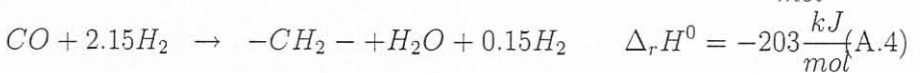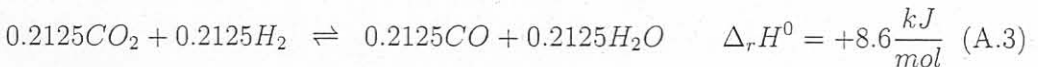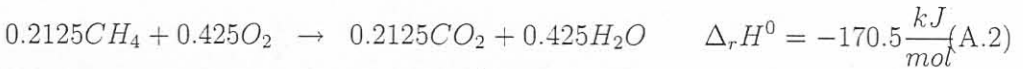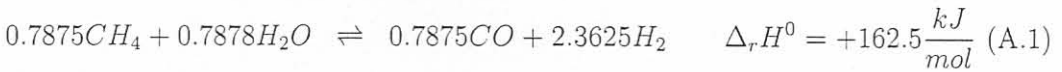# Appendix A

Process synthesis

When analyzing the GTL process and the overall stoichiometry of the process it can be shown that the process is a net exporter of energy (see equation A.5). This was already shown in the main part of the report, but is given again in this section to show the importance of this fact.

If we are interested in what H_2:CO syngas ratio we can ideally obtain without having any CO_2 we can do the following: Take one mol of methane and reform 0.8 mol and burn 0.2 mol (for ideal adiabatic combustion). Take the 0.2 mol of CO_2 and shift it by using 0.2 mol of H_2 from the reforming section. The result is 0.8 + 0.2 = 1 mol of CO, 2.4 - 0.2 = 2.2 mol of H_2, which gives a H_2:CO ratio of 2.2:1 for a 100% C efficiency. Comparing this ratio to the ratio of 2.15 used in this study, there is not much of a difference. This H_2:CO ratio of 2.15 was necessitated by the fact that we want a Schulz–Flory alpha value of 0.95 in the SBR (refer once again to the main report). See equations A.1, A.2, A.3 for the reactions taking place in the reformer and equation A.4 for the reaction taking place in the SBR.

$$0.7875CH_4 + 0.7878H_2O \rightleftharpoons 0.7875CO + 2.3625H_2 \qquad \Delta_r H^0 = +162.5\frac{kJ}{mol} \quad (A.1)$$

$$0.2125CH_4 + 0.425O_2 \rightarrow 0.2125CO_2 + 0.425H_2O \qquad \Delta_r H^0 = -170.5\frac{kJ}{mol}(A.2)$$

$$0.2125CO_2 + 0.2125H_2 \rightleftharpoons 0.2125CO + 0.2125H_2O \qquad \Delta_r H^0 = +8.6\frac{kJ}{mol} \quad (A.3)$$

$$CO + 2.15H_2 \rightarrow -CH_2- + H_2O + 0.15H_2 \qquad \Delta_r H^0 = -203\frac{kJ}{mol}(A.4)$$

When combining all of the above equations, the resulting equation can be seen in equation

A.5.

$$CH_4 + 0.425O_2 \rightarrow -CH_2- +0.85H_2O + 0.15H_2 \qquad \Delta_r H^0 = -202.4\frac{kJ}{mol} \qquad \text{(A.5)}$$
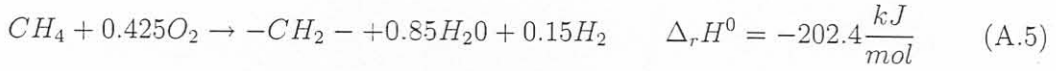
Thus from equation A.5 it can be seen that a surplus of 0.15 mol of H_2 will be produced for every 1 mol of CH_4 fed to the reformer. This is for near ideal adiabatic conditions in the ATR. This equation also shows that the process will be a net exporter of energy. The idea was thus to design the process to realise this goal. But it was kept in mind that the export of energy would only be possible with a very high total carbon efficiency (which is not always practical). This led to the main objectives for designing this process:

- optimization of product yield (i.e. maximum carbon efficiency) and

- minimum energy requirements.

Appendix B

The SBR product distribution

The importance of the H_2:CO consumption ratio in the Fischer-Tropsch reactor was already discussed in the literature survey. This ratio will determine the product distribution in the Fischer-Tropsch reactor, together with the type of catalyst, temperature and reactor type. To manipulate the H_2:CO ratio of the syngas in the ATR, either the temperature, S/C ratio, O_2/C ratio or the amount of CO_2 recycled can be used (Ernst et al., 2000).

In this study the specific syngas H_2:CO consumption ratio is 2.15 to obtain a Schulz-Flory alpha value of 0.95. Refer here to figure B.1 and to the literature survey on H_2:CO ratios and the Schulz-Flory alpha values. The H_2:CO consumption ratios were calculated by determining the product distribution according to the Flory–Schulz distribution (see equation B.1)

$$y_n = (1 - p)p^{(n-1)} \tag{B.1}$$

and then determining the H_2:CO consumption ratios accordingly (see equation B.2):

$$ratio = \frac{2n + 1}{n} \cdot y_n \tag{B.2}$$

It is also known that a higher H_2:CO ratio would increase the reaction rate, but can decrease the selectivity. For this study it was assumed that a syngas H_2:CO ratio of 2.15 is sufficient for a reasonable selectivity and a high rate of reaction.
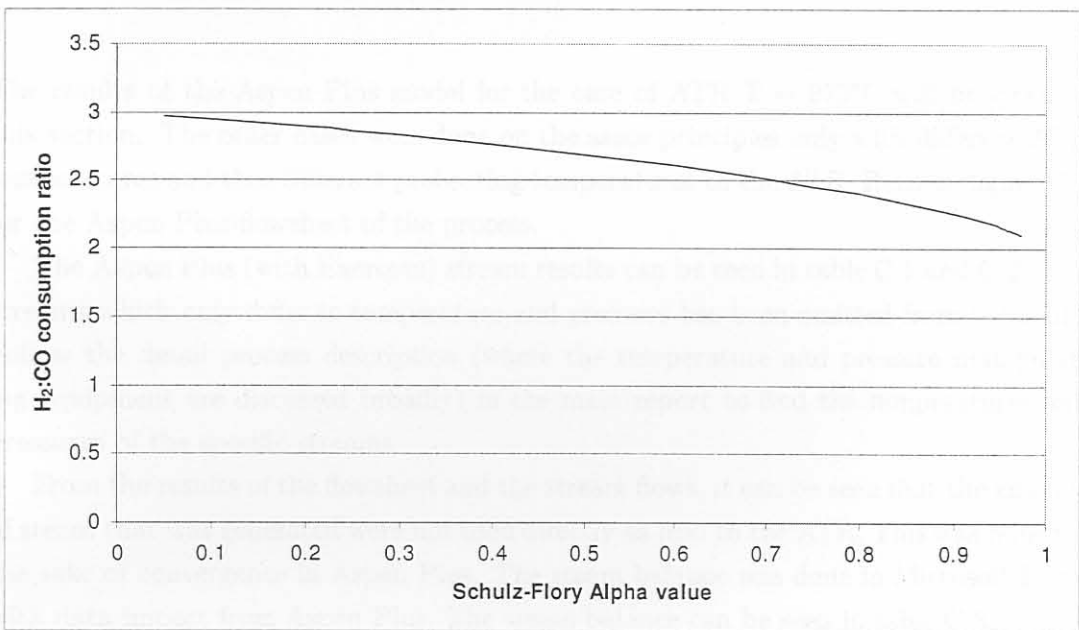
Figure B.1: The H_2:CO consumption ratios

Appendix C

Aspen Plùs modelling results

The results of the Aspen Plus model for the case of ATR T = 975°C will be given in this section. The other cases were done on the same principles only with different ATR temperatures and thus different preheating temperatures to the ATR. Refer to figure C.1 for the Aspen Plus flowsheet of the process.

The Aspen Plus (with Exercom) stream results can be seen in table C.1 and C.2. The streams which only differ in temperature and pressure has been omitted from the table. Follow the detail process description (where the temperature and pressure manipulating equipment are discussed broadly) in the main report to find the temperatures and pressures of the specific streams.

From the results of the flowsheet and the stream flows, it can be seen that the amount of steam that was generated were not used directly as feed to the ATR. This was done for the sake of convergence in Aspen Plus. The steam balance was done in Microsoft Excel with data import from Aspen Plus. The steam balance can be seen in table C.3.

As can be seen from table C.3 the steam generated on the plant was integrated between the Fischer-Tropsch reactor and the ATR. The Fischer-Tropsch reactor operates at 260°C and therefore it can only produce saturated steam at the required pressure. The maximum amount of saturated steam was produced in each scenario for the heat available from the FT reactor.

This saturated steam was then superheated by the hot exit gases from the ATR. The superheated steam generated was then used as feed to the ATR.

In both cases (the FT reactor and the ATR) if surplus steam were generated, the surplus steam was sent through a steam turbine to generate electricity. In some cases (very low and very high ATR temperatures) more saturated steam had to be imported for producing enough superheated steam as feed to the ATR.
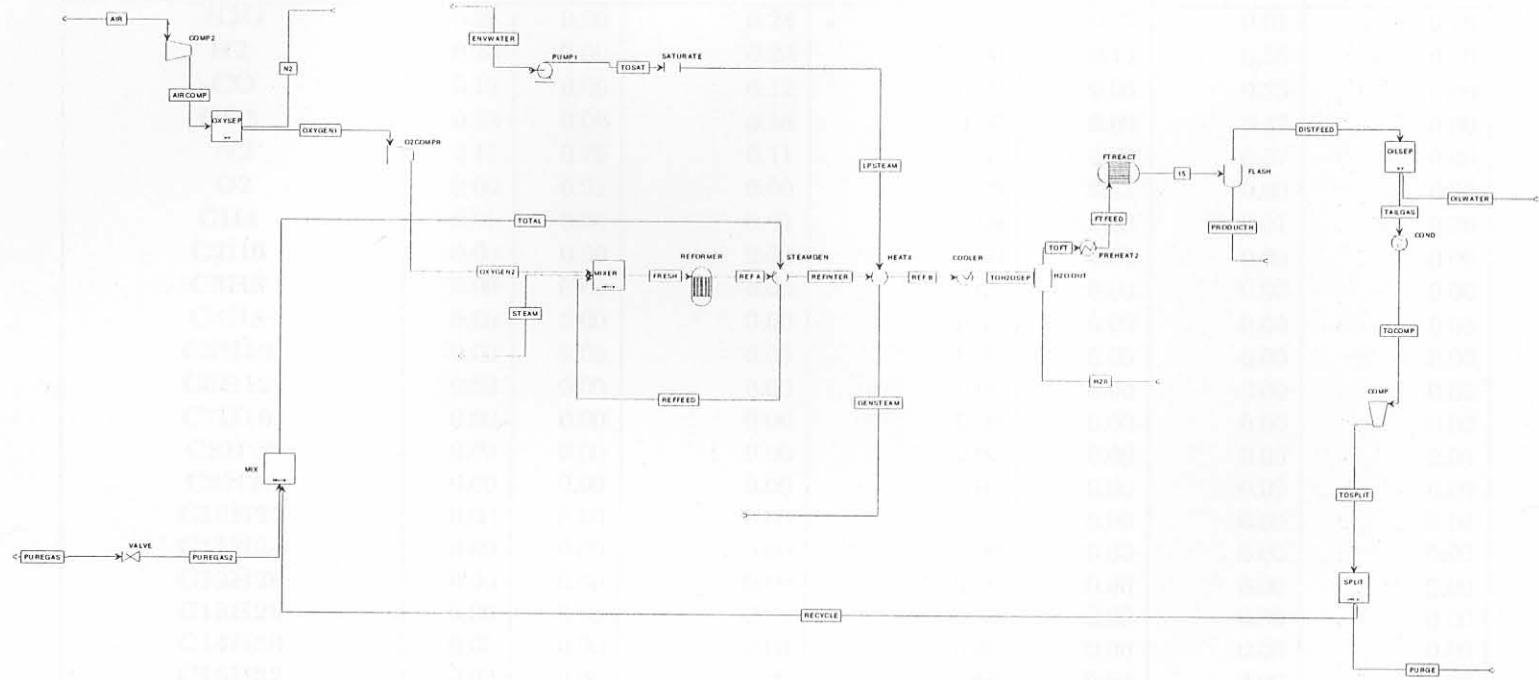
Figure C.1: The Aspen Plus process flowsheet for the GTL process

Table C.1: Stream results for the case of ATR T=975°C

Mole Fraction	15	AIR	DISTFEED	ENVWATER	FRESH	FTFEED	OILWATER
H2O	0.28	0.00	0.28	1.00	0.37	0.01	0.96
H2	0.28	0.00	0.28	0.00	0.13	0.55	0.00
CO	0.12	0.00	0.12	0.00	0.06	0.25	0.00
CO2	0.18	0.00	0.18	0.00	0.09	0.12	0.00
N2	0.11	0.79	0.11	0.00	0.06	0.07	0.00
O2	0.00	0.21	0.00	0.00	0.11	0.00	0.00
CH4	0.01	0.00	0.01	0.00	0.18	0.01	0.00
C2H6	0.00	0.00	0.00	0.00	0.01	0.00	0.00
C3H8	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C4H8	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C5H10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C6H12	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C7H16	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C8H18	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C9H20	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C10H22	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C11H24	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C12H26	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C13H28	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C14H30	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C15H32	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C16H34	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C17H36	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C18H38	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C19H40	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C20H42	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C21H44	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C22H46	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C23H48	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C24H50	0.01	0.00	0.00	0.00	0.00	0.00	0.01
Total Flow KMOL/HR	9764	8902	9713	6550	16891	15151	2884
Total Flow KG/HR	235522	256826	221473	118000	349172	235522	72504
Temperature C	260	25	261	25	716	260	261
Pressure BAR	23	1	23	1	24	23	23

Table C.2: Stream results (continued) for the case of ATR T=975°C

Mole Fraction	OXYGEN2	PRODUCTH	PUREGAS	RECYCLE	REF-A	REFFEED	STEAM
H_2O	0.00	0.10	0.00	0.00	0.30	0.00	1.00
H_2	0.00	0.01	0.00	0.40	0.39	0.26	0.00
CO	0.00	0.01	0.00	0.17	0.18	0.11	0.00
CO_2	0.00	0.02	0.01	0.26	0.08	0.17	0.00
N_2	0.07	0.01	0.02	0.15	0.05	0.11	0.00
O_2	0.93	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	0.00	0.00	0.95	0.01	0.00	0.35	0.00
C_2H_6	0.00	0.00	0.03	0.00	0.00	0.01	0.00
C_3H_8	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_4H_8	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_5H_{10}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_6H_{12}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_7H_{16}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_8H_{18}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C_9H_{20}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$C_{10}H_{22}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$C_{11}H_{24}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$C_{12}H_{26}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$C_{13}H_{28}$	0.00	0.01	0.00	0.00	0.00	0.00	0.00
$C_{14}H_{30}$	0.00	0.01	0.00	0.00	0.00	0.00	0.00
$C_{15}H_{32}$	0.00	0.01	0.00	0.00	0.00	0.00	0.00
$C_{16}H_{34}$	0.00	0.01	0.00	0.00	0.00	0.00	0.00
$C_{17}H_{36}$	0.00	0.01	0.00	0.00	0.00	0.00	0.00
$C_{18}H_{38}$	0.00	0.02	0.00	0.00	0.00	0.00	0.00
$C_{19}H_{40}$	0.00	0.02	0.00	0.00	0.00	0.00	0.00
$C_{20}H_{42}$	0.00	0.03	0.00	0.00	0.00	0.00	0.00
$C_{21}H_{44}$	0.00	0.03	0.00	0.00	0.00	0.00	0.00
$C_{22}H_{46}$	0.00	0.03	0.00	0.00	0.00	0.00	0.00
$C_{23}H_{48}$	0.00	0.04	0.00	0.00	0.00	0.00	0.00
$C_{24}H_{50}$	0.00	0.62	0.00	0.00	0.00	0.00	0.00
Total Flow KMOL/HR	1973	51	3101	5599	21459	8701	6218
Total Flow KG/HR	62563	14049	52437	122155	349172	174591	112017
Temperature C	650	261	279	57	975	885	430
Pressure BAR	24	23	60	26	24	26	24

Table C.3: Steam balance for the case of ATR T=975°C

Type of steam	Value	Unit
Sat. steam generated by FT-Reactor	163006.1	kg/hr
Sat. steam used for superheated steam generation	118000.0	kg/hr
Sat. steam exported	45006.1	kg/hr
Sat. steam exported (Exergy)	11700558.4	Watt
Sat. steam exported (Exergy/ton product)	1.2	GJ / t C5-C25 product
Superheated steam generated	118000.0	kg/hr
Superheated steam exported	5990.0	kg/hr
Superheated steam exported (Exergy)	2099300.0	Watt
Superheated steam exported (Exergy/ton product)	0.2	GJ / t C5-C25 product

The summary of the energy and exergy balances were already given in the main report in table 5.3. The energy and exergy stream values for the case of ATR T = 975°C can be seen in table C.4 and table C.5.

The other important information for completing the energy and exergy balances are the electricity generation values. These values can be seen in table C.6.

The efficiencies that were used for the turbines are accounted for by Williams & Larson (1993) and Smith *et al.* (1996). The highest possible conversion for a combined cycle were used with the incineration of the gas in a gas turbine to generate steam. This steam is again used in a steam turbine to generate electricity. This was taken from Williams & Larson (1993).

The steam turbine efficiencies (Smith *et al.*, 1996) were obtained from the best efficiency values of current steam turbines.

The generation of electricity for the other scenario cases can be seen in the main report in figure 5.12.

Table C.4: Energy and exergy stream values for the case of ATR T=975°C

Property (Watt)	15	AIR	DISTFEED	ENVWATER	FRESH	FTFEED	OILWATER
Chemical Enthalpy	5.30E+08	-2.00E+04	3.63E+08	-8.01E+07	7.10E+08	6.81E+08	2.46E+08
Mix Enthalpy	-5.87E-08	-9.41E+01	6.54E+05	0.00E+00	2.55E+05	1.61E+05	1.45E+05
Physical Enthalpy	5.93E+07	2.62E+02	5.60E+07	-4.11E+01	2.02E+08	3.02E+07	4.32E+07
Total Enthalpy	5.90E+08	-1.99E+04	4.20E+08	-8.01E+07	9.13E+08	7.12E+08	2.89E+08
Chemical Exergy	7.94E+08	3.47E+06	6.14E+08	1.64E+06	9.78E+08	8.66E+08	2.98E+08
Mix Exergy	-1.12E+07	-3.15E+06	-1.07E+07	0	-2.04E+07	-1.21E+07	-3.92E+05
Physical Exergy	3.45E+07	-80638.1	3.31E+07	-51.05045	1.15E+08	4.06E+07	1.48E+07
Total Exergy	8.18E+08	2.37E+05	6.36E+08	1.64E+06	1.07E+09	8.95E+08	3.13E+08

Table C.5: Energy and exergy stream values (continued) for the case of ATR T=975°C

Property (Watt)	OXYGEN2	PRODUCTH	PUREGAS	RECYCLE	REF-A	REFFEED	STEAM
Chemical Enthalpy	-5.16E+03	1.69E+08	6.89E+08	9.42E+07	6.08E+08	7.83E+08	-7.60E+07
Mix Enthalpy	1.98E+01	3.24E+04	1.28E+04	2.29E+05	2.82E+05	3.61E+04	0.00E+00
Physical Enthalpy	1.10E+07	2.31E+06	9.20E+06	1.08E+06	2.72E+08	9.23E+07	1.03E+08
Total Enthalpy	1.10E+07	1.71E+08	6.98E+08	9.55E+07	8.81E+08	8.75E+08	2.69E+07
Chemical Exergy	2.05E+06	1.81E+08	7.16E+08	2.58E+08	8.68E+08	9.74E+08	1.55E+06
Mix Exergy	-3.49E+05	-42424.07	-5.67E+05	-5.28E+06	-2.06E+07	-9.33E+06	0
Physical Exergy	9.46E+06	6.59E+05	1.13E+07	1.24E+07	1.72E+08	7.06E+07	3.77E+07
Total Exergy	1.12E+07	1.82E+08	7.26E+08	2.66E+08	1.02E+09	1.04E+09	3.93E+07

Table C.6: Electricity balance for the case of ATR T=975°C

UNIT	Exergy in (Watt)	Exergy out (Watt)	Electr. generated (Watt)	Efficiency	Electr. generated (GJ/t C5-C25 product)
Tail Gas Combustion	5.83E+07	2.91E+07	2.91E+07	0.50	2.8689
Sup. steam turbine	2099300.00	1.47E+06	6.30E+05	0.70	0.0620
Sat. steam turbine	1.17E+07	8.19E+06	3.51E+06	0.70	0.3455

Appendix D

Exergy analysis results

D.1 Internal exergy loss

The exergy results from the Exercom routines were used to calculate the irreversibility of each process unit. The exergy balance for each unit will be shown in this section only for the case of ATR T = 975°C.

The irreversibilities were calculated by using equation 2.19. The duties associated with each unit can be seen in table D.1.

Table D.1: Work duties of important unit processes for ATR T = 975°C

Process Unit	Duties (GJ/ton product)
Blower	0.0987
Water separation cooler	-17.0722
FT-Reactor	-12.0139
Steam generator	1.4572
FT-Reactor preheater	2.7096
ATR feed preheater	8.0383
Total water pumped	0.2226

D.1.1 The reformer irreversibility

The ATR was modelled with no external heat supplied to the reformer. All the heat supplied to the ATR were by means of feed preheating (with exhaust gases) and methane burnt in the ATR. After applying the exergy balance (equation 2.19) to the reformer (with the irreversibility of the mixing of the feed included) an irreversibility of 6.52 GJ/ton

product (where the product is defined as the C_1–C_{25} cut produced in the work-up) was obtained.

D.1.2   The ATR feed preheater irreversibility

The amount of feed preheating to the ATR were done without taking into consideration the effect of sooting. With this assumption, a two stream heat exchanger model was used in Aspen Plus with a design constraint on the outlet temperature of the cold stream at $(T_{ref} - 75)°C$. This was a rough estimation without any mean-temperature driving force (ΔT) and without any consideration of the transport equation:

$$Q = UA\Delta T_m \tag{D.1}$$

where U is the overall heat transfer coefficient, A is the area for heat transfer and ΔT_m is the mean temperature-driving force for heat transfer.

Equation 2.19 were used on the heat exchanger only considering the two input exergy flows and the two output exergy flows. No internal heat losses were considered. The resulting irreversibility was 0.896 GJ/ton product.

D.1.3   The steam generator irreversibility

Environmental water are pressurised (by a pump) to 24 bar and saturated to vapour (2800.9 kJ/kg, 24 bar) by the heat from the Fischer-Tropsch reactor. This saturated vapour steam is then superheated (h=3297.5 kJ/kg, 24 bar) by the reformer tailgas. The design constraint of 430°C was put on the cold stream outlet temperature. This results in saturated vapour being heated from 222°C to 430°C which is superheated steam at the correct temperature and pressure for feed to the reformer.

The amount of saturated steam that is generated by the FT reactor is 163006 kg/hr. The amount of heat available from the hot reformer outlet gas can superheat 118000 kg/hr of saturated steam. Thus 163006 - 118000 = 45006 kg/hr of saturated steam can be exported to the steam turbines for electricity generation.

But of the 118000 kg/hr of superheated steam generated, only 112010 kg/hr is necessary as feed to the ATR. This then implies a superheated steam export of 5990 kg/hr which is also used for electricity generation.

The irreversibility of the steam generator was calculated with the exergy balance. The balance consisted of the two inlet and two outlet exergy flows to the steam generator.

The irreversibility was 0.217 GJ/ton product.

D.1.4   The Fischer-Tropsch (FT) reactor irreversibility

The thermal exergy was calculated by multiplying the FT reactor duty with the Carnot factor. This can be seen in equation D.2. T_r was taken as 533K and T_0 as 298K.

$$Q \cdot (1 - \frac{T_0}{T_r}) \qquad \text{(D.2)}$$

After applying the exergy balance (equation 2.19) over the FT reactor an irreversibility of 2.29 GJ/ton product was obtained.

D.1.5   The work-up irreversibility

The irreversibility of the work-up unit was not calculated. since this unit was not yet modelled in detail and since the condenser temperature in the distillation column was close to the reference temperature. The condenser was thus a pseudo unit to model the condenser of the separation column (the Sep block was used in Aspen Plus). Therefore the irreversibility of the condenser was not calculated.

D.1.6   The blower irreversibility

The work exergy was taken as equal to the blower duty. After applying the exergy balance over the blower an irreversibility of 0.025 GJ/ton product was obtained. This loss would have been much greater if the blower was not modelled as isentropic in Aspen Plus. The isentropic compressor efficiency was kept at the default value of 0.72.

D.2   External exergy loss

The external exergy losses are shown in table D.2.

As can be seen from table D.2, the waste streams (or streams not associated with product streams) are included in external exergy losses. The purge combusted stream refers to the purge stream in the recycle loop that is combusted in the combined cycle to produce electricity. An attempt was made to utilise the maximum amount of exergy available from each waste stream in the process.

Table D.2: External exergy losses for ATR T = 975°C case

Stream	Exergy loss (GJ/ton product)
N_2 stream in oxygen separation	1.398
H_2O separated before FT reactor	0.178
Water condensed after used as steam	0.223
Purge combusted stream (for electricity)	5.565