

Appendix A

Flowsheeting

This appendix shows the flowsheet from HYSYS. Figure I show the whole process including the heat exchanger networks and spreadsheets, whilst Figure II shows an enlarged image of the main process.

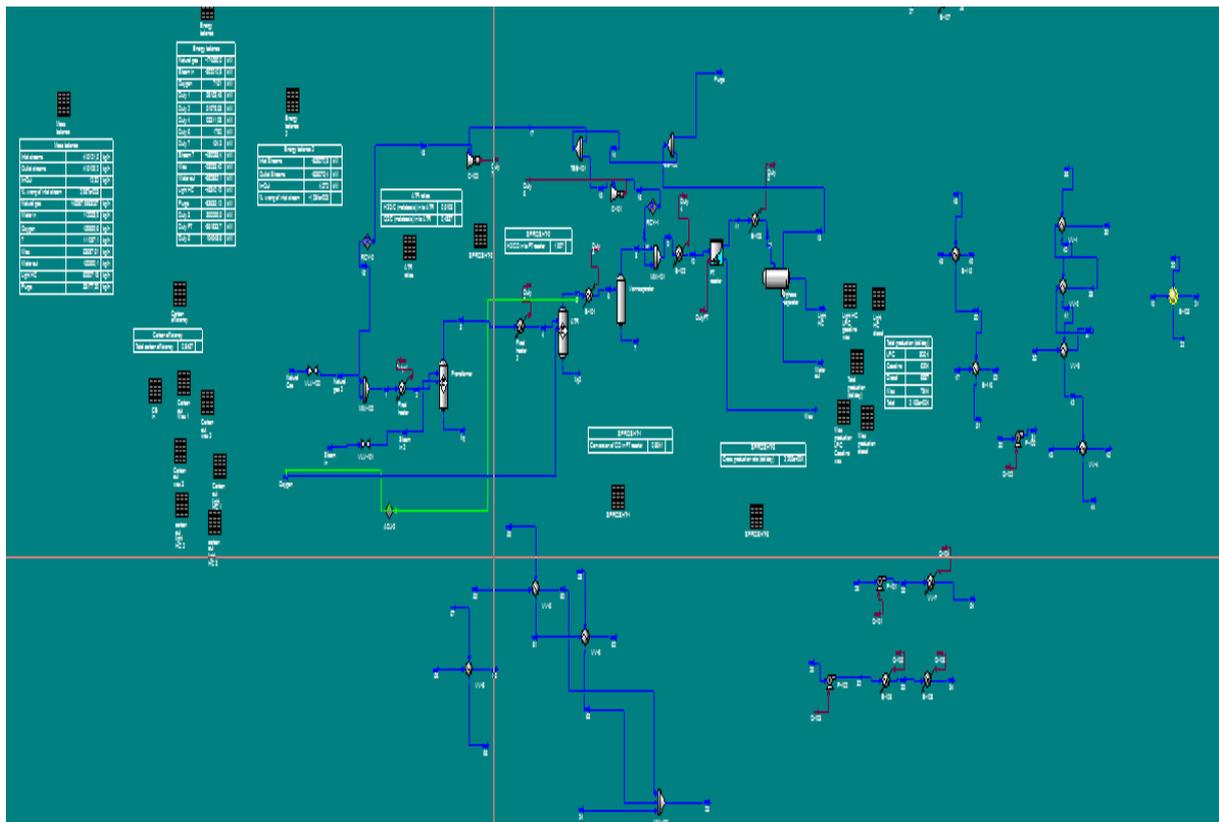


Figure I - HYSYS flowsheet

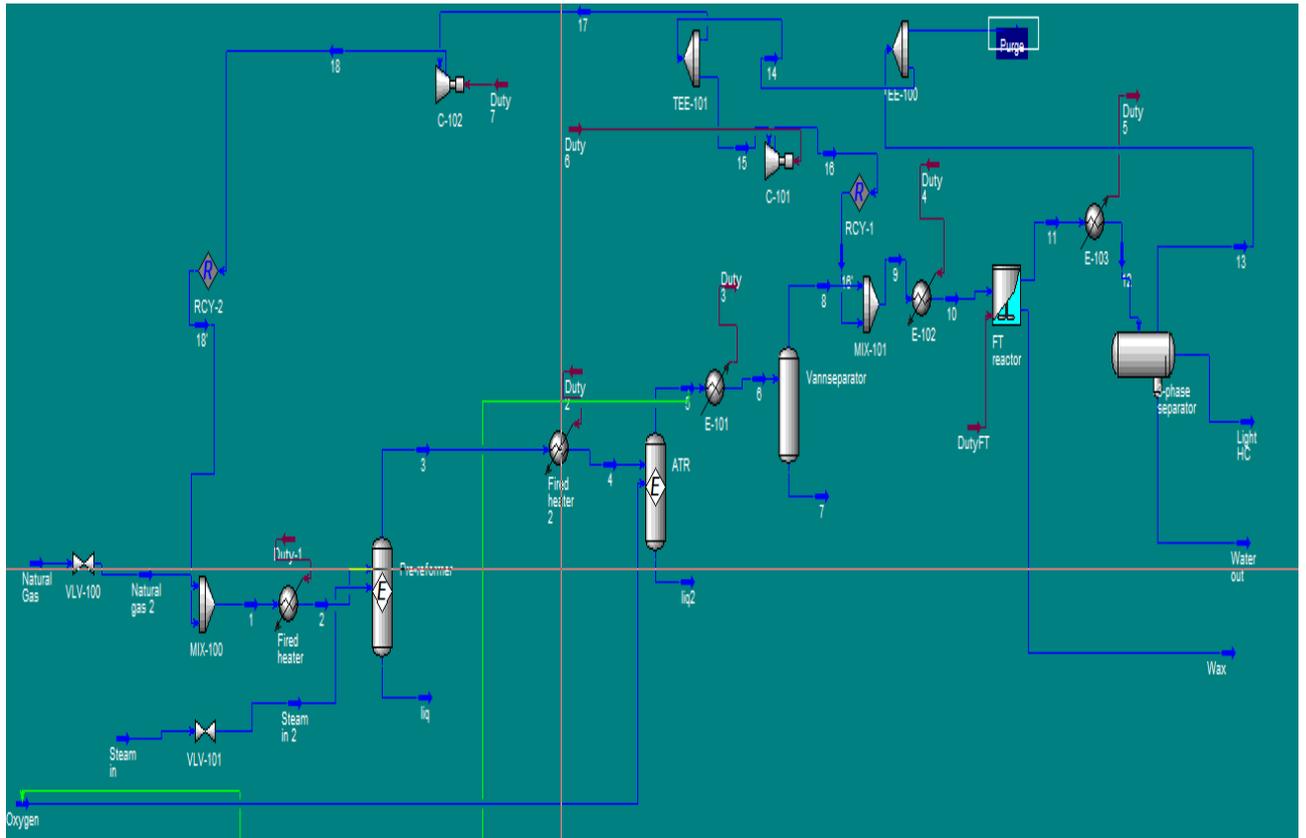


Figure II - HYSYS flowsheet 2

Appendix B

ASF distribution

This appendix shows how the U' and p_i values in equation 4 in the main report are calculated

To calculate the values, formulas given in literature (1) and MATLAB was used. The formulas needed are given under.

$$p_i = (1 - \alpha)^2 \alpha^{i-1} \quad (\text{B.1})$$

$$U' = 3 - \alpha \quad (\text{B.2})$$

$$\sum_{i=1}^{\infty} ip_i = 1 \quad (\text{B.3})$$

Equation B.2 and B.3 are used to calculate p_i and U' , and the last equation is to make sure that the sum adds up to 1 according to the weight ASF distribution (1).

The MATLAB code is given under.

```
clear all
clc
format long

%Rx: CO + UH2 --> p1C1 + p2C2 + ... + p20C20 +sum(pnuCnu) + H2O
%ASF distribution
alfa=0.90;
N=21;

%average carbon number of lump
Xnu=N+(alfa/(1-alfa))
U=3-alfa
%calculating pi values

for i=1:N-1
    p(i)=(1-alfa)^2*(alfa^(i-1));
end

for i=N:999
    pnu(i)=(1-alfa)^2*(alfa^(i-1));
end

disp (p)
pn=sum(pnu)

%checking if the sum adds up to 1
for i=1:999
    p(i)=(1-alfa)^2*(alfa^(i-1));
    y(i)=sum(i*p(i));
end
Y=sum(y(1:i))
```

Appendix C

Optimization

Recycle to FT reactor

To find the recycle ratio back to the FT reactor, the recycle ratio was compared against the mass flow of steam into the system, the gross production rate and the steam/carbon ratio, whilst all other variables were held constant. First a rough interval was tested, and then narrowed down to a smaller interval. Table I shows the different configurations when testing, and the constants. The purge ratio and reactor volume were constant in all cases. The temperature out of the ATR was 1030 ± 1 , and the H_2/CO ratio was 2.0 ± 0.1 .

Table I - Rough interval for FT recycle test

Variable	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Units
Recycle to FT reactor	50	60	70	80	90	100	%
H_2O/C ratio	3.323	3.22	3.148	2.13	1.096	0.2238	
H_2/CO ratio	1.966	1.948	2.08	1.964	2.01	1.991	
Conversion CO	0.377	0.417	0.4846	0.6479	0.7512	0.696	
T_{out} ATR	1029	1031	1030	1030	1031	1031	$^{\circ}C$
Gross Production	1517	4701	9896	$1.88 \cdot 10^4$	$2.19 \cdot 10^4$	$1.99 \cdot 10^4$	bbl/day
Mass flow water in	$5.13 \cdot 10^6$	$4.14 \cdot 10^6$	$2.88 \cdot 10^6$	$8.83 \cdot 10^5$	$2.76 \cdot 10^5$	$4.86 \cdot 10^4$	kg/h
Reactor volume	1000						m^3
Purge ratio	3.40						%

These results were plotted in Figure III, Figure IV and Figure V.

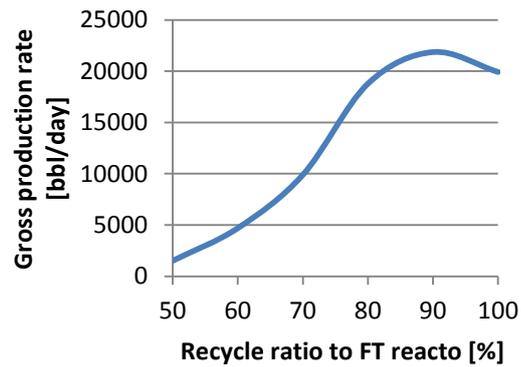
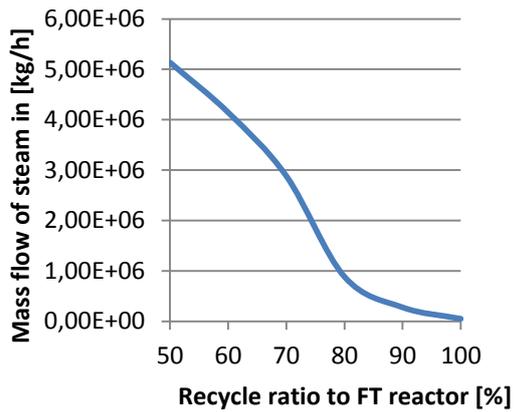


Figure III - Recycle ratio vs. Mass flow steam

Figure IV - Gross production rate vs. Recycle ratio

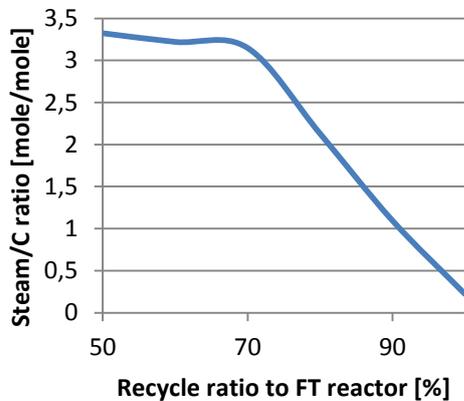


Figure V - Recycle ratio vs. Steam/C ratio

From these figures it can be seen that the production rate is at its highest in the interval 90-100 %, and the steam consumption is also lowest in that interval, so it was decided to look more closely into that interval. Table II Shows the new variables and constants for the second test

Table II - Variables and constants for the second test

Variables	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Units
Recycle ratio to FT reactor	90	92	94	96	98	100	%
H ₂ O/C	1.096	0.8956	0.7317	0.5437	0.4048	0.2238	
H ₂ /CO	2.01	1.965	1.964	1.97	2.025	1.991	
Conversion CO	0.7512	0.7523	0.7551	0.7576	0.7498	0.696	
T _{out} ATR	1031	1029	1031	1031	1030	1031	°C
Gross production rate	2.19*10 ⁴	2.22*10 ⁴	2.23*10 ⁴	2.22*10 ⁴	2.17*10 ⁴	1.99*10 ⁴	bbl/day
Mass flow steam in	2.76*10 ⁵	2.13*10 ⁵	1.66*10 ⁵	1.19*10 ⁵	8.65*10 ⁴	4.86*10 ⁴	kg/h
Reactor volume	1000						m ³
Purge ratio	3.40						%

Using these values, the plots in Figure 3 in the main report are gotten.

Purge ratio

To find the optimal purge ratio, the purge ratio was compared against the gross production rate, the steam consumption, the steam/carbon ratio and the carbon efficiency, whilst all other variables were held constant. First a rough interval was tested, and then narrowed down to a smaller interval.

Table III shows the different configurations and constants. The recycle ratio back to the FT reactor and reactor volume were constant in all cases. The temperature out of the ATR was 1030 ± 1 , and the H_2/CO ratio was 2.0 ± 0.1 .

Table III - Variables and constant for rough purge ratio test

Variable	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Units
Purge ratio	1	2	4	6	8	10	%
H_2O/C	1.398	0.7641	0.5437	0.4176	0.3592	0.3353	
H_2/CO	2.059	2.031	1.97	2.042	2.031	2.01	
Conversion CO	0.5097	0.6933	0.7576	0.8202	0.8370	0.8490	
T_{out} ATR	1029	1029	1031	1029	1029	1031	$^{\circ}C$
Gross production rate	$2.14*10^4$	$2.24*10^4$	$2.22*10^4$	$2.17*10^4$	$2.13*10^4$	$2.11*10^4$	bbl/day
Steam consumption	$3.92*10^5$	$1.75*10^5$	$1.19*10^5$	$8.97*10^5$	$7.75*10^5$	$7.21*10^5$	kg/h
Carbon efficiency	0.8087	0.8431	0.8396	0.821	0.8093	0.8003	
Recycle ratio to FT reactor	96						%
Reactor volume	1000						m^3

The results were plotted in Figure VI, Figure VII, Figure VIII and Figure IX below

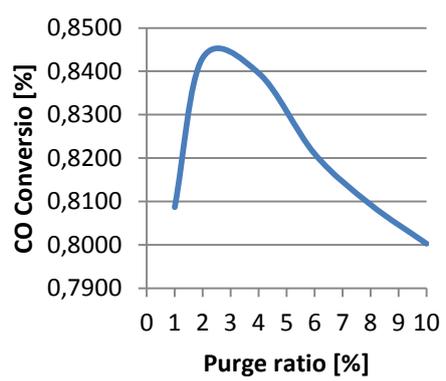
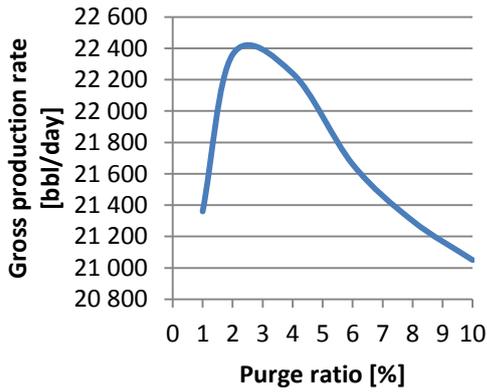


Figure VI - Purge ratio vs. Gross production rate

Figure VII - Purge ratio vs. Carbon efficiency

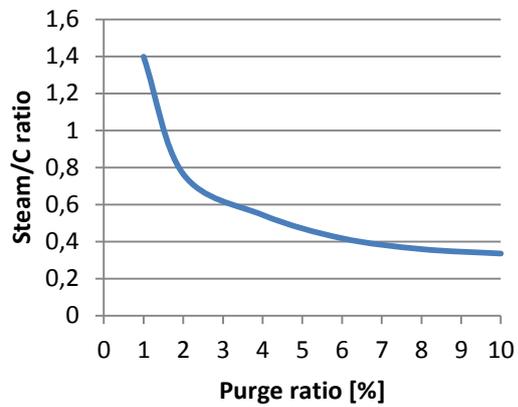
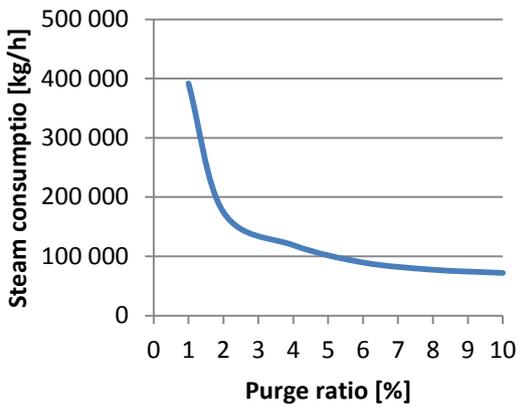


Figure VIII - Purge ratio vs. Steam consumption

Figure IX - Purge ratio vs. H₂O/C ratio

From these figures it can be seen that the optimal purge ratio is between 2-4 %, because the production is highest there, and the steam consumption is acceptable. The new interval from 2-4 % was investigated more thoroughly, and the results are given in Table IV. These are the values the plots in Figure 4 in the main report are gotten from.

Table IV - Purge ratio test 2

Variables	Test 1	Test 2	Test 3	Test 4	Test 5	Units
Purge ratio	2.0	2.5	3.0	3.5	4.0	%
H ₂ O/C	0.7641	0.6745	0.6083	0.5539	0.5437	
H ₂ /CO	2.031	1.968	2.050	2.045	1.970	
Conversion CO	0.6933	0.7174	0.7535	0.7708	0.7576	
T _{out} ATR	1029	1031	1030	1029	1031	°C
Gross production rate	22 360	22 350	22 320	22 200	22 190	bbl/day
Steam consumption	174 700	150 400	133 700	120 700	118 900	kg/h
Carbon efficiency	0.8431	0.8429	0.8423	0.8400	0.8350	
Recycle to FT reactor	96					%
Reactor volume	1000					m ³

Reactor volume

To find the optimal reactor volume, the reactor volume was compared against the gross production rate, whilst holding all other variables constant. The results used in Figure 5 in the main report are given in Table V below.

Table V - Test for reactor volume

Variables								Units
Reactor volume	500	1000	1500	2000	2500	3000	5000	m ³
H ₂ O/C	0.5463	0.5514	0.5536	0.5547	0.5556	0.5561		
H ₂ /CO	2.021	1.990	1.979	1.975	1.975	1.975		
Gross production rate	21 530	22 280	22 450	22 580	22 630	22 700	22 760	bbbl/day
Carbon efficiency	0.8205	0.841	0.8444	0.8476	0.8483	0.8502		
Conversion CO	0.6277	0.7602	0.8132	0.8427	0.8619	0.8753	0.9037	
T _{out} ATR	1029	1031	1031	1031	1031	1031		°C
Purge ratio	3.5							%
Recycle ratio to FT reactor	96							%

Appendix D

Heat integration

This appendix shows more detailed heat integration, and heat exchanger networks.

E-101

This heat exchanger is actually a steam drum and four exchangers as shown in Figure X.

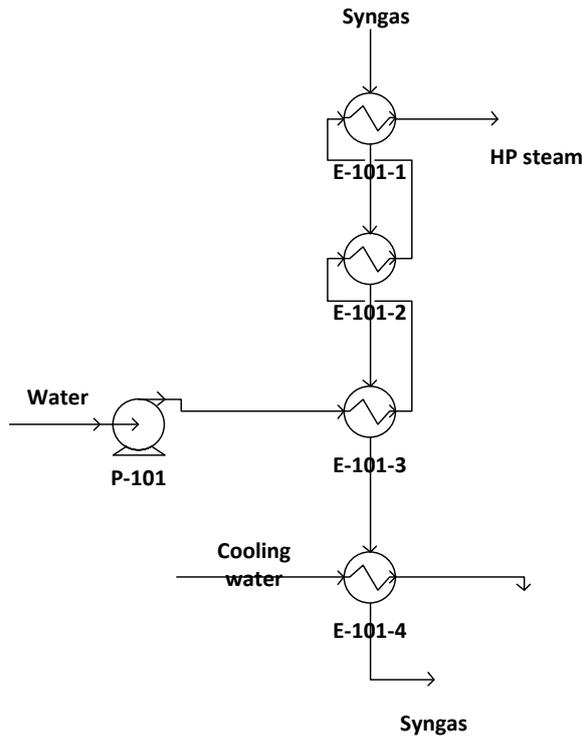


Figure X - E-101

The syngas leaving the ATR at 1030 °C is cooled down while HP steam at 510 °C and 110 bars is produced. The ΔT_{\min} value was set to 10 °C. A bit of trials and errors was done before the plot in Figure 6 in the main report was achieved. The amount of cooling water needed can be calculated by eq. D.1.

$$Q = m^* C_p \Delta T \quad (\text{D.1})$$

The cooling water enters at 8.5 °C and leaves at 18.5 °C (2).

E-102

Several possibilities were examined for this heat exchanger. The first possibility was to pair it against E-103 with a ΔT_{\min} at 10 °C. The pinch analysis is shown in Figure XI

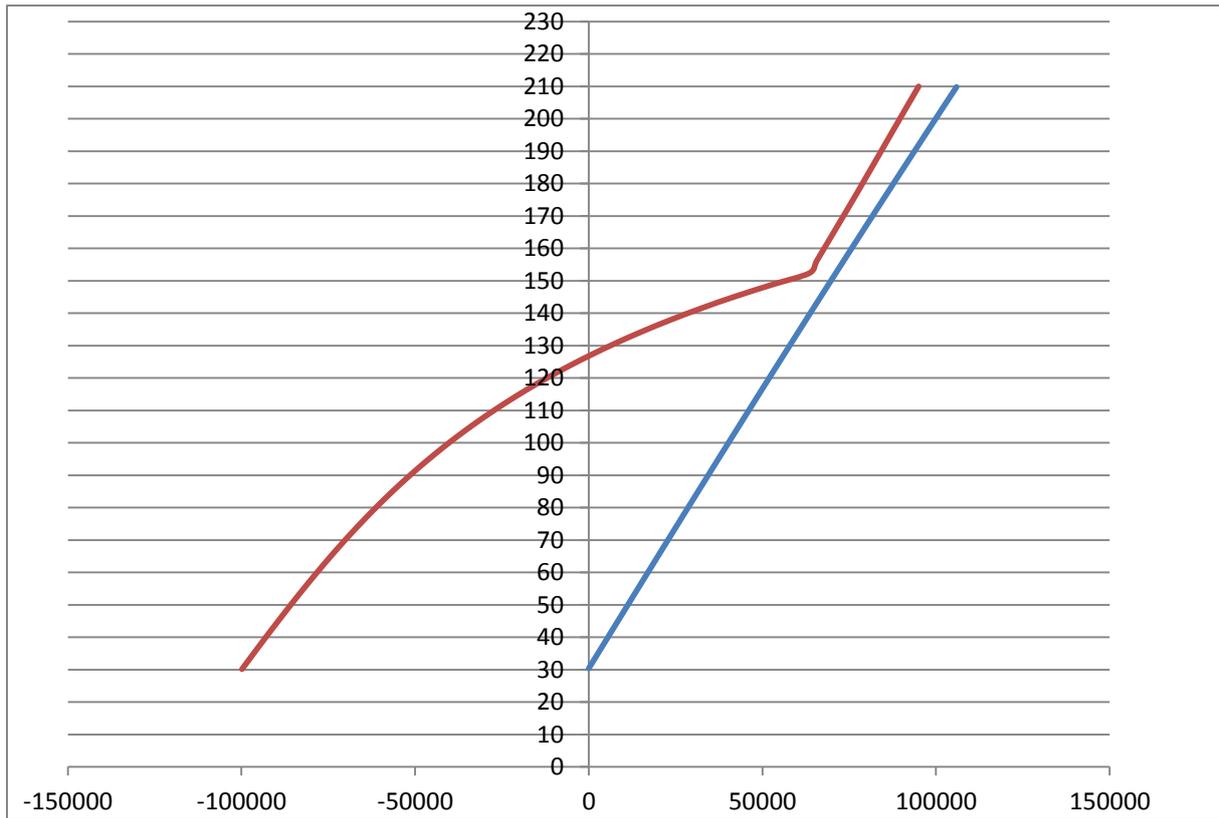


Figure XI - Pinch analysis for E-102 and E-103

This configuration needs both steam and cooling water to utilize. The next step was to lower the inlet temperature to the FT reactor so that no external warming was needed. This configuration only requires cooling water, but the heat exchangers gets to huge because of bad heat transfer between two hydrocarbon fluids, thus it was decided to use steam to heat up stream 9, and cooling water to cool stream 11.

Stream 9 is heated with both LP and HP steam to reach decided temperature. Figure XII shows the heat exchanger network. Figure II shows where streams 9 and 11 are in the process.

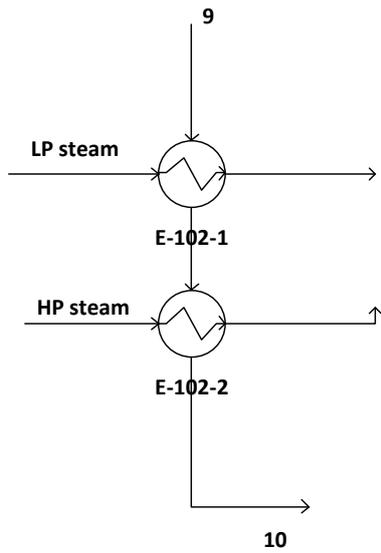


Figure XII - Heat exchanger network for E-102

Reaction heat

The energy from the reaction is used to produce LP steam at 190 °C and 10 bars. The amount of steam that can be produced is calculated from eq. D.1. Inside the reactor there are cooling tubes for heat transfer, and the tubes are connected to a steam drum.

E-103

The last heat exchanger uses cooling water to cool down the products. The amount of cooling water needed is calculated from eq. D.1.

Appendix E

Values used in economic calculations

ASU

The cost for the air separation unit is 125 000 000 NOK (2001 price) for a 325 ton O₂/day, with a scaling factor of 0.7. The energy demand is 0.8 kWh/kg O₂ (3).

Pressure vessels

The pre-reformer, ATR, separators, FT reactor and steam drums are modeled as pressure vessels. To find the volume of separators and steam drums a residence time of 5 minutes is assumed (4), and a height/diameter ratio of 3 (5). The pre-reformer is assumed to be 4 meters in diameter and 6 meters high, the ATR is assumed to be 8 meters in diameter and 6 meters high (6). The FT reactor is assumed to have a height/diameter ratio of 3 (5).

The design pressures of the vessels are assumed to be 10% larger than the actual pressure, and the maximum allowable stress is found from a temperature dependency in literature (4). The thickness of the vessels are then calculated from equation E.1

$$t = \frac{P_i D}{2\sigma - P_i} \quad \text{E.1}$$

σ is the maximum allowed stress, D is the diameter and P_i is the design pressure.

A summary of the design pressures, temperatures, maximum allowable stresses and thicknesses are given in Table VI under.

Table VI - Equipment summary

Equipment	Design pressure (bar)	Temperature (°C)	Max. stress (ksi)	Thickness (m)
Pre-reformer	32.615	465	11.7	0.083
ATR	31.515	1030	11.5	0.163
FT-reactor	29.315	210	14	0.162
Steam drum 1	121	510	10.8	0.211
Steam drum 2	11	210	14	0.015
Separator	30.415	30	21	0.035
3-phase separator	28.215	30	21	0.040

Heat-Exchangers

All heat exchangers are modeled as U-tube shell and tube exchangers, except the one inside the FT reactor which is cooling tubes.

U-tube

For the U-tube exchangers the UA value gotten from HYSYS is used, and U values are found in literature (4). Then the area is calculated. A summary is given in Table VII under.

Table VII - Summary of heat exchangers

Heat exchanger	UA (W/°C)	U (W/(m ² °C))	A (m ²)
E-101-1	1.03*10 ⁵	750	137
E-101-2	4.17*10 ⁵	1000	417
E-101-3	2.54*10 ⁶	700	3 627
E-101-4	9.72*10 ⁵	750	1 296
E-102-1	2.27*10 ⁶	1000	2 269
E-102-2	5.78*10 ⁴	1000	58
E-103	2.31*10 ⁶	750	3 085

Cooling tubes

To find the cost of the cooling tubes the duty and temperatures from HYSYS were used, and the area was found from equation E.2.

$$Q = UA\Delta T_{lm} \quad (\text{E.2})$$

Then the total length of tubes was found from equation E.3

$$A = \pi LD \quad (\text{E.3})$$

The diameter of the tubes is approximately 5 centimeters (7). When the length of the tubes was found, a correlation in literature (8) said that the price was approximately 2 \$/feet of tube (1991 price).

Catalyst

Inside the pre-reformer and ATR nickel catalyst is used. The price of nickel catalyst is approximately 100 NOK/liter (6). Inside the FT reactor there is a cobalt based catalyst, and the price of finished catalyst is about 30 \$/lb (9). The amount of catalyst inside the reactors are 10 vol% according to the maximum allowed concentration (6).

Bibliografi

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