kg CO_2-eq/GJ*
= 3,05 kg CO_2-eq/$kg_{ethylene}$	*Total emissions before allocation*

Translating natural gas input to GHG emissions related to burning:

2254,10 MMBTU	
= 2380,04 GJ	*MMBTU to GJ*
= 2380036,57 MJ	*For a production of 125 tons ethylene/h*
= 19,04 MJ/$kg_{ethylene}$	*Specific energy of natural gas: 53,6 MJ/kg*
= 0,36 kg natural gas/$kg_{ethylene}$	*Emission factor: 0,7 kg CO_2-eq/kg (Idemat 2015)*
= 0,25 kg CO_2-eq/$kg_{ethylene}$	

Following this method, an emission factor of 13,82 kg CO_2-eq/MMBTU was obtained. For computing GHG emissions, the emission factor of 15,19 by You et al. [44] was used. Reasons for the difference: specific energy differs for other natural gas compositions or updated emission factor used from more recent EcoInvent database.

Table A3: *Total life cycle GHG emissions for manufacturing ethylene by thermal cracking (mass allocation)*

Ethylene from thermal cracking of shale gas				**Percentage of total**
Total emissions	Shale gas extraction:	0,53	kg CO_2-eq/$kg_{ethylene}$	32%
	Shale gas processing:	0,11		6%
	Ethylene production:	1,02		61%
	Transportation of ethane and shale gas:	0,01		1%
	Total:	1,68		100%

Table A4: *Total life cycle GHG emissions for manufacturing ethylene by thermal cracking (economic allocation)*

Ethylene from thermal cracking of shale gas				**Percentage of total**
Total emissions	Shale gas extraction:	0,43	kg CO_2-eq/$kg_{ethylene}$	26%
	Shale gas processing:	0,09		5%
	Ethylene production:	1,11		67%
	Transportation of ethane and shale gas:	0,01		1%
	Total:	1,64		100%

Table A5: *Total life cycle GHG emissions for manufacturing ethylene by thermal cracking (values from literature [44])*

Ethylene from thermal cracking of shale gas (reference)				**Percentage of total**
Total emissions	Shale gas extraction:	0,40	kg CO_2-eq/$kg_{ethylene}$	28%
	Shale gas processing:	0,10		7%
	Ethylene production:	0,92		64%
	Transportation of ethane and shale gas:	0,01		1%
	Total:	1,44		100%

8.1.2 Ethylene manufacturing from biomass

8.1.2.1 Corn stover pathway

Table A6: *GHG emissions related to production of host nutrients*

Nutrients	Fraction	Mass of nutrient (for 0,0053 kg host nutrients)	GHG emissions (kg CO_2-eq/$kg_{ethylene}$)
Ammonium phosphate	0,34	0,0018	0,0040
Potassium phosphate	0,49	0,0026	0,0001
Magnesium sulfate	0,07	0,0004	0,0002
Calcium chloride	0,10	0,0005	0,0005
		Emission factor:	**0,0048**

Table A7: *Calculation of emission factor for corn steep liquor, glucose, diammonium phosphate and potassium phosphate. Data extracted from GREET 2018*

Corn steep liquor (CSL)

Total emissions (transportation + production)	g per ton CSL	kg per kg CSL	kg CO_2-eq/kg_{CSL}
CH_4	1751,21	0,00	0,05
N_2O	2522,78	0,00	0,72
CO_2	736159,69	0,74	0,74
		Emission factor:	**1,50**

Glucose

Total emissions (transportation + production)	g per ton glucose	kg per kg glucose	kg CO_2-eq/$kg_{glucose}$
CH_4	1233,68	0,00	0,04
N_2O	753,18	0,00	0,22
CO_2	450290,09	0,45	0,45
		Emission factor:	**0,70**

Diammonium phosphate (DAP)

Total emissions (transportation + production)	g per ton DAP	kg per kg DAP	kg CO_2-eq/kg_{DAP}
CH_4	2572,75	0,00	0,07
N_2O	21,33	0,00	0,01
CO_2	1009.50	1,01	1,01
		Emission factor:	**1,09**

Potassium phosphate (PP)

Total emissions (transportation + production)	**g per ton PP**	**kg per kg PP**	**kg CO_2-eq/kg_{PP}**
CH_4	58,00	0,00	0,00
N_2O	0,17	0,00	0,00
CO_2	40.70	0,04	0,04
		Emission factor:	**0,04**

Table A8: *Total life cycle GHG emissions ethylene manufacturing from corn stover (mass allocation)*

Ethylene from corn stover				**Percentage of total (excluding sequestration)**
Total emissions	Feedstock production:	0,63	kg CO_2-eq/$kg_{ethylene}$	29%
	Ethanol production:	0,99		47%
	Ethylene production:	0,50		23%
	Transportation:	0,01		1%
	Sequestration	-3,10		/
	Total:	-0,97		100%

Table A9: *Total life cycle GHG emissions ethylene manufacturing from corn stover (economic allocation)*

Ethylene from corn stover				**Percentage of total (excluding sequestration)**
Total emissions	Feedstock production:	0,58	kg CO_2-eq/$kg_{ethylene}$	29%
	Ethanol production:	0,92		46%
	Ethylene production:	0,50		25%
	Transportation:	0,01		1%
	Sequestration	-3,10		/
	Total:	-1,09		100%

Table A10: *Total life cycle GHG emissions for manufacturing ethylene from corn stover (values from literature [44])*

Ethylene from corn stover (reference)				**Percentage of total (excluding sequestration)**
Total emissions	Feedstock production:	0,57	kg CO_2-eq/$kg_{ethylene}$	28%
	Ethanol production:	0,99		48%
	Ethylene production:	0,48		24%
	Transportation:	0,01		1%
	Sequestration	-3,10		/
	Total:	-1,05		1

8.1.2.2 Corn grain pathway

Table A11: *Calculation of emission factor for alpha-amylase, glucoamylase and yeast. Data from GREET 2018.*

Alpha-amylase

Total emissions (transportation + production)	**g per ton alpha-amylase**	**kg per kg alpha-amylase**	**kg CO_2-eq/$kg_{alpha\text{-}amylase}$**
CH_4	2566,25	0,00	0,07
N_2O	21,98	0,00	0,01
CO_2	1126.90	1,13	1,13
		Emission factor:	**1,21**

Glucoamylase

Total emissions (transportation + production)	**g per ton glucoamylase**	**kg per kg glucoamylase**	**kg CO_2-eq/$kg_{glucoamylase}$**
CH_4	10891,17	0,01	0,31
N_2O	810,86	0,00	0,23
CO_2	4973.24	4,97	4,97
		Emission factor:	**5,51**

Yeast

Total emissions (transportation + production)	**g per ton yeast**	**kg per kg yeast**	**kg CO_2-eq/kg_{yeast}**
CH_4	6579,24	0,01	0,18
N_2O	63,74	0,00	0,02
CO_2	2149.67	2,15	2,15
		Emission factor:	**2,35**

Table A12: *Total life cycle GHG emissions for ethylene manufacturing from corn grain (mass allocation)*

Ethylene from corn grain				**Percentage of total (excluding sequestration)**
Total emissions	Feedstock production:	0,66	kg CO_2-eq/$kg_{ethylene}$	33%
	Ethanol production:	0,80		40%
	Ethylene production:	0,50		25%
	Transportation:	0,05		3%
	Sequestration	-3,10		/
	Total:	-1,09		100%

Table A13: *Total life cycle GHG emissions for ethylene manufacturing from corn grain (economic allocation)*

Ethylene from corn grain				**Percentage of total (excluding sequestration)**
Total emissions	Feedstock production:	1,00	kg CO_2-eq/$kg_{ethylene}$	36%
	Ethanol production:	1,22		44%
	Ethylene production:	0,50		18%
	Transportation:	0,05		2%
	Sequestration	-3,10		/
	Total:	-0,34		100%

Table A14: *Total life cycle GHG emissions for manufacturing ethylene from corn grain (values from literature [44])*

Ethylene from corn grain (reference)				**Percentage of total (excluding sequestration)**
Total emissions	Feedstock production:	0,96	kg CO_2-eq/$kg_{ethylene}$	37%
	Ethanol production:	1,12		43%
	Ethylene production:	0,47		18%
	Transportation:	0,05		2%
	Sequestration	-3,10		/
	Total:	-0,50		100%

8.1.3 Ethylene production through plasma-assisted methane coupling

8.1.3.1 Gas phase system (total purge stream combustion)

Translating raw shale gas input to GHG emissions related to shale gas extraction:

241,9 kg/h	*Input of raw shale gas*
= 61,40 m^3/h	*Raw shale gas has a heating value of 43,9 MJ/m3*
= 2695,46 MJ/h	*Emission factor: 8,8 kg CO_2-eq/GJ*
= 23,72 kg CO_2-eq/h	*Total GHG emissions related to feedstock production*
= 0,26 kg CO_2-eq/$kg_{ethylene}$	*For a production of 88,96 $kg_{ethylene}$/h*

Table A15: *GHG emissions related to cooling systems (Gas phase system, total purge stream combustion)*

Electricity demand for cooling systems	**1 kg ethylene**	**GHG emissions (kg CO_2-eq/$kg_{ethylene}$)**	
		Mass allocation	**Economic allocation**
Methane compression (kW)	4,49	1,13	1,58
Methane expansion (kW)	-1,22	-0,31	-0,43

Table A16: *Total life cycle GHG emissions for plasma-assisted ethylene production (Gas phase system, total purge stream combustion, mass allocation)*

				Percentage of total
Total emissions	Shale gas extraction:	0,26	kg CO_2-eq/$kg_{ethylene}$	3%
	Shale gas dehydration:	0,02		0%
	Ethylene production:	7,94		96%
	Transportation:	0,01		0%
	Total:	8,24		100%

GHG emissions from power consumption:	7,10	kg CO_2-eq/$kg_{ethylene}$
Percentage of total emissions:	86%	
Total emissions when using renewable energy sources:	1,31	kg CO_2-eq/$kg_{ethylene}$

Table A17: *Total life cycle GHG emissions for plasma-assisted ethylene production (Gas phase system, total purge stream combustion, economic allocation)*

				Percentage of total
Total emissions	Shale gas extraction:	0,26	kg CO_2-eq/$kg_{ethylene}$	2%
	Shale gas dehydration:	0,03		0%
	Ethylene production:	11,05		97%
	Transportation:	0,01		0%
	Total:	11,35		100%

GHG emissions from power consumption:	9,87	kg CO_2-eq/$kg_{ethylene}$
Percentage of total emissions:	87%	
Total emissions when using renewable energy sources:	1,65	kg CO_2-eq/$kg_{ethylene}$

8.1.3.2 Gas phase system (partial purge stream combustion)

Table A18: *GHG emissions related to cooling system (Gas phase system, partial purge stream combustion)*

Electricity demand for cooling systems	**1 kg ethylene**	**GHG emissions** (kg CO_2-eq/$kg_{ethylene}$)	
		Mass allocation	**Economic allocation**
Methane compression (kW)	4,49	0,99	1,54
Methane expansion (kW)	-1,22	-0,27	-0,42

Table A19: *Total life cycle GHG emissions for plasma-assisted ethylene production (Gas phase system, partial purge stream combustion, mass allocation)*

				Percentage of total
Total emissions	Shale gas extraction:	0,26	kg CO_2-eq/$kg_{ethylene}$	4%
	Shale gas dehydration:	0,02		0%
	Ethylene production:	6,62		95%
	Transportation:	0,01		0%
	Total:	6,91		100%

GHG emissions from power consumption:	6,18	kg CO_2-eq/$kg_{ethylene}$
Percentage of total emissions:	89%	
Total emissions when using renewable energy sources:	0,87	kg CO_2-eq/$kg_{ethylene}$

Table A20: *Total life cycle GHG emissions for plasma-assisted ethylene production (Gas phase system, partial purge stream combustion, economic allocation)*

				Percentage of total
Total emissions	Shale gas extraction:	0,26	kg CO_2-eq/$kg_{ethylene}$	2%
	Shale gas dehydration:	0,03		0%
	Ethylene production:	10,35		97%
	Transportation:	0,01		0%
	Total:	10,66		100%

GHG emissions from power consumption:	9,68	kg CO_2-eq/$kg_{ethylene}$
Percentage of total emissions:	91%	
Total emissions when using renewable energy sources:	0,12	kg CO_2-eq/$kg_{ethylene}$

8.1.3.3 Hybrid process (total purge stream combustion)

Table A21: *GHG emissions related to cooling system (Hybrid system, total purge stream combustion)*

Electricity demand for cooling systems	**1 kg ethylene**	**GHG emissions** (kg CO_2-eq/$kg_{ethylene}$)	
		Mass allocation	**Economic allocation**
Methane compression (kW)	4,27	1,20	1,55
Methane expansion (kW)	-1,16	-0,33	-0,42

Table A22: *Total life cycle GHG emissions for plasma-assisted ethylene production (Hybrid system, total purge stream combustion, mass allocation)*

				Percentage of total
Total emissions	Shale gas extraction:	0,21	kg CO_2-eq/$kg_{ethylene}$	3%
	Shale gas dehydration:	0,02		0%
	Ethylene production:	7,48		97%
	Transportation:	0,01		0%
	Total:	7,72		100%

GHG emissions from power consumption:	6,58	kg CO_2-eq/$kg_{ethylene}$
Percentage of total emissions:	85%	
Total emissions when using renewable energy sources:	1,27	kg CO_2-eq/$kg_{ethylene}$

Table A23: *Total life cycle GHG emissions for plasma-assisted ethylene production (Hybrid system, total purge stream combustion, economic allocation)*

				Percentage of total
Total emissions	Shale gas extraction:	0,21	kg CO_2-eq/$kg_{ethylene}$	2%
	Shale gas dehydration:	0,02		0%
	Ethylene production:	9,61		98%
	Transportation:	0,01		0%
	Total:	9,86		100%

GHG emissions from power consumption:	8,46	kg CO_2-eq/$kg_{ethylene}$
Percentage of total emissions:	86%	
Total emissions when using renewable energy sources:	1,53	kg CO_2-eq/$kg_{ethylene}$

8.1.3.4 Hybrid process (no purge stream combustion)

Table A24: *GHG emissions related to cooling system (Hybrid system, no purge stream combustion)*

Electricity demand for cooling systems	**1 kg ethylene**	**GHG emissions** (kg CO_2-eq/$kg_{ethylene}$)	
		Mass allocation	**Economic allocation**
Methane compression (kW)	4,27	1,01	1,51
Methane expansion (kW)	-1,16	-0,28	-0,41

Table A25: *Total life cycle GHG emissions for plasma-assisted ethylene production (Hybrid system, no purge stream combustion, mass allocation)*

				Percentage of total
Total emissions	Shale gas extraction:	0,21	kg CO_2-eq/$kg_{ethylene}$	3%
	Shale gas dehydration:	0,02		0%
	Ethylene production:	5,96		96%
	Transportation:	0,01		0%
	Total:	6,20		100%

GHG emissions from power consumption:	5,55	kg CO_2-eq/$kg_{ethylene}$
Percentage of total emissions:	90%	
Total emissions when using renewable energy sources:	0,76	kg CO_2-eq/$kg_{ethylene}$

Table A26: *Total life cycle GHG emissions for plasma-assisted ethylene production (Hybrid system, no purge stream combustion, economic allocation)*

				Percentage of total
Total emissions	Shale gas extraction:	0,21	kg CO_2-eq/$kg_{ethylene}$	2%
	Shale gas dehydration:	0,02		0%
	Ethylene production:	8,90		97%
	Transportation:	0,01		0%
	Total:	9,14		100%

GHG emissions from power consumption:	8,28	kg CO_2-eq/$kg_{ethylene}$
Percentage of total emissions:	91%	
Total emissions when using renewable energy sources:	0,97	kg CO_2-eq/$kg_{ethylene}$

8.2 Comparison

Table A27: *Comparison of the five different ethylene production processes in terms of water consumption, chemicals consumption, electricity demand, GHG emissions and breakeven ethylene price*

	Thermal cracking pathway	Corn grain pathway	Corn stover pathway	One step plasma process (TPSC)	One step plasma process (PPSC)	Hybrid plasma process (TPSC)	Hybrid plasma process (NPSC)
Water consumption ($kg/kg_{ethylene}$)	11,50	14,63	14,79	23,39	23,39	91,70	91,70
Chemicals consumption ($kg/kg_{ethylene}$)	0,0008	0,07	0,81	0,29	0,29	0,24	0,24
Electricity consumption ($kWh/kg_{ethylene}$)	1,86	0,69	0,23	28,10	28,10	23,33	23,33
GHG emissions (kg CO_2-eq/ $kg_{ethylene}$; mass allocation)	1,68	2,01	2,13	8,24	6,91	7,72	6,20
GHG emissions (kg CO_2-eq/ $kg_{ethylene}$; economic allocation)	1,64	2,76	2,01	11,35	10,66	9,86	9,14
Breakeven ethylene price ($/kg)	0,35	1,25	2,03	3,35	3,35	2,71	2,71

Table A28: *Life cycle GHG emissions using different energy sources (kg CO_2-eq/$kg_{ethylene}$)*

		Thermal cracking	Corn grain	Corn stover	One step plasma process (TPSC)	One step plasma process (PPSC)	Hybrid plasma process (TPSC)	Hybrid plasma process (NPSC)
Mass allocation	**US energy mix**	1,68	2,01	2,13	8,24	6,91	7,72	6,20
	Wind	1,59	1,83	2,03	1,31	0,87	1,27	0,76
	Solar	1,60	1,84	2,04	1,65	1,17	1,58	1,03
Economic allocation	**US energy mix**	1,64	2,76	2,01	11,31	10,61	9,82	9,10
	Wind	1,57	2,53	1,91	1,72	1,21	1,56	1,03
	Solar	1,57	2,54	1,92	2,19	1,67	1,97	1,42