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Seksjon 1

1 OPPGAVE

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PROJECT TITLE:

Creating a Simulation Model of a Hydrogen Liquefaction Process

By

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Abstract

In this project, a proposed model of a highly efficient hydrogen liquefaction process was implemented in Aspen HYSYS. A simulation model was created, and a sensitivity analysis suggested that this model was close to optimized. It is expected that the simulation model will be made dynamic in future work.

Contents

1 Introduction

Finnmark, Norway has exceptionally stable wind conditions, something that makes it an ideal place for renewable electricity production from wind turbines. Current wind turbines are in full production over 4000 hours a year, corresponding to a capacity factor of up to 50%. Companies are now planning to set up additional wind turbines (without subsidies) that are supposed to deliver 3.6TWh a year. [8]

There are, however, already problems with the capacity in the grid. One possible solution to this, is to use the extra electricity to produce hydrogen via electrolysis. Japan and Japanese companies are investing heavily in hydrogen technologies [9], and Kawasaki in particular are designing ships to transport liquid hydrogen. [7] If they were to succeed, hydrogen from Finnmark could be transported to Japan via the Northeast Passage.

For this solution to become economically viable, an efficient liquefaction process has to be realized. Current hydrogen liquefaction plants have a power consumption in the range of 8-12 kWh/kg [2], which is considered too high. There are however several proposed liquefaction processes with lower energy requirements. One of them, proposed by Valenti and Macchi (2008) [1], have a power consumption that is estimated to be as low as 5 kWh/kg.

This number, however, is calculated for a steady state process. Wind power is a variable energy source, so a potential liquefaction plant needs to be able to handle changes. It is therefore desirable to create a dynamic model of a liquefaction process, to see how it behaves under various conditions.

The aim in this project is to implement the model created by Valenti and Macchi into to a simulation program like Aspen HYSYS, and check if it is optimized. When this is done, it should be possible in later work to make a dynamic model of the process.

2 Process description

This section describes some common liquefaction processes. All processes take advantage of the fact that gases cool upon adiabatic expansion. It can either occur without extraction of mechanical energy by using a throttling valve, or it can occur with the extraction of mechanical energy by using an expander. The latter case usually results in a liquid with lower temperature, whereas the fluid in the former case usually needs to go through a flash tank to let warmer gas flash off so that the liquid product gets cold enough. The warmer gas is recycled. [2]

2.1 Linde-Hampson cycle

The Linde-Hampson cycle is the most basic liquefaction process.[2][4]. The simplest version uses only one throttling valve where all the expansion takes place. After the valve, the fluid goes through a flash tank where the warmer flash gas is recycled and the colder liquid is removed as a product. The flash gas goes through a heat exchanger where it is used to cool the compressed gas, before it is mixed with the makeup gas and then compressed. The gas is cooled during compression so that the temperature is kept constant. [5] A diagram of the process is given in Figure 1.

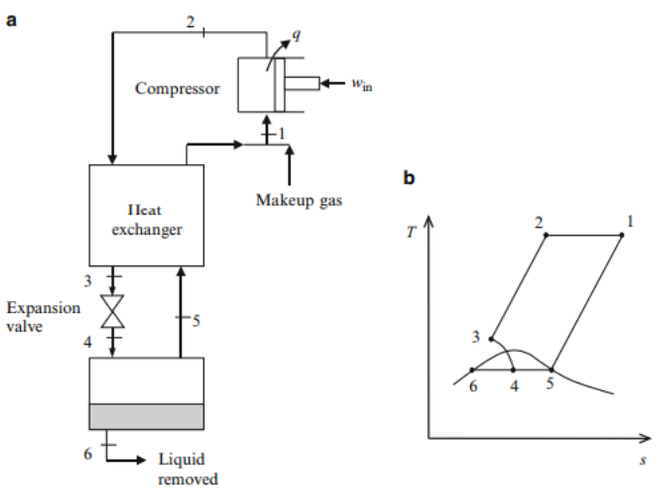

Figure 1: a) gives a schematic representation of a simple Linde-Hampson cycle and b) gives a qualitative picture of how temperature and entropy changes between different stages. [5]

The Linde-Hampson process is not very efficient. According to Verfondern [4], the energy consumption of an optimized version is 13.12 kWh/kg plus 6.7 kg of liquid nitrogen per kg of liquid hydrogen.

2.2 Claude cycle

The Claude cycle uses expanders in addition to the throttling valves. This allows for more efficient cooling.[4] There are multiple variants and configurations of the cycle. The simplest case employ a total of three heat exchangers and an expander (Figure 2a). Figure 2b and c illustrates a cycle with two compression stages and a cycle with a precooling stage respectively.

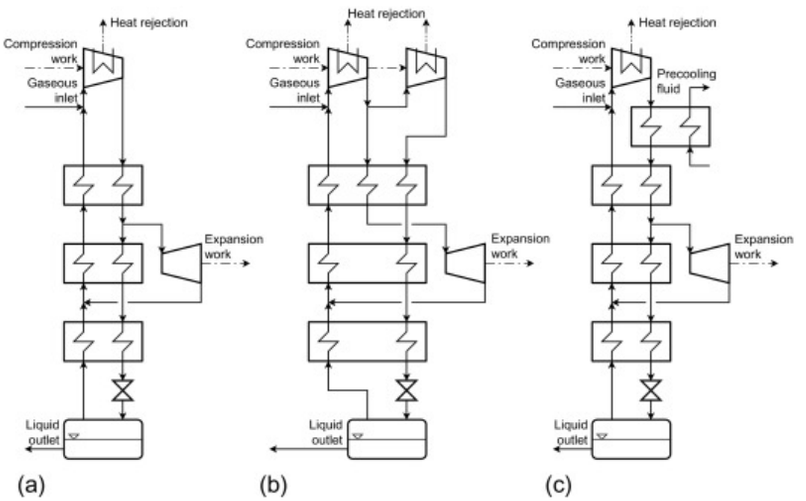

Figure 2: a) Simple Claude cycle, b) Claude cycle with two compression stages, c) Claude cycle with precooling. [2]

Variants of the Claude cycle are the most common configuration in existing liquefaction plants. [6] In these plants, energy consumptions range from 8-12 kWh/kg. [2]

2.3 Brayton cycle

The Claude cycle can be modified by having a refrigerant cycle that is separate from the hydrogen and cools it only via heat exchangers. The gas in this cycle (typically helium or neon) operates only in the gas phase and uses only expanders for cooling. This is called a reversed Joule-Brayton cycle [2] or simply a Brayton cycle [6]. The basis for this report uses this kind of refrigeration cycle (Section 3).

3 Design basis

The basis for this project was the report *"Proposal of an innovative, high-efficiency, large-scale hydrogen liquefier"* by Valenti and Macchi (2008)[1] (frequently referred to as the "reference case" in this report). The report describes a hydrogen liquefaction process with helium as the refrigerant, arranged in four recuperative Joule-Brayton cycles. The hydrogen is cooled by these four cycles down to 20.57 K before it is expanded to storage conditions using a single expander. This method avoids the formation of flash gas and the extra recycling that is needed to handle this. A flowchart of the process is given in Figure 3.

The process was simulated in Aspen Plus ver. 13.2. The built-in Soave-Redlich-Kwong fluid property pack was used for helium, but for hydrogen, a whole new thermodynamic package was developed with basis in the literature and validated against the hydrogen liquefier that was situated in Ingolstadt, Germany. [6]

The liquefaction capacity of the plant was set to 10 kg/s. The calculated energy consumption was 5 kWh/kg, which is well below current liquefiers (8-12 kWh/kg [2]).

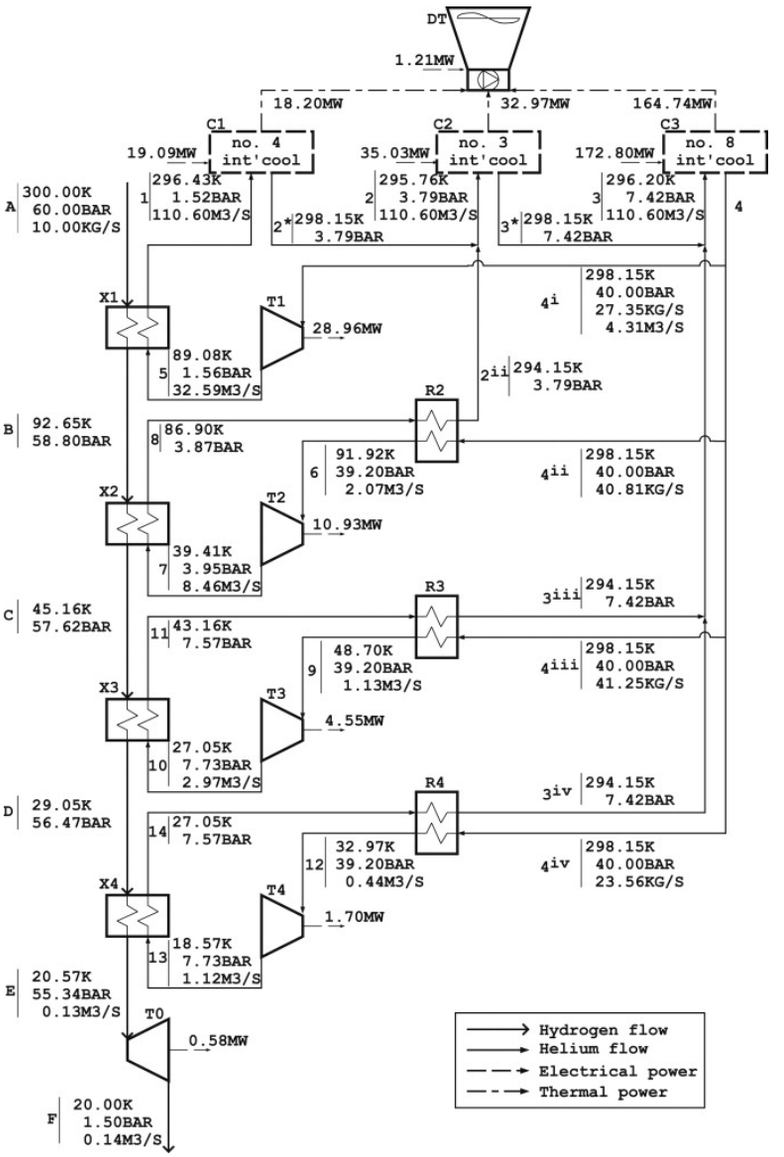

Figure 3: Flowchart of the process proposed by Valenti and Macchi.[1]

4 Model fitting

All simulations were carried out in Aspen HYSYS V9, using the Soave-Redlich-Kwong (SRK) fluid package for all components. SRK gives good results around the critical point and is, among other applications, used for cryogenic gas processing. [12]

4.1 Specifications

The basis for the model was, as mentioned in Section 3, the process proposed by Valenti and Macchi [1]. A flowsheet of the model is given in Figure 4. An overview of the specifications are given in this section.

4.1.1 Helium compressors

Valenti and Macchi [1] proposes a compressor train with 15 compressors and coolers. This is modeled as three single centrifugal compressors, each with an accompanying cooler. The polytropic efficiencies were set to 92.

4.1.2 Turbines

The turbines were modeled as expanders with the following polytropic efficiencies: Turb1=93, Turb2=92, Turb3=90, Turb4=88 and Hydrogen_turbine=85.

4.1.3 Heat exchangers

The heat exchangers were specified to have one tube pass per shell pass, effectively making them simple plate exchangers. The pressure drops were set to zero for the helium side of the heat exchangers. The pressure drops for the hydrogen side of the heat exchangers were not specified in the heat exchangers because these pressures were specified in the streams themselves (see Table 1). The UA-values were not specified at this stage, but rather calculated via stream data (Section 4.2.2). Liquid hold-ups were not emphasised at this stage.

4.1.4 Stream specifications

All stream parameters that were specified during the model fitting are listed in Table 1. Valenti and Macchi[1] proposes a production capacity of 10 kg/s, but during the model fitting, this was reduced to 9.8 kg/s to avoid a temperature crossover in the first heat exchanger (Hex1).

Table 1: An overview of all the stream parameters that were specified. All other stream values were calculated by Aspen HYSYS V9. The stream compositions are included to aid the reader.

Stream	T [K]	P [bar]	Mass flow $[\frac{kg}{s}]$	Composition
1	300.00	60.00	9.80	Hydrogen
2	92.65	58.80	-	Hydrogen
3	45.16	57.62	-	Hydrogen
4	29.05	56.47	-	Hydrogen
5	20.57	55.34	-	Hydrogen
6	-	1.50	-	Hydrogen
7	-	-	27.35	Helium
8	-	1.56	-	Helium
11	298.15	3.95	-	Helium
12	-	-	40.81	Helium
13	91.92	-	-	Helium
14	-	3.95	-	Helium
19	298.15	7.73	-	Helium
20	-	-	41.25	Helium
21	48.70	-	-	Helium
22	-	7.73	-	Helium
25	-	-	23.56	Helium
26	32.97	-	-	Helium
27	-	7.73	-	Helium
32	298.15	40.00	-	Helium

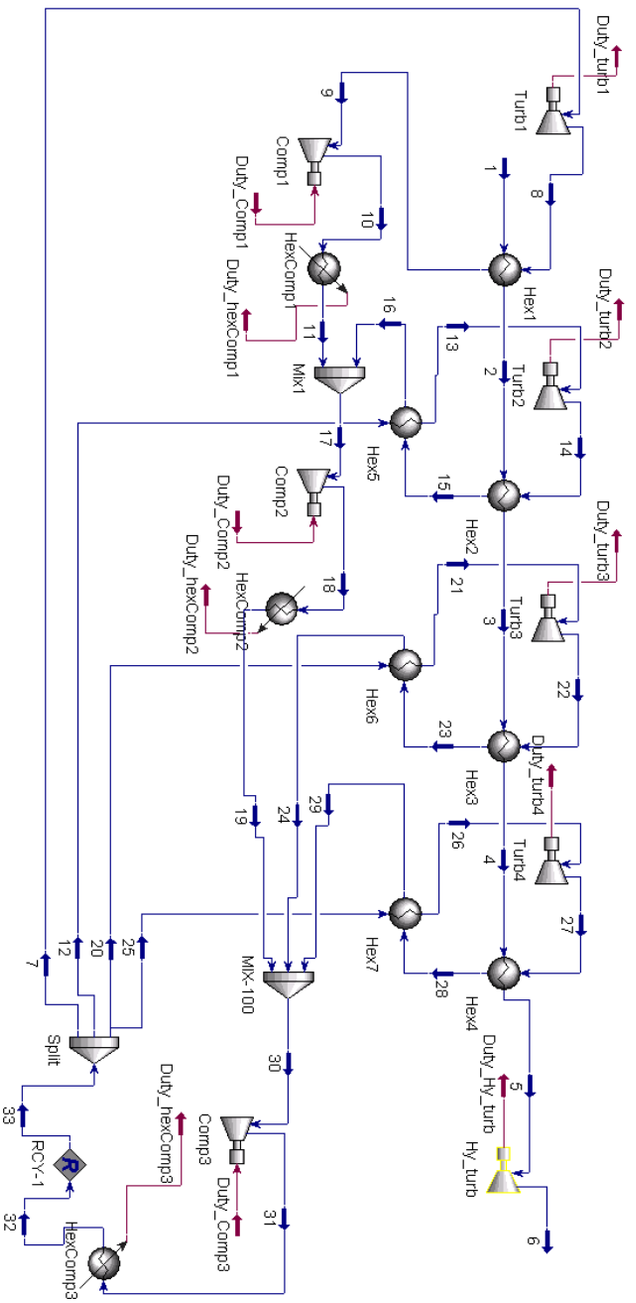

Figure 4: Flowsheet of the model implemented in Aspen HYSYS.

4.2 Results from the model fitting

This section includes comparisons of the HYSYS-model with the reference case. In addition, the calculated UA-values are listed here.

4.2.1 Calculation differences

Table 2 shows the stream data with the largest deviations. Table 3 and 4 compares the performance of the HYSYS-model and the reference case. A table of all the stream data is given in Appendix A.

Table 2: The stream data with the largest deviations. T and P refers to the temperature and pressure in the HYSYS streams. T_{ref} og P_{ref} refers to the temperatures and pressures of the corresponding streams in the reference case (see Section 3)

Stream	T [K]	T_{ref} [K]	Deviation [K]	P [bar]	P_{ref} [bar]	Deviation [bar]]
15	83.19	86.90	-3.71	3.95	3.87	0.08
16	289.50	294.15	-4.65	3.95	3.79	0.16
17	292.97	295.76	-2.79	3.95	3.79	0.16

Table 3: Total mechanical work. It includes the energy demand of the compressor minus the mechanical work generated in the expanders.

	HYSYS model [MW]	Reference case [MW]	Deviation [MW]
Total work	221.65	180.20	41.45

Table 4: Energy consumption per kg liquid hydrogen produced

	HYSYS model $[\frac{kWh}{kg}]$	Reference case $[\frac{kWh}{kg}]$	Deviation $[\frac{kWh}{kg}]$
Consumption	6.28	5.01	1.27

4.2.2 UA-values

Table 5 shows UA-values for each heat exchanger. These values are calculated by HYSYS using simple energy balances on the inlet and outlet streams. They will later be used to create the simulation model.

Table 5: Calculated UA-values

Heat exchanger	UA [MW/K]
Hex1	15.47
Hex2	1.26
Hex3	1.89
Hex4	0.71
Hex5	5.04
Hex6	10.92
Hex7	7.59

5 Simulation model

5.1 Creating the Simulation model

To create the simulation model, the UA-values calculated in Section 4.2.2 were used to specify the heat exchangers. In addition, some stream parameters that were specified during the model fitting were now left unspecified. It was also necessary to add three recycle blocks in the helium loops. An adjust block was added to let the temperature in Stream 5 be controlled at a constant value by changing the outlet pressure from Stream 27. The resulting flowsheet is given in Figure 5. A table of the specified stream parameters are given in Table 6.

Table 6: An overview of all the specified stream parameters in the simulation model. The stream compositions are included to aid the reader.

Stream	T [K]	P [bar]	Mass flow $[\frac{kg}{s}]$	Composition
1	300.00	60.00	9.80	Hydrogen
2	-	58.80	-	Hydrogen
3	-	57.62	-	Hydrogen
4	-	56.47	-	Hydrogen
5	20.57	55.34	-	Hydrogen
6	-	1.50	-	Hydrogen
7	-	-	27.35	Helium
8	-	1.56	-	Helium
11	298.15	3.95	-	Helium
12	-	-	40.81	Helium
14	-	3.95	-	Helium
19	298.15	7.73	-	Helium
20	-	-	41.25	Helium
22	-	7.73	-	Helium
25	-	-	23.56	Helium
32	298.15	40.00	-	Helium

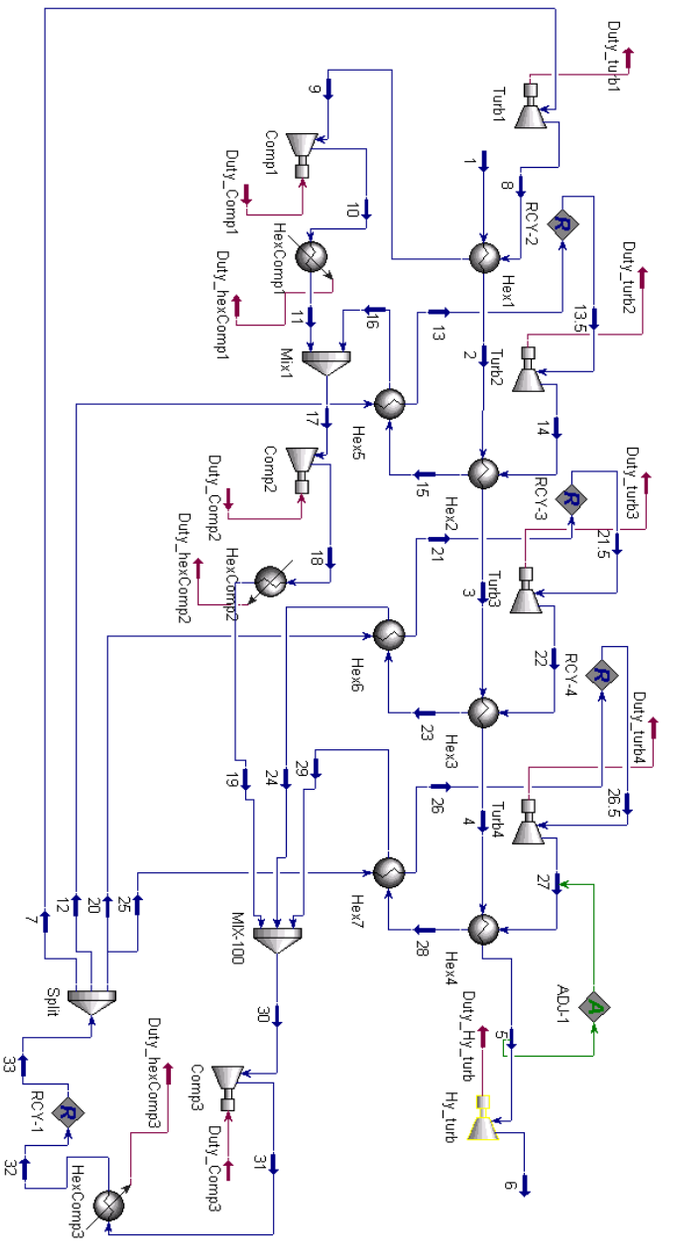

Figure 5: Flowsheet of the simulation model.

5.2 Sensitivity analysis

A sensitivity analysis was performed by changing the outlet pressures for each turbine, and by changing the mass flow of helium through each turbine. Turb4 was not included because its exit pressure was already used to control the temperature in Stream 5. The results are given in Table 7 and 8

Table 7: Changes in energy requirements when the exit pressures for Turb1, Turb2 and Turb3 were changed. Inc. refers to an increase. Dec refers to a decrease. The pressures were changed by 10% in each direction.

	Original	Inc.Turb1	Dec.Turb1	Inc.Turb2	Dec.Turb2	Inc.Turb3	Dec.Turb3
Comp1	21.1	18.6	24.1	21.1	21.1	21.1	21.1
Comp2	35.2	35.2	35.2	35.2	41.7	35.2	35.2
Comp3	214.1	231.2	214.1	239.1	214.2	242.1	233.8
TurbHy	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Turb1	30.0	29.5	30.5	30.0	30.0	30.0	30.0
Turb2	11.6	11.9	11.3	11.3	11.9	11.6	11.6
Turb3	4.9	5.0	4.9	5.1	4.8	4.8	5.1
Turb4	1.9	2.0	1.7	2.0	1.7	2.0	1.7
Total work	221.7	236.1	224.6	246.6	228.2	249.6	241.3

Table 8: Changes in energy requirements mass flows through Turb1, Turb2 and Turb3 were changed. Inc. refers to an increase. Dec refers to a decrease. The mass flows were changed by 10% in each direction.

	Original	Inc.Turb1	Dec.Turb1	Inc.Turb2	Dec.Turb2	Inc.Turb3	Dec.Turb3
Comp1	21.1	22.0	infeasible	21.1	21.1	21.1	21.1
Comp2	35.2	36.6	infeasible	37.2	33.2	35.2	35.2
Comp3	214.1	218.6	infeasible	220.8	262.0	220.6	242.8
TurbHy	0.5	0.5	infeasible	0.5	0.5	0.5	0.5
Turb1	30.0	33.0	infeasible	30.0	30.0	30.0	30.0
Turb2	11.6	11.3	infeasible	12.5	10.6	11.6	11.6
Turb3	4.9	4.9	infeasible	4.7	5.2	5.4	4.5
Turb4	1.9	1.7	infeasible	1.6	2.2	1.7	2.1
Total work	221.7	225.9	infeasible	229.8	267.9	227.9	250.6

6 Discussion

There are some deviations between the reference model and the model implemented in HYSYS (Section 4.2.1). This is to be expected. Not only because the reference model was generated in Aspen Plus, but also because the Soave-Redlich-Kwong property package was used for the hydrogen in the HYSYS-model while an independent package was developed in the reference case (Section 3). This is thought to be the main reasons for the temperature deviations.

The pressure deviations on the other hand, are thought to be mainly caused by the assumption that there was zero pressure drop over the heat exchangers(Section 4.1.3). Even with this simplification, the deviations are not that high (Table A.1).

The total work, however, is significantly higher in the HYSYS-model than in the reference case (Table 3). This is mainly due to the compressor simplifications(Section 4.1.1). The 15 compressors used in the reference case have a lot of intermediate cooling, whereas the HYSYS-model only has three compressors and coolers. This causes much higher temperatures, and results in higher energy consumption during compression. The total work is however still below existing liquefaction plants (Section 2.2).

The UA-values are, as mentioned in Section 4.2.2, calculated by HYSYS using simple energy balances. This could make it hard to tell if they are reasonable, but because the deviations in the calculated temperatures of the stream are not very large, it is likely that the deviation for the UA-values are small also.

A thing that was not emphasized in this report, was the liquid holdup in the heat exchangers, even though the hydrogen is cooled below the critical temperature in Hex3 and Hex4 (Table B.1 and Table A.1) . This is something that needs to be addressed before proceeding to a dynamic model.

The results from the sensitivity analysis (Section 5) shows that the original case is the most energy efficient among the cases tested. This indicates that the model is close to optimum already, although it is worth noting that analysis was very limited.

7 Conclusion and further work

A proposed highly efficient hydrogen liquefaction process has been implemented in Aspen HYSYS. The resulting model showed in general small deviations from the original case, except for efficiency in the compression stage.
A sensitivity analysis was performed, and it was concluded that the model was already optimized.
There are however some things that should be addressed before moving to a dynamic model. These include doing a more accurate modelling of the heat exchangers by including pressure drops an liquid holdups. The structure of the compression stage should also be changed to increase the efficiency.

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A Stream data

Table A.1: Overview of stream data from the model fitting. Stream 1-6 contain hydrogen, and the rest contain helium. T and P refers to the temperature and pressure of the streams. T_{ref} and P_{ref} refers to the temperature and pressure of the corresponding streams in the reference case (Valenti and Macchi [1]). The mass flows are equal in both the model and the reference case, except for stream 1-5 which are 9.8 kg/s in the design and 10 kg/s in the reference case. Numbers in red indicate values from the reference case. Number in blue indicate values that were specified in the model. Black numbers are values calculated by the simulation program.

Stream	T [K]	T_{ref} [K]	Deviation [K]	P [bar]	P_{ref} [bar]	Deviation [bar]	Mass flow [$\frac{kg}{s}$]
1	300.00	300.00	-	60.00	60.00	-	9.80
2	92.65	92.65	-	58.80	58.80	-	9.80
3	45.16	45.16	-	57.62	57.62	-	9.80
4	29.05	29.05	-	56.47	56.47	-	9.80
5	20.57	20.57	-	55.34	55.34	-	9.80
6	19.33	20.00	-0.67	1.50	1.50	-	9.80
7	298.15	298.15	-	40.00	40.00	-	27.35
8	89.50	89.08	0.42	1.56	1.56	-	27.35
9	298.93	296.43	2.50	1.56	1.52	0.04	27.35
10	447.59	-	-	3.95	-	-	27.35
11	298.15	298.15	-	3.95	3.95	-	27.35
12	298.15	298.15	-	40.00	40.00	-	40.81
13	91.92	91.92	-	40.00	39.20	0.80	40.81
14	39.49	39.41	0.08	3.95	3.95	-	40.81
15	83.19	86.90	-3.71	3.95	3.87	0.08	40.81
16	289.50	294.15	-4.65	3.95	3.79	0.16	40.81
17	292.97	295.76	-2.79	3.95	3.79	0.16	68.16
18	392.19	-	-	7.73	-	-	68.16
19	298.15	298.15	-	7.73	7.73	-	68.16
20	298.15	298.15	-	40.00	40.00	-	41.25
21	48.70	48.70	-	40.00	39.20	0.80	41.25
22	27.14	27.05	0.09	7.73	7.73	-	41.25
23	43.29	43.16	0.13	7.73	7.57	0.16	41.25
24	293.68	294.15	-0.47	7.73	7.42	0.31	41.25
25	298.15	298.15	-	40.00	40.00	-	23.56
26	32.97	32.97	-	40.00	39.20	0.80	23.56
27	18.56	18.57	-0.01	7.73	7.73	-	23.56
28	27.64	27.05	0.59	7.73	7.57	0.16	23.56
29	294.69	294.15	0.54	7.73	7.42	0.31	23.56
30	296.15	296.20	-0.05	7.73	7.42	0.31	132.97
31	604.67	-	-	40.00	-	-	132.97
32	298.15	298.15	-	40.00	40.00	-	132.97
33	298.15	-	-	40.00	-	-	132.97

Table A.2: Overview of the energy streams of the model. Black numbers are calculated by Aspen HYSYS. Red numbers indicate values from the reference case.

Energy stream	HYSYS calculations [MW]	Reference case [MW]	Deviation [MW]
Duty_turb1	29.97	28.96	1.01
Duty_turb2	11.60	10.93	0.67
Duty_turb3	4.94	4.55	0.39
Duty_turb4	1.86	1.7	0.16
Duty_Comp1	21.14	19.09	2.05
Duty_hexComp1	21.23	18.2	3.03
Duty_Comp2	35.21	35.03	0.18
Duty_hexComp2	33.29	32.97	0.32
Duty_Comp3	214.15	172.8	41.35
Duty_hexComp3	211.46	164.74	46.72
Duty_Hy_turb	0.48	0.58	-0.10
Total work	221.65	180.20	41.45

B Properties of Hydrogen

This section lists vapor pressures for hydrogen in the two-phase region. It also includes an explanation regarding the spin isomers of hydrogen.

B.1 Vapor pressure

Table B.1: Vapor pressure of para hydrogen at temperatures ranging from the triple point to the critical point.[11]

T [K]	P [kPa]
13,8033	7,041
14	7,884
15	13,434
16	21,548
17	32,886
18	48,148
19	68,071
20	93,414
20,271	101,325
21	124,96
22	163,5
23	209,83
24	264,78
25	329,17
26	403,84
27	489,65
28	587,5
29	698,33
30	823,19
31	963,29
32	1120,3
32,938	1285,8

Table B.2: Vapor pressure of normal hydrogen at temperatures ranging from the triple point to the critical point.[11]

T [K]	P [kPa]
13,957	7,358
14	7,541
15	12,898
16	20,755
17	31,759
18	46,602
19	66,006
20	90,717
20,369	101,325
21	121,5
22	159,13
23	204,38
24	258,07
25	321
26	393,99
27	477,89
28	573,59
29	682,05
30	804,32
31	941,65
32	1095,7
33	1269,3
33,145	1296,5

B.2 Spin isomers of Hydrogen

Molecular hydrogen occurs as two different spin isomers. This isomerism arises from the nuclear spin of the two hydrogen nuclei. If the nuclei has parallel spin, the molecule is said to be in the ortho state. If the spin of the nuclei is antiparallel, the molecule is said to be in the para state. The ortho state has slightly higher energy ($\Delta H_{ortho \rightarrow para} = -1.5$ kJ/mol).[10]

At room temperature, the ratio between the two forms is roughly 75% orthohydrogen and 25% parahydrogen, and the mixture is refered to as normal hydrogen. This equilibrium shifts towards parahydrogen at decreasing temperatures, and at the boiling point of hydrogen (20.3 K), the equilibrium composition is >99% parahydrogen.

The transition from ortho to para is slow. If hydrogen is cooled from room temperature down to below the boiling point, the resulting liquid can therefore end up far from equilibrium. Keeping in mind the exothermic nature of the ortho to para transition (−1.5 kJ/mol), the slow conversion from ortho to para during storage can lead to considerable energy release and subsequent boil-off. This can cause a serious challenge if it's not dealt with properly. Luckily there are catalysts that (typically Iron oxide) can speed up the process. These catalysts can be placed inside the heat exchanger so that continuous conversion is allowed. [2]