Chapter 5

Results and discussion

5.1 The process synthesis study to determine the governing interaction variables of the process

The process synthesis study on the GTL process was done to find the governing interaction variables of the combined reforming and FT processes (with external recycle). The results of the process synthesis study was used to construct the basic process layout.

The simulation used in this section was discussed in the design chapter (chapter 3) and for this section no process integration was used. The reason for this is that the integration complicates the interaction between the units. To determine the governing interaction variables in order to improve our basic understanding of the GTL process, the process was studied in its simplest form.

5.1.1 Controlling the H_2:CO ratio of the syngas

At the exit of the reformer, the syngas (product from the reformer) will be the equilibrium of the methane reforming and the water gas shift reactions (see equations 3.1 and 3.2). Equilibrium thermodynamics determine syngas composition by the adiabatic heat balance. Main variables are exit pressure and feed ratios: H_2O/C, CO_2/C and O_2/C. Reformer temperature is directly linked to O_2/C feed ratio. The equilibrium simulation results can be seen in figure 5.1 and 5.2.

Figure 5.1 shows the simulation results of the syngas ratio and oxygen consumption dependence of the H_2O/CH_4 feed ratio. The temperature in the reformer is dependent on the amount of oxygen fed, thus the temperature varied accordingly between 900°C and 1200°C.

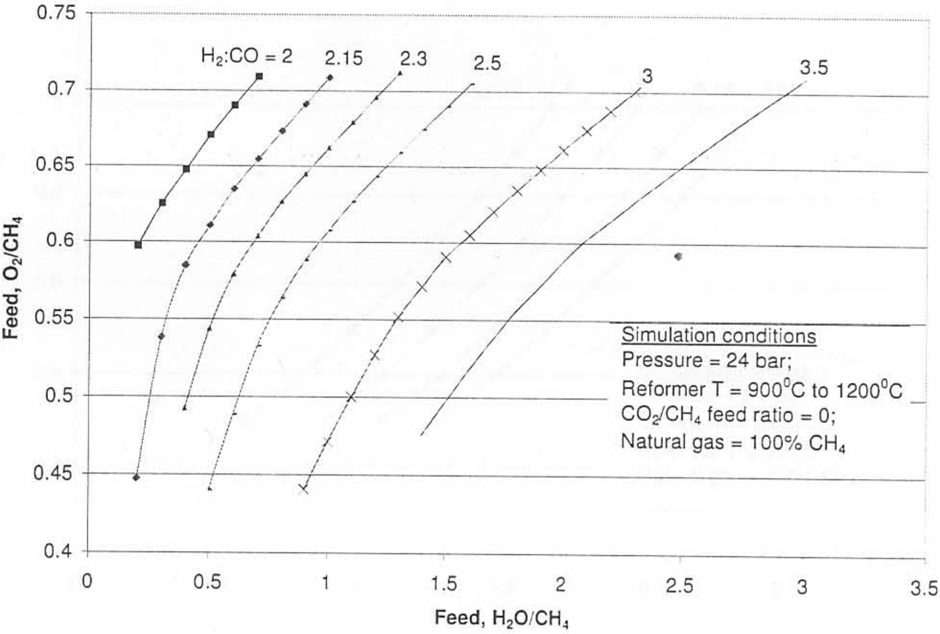

Figure 5.1: The H_2:CO ratios of the syngas without CO_2 feed

Traditionally, ATR plants operate at H_2O/C ratios of 2.0 to 3.5 yielding H_2:CO ratios of between 3.3 and 4.0 (Christensen & Primdahl, 1994). Production of H_2/CO ratio below 2.2 requires CO_2 addition. The effect of adding (recycle or import) CO_2 is illustrated in figure 5.2, which shows that curves for constant H_2:CO ratios are dependent on two feed ratios: H_2O/C and CO_2/C.

The most important curve for our study is the constant H_2:CO ratio curve of 2.15. To obtain maximum carbon efficiency, maximum CO_2 recycle is required while maintaining a H_2:CO syngas ratio of 2.15. This temperature is a function of the O_2/CH_4 feed ratio. Thus the optimum temperature of the reformer needs to be targetted, because the temperature in the reformer would determine the maximum amount of CO_2 which could be recycled and also the success of integration that could take place between the process units.

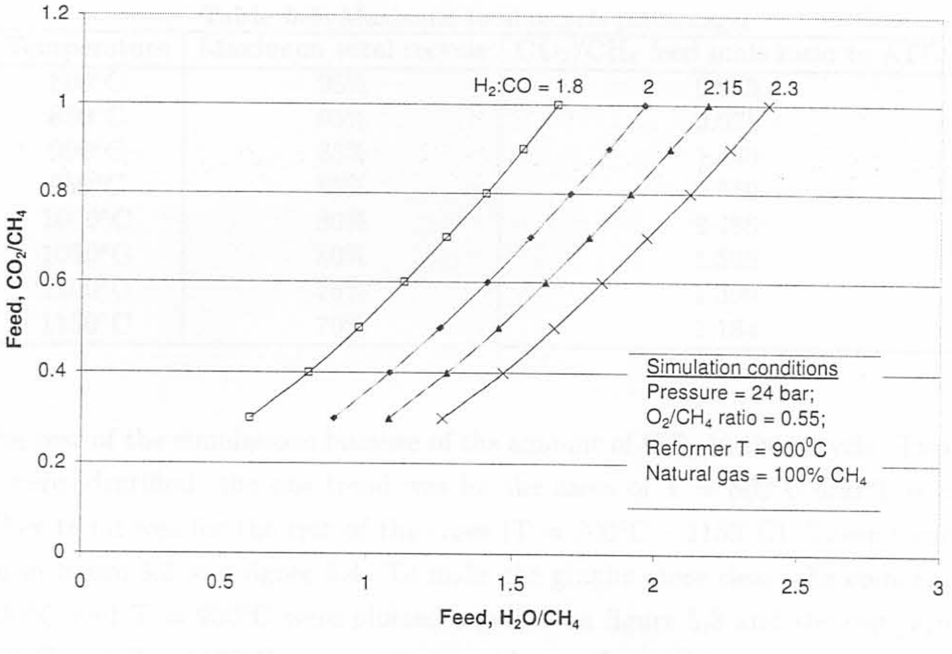

Figure 5.2: The H_2:CO ratios of the syngas with CO_2 feed

5.1.2 Varying ATR temperature with maximum amount of CO_2 recycling

An Aspen Plus simulation was used for varying the ATR temperature between 800°C and 1150°C with intervals of 50°C. The O_2/C feed ratio was manipulated to a minimum to maintain the specific temperature. The H_2O/C feed ratio was also manipulated to a minimum to maintain a H_2:CO syngas ratio of 2.15. Taking all the said conditions into account, the external recycle was varied between 0 and maximum. Maximum external recycle flow is reached when it is impossible to maintain a H_2:CO syngas ratio of 2.15, because the CO_2 in the external recycle lowers the H_2:CO syngas ratio. In other words there exists a maximum recycle capability for every specific ATR temperature with the other manipulated variables (O_2/C and H_2O/C feed ratios) at a minimum.

The maximum total recycle percentages that were achieved can be seen in table 5.1 as well as the maximum amount of CO_2 recycled given as a fraction of the total amount of CH_4 fed to the reformer.

A total recycle of 95% implies that 95% of the work–up tailgas is recycled and 5% is purged. From table 5.1 it can be seen that the simulations at 800 and 850°C differ

Table 5.1: Maximum total recycle percentages

Temperature	Maximum total recycle	CO_2/CH_4 feed mole ratio to ATR
800°C	95%	0.069
850°C	95%	0.075
900°C	85%	1.440
950°C	85%	2.550
1000°C	80%	2.488
1050°C	80%	1.538
1100°C	75%	1.399
1150°C	70%	1.134

from the rest of the simulations because of the amount of CO_2 in the recycle. Two basic trends were identified: the one trend was for the cases of T = 800°C and T = 850°C. The other trend was for the rest of the cases (T = 900°C - 1150°C). These trends can be seen in figure 5.3 and figure 5.4. To make the graphs more clear, the comparison of T = 800°C and T = 950°C were plotted together on figure 5.3 and the comparison of T = 950°C and T = 1150°C were plotted together on figure 5.4.

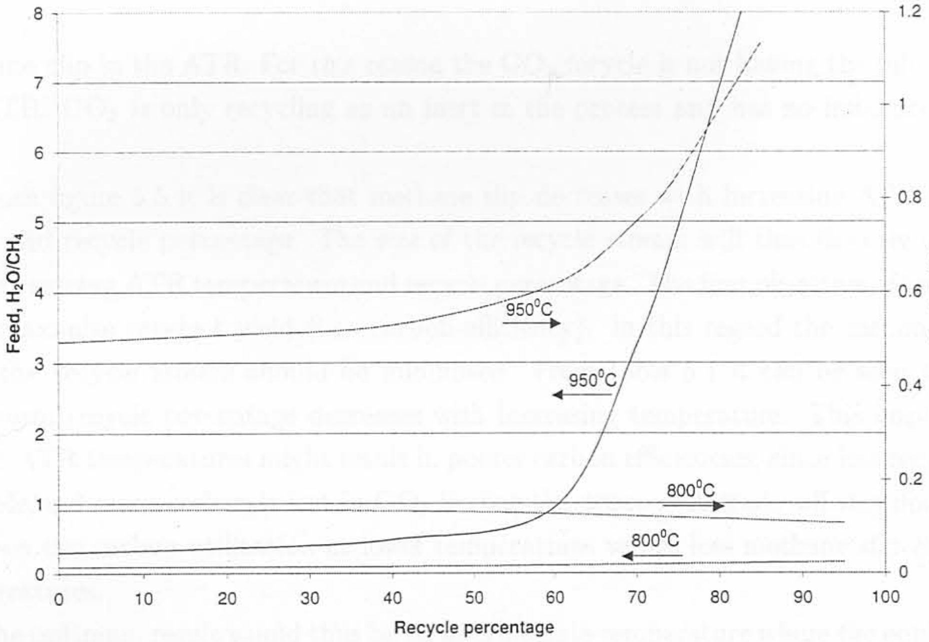

Figure 5.3: The steam/methane and oxygen/methane feed ratios to the ATR (1st scenario)

The trend for the T = 800°C case is due to the low temperature which encourages

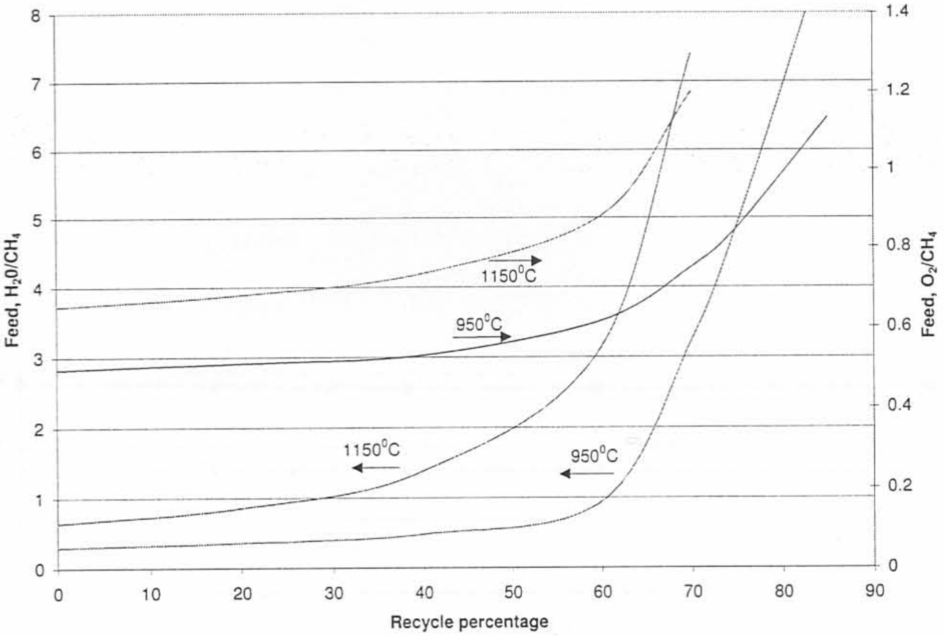

Figure 5.4: The steam/methane and oxygen/methane feed ratios to the ATR (2nd scenario)

methane slip in the ATR. For this reason the CO_2 recycle is not having the full effect in the ATR. CO_2 is only recycling as an inert in the process and has no influence on the ATR.

From figure 5.5 it is clear that methane slip decreases with increasing ATR temperature and recycle percentage. The size of the recycle stream will thus directly decrease with increasing ATR temperature and recycle percentage. The first objective of this study is to maximise product yield (i.e. carbon efficiency). In this regard the carbon purged from the recycle stream should be minimised. From table 5.1 it can be seen that the maximum recycle percentage decreases with increasing temperature. This implies that higher ATR temperatures might result in poorer carbon efficiencies, since less recycling is possible and more carbon is lost in CO_2 leaving the process. A trade–off therefore exists between the carbon utilization at lower temperatures versus less methane slip at higher temperatures.

The optimum result would thus be an intermediate temperature where the equilibrium in the reactor is sufficient to decrease methane slip and increase the external recycle percentage (which will contribute to a higher carbon efficiency). An added benefit will be the smaller amount of O_2 needed to maintain the ATR temperature as well as a smaller

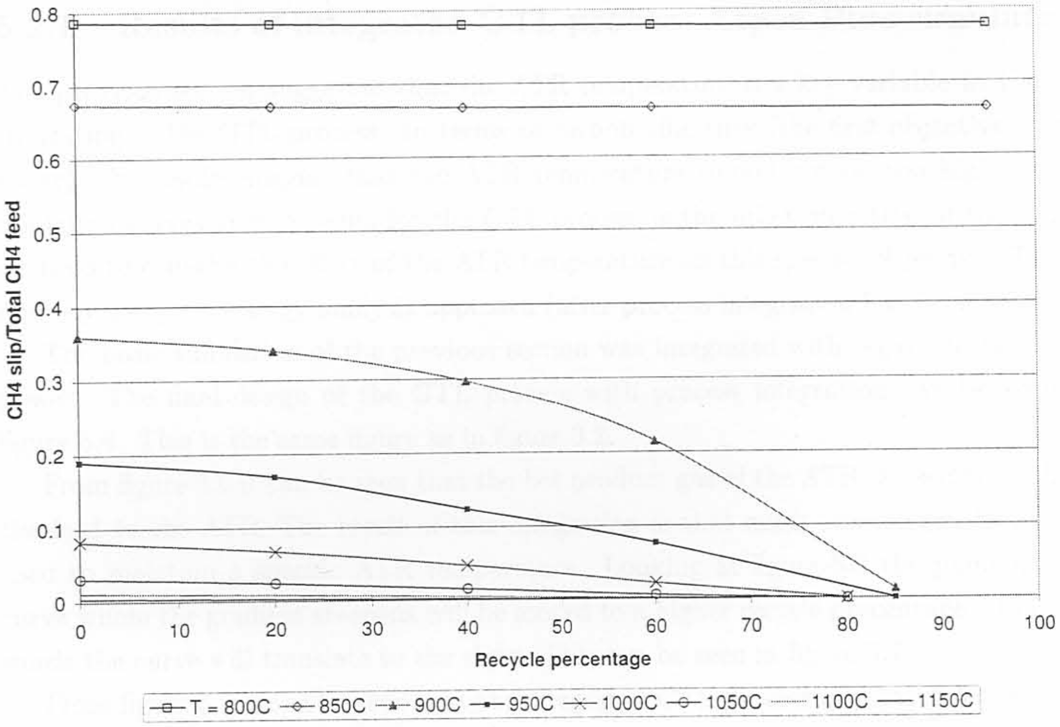

Figure 5.5: The methane slip percentage as a function of total methane fed to the ATR

H_2O/C ratio to maintain the desired H_2:CO ratio (see figures 5.3 and 5.4).

All of these simulations were done without any process integration. Integration will complicate the interaction between the units and could have a positive or negative influence on the process.

5.2 Determining optimum ATR temperature with exergy analysis and process integration

5.2.1 Results of integrated GTL process Aspen Plus simulation

The previous section suggested that the ATR temperature is a key variable in the optimization of the GTL process. In terms of carbon efficiency (the first objective of the study), the results suggest that the ATR temperature should not be too high. Since minimum energy requirements for the GTL process is the other objective of the study, we need to consider the effect of the ATR temperature on this specific objective. This is done by using the exergy analysis approach (after process integration has been done).

The basic simulation of the previous section was integrated with regard to heat and power. The final design of the GTL process with process integration can be seen in figure 5.6. This is the same figure as in figure 3.2.

From figure 5.6 it can be seen that the hot product gas of the ATR is used to preheat the feed to the ATR. The result of this integration is that much less oxygen has to be used to maintain a specific ATR temperature. Looking at figure 5.3 the point on the curve where the gradient steepens will be moved to a higher recycle percentage – in other words the curve will translate to the right. This can be seen in figure 5.7.

From figure 5.7 it can be seen that the integrated GTL process uses much less oxygen in the reformer than the non-integrated GTL process. Both the simulations were done at an ATR temperature of 900°C and a H_2:CO syngas ratio of 2.15.

Results for maximum external recycling and optimum feed to ATR

An integrated Aspen Plus simulation of the GTL process was used for varying the ATR temperature with maximum CO_2 recycling to the reformer. The H_2:CO syngas ratio was again kept at 2.15 with the minimum H_2O/C and O_2/C feed ratio. Temperatures of the ATR were varied between 905°C and 1170°C. The maximum recycle percentages that were achieved while maintaining a H_2:CO syngas ratio of 2.15 can be seen in table

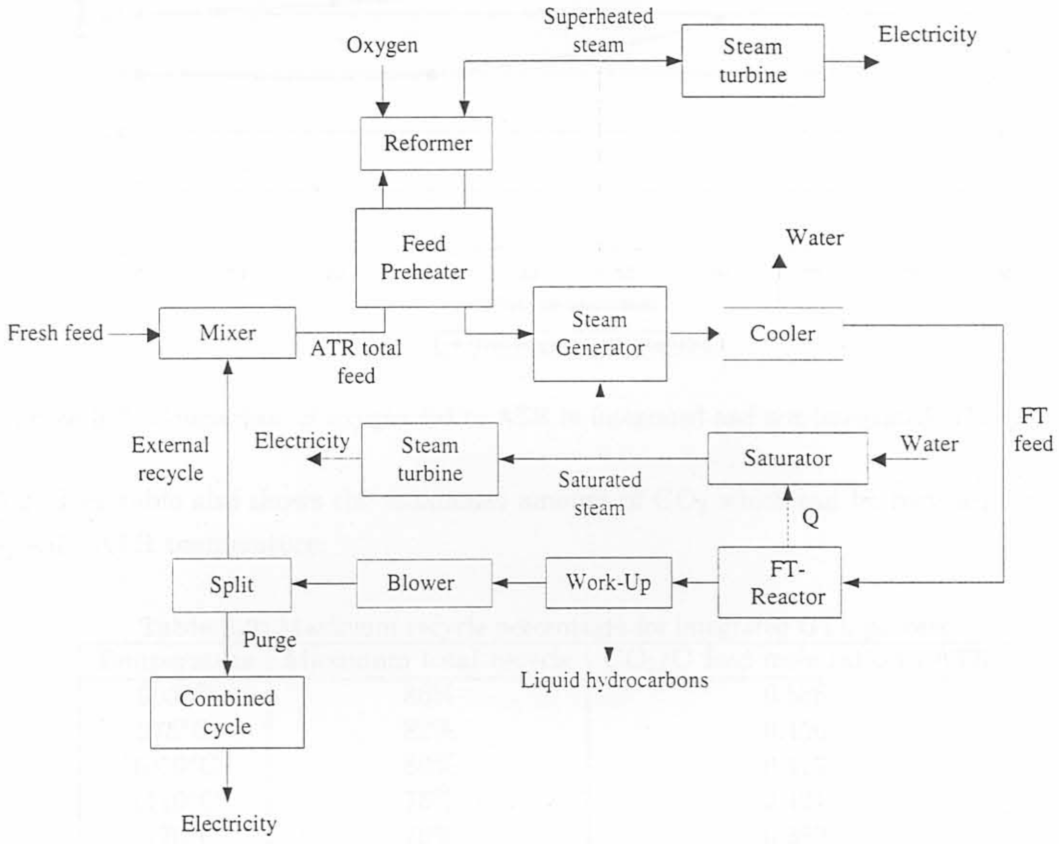

Figure 5.6: The final design of the GTL process with process integration

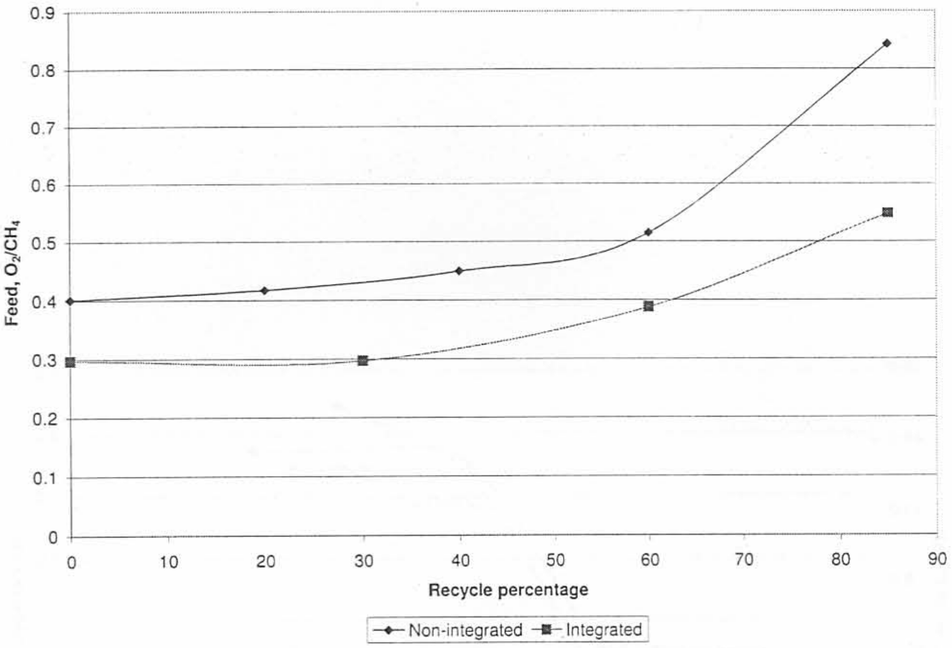

Figure 5.7: Comparison of oxygen fed to ATR in integrated and non-integrated GTL process

5.2. This table also shows the maximum amount of CO_2 which can be recycled for this specific ATR temperature.

Table 5.2: Maximum recycle percentages for integrated GTL process

Temperature	Maximum total recycle	CO_2/C feed mole ratio to ATR
905°C	86%	0.566
975°C	82%	0.456
1010°C	80%	0.413
1110°C	75%	0.421
1170°C	70%	0.362

The result of the simulation for the feed to the ATR can be seen in figure 5.8.

The steam/carbon feed ratio in figure 5.8 shows that the minimum feed results between 905°C and 1010°C. But with regard to expensive oxygen use, the lowest temperature possible would be the optimum.

Table 5.2 clearly indicates that a lower temperature in the ATR would result in higher maximum external recycling which would imply higher carbon efficiencies. The carbon efficiencies can be seen in figure 5.9.

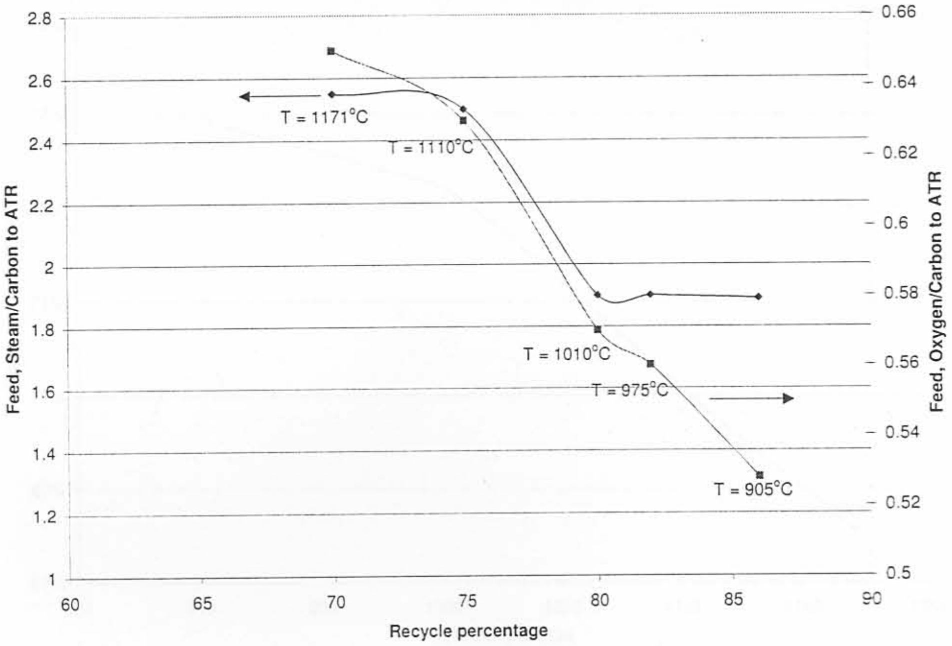

Figure 5.8: The steam/carbon and oxygen/carbon feed ratio to the ATR at maximum recycle (integrated process)

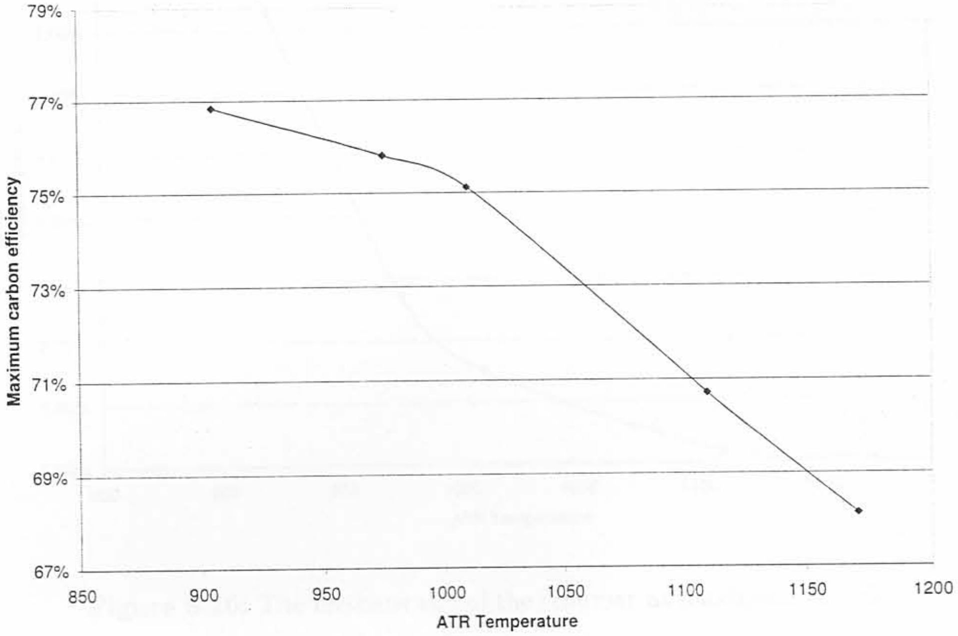

Figure 5.9: The maximum carbon efficiencies of the GTL process at different ATR temperatures

It can be seen from figure 5.9 that the carbon efficiency of the GTL process decreases with an increase in ATR temperature (extreme values between 77% for ATR T = 905°C and 68% for ATR T = 1171°C). Therefore the carbon efficiency would also be maximised with the lowest possible ATR temperature. The only negative impact of the high rate of external recycling is the increase in methane slip in the reformer. The results of the methane slip can be seen in figure 5.10.

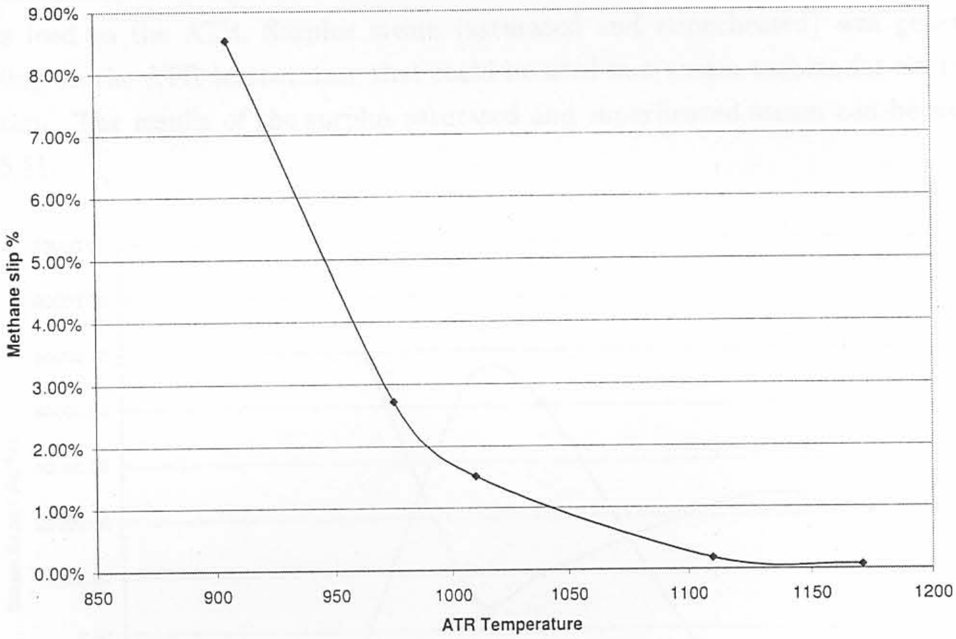

Figure 5.10: The methane slip of the reformer at maximum recycle

From the results of the methane slip in the reformer it is clear that the methane slip decreases with an increase in ATR temperature. This implies that we would rather want to operate the ATR at a higher temperature, because CH_4 conversion increases with a decrease in methane slip. But a methane slip of 8.53% (the highest case in this study) is still acceptable. From Rostrup-Nielsen (2002) it is known that acceptable CH_4 conversions of 70% can be attained with a methane slip of 8%. Thus for this study the lowest operating ATR temperature of 905°C has an acceptable methane slip.

Results for steam and electricity generation

The heat and power integration also provides a new design variable which should be considered – electricity generation. But before the results of the electricity generation can be analysed, the amount of steam exported for electricity generation should be considered. Since all steam was generated at a pressure of 24 bar, the steam was divided into saturated (222°C) and superheated (430°C) steam. The saturated steam was generated with the heat from the Fischer–Tropsch reactor and the superheated steam with the heat from the reformer product gas. The saturated steam generated with the FT reactor was used as feed to the superheated steam generation. The maximum amount of saturated and superheated steam were generated with the heat available. The superheated steam was used as feed to the ATR. Surplus steam (saturated and superheated) was generated depending on the ATR temperature that could be used in a steam turbine for electricity generation. The results of the surplus saturated and superheated steam can be seen in figure 5.11.

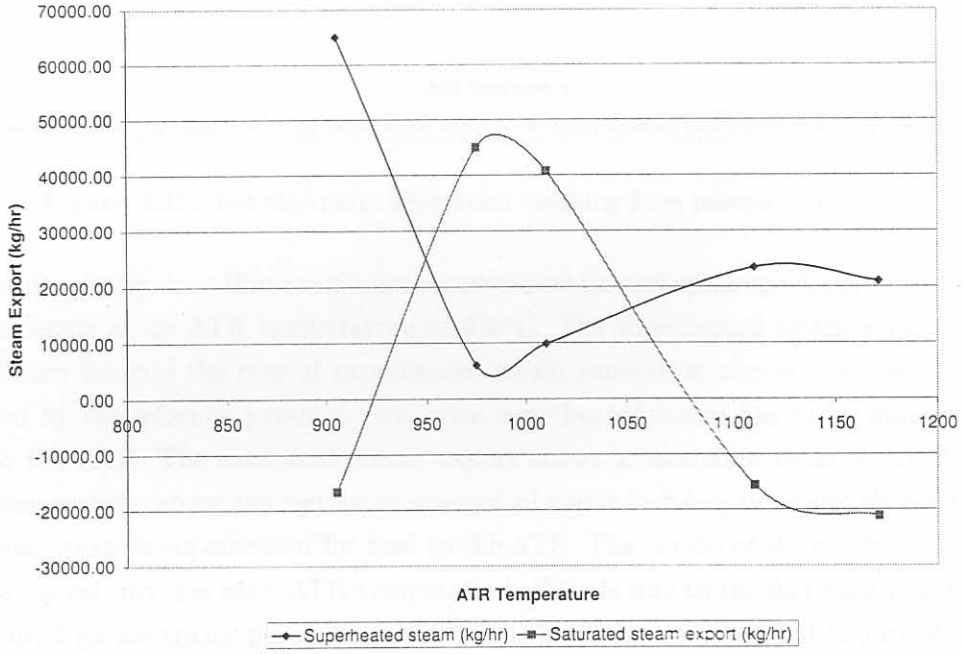

Figure 5.11: The surplus steam for electricity generation resulting from process integration

These results will be discussed together with the results of electricity generation which can be seen in figure 5.12.

Firstly it should be mentioned that the negative values on the surplus steam figure indicate that extra saturated steam had to be generated (or could be imported). This implies that import heat was necessary to generate sufficient saturated steam for feed to the superheated steam generator, because the heat from the FT reactor was not enough.

5.2.2 Results of the exergy analysis

Exergy losses and target exergy values for different ATR temperature scenarios

The exergy results can be seen in figures 5.13 and 5.14.

Table 5.3 presents energy and exergy figures for the different ATR temperatures on an absolute basis per unit C_5–C_{25} yield. Since absolute exergy losses are invariant and directly reflect the amount of work–potential being lost, regardless of the total amount of incoming energy and exergy, these are recommended rather than exergetic efficiencies when reporting on exergy analysis.

According to Hinderink *et al.* (1996) exergetic efficiencies are a more ambiguous measure, since they can be defined in numerous ways.

From table 5.3 it is clear that the amount of natural gas needed to make one ton of product increases with an increase in ATR temperature. With the exception of the process inputs water and air, which do not significantly contribute to the overall incoming energy and exergy, all inputs are associated with the application of natural gas, when generation efficiencies for power and import exergy are accounted for.

Approximately, 56–62% of the total incoming exergy is retained in the C_5–C_{25} product. This is known as target exergy and is also shown in figure 5.14. The exergy loss figures in the table are also represented in figure 5.13. These results will now be discussed along with figures 5.13 and 5.14.

The total exergy losses can be divided into internal and external exergy losses. Internal losses, also called irreversibilities, take place due to internal degradation of energy, while external losses can occur if process streams are emitted into the environment. From the results it can be seen that the total exergy loss increases with an increase in ATR temperature. The loss is at an even steeper gradient when the temperature is above 1010°C. This clearly indicates that the GTL process should rather be run at a low ATR temperature. This result is also supported by the results of the exergy contained in the product and is even more specific at which temperature the ATR should be run. If the exergy contained in the product is divided by the total exergy input, a maximum is obtained at an ATR temperature of 975°C. The actual exergy contained in the product decreases with an increase in ATR temperature and this is due to the lower carbon efficiency with higher ATR temperature. This result is based upon target exergy. Target exergy is denoted as a comparison between the actual input of exergy to exergy stored in the final product. In theory, a quantity of exergy equal to the target exergy, more or less

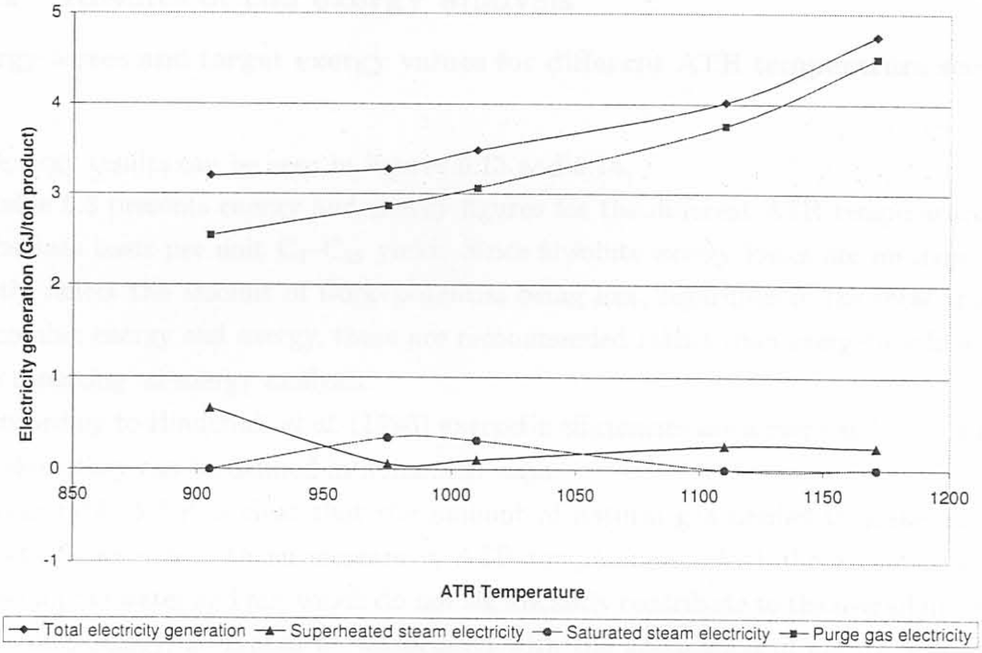

Figure 5.12: The electricity generation resulting from process integration

The results clearly show that maximum saturated steam and minimum superheated steam export occurs at an ATR temperature of 980°C. The superheated steam export shows a minimum because the rate of superheated steam generation almost matches the heat supplied by the reformer product. No extra superheated steam has to be imported for feed to the ATR. The saturated steam export shows a maximum because the ATR is at a temperature where the optimum amount of steam is being used and therefore less saturated steam is superheated for feed to the ATR. The results of electricity generation show a logical increase with ATR temperature. This is due to the fact that besides the steam used for electricity generation, the tailgas from the work–up that is purged at the recycle split is also used for electricity generation. From the previous results discussion it is known that the amount of purge gas increases with an increase in ATR temperature. Thus more electricity will be generated at higher ATR temperatures, also due to the fact that more heat is available. *It should be kept in mind that the goal of the process is to make a diesel product and not to generate electricity.*

With this steam and electricity generation in mind the discussion could now be focused on the exergy analysis results.

Table 5.3: Energy and exergy figures for various ATR temperatures

					Useful exergy output (GJ/t product)		Exergy loss (GJ/t product)		
T	Feedstock NG (N m^3/t product)	Fuel NG (N m^3/t product)	Total energy input (GJ/t product)	Total exergy input (GJ/t product)	C_5–C_{25} product	Electricity	Internal	External	Total
905°C	2075	145	58.0	77.5	48.7	3.2	18.43	6.73	25.15
975°C	2103	154	56.9	77.2	48.7	3.3	18.70	7.36	26.07
1010°C	2122	162	57.4	77.8	48.7	3.5	18.98	7.77	26.76
1110°C	2254	258	57.1	83.3	48.7	4.0	23.37	9.42	32.79
1170°C	2340	298	58.9	86.8	48.7	4.7	25.43	11.01	36.44

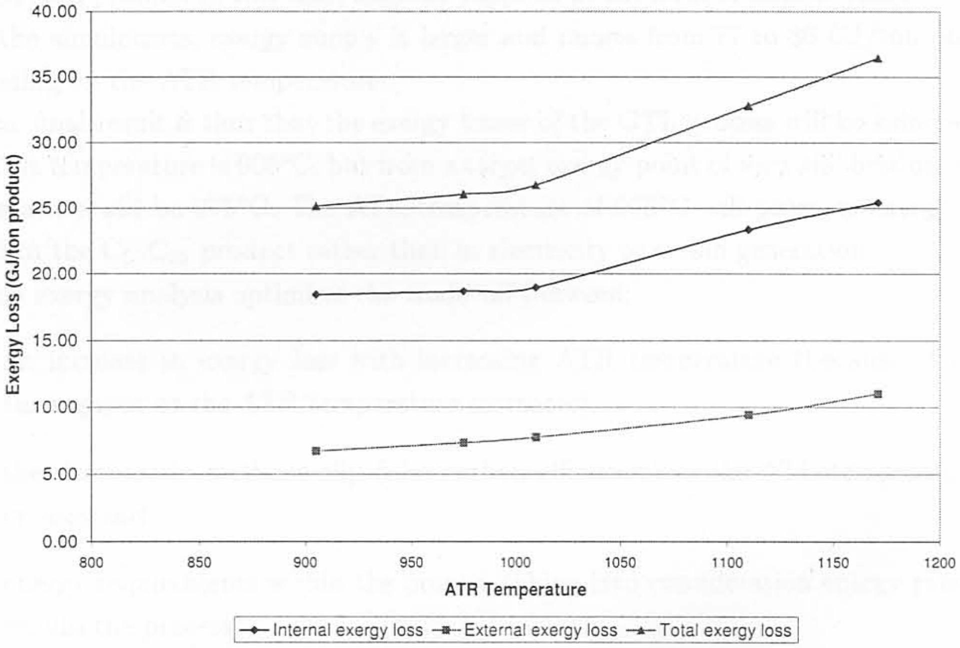

Figure 5.13: The total exergy loss (internal and external) of the GTL process

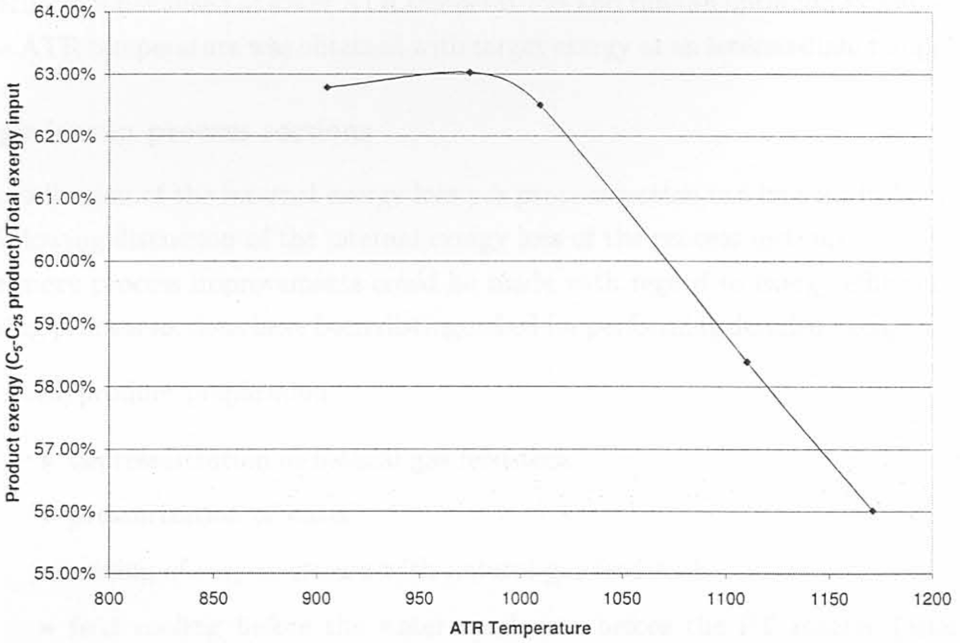

Figure 5.14: The exergy contained in the C_5 – C_{25} product of the GTL process

48.7 GJ/ton product in this case, must be supplied in the form of natural resources. But from the simulations, exergy supply is larger and ranges from 77 to 86 GJ/ton product depending on the ATR temperature.

The final result is thus that the exergy losses of the GTL process will be minimised if the ATR temperature is 905°C, but from a target exergy point of view the best operating temperature will be 975°C. The ATR temperature of 975°C will promote exergy to be stored in the C_5–C_{25} product rather than in electricity or steam generation.

The exergy analysis optimises the trade–off between:

- an increase in exergy loss with increasing ATR temperature (because of bigger throughput as the ATR temperature increases),
- the decrease in methane slip (also carbon efficiency) as the ATR temperature increases and
- energy requirements within the process taking into consideration energy produced within the process.

An advantage of exergy analysis is that all products of the process (including export electricity) can be evaluated and compared. Misdirected energy in the form of export electricity was penalised at lower ATR temperatures and thus an optimum exergy solution for the ATR temperature was obtained with target exergy at an intermediate temperature.

Exergy loss in process sections

The subdivision of the internal exergy loss per process section can be seen in figure 5.15. The following discussion of the internal exergy loss of the process sections could indicate where more process improvements could be made with regard to exergy efficiency. The following process sections have been distinguished for performing detailed exergy analyses:

1. Feed/product preparation
    - depressurization of natural gas feedstock
    - pressurization of water
    - mixing of recycle stream with natural gas feedstock
    - feed cooling before the water condenser before the FT reactor (after heat exchange with ATR feed and superheated steam generation)
    - feed preheating to the FT reactor

    - blower in recycle to the ATR.

2. ATR reaction section
    - autothermal reformer
    - mixing feeds
3. Heat recovery – ATR reaction section
    - feed preheater
    - steam generator
4. SBR reaction section
    - SBR reactions
5. Heat recovery – SBR reaction section
    - saturated steam generation with heat from SBR
6. Air separation
    - air compressors
    - oxygen and nitrogen separation
7. Power generation
    - generation of electricity with saturated and superheated steam
    - generation of electricity with combined cycle (purge tailgas)

As could be seen from figure 5.13, the overall internal exergy loss increases with an increase in ATR temperature. Figure 5.15 shows a more detailed subdivision of the reasons for the increase in exergy loss.

The feed/product preparation internal exergy loss increase tremendously with an increase in ATR temperature, mainly because of the large amount of cooling that has to be done for the water to condense during feed preparation before the SBR.

The exergy losses in the ATR reaction section also increase with an increase in temperature, because the thermodynamic driving forces become too large and are unnecessary.

The heat recovery section for the ATR shows lowest internal exergy losses at a temperature of 1010°C. This is due to the large amount of saturated steam available for

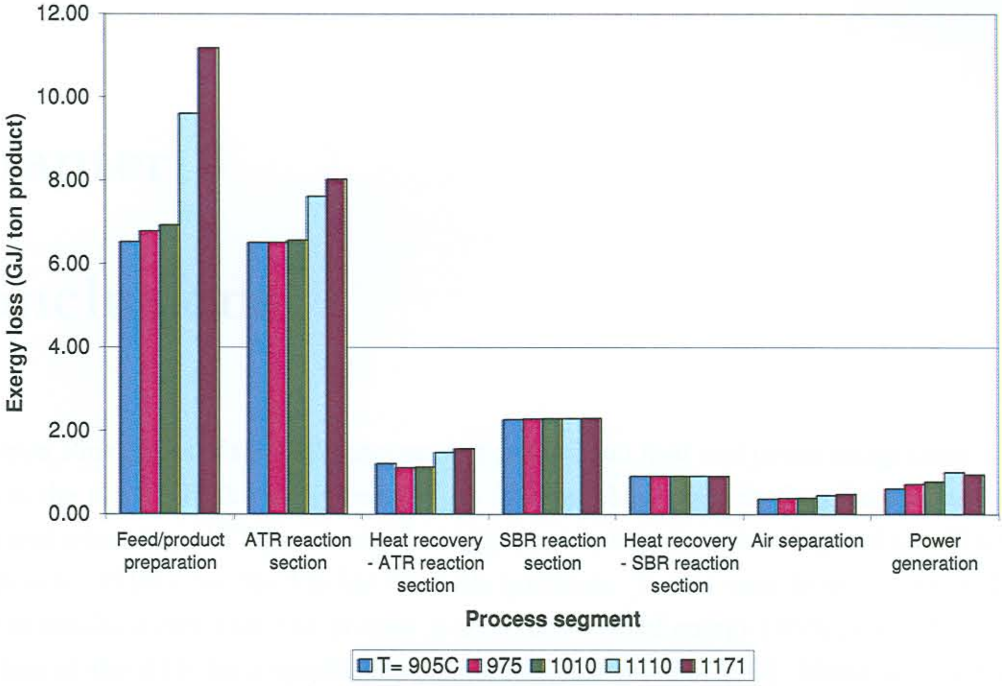

Figure 5.15: Subdivision of internal exergy loss per process section

superheated steam generation and also because of a very good ΔT for the feed preheat exchanger (best ΔT in all simulations).

The conditions in the SBR didn't change with the change in the ATR temperature and thus the internal exergy loss for all the simulations remained constant. The same with the heat recovery for the SBR reaction section.

The contribution of the air separation internal exergy losses are small compared to the other process sections. The exergy losses do increase with a need for more oxygen as the ATR temperature increases.

The losses with the power generation also increases as the internal exergy loss with the larger purge gas combustion increase.

The final remark is that the largest contributors to internal exergy loss are the feed/product preparation and the ATR reaction section. Further improvements in a follow-up study in these sections could result in ultimate optimization.