

# Reducing the CO<sub>2</sub> emissions of a Gas Cracker by Reforming Fuel Gas

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## Abstract

Ethylene is the most produced organic substance in the world and is a pillar in the chemical process industry. The production pathway is energy intensive and has a corresponding high carbon footprint. This work explores, simulates, and presents the possibility of reforming the fuel gas of a steam cracking furnace. Currently, methane (CH<sub>4</sub>) and hydrogen (H<sub>2</sub>) from the cracking furnace outlet makes up the fuel source. If H<sub>2</sub> produced by reformation of the current fuel can cover the energy demand of the steam cracking furnace, it can drastically reduce the CO<sub>2</sub> emissions.

*Keywords:* Decarbonizing, ethylene, steam cracking, reforming, fuel substitution, hydrogen production, ATR, Aspen HYSYS

## 1. Introduction

Cracking of hydrocarbons is the dominating ethylene production method. The highly endothermic reaction requires high temperatures to produce the desired products. Combustion of fossil fuel to produce the heat adds to the emissions and energy demand, resulting in 1-2 tons of CO<sub>2</sub> for every ton of produced ethylene. The combustion of fossil fuels to supply the steam cracking process, resulted in an emission of 200 million tons of CO<sub>2</sub> in 2000 and 300 million tons CO<sub>2</sub> in 2019 (Ren *et al.*, 2008; Amghizar *et al.*, 2020). With the Paris agreement from 2015, and the national goals of Norway towards a greener society, the exploration of different CO<sub>2</sub> reduction methods has become necessary.

Decarbonizing and/or reduction of the energy consumption in the industrial sector is a necessity to reach the climate goals of Norway. The possibilities are numerous in the refinery sector and can be divided into seven categories, namely fuel substitution, feedstock substitution, process intensification and optimization, recycling, product solution, energy recovery and Carbon Capture and Storage (CCS) or re-use (Negri and Lighthart, 2021). Industrial GreenTech (IGT) has a vision of making the industrial region in Grenland climate neutral by 2040 and have mapped out the current emission status and suggested some reduction possibilities. One of the suggested methods for evaluation is replacing the fuel to the crackers at INEOS. If this fuel gas is reformed to pure hydrogen, it can potentially reduce the current emissions of CO<sub>2</sub> (Aas *et al.*, 2020).

A steam cracker with ethane as feedstock, such as INEOS, has a product stream consisting mainly of ethylene, unconverted ethane, hydrogen, methane and some amount ethyne, propane, propene, propadiene, butane, butene, butadiene, pygas, and fuel oil (Ullmann's Encyclopedia of Industrial Chemistry, 1988). INEOS has ethylene as their most important product and the separated methane and hydrogen is burned in the cracker as fuel. The outlet of the combusted fuel is primarily H<sub>2</sub>O and CO<sub>2</sub> and is usually utilized for heating or steam export before being emitted to the atmosphere.

When producing hydrogen from hydrocarbon sources, the production pathway is most commonly divided into 3 sections. First a section to produce syngas, short for synthesis gas, which in this context refers to a mixture of H<sub>2</sub> and CO. The syngas can originate from both natural gas, heavier hydrocarbons or coal. Depending on application and the following process, the syngas is sent for processing to second section. This processing can be water-gas-shift (WGS) reaction, CO removal, or other treatments to obtain the desired composition and/or CO/H<sub>2</sub> ratios. The third section relates to reach the specifications of the H<sub>2</sub>, regarding purity and content of different contaminations (Moulijn *et al.*, 2013).

Mature methods for H<sub>2</sub> production originating from hydrocarbons is Steam Methane Reforming (SMR), Partial Oxidation (POX), Catalytic Partial Oxidation (CPOX) and Auto Thermal Reforming (ATR). Among more advanced, novel and/or promising methods for H<sub>2</sub> production originating from hydrocarbons is methane pyrolysis, integrated membrane reactors, integrated sorption-enhanced

systems, chemical looping variations and electric reforming (Wismann *et al.*, 2019; Basile *et al.*, 2015; Voldsund *et al.*, 2016).

## 2. Process Description

The reforming method utilized in this work is ATR, which is a highly developed and well-tested technology. ATR utilize O<sub>2</sub> and the production of the O<sub>2</sub> contributes to a higher production cost of the hydrogen. Even so, it is regarded as a more attractive option due to the planned construction of water electrolysis at Herøya Industry Park, close to the INEOS production plant (INOVYN, 2021; Krohn-Fagervoll, 2020). This opens the opportunity to purchase O<sub>2</sub> at a lower cost.

ATR is a combination of SMR and POX, where the reactor consists of a burner, a combustion section, and a catalyst bed section. The system is simulated in Aspen HYSYS v12 with various configurations, and partly maximized for hydrogen production. An ATR system along with the primary occurring reactions is illustrated in Figure 1. The methane is fed into the top section along with steam and oxygen. The reaction between CH<sub>4</sub> and O<sub>2</sub> is exothermic. The surplus heat is utilized in the endothermic section in the catalytic bed. This combination of reactions is making the reactor self-supplied with energy (Nielsen and Christiansen, 2011).

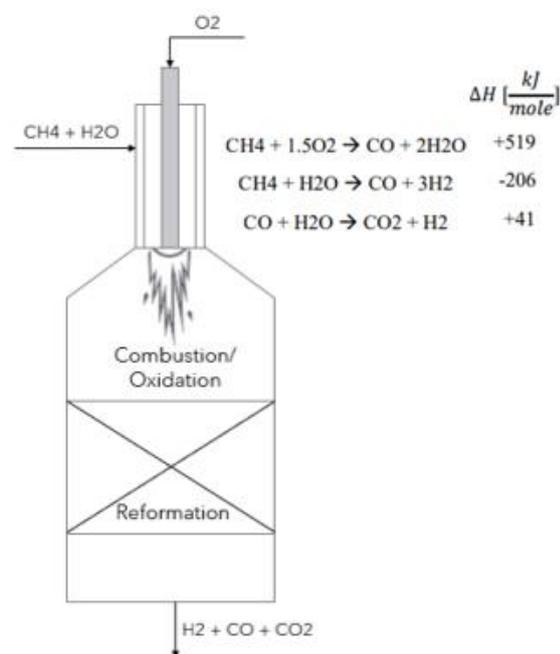


Figure 1: Illustration of an ATR based on a figure from Rostrup-Nielsen and Christiansen(2011). From Rustad (2021)

Compared to a fired furnace (SMR) the ATR is a system with reduced size and complexity. With no external heat supply required, the fuel cost to the reformer will disappear and lead to a reduction in the

CO<sub>2</sub> emission. Another advantage is that the ATR needs less water than an SMR. This is because the high temperature in an ATR leads to a high methane conversion. Additionally, oxygen helps with the prohibition of soot formation (Baltrusaitis and Luyben, 2015). There is a balance between the inlet oxygen flow rate and the temperature in the ATR, where more oxygen will lead to higher temperature. However, the temperature is limited by material and construction cost.

## 3. Simulations

The specifications and input to the simulation is based on several previous studies and literature (Moulijn *et al.*, 2013; Nielsen and Christiansen, 2011; Jakobsen, 2016; Soltani *et al.*, 2014; Chen *et al.*, 2010). Additionally, some input has been based on assumptions and simplifications.

All the simulations use the Peng Robinson equation of state. The pressure-drop over every heat exchanger is set to 10 kPa and there is assumed not to be a pressure drop in the reactors. There is also assumed no heat loss in the system and the adiabatic efficiency of the compressor is 75 %. All the reactors are simulated as Gibbs reactors (minimizing the Gibbs free energy). There is also assumed to be no build-up in the system. The initial separation step is suggested to be a membrane that separates out 95 mol% of the inlet hydrogen prior to the reforming system to a purity of 100 %. This is simulated as a component splitter. The component splitter is also used for simulating the CO<sub>2</sub> separation and the H<sub>2</sub> purification. The component splitters are merely to exemplify the possibility of different separation steps.

### 3.1. Burner comparison

The main goal of this project is to investigate if there are enough energy to cover the requirement of a steam cracker with reformed fuel. The natural starting point is to determine how much hydrogen is the minimum to keep the same production rate of ethylene. The current energy supply is combustion of the methane and the hydrogen that are products of the cracker. The amount of CH<sub>4</sub> and H<sub>2</sub> that is burned is the total amount of these components exiting the cracker. A typical amount is 5.5 wt% CH<sub>4</sub> and 4.0 wt% H<sub>2</sub> in the exit gas of the cracking furnace (Mathisen, 2021). This is in the same range as a standard steam cracker for ethylene production with ethane as feed (Ullmann, 1988) and is therefore assumed to be comparable with the actual composition at INEOS. The comparison is illustrated in Figure 2.

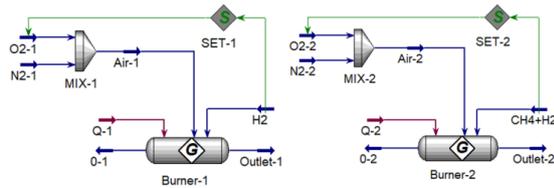


Figure 2: Flowsheet from Aspen HYSYS simulation of burners. Left is Burner 1 and right is Burner 2. From Rustad (2021)

An inlet flow of 150 ton ethane per hour will result in a flow of 514.2 kmole/h CH<sub>4</sub> and 2976.3 kmole/h H<sub>2</sub> on a molar basis. To simplify and to make the comparison on the same terms is two burners simulated in Aspen HYSYS. Burner 1 has pure hydrogen (100 mole%) as fuel and Burner 2 has a mix of hydrogen (14.73 mole%) and methane (85.27 mole%) as fuel. Both are combusted in air with a flow rate that gives 100 % conversion of the fuel, and both burners have the same inlet and outlet pressure and temperature. Burner 1 has a flow rate of 423 kmole/h, corresponding to the flow of hydrogen that enters the burner after reformation in Case 0 (base case, presented in 3.2). Burner 2 has a flow rate of 3491 kmole/h, corresponding to the flow of CH<sub>4</sub> and H<sub>2</sub> that exits the steam cracker (and is the inflow to the reforming process). Burner 1 and Burner 2 has a heat flow of  $-6.935 \times 10^8$  kJ/h and -

$7.478 \times 10^8$  kJ/h, respectively. The negative sign indicating that heat is going out.

### 3.2. Case 0 Base case

A snapshot of the base case simulation from Aspen HYSYS is presented in Fig. 3. The feed to the system is “Inlet flow, CH<sub>4</sub> and H<sub>2</sub>” with a flow rate of 514.2 kmole/h CH<sub>4</sub> and 2976.3 kmole/h H<sub>2</sub>. This is fed into a membrane where 95 mol% of the H<sub>2</sub> is separated out and sent directly to the burner. The retentate side of the membrane is mixed with steam with a ST/C ratio of 1.62 and compressed to 2300 kPa. The compressed flow is heated to 650 °C before entering the ATR. O<sub>2</sub> is added to the ATR with a O<sub>2</sub>/C ratio of 0.6, and the occurring reactions are highly exothermic, eliminating the need of external energy. The ATR outlet temperature is 1050 °C and the stream is partly utilized to heat the inlet flow to the ATR. The outlet of the ATR is cooled before being fed to two WGS reactors. One high temperature water-gas-shift (HT-WGS) and one low temperature water-gas-shift (LT-WGS) with the inlet temperature at 300 °C and 175 °C, respectively. The WGS reaction is slightly exothermic, and the process stream must be cooled both before and after the reactors.

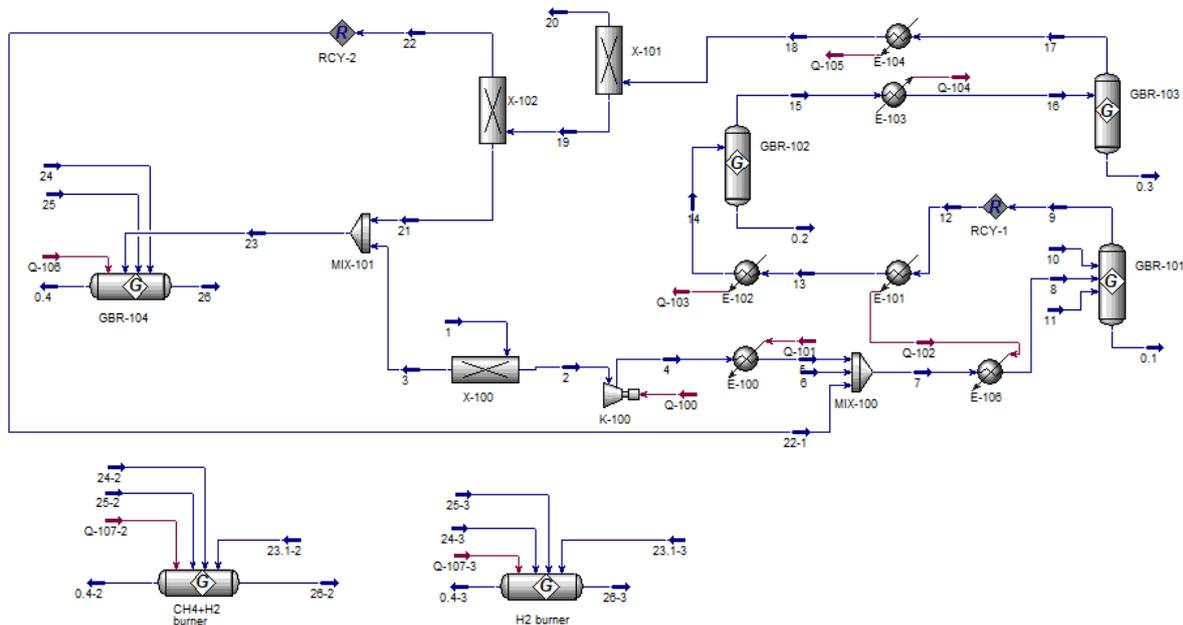


Figure 3: Flowsheet for Base Case. From Rustad (2021)

After the WGS reactors there are two separation processes simulated as component splitters. The first separates out 90 mol% of the CO<sub>2</sub> to a purity of 99.55 mol% and the second one separates out 90 mol% of the H<sub>2</sub> to a purity of 96.8 mol%. The two flows of hydrogen are sent to a burner. The combustion receives stoichiometric amount of air, and the outlet stream of the burner is mainly water

and nitrogen. The energy released from the combustion process (“Burner” in Figure 3) is representing the energy supplied to the steam cracking furnace

### 3.3. Case 1 Recycle stream

Case 1 has all the equal input parameters as Case 0 with one exception, being the gas exiting the H<sub>2</sub>

purification unit is recycled back and enters along with the steam prior to compression. The stream consists of approximately 60 mol% H<sub>2</sub>O, 27 mol% H<sub>2</sub>, 1 mol% CO<sub>2</sub> and minor amounts of CO and unconverted CH<sub>4</sub>. The flow amounts to 624.4 kmole/h. A snapshot of the simulation is presented in Figure 4. Recycling of this stream leads to a few observations. One being the reduced flow of inlet water, from 835 to 450.6 kmole/h, while remaining the ST/C ratio of 1.62. This is due to the content of water in the recycle. This will also result in a lower temperature at the ATR outlet which generally relates to lower conversion of methane. This can be seen from the increased flow of methane, from approximately 3 to 12 kmole/h. This can be compensated by increasing the inlet temperature of the inlet flow(s) or by increasing the flow of oxygen.

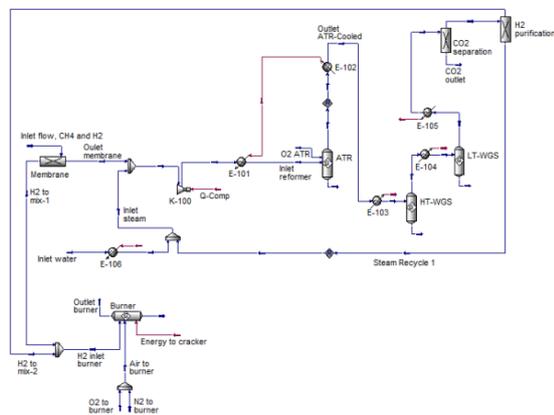


Figure 4: Case 1 Implementing a recycle. From Rustad (2021)

An optimization of the process is not completed at this stage for this case. The process flow in the system from the compressor and for all following the units is increased, and the result is a need for equipment and vessels with higher capacity and therefore higher cost. However, valuable H<sub>2</sub> will be fed back into the system causing the overall hydrogen production to increase.

### 3.4. Case 2 Additional inlet stream

Neither Case 0 nor Case 1 fulfilled the required amount of hydrogen to satisfy the desired energy supply. There are multiple approaches to increase the amount of hydrogen to the burner. The chosen approach was to have an additional inflow of ethane to the reforming system. The ethane is assumed to be available on site or easy to purchase since this is the raw material to the cracker. More specifically, the ethane is added between the membrane and the compressor, together with the recycle stream. This can be seen from Figure 5. The ethane flow was adjusted until the desired flow of hydrogen to the burner was reached. Note that this both increases the steam and oxygen consumption, as discussed in the

following chapters. If all ratios, temperatures, and pressures from the base case are kept constant, the inflow of ethane is adjusted to approximately 40 kmole/h.

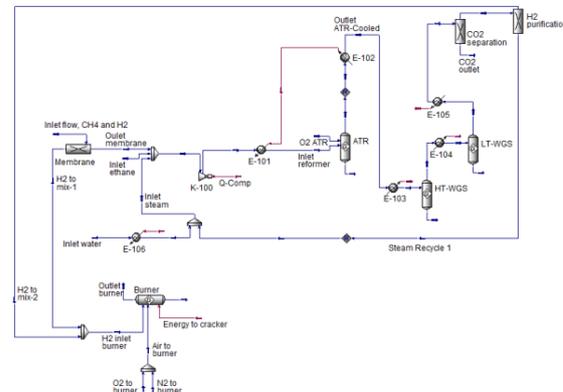


Figure 5: Case 2 Adding ethane to the process. From Rustad (2021)

### 3.5. Case 3 Adding CO<sub>2</sub>

The main advantage of the ATR process is its self-supply of thermal energy. However, there are some challenges related to this reforming method. The temperature in the reactor may exceed the limits of the material and/or lead to total combustion. In the previous cases (Case 0, 1, and 2) this temperature was altered by selecting an appropriate ST/C and O<sub>2</sub>/C ratio. More steam or less oxygen leads to a lower temperature and vice versa. The optimum is a tradeoff between conversion, consumption and cost, but that is not pursued here. Reforming by CO<sub>2</sub> is referred to as dry reforming and has received some attention in literature, both encouraging and constructive. It is regarded as an unfavorable option compared to other methods available (Oyama *et al.*, 2012). It is in this work chosen to add a CO<sub>2</sub> flow as an example.

### 3.6. Case 4 Replacing HT-and LT WGS with MT-WGS

Replacing two reactors of high and low temperature with one medium temperature reactor has obvious advantages, considering the reduction in number of units. Regarding hydrogen production, an MT-WGS reactor is an attractive solution, because it potentially reduces the required steam to the process. It is more challenging to develop a catalyst which functions adequately in the whole interval, being active in the lower region and stable in the higher region. However, the advances in catalyst technology have made the MT-WGS the preferred solution when producing hydrogen. (Moulijn *et al.*, 2013)

The MT-WGS reactor is illustrated in Figure 6 and has an inlet temperature of 225 °C. The outlet temperature increases to 366 °C. This is an increase

of 141 °C compared with the increase in HT and LT in Case 0 of 121.8 and 45.3 °C, respectively.

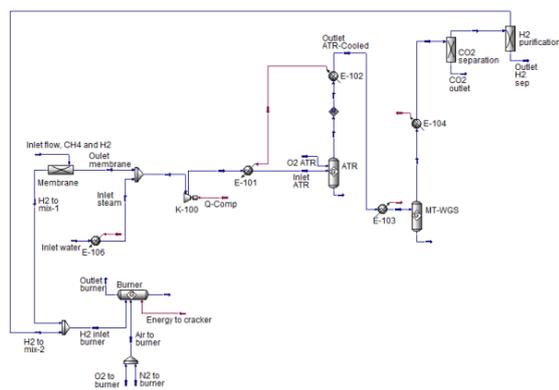


Figure 6: Case 4 Replacing HT- and LT WGS with MT-WGS. From Rustad (2021)

#### 4. Comparisons

Using Case studies in Aspen HYSYS is a method that can be used to analyze the effect of a parameter variation in a process. This is done by choosing an independent variable which is varied within a chosen interval, and with a chosen step size. The dependent variables of interest are selected and there is only one independent variable that varies at the time. The input and results from Case studies of Case 2 are presented.

The ST/C ratio was varied from 0.5 to 5.0, corresponding to an inlet flow of water in the range of 300 to 3000 kmole/h. The result was that increased ratio led to a decrease in the outlet temperature of the ATR. Not surprisingly did it also lead to an increase in the energy stream to the heat exchanger prior to the ATR (E-102), because of a higher flow. The outlet molar composition flow of H<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> increased, while for CO it decreased. The flow of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> only changed slightly, while the O<sub>2</sub> remained at zero.

The O<sub>2</sub>/C ratio was varied from 0.2 to 1.0, corresponding to 120 to 600 kmole/h of O<sub>2</sub>. This ratio should be one of the last parameters to be optimized due to the fact that it depends on the pressure, temperature and the ST/C ratio. (de Souza, 2015) Too much oxygen could also lead to total combustion which will result in a lower hydrogen production and temperature above material restrictions. The increase in the O<sub>2</sub>/C ratio gave an increase in the outlet temperature of the ATR (725 to 1936 °C). The energy stream to E-102 remained constant because the identical flow was risen to the identical temperature throughout the case study. The outlet molar composition changes after all the CH<sub>4</sub> is consumed. This happened at an O<sub>2</sub> flow of 375 kmole/h (which is a O<sub>2</sub>/C ratio of 0.635). Until that point is there an increase in CO and a decrease in CO<sub>2</sub>. Hydrogen reaches its highest fraction when the flow of O<sub>2</sub> is at 315 kmole/h (which is a O<sub>2</sub>/C ratio

of 0.53). The composition of H<sub>2</sub>O decreases until it turns before the flow of O<sub>2</sub> reached 300 kmole/h.

The case study for the pressure in the ATR was conducted by reusing the ATR in the Case 2 and complete this study without the upstream and downstream part. The case study involves a pressure from 2000 to 10000 kPa. The result was that an increase in pressure gave an increase in temperature. The outlet molar composition has less H<sub>2</sub> and CO and more H<sub>2</sub>O. CH<sub>4</sub> increased slightly and CO<sub>2</sub> decreased slightly.

The case study for the temperature of oxygen to the ATR was in the interval of 20 to 750 °C. The increase in temperature of O<sub>2</sub> also increased the outlet temperature of the ATR (from 1050 to 1161 °C). This caused the outlet molar composition to have more CO and less CO<sub>2</sub>, a slight increase in the H<sub>2</sub>O content and decrease in H<sub>2</sub>, while CH<sub>4</sub> did not change substantially, and the oxygen and ethane remained unchanged.

The case study for the inlet temperature to the HT-WGS was conducted between 250 and 450 °C. Not surprisingly did the outlet temperature increase along with the inlet temperature. It also showed that outlet CO and H<sub>2</sub>O molar composition increased, and CO<sub>2</sub> and H<sub>2</sub> decreased. CH<sub>4</sub> (inert), C<sub>2</sub>H<sub>6</sub> (inert) and O<sub>2</sub> remained constant. The molar H<sub>2</sub>/CO ratio in the outlet got lower when the temperature got higher with 13.3 at 300 °C and 10.7 at 350 °C.

The same trend lines can be observed when increasing the inlet temperature for the LT-WGS in the range from 150 to 250 °C. The H<sub>2</sub>/CO ratio decreased from 14.1 at 175 °C to 95.2 at 200 °C.

The case study for varying the flow of oxygen (and nitrogen) was varying from 1000 to 3000 kmole/h. Heat is released and is representing the energy supply to the ethane cracking furnace, meaning that the highest absolute value of the heat flow is desired. This value is at 2201 kmole/h of oxygen, in the case study this is exactly stoichiometrically. Before the amount reaches the stoichiometric amount there is a descending flow of H<sub>2</sub> and CO. When the flow surpasses the stoichiometric amount of O<sub>2</sub>, the H<sub>2</sub> and CO are stable at zero, while the molar composition of CO<sub>2</sub> and H<sub>2</sub>O decreases and oxygen increases.

The case study varying the temperature into the ATR varied in the range of 600 to 800 °C. Increased temperature leads naturally to a higher heat flow to the heat exchanger before the reformer. Keeping all other variables constant, it is observed that increased temperature leads to increased CO and H<sub>2</sub>O composition in the ATR outlet, and a decrease for H<sub>2</sub> and CO<sub>2</sub>. This might appear unfavorable but the increase in the CO results in higher possible conversion in the following WGS reactors. The overall molar flow of the hydrogen increases.

Tab.1 presents a summary of the effects on outlet flow of CO<sub>2</sub> and the overall H<sub>2</sub> production. The

base case simulation had a molar flow of 524 kmole/h of CO<sub>2</sub> and 4450 kmole/h of H<sub>2</sub>. The numbers presented in the table are in a range, representing the lowest and highest values achieved within the limits used in the corresponding case study and again is the recycle not attached. The pressure in the ATR was analyzed by reusing the

reactor in Aspen HYSYS, eliminating the possibility to see the CO<sub>2</sub> and H<sub>2</sub> molar flow rates directly. The interval given in the table is therefore the minimum and maximum found when manually testing various pressures in the interval of 100 to 5000 kPa.

Table 1: Summary of CO<sub>2</sub> outlet flow and H<sub>2</sub> production for the various case studies. From Rustad (2021)

Variables	CO <sub>2</sub> outlet flow [kmole/h]	H <sub>2</sub> production [kmole/h]	Note
ST/C-ratio	361.3-535.7	4258-4614	Higher ratio results in higher CO <sub>2</sub> and H <sub>2</sub> molar flows
O <sub>2</sub> /C-ratio	235.1-534.1	3747-4464	Higher ratios result in higher CO <sub>2</sub> . H <sub>2</sub> production peaks when O <sub>2</sub> /C is 0.57
Inlet temp. HT- and LT-WGS	HT: 526.0-516.3 LT: 504.5-528.0	HT: 4444-4451 LT: 4434-4453	Increasing temperature results in degreasing flows of CO <sub>2</sub> and H <sub>2</sub>
Inlet temp. MT-WGS	386.9-419.9	4227-4252	Increasing temperature results in degreasing flows of CO <sub>2</sub> and H <sub>2</sub>
Pressure ATR	522.7-525.8	4432-4457	Increasing pressure results in degreasing flow of CO <sub>2</sub> and H <sub>2</sub>
Inlet temp. ATR	523.0-525.0	4445-4455	Increasing temperature results in increase in flow of CO <sub>2</sub> and H <sub>2</sub>
Inlet temp. of O <sub>2</sub> to ATR	524.0-524.9	4450-4454	Increasing temperature results in slightly increase in flow of CO <sub>2</sub> and H <sub>2</sub>
Flow of CO <sub>2</sub> to ATR	420.4-581.4	4182-4222	Increasing flow results in increase in flow of CO <sub>2</sub> and decrease in flow of H <sub>2</sub>

As can be seen from Tab.1 hydrogen production is favored at high ST/C ratio, O<sub>2</sub>/C ratio of 0.57, low inlet temperatures to the WGS reactors, low pressure, low flow of CO<sub>2</sub> and high temperature in the ATR. A 'perfect' system has minimum amount of CO<sub>2</sub> produced and maximum amount of H<sub>2</sub> produced.

#### 4.1. Evaluation and discussion

The most important output of each simulation is the energy requirement for the ethane steam cracking furnace. Case 2 has enough energy to meet this requirement. However, it is highly advantageous that the process operates economically, in a sense that consumption of ethane and oxygen is at minimum, as this is purchased. The increase in flow throughout the system will also be a determining factor when sizing the equipment, which will affect the investment cost. So, there will be a tradeoff

between efficiency, amount produced, operational cost and capital cost.

The selection of optimal operation conditions in an overall sense is not possible to complete properly when the cost is not a part of the equation and only one parameter is evaluated at the time. Nevertheless, there are some parameters that are more advantageous to promote than others. CH<sub>4</sub> and ethane conversion, H<sub>2</sub> and CO<sub>2</sub> production, as well as the possibility of steam export. This system will by no means be completely optimized, neither for production or conversion, nor for cost. This is a feasibility study and an investigation of the possibility to implement a reforming process for a cracking production plant, such as INEOS. The focus will therefore be on high hydrogen production. But there are some advantages and disadvantages related to all the cases described and the main ones are summarized in Table 2.

From Tab.1 and Tab.2 it is observable that some choices for further work are more appealing than others. Case 2 and 4 are the ones that overall comes out on the winning side of the selection. Both may accomplish a satisfactory production of hydrogen, both consists of well tested technologies that are ready for implementation, and both have potential for further optimization along with their possible

steam export. The hydrogen production is likely to increase when optimal conditions are chosen.

To summarize what favors conversion of hydrocarbons and production of hydrogen, the following points as seen from the simulations, case studies, and literature research. The trend lines are in agreement with previous studies (Nielsen and Christiansen, 2011; Baltrusaitis and Luyben, 2015; Rashid, 2019; Jakobsen, 2016; Souza *et al.*, 2015).

Table 2: Main advantages and disadvantages for the simulated cases (Case 0 - 4). From Rustad (2021)

Cases	Main advantages	Main disadvantages
Case 0	Lowest complexity	Does not produce enough H2 Low utilization of resources
Case 1	Increased utilization of resources Higher H2 production (less lost)	Does not produce enough H2
Case 2	Produce enough hydrogen	Higher flow throughout the system
Case 3	Produce enough hydrogen Easier temperature control	Lower conversion
Case 4	One less reactor and heat exchanger	Lower H2 production (but can be compensated with ethane inflow) Higher flow throughout the system

Low pressure. It should be as low as possible and is generally limited by the downstream purification steps, the volumetric flow through the system (which affect the dimensions), and carbon formation.

High temperatures, both in the inlet and outlet of the ATR are generally limited by the material and the risk of total combustion.

High ST/C ratio. The steam contributes to higher hydrogen production, as well as reduction of coke formation. The downside is increased energy requirement (because the temperature drops with an increase of steam) and the flow through the system. O<sub>2</sub>/C ratio gave varying results and highly affects the outlet temperature. Keeping a ST/C ratio of 1.62 was the highest fraction of H<sub>2</sub> in the outlet when the O<sub>2</sub>/C ratio was 0.53. The optimum ratio is affected by the inlet temperature, ST/C ratio and pressure, and should therefore be the last parameter to be optimized. This is not evaluated further but a ST/C ratio in the range 0.5-0.6 should be adequate for this purpose.

Low inlet temperature to the WGS reactors should be as low as possible within the limits of the catalyst and the dew point of the inlet gas. The energy out of the burner (to the cracking furnace) is maximized when the inlet is combusted stoichiometrically.

#### 4.2. Case 5 Partly maximized for H<sub>2</sub> production

Case 5 has its starting point from Case 2 and the goal is to increase the H<sub>2</sub> production. The snapshot from Aspen HYSYS is identical to Case 2 (Figure 5). Since the CO<sub>2</sub> separation and H<sub>2</sub> purification is not decided, and absorption with MDEA and PSA is considered as the state-of-the-art technology the

pressure is not reduced further. The reduction would improve the production rate but since there is likely to be a pressure requirement down the process line it is kept the same. The ST/C ratio is increased to 2, which is the highest value within the normal operating condition of an ATR. The inlet temperature to the ATR is risen from 650 to 750 °C, and not higher due to assumed material and corrosion restrictions. Lastly is a case study to find the optimal O<sub>2</sub>/C ratio for this system and the peak in hydrogen production is when the flow of O<sub>2</sub> is 310 kmole/h, which corresponds to a ratio of 0.52, slightly lower than the one observed for Case 2 (0.53). It should be noted that the amount and the composition in the recycle steam changes when parameter changes, causing some small variations in the ratios. Next is that the inlet temperature to the HT- and LT-WGS reactors are kept at the (normal) minimum of 300 and 175 °C, respectively. It is not unlikely that these temperatures can be even lower in the near future, if the catalyst development continues. The hydrogen produced in this system amounts to 4659 kmole/h H<sub>2</sub>, exceeding the amount that in section 6.1 was stated as the minimum (4565 kmole/h) if the same ethylene production rate were to be kept. When burned stoichiometrically the energy supply to the cracker is 7.615\*10<sup>8</sup> kJ/h. This is above what is necessary and can be reduced by reducing the ethane feed again.

If the ethane is reduced to 22 kmole/h (keeping temperature and ratios the same) the hydrogen to the burner will be 4571 kmole/h. This is a sufficient amount and the energy from the burner to the cracker will be 7.485\*10<sup>8</sup> kJ/h. An initial calculation of steam export of case 5 was found to be 21 MW. Case

5 is an attractive solution. It is recommended to develop this alternative further.

## 5. Conclusion

The main goal of this work was to investigate if fuel replacement by reforming the current fuel to only hydrogen can cover the energy demand in a steam cracking furnace for ethylene production.

The selected method for hydrogen production was an autothermal reforming process (ATR) with integrated pre-combustion CO<sub>2</sub> capture. The process is simulated in Aspen HYSYS and partly maximized for the hydrogen production. Five different configurations and nine case studies were examined for optimization.

The result was a system with a pressure of 2290 kPa (in the ATR), Steam/Carbon-ratio of 2, O<sub>2</sub>/C-ratio of 0.52, and an inlet temperature to the ATR of 750 °C. The inlet temperature to the high and low-temperature water-gas-shift reactors was 300 °C and 175 °C, respectively. The inlet flow was 514 kmole/h methane and 2976 kmole/h hydrogen, where 95 mol-% of the hydrogen is separated prior to the reformation process.

To cover the gap between the simulated and desired flow of hydrogen, an inlet flow of ethane was added to the process. By adding only 22 kmole/h of ethane, a sufficient amount of hydrogen flow was reached. Potential steam export was found to be 21 MW, excluding the heat required for a CO<sub>2</sub> and H<sub>2</sub> separation unit.

Fuel replacement in industrial furnaces can have a significant impact towards decarbonization of ethylene production. Reforming traditional fuels containing hydrocarbons to hydrogen is shown to have potential.

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