

# Chapter 2

## Literature survey

### 2.1 GTL processing steps

The GTL process has three main processing steps (see figure 2.1), all of which has been proven commercially (Lutz, 2001).

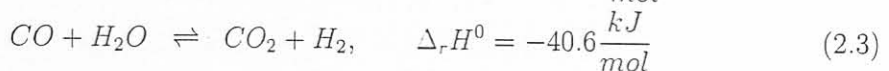
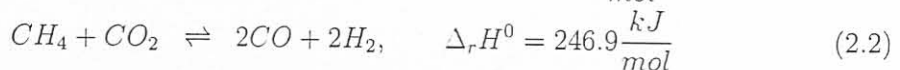
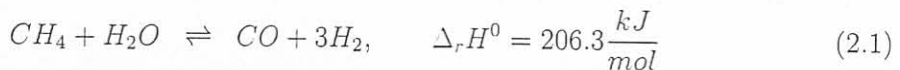


Figure 2.1: The basic GTL process

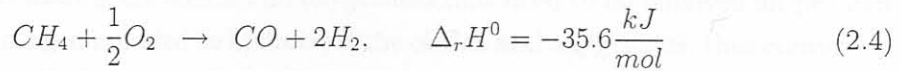
#### 2.1.1 Natural gas reforming

This step converts natural gas (largely methane) into synthesis gas, also known as syngas (a mixture of hydrogen and carbon monoxide). The production of syngas is obtained by reforming natural gas with either steam or carbon dioxide, by partial oxidation or by a combination of the three. Due to the presence of water, the water gas shift reaction plays an important role.

The principal reactions of steam reforming are:



The principal partial oxidation reaction is:

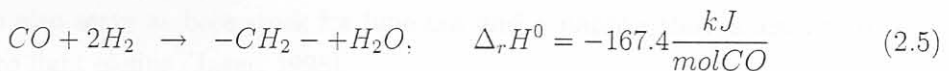


The Fischer-Tropsch conversion step requires a stoichiometric  $H_2:CO$  ratio of about 2. The above mentioned reforming reactions give syngas with  $H_2:CO$  ratios ranging from less than 1 to more than 3. A combination of these reactions in the presence of a catalyst is normally practiced to obtain a suitable  $H_2:CO$  ratio. This may be done in a tubular catalytic steam reformer with a furnace to provide external heat, in an autothermal reformer where partial oxidation is combined with adiabatic catalytic steam reforming, or in a partial oxidation reformer followed by a shift reactor. When reforming is followed by Fischer-Tropsch (FT) conversion, it is possible to recycle FT tail gas to the feed of the reforming process in order to manipulate the  $H_2:CO$  ratio of the reformer outlet.

### 2.1.2 Fischer-Tropsch conversion

The second step, Fischer-Tropsch conversion, upgrades the syngas into waxy hydrocarbons by using the low temperature Fischer-Tropsch (LTFT) reactor. Originally LTFT was practiced in tubular fixed bed reactors. Currently Sasol in South Africa is using slurry phase reactors to overcome problems and limitations associated with tubular fixed bed reactors (Jager, 1998).

The simplified FT reaction can be represented as:



Preheated syngas is fed to the bottom of the slurry reactor where it diffuses into the slurry. The syngas is converted into more wax by the FT reaction.

The lighter, more volatile fractions leave the reactor in a gas stream from the top of the reactor. The gas stream is cooled to recover the lighter cuts and water. The hydrocarbon streams (i.e. the wax and lighter cuts) are sent to the product upgrading unit, while the water stream is treated in the water recovery unit (Lutz, 2001).

### 2.1.3 Product upgrading

In the third step, the waxy syncrude is upgraded to middle distillate fuels: mainly GTL Fuel and some naphtha (Lutz, 2001).

The products from the slurry phase reactor are predominantly paraffinic, but the lighter products contain some olefins and oxygenates that need to be removed for product stabilization. Hydrogen is added to hydrotreat the olefins and oxygenates, thus converting them to paraffins. Hydrogen is also added to the mild hydrocracker, which breaks the long chain waxes into naphtha and GTL Fuel. The products are separated out in a fractionation section (Lutz, 2001).

In this study, the total product upgrading will not be considered. Only the first stage will be considered. The first stage of upgrading consists of cooling the gas stream to recover the lighter cuts and water. The lighter cuts is then recycled to the reformer or the FT reactor.

## 2.2 Background on Fischer-Tropsch synthesis

### 2.2.1 The low temperature Fischer-Tropsch (FT) reactor

Conversion of natural gas to Naphtha and GTL Fuel can be achieved by means of the FT process. The FT process can be operated at low temperatures (LTFT) to produce a syncrude with a large fraction of heavy, waxy hydrocarbons or it can be operated at higher temperatures (HTFT) to produce a light syncrude and olefins. With HTFT the primary products can be refined to environmentally friendly gasoline and diesel, solvents and olefins. With LTFT, the heavy hydrocarbons can be refined to speciality waxes. The heavy hydrocarbons can also be hydrocracked and/or isomerised to produce high quality diesel. It can also serve as base stock for lube oils and a naphtha that is ideal feedstock for cracking to light olefins (Jager, 1998).

The composition of the hydrocarbon product fraction ( $-\text{CH}_2-$ ) (see equation 2.5) can be described by the Schulz-Flory distribution. These products are then also known by trivial names in the industry, which can be seen in table 2.1.

### 2.2.2 The influence of $\text{CO}_2$ and $\text{H}_2\text{O}$ on the Fischer-Tropsch reactor performance

Cobalt catalysts are more resistant towards reoxidation than iron based catalysts, but a certain degree of oxidation does still take place. The rate of oxidation of supported cobalt catalysts is a function of the operating temperature, partial pressure of water and crystallite size of the catalyst. Thus water will have a deactivation effect on the cobalt

**Table 2.1:** Trivial names of the main products of the FT synthesis

Chain Length	Trivial Name
C <sub>1-2</sub>	Fuel Gas
C <sub>3-4</sub>	LPG
C <sub>5-12</sub>	Benzine
C <sub>5-10</sub>	Naphtha
C <sub>11-13</sub>	Kerosene
C <sub>13-17</sub>	Diesel
C <sub>10-20</sub>	Middle distillates
C <sub>19-23</sub>	Soft waxes
C <sub>24-35</sub>	Medium waxes
C <sub>35+</sub>	Hard waxes

catalyst after long periods of operation (Espinoza *et al.*, 1999).

There is general consensus in the literature that carbon dioxide and water does not have an inhibiting effect on the rate of FT synthesis for catalysts that are not active for the water gas shift (WGS) reaction, such as the cobalt catalyst (Espinoza *et al.*, 1999). This is due to the fact that the FT rate for cobalt catalysts are more related to the ratio of the partial pressures of H<sub>2</sub>:CO, while for iron catalysts it is more related to the absolute partial pressures of the reactants (Espinoza *et al.*, 1999).

In this study only the effect of the cobalt catalyst will be analysed.

### 2.2.3 The H<sub>2</sub>:CO molar ratio and the Schulz-Flory alpha value in the Fischer-Tropsch reactor

The alpha value is the probability of carbon chain growth in the Fischer-Tropsch reactor. If the value is low and approaches zero, chain growth is not probable and the main product will be mainly methane. On the other hand, alpha approaches 1 and is high when longer carbon chains are formed.

For this study, the following equation was used to determine alpha (Lox & Froment, 1993):

$$\alpha = \frac{k_1 P_{CO}}{k_1 P_{CO} + k_5 P_{H_2} + k_6} \quad (2.6)$$

It can be seen from equation 2.6 that the alpha distribution will decrease with an increase in H<sub>2</sub>:CO syngas ratio. The opposite is also true; the alpha distribution will increase with a decrease in H<sub>2</sub>:CO syngas ratio.

The goal of the Fischer-Tropsch reactor in the GTL process is to make a product slate

with a typical alpha value of 0.95. This indicates that the product slate mainly consists of waxes (long carbon chains). These waxes can then be converted into many valuable products.

## 2.3 Existing technologies

### 2.3.1 Syngas generation

Fischer-Tropsch (FT) chemistry is often regarded as the key technological component of schemes for converting synthesis gas (or 'syngas') to transportation fuels and other liquid products. However, syngas production itself accounts for more than half the capital investment and a disproportionate share of the operating costs for a gas-to-liquids (GTL) complex. A recent study by SFA Pacific (see table 2.2) examines the full range of commercial and developmental synthesis gas production technologies and provides an independent assessment of syngas production options and costs for GTL applications (Karp *et al.*, 1998).

The manner in which syngas is produced can be influenced by, and in turn can profoundly impact, many facets of the overall GTL process design, such as (Wilhelm *et al.*, 2001):

- Plant size and location;
- The need for an oxygen plant or oxygen enrichment facilities;
- The physical size of downstream gas-handling equipment;
- Syngas composition and its associated effects on FT chemistry and yields;
- Heat integration and gas recycle options;
- Gas compression requirements;
- The scope and configuration of power generation alternatives.

This section examines the status of commercial and developmental syngas production technologies in the context of GTL production based on FT synthesis.

## Syngas generation technologies

In principle, synthesis gas may be generated from any hydrocarbon feedstock. This is reflected in industrial practice, which includes large-scale syngas production from a wide variety of materials that includes natural gas, naphtha, residual oil, petroleum coke and coal. However, in the context of GTL applications, low-value natural gas is the predominant (if not the only) feedstock of interest (Wilhelm *et al.*, 2001).

In large part, this is a reflection of the high investment costs of GTL processes, which, in the absence of special circumstances, require a low or, even better, negative value feedstock to achieve attractive overall economics. Low quality residual oil or coke can have a low or even negative value. However, conversion of such feedstocks (via gasification) entails greater capital investment, in part due to the costs associated with materials handling, soot removal and syngas cooling and purification. The focus for GTL has thus been on associated gas, so-called stranded or remotely located gas reserves, and larger gas reserves that are not currently being economically exploited. In the near-term, associated gas may offer the greatest potential, particularly where such gas is subject to flaring constraints and associated reinjection costs (Wilhelm *et al.*, 2001).

The principal technologies for producing syngas from natural gas feed are summarized and compared in table 2.2. The predominant commercial technology for syngas generation has been, and continues to be, steam methane reforming (SMR), in which methane and steam are catalytically and endothermically converted to hydrogen and carbon monoxide. An alternative approach is partial oxidation, the exothermic, non-catalytic reaction of methane and oxygen to produce a syngas mixture. SMR and partial oxidation inherently produce syngas mixtures having appreciably different compositions. In particular, SMR produces a syngas having a much higher  $H_2:CO$  ratio. This, of course, represents a distinct advantage for SMR in hydrogen-production applications and, in large measure, accounts for its overall dominance among syngas production technologies to date (Wilhelm *et al.*, 2001).

As shown in table 2.3 and table 2.4, the product syngas composition from either process can, within limits, be manipulated by altering various process conditions and/or by means of additional process steps (Wilhelm *et al.*, 2001). Nonetheless, even with such manipulation; neither SMR nor partial oxidation is ideally suited to GTL applications. This is due to the fact that FT synthesis calls for an  $H_2:CO$  ratio of about 2, a value higher than that achievable with partial oxidation and lower than that obtainable with SMR.

A solution to this dilemma is to use both technologies. For example, partial oxida-

tion and SMR may be used in parallel to produce syngas streams that have differing compositions but, when mixed, form a total FT feedstock of the desired composition. An alternative to this approach is autothermal reforming (ATR), which combines partial oxidation with catalytic steam reforming in one reactor. The process is 'autothermal' in that the endothermic reforming reactions proceed with the assistance of the internal combustion or oxidation of a portion of the feed hydrocarbons-in contrast to the external combustion of fuel characteristic of conventional tubular reforming.

ATR properly refers to a stand-alone, single-step process for feedstock conversion to syngas. However, the same basic idea can be applied to reactors fed by partially reformed gases from a primary reformer. Such reactors form a subcategory of ATR that is commonly called secondary reforming. Due to feed composition differences-in particular, the lower concentration of combustibles in secondary reformer feeds-ATR reactors and secondary reformers have different thermal and soot-forming characteristics that require different burner and reactor designs. Nonetheless, the distinction between ATR and secondary reforming is not consistently drawn by technology users and vendors, with the result that secondary reformers often are referred to as ATRs (Wilhelm *et al.*, 2001).

### Air-blown vs. oxygen-blown autothermal reforming

The importance of syngas production to overall GTL costs is vividly illustrated in Table 2.5, which shows the cost distribution for a facility that is based on the use of oxygen-blown ATR. As shown, GTL costs are dominated by capital charges, which comprise about two-thirds of the total costs. Syngas production, in turn, accounts for about half of the capital investment, in part due to the significant capital cost of the oxygen plant (Wilhelm *et al.*, 2001; Jager, 1998).

Not surprisingly, the oxygen plant investment has been an attractive target of GTL cost-cutting strategies. This target has spawned both long-term strategies (e.g., the previously mentioned ceramic membrane reactor) and short-term strategies (e.g., air-blown ATR). It remains to be seen how successful ceramic membrane reactor development will be. However, SFA Pacific sees no apparent advantage that would favour air-blown over oxygen-blown systems (Wilhelm *et al.*, 2001). Indeed, air-blown reforming technology is unlikely to be economically competitive with oxygen-blown systems and appears much less flexible. Factors which more than negate the savings associated with elimination of the oxygen plant include: lower thermal efficiency, high air compression power requirements, the inability (because of its composition) to recycle FT tail gas, and the larger downstream equipment sizes and pressure drop associated with handling the much larger

**Table 2.2:** Comparison of syngas generation technologies (natural gas feed)(Karp *et al.*, 1998)

Technology	Advantages	Disadvantages
SMR	<p>Most extensive industrial experience</p> <p>Oxygen not required</p> <p>Lowest process temperature requirement</p> <p>Best H<sub>2</sub>:CO ratio for hydrogen production applications</p>	<p>H<sub>2</sub>:CO ratio often higher than required when CO also is to be produced</p> <p>Highest air emissions</p>
Heat exchange reforming	<p>Compact overall size and ‘footprint’</p> <p>Application flexibility offers additional options for providing incremental capacity</p>	<p>Limited commercial experience</p> <p>In some configurations, must be used in tandem with another syngas generation technology</p>
Two-step reforming <sup>a</sup>	<p>Size of SMR is reduced</p> <p>Low methane slip favours high purity syngas applications</p> <p>Syngas methane content can be tailored by adjusting secondary reformer outlet temperature</p>	<p>Increased process complexity</p> <p>Higher process temperature than SMR</p> <p>Usually requires oxygen</p>
ATR	<p>Natural H<sub>2</sub>:CO ratio often is favourable</p> <p>Lower process temperature requirement than POX</p> <p>Low methane slip</p> <p>Syngas methane content can be tailored by adjusting reformer outlet temperature</p>	<p>Limited commercial experience</p> <p>Usually requires oxygen</p>
POX	<p>Feedstock desulfurization not required</p> <p>Absence of catalyst permits carbon formation and, therefore, operation without steam, significantly lowering syngas CO content</p> <p>Low methane slip</p> <p>Low natural H<sub>2</sub>:CO ratio is an advantage for applications requiring ratio &lt; 2.0</p>	<p>Low natural H<sub>2</sub>:CO ratio is a disadvantage for applications requiring ratio &gt;2.0.</p> <p>Very high process operating temperatures</p> <p>Usually requires oxygen</p> <p>High temperature heat recovery and soot formation handling adds process complexity</p> <p>Syngas methane content is inherently low and not easily modified to meet downstream processing requirements</p>

<sup>a</sup>SMR followed by oxygen-blown secondary reforming



**Table 2.3:** Techniques for adjusting syngas H<sub>2</sub>:CO ratios (Karp *et al.*, 1998)

	Decreases ratio	Increases ratio
Recycle CO <sub>2</sub>	×	
Import CO <sub>2</sub>	×	
Remove H <sub>2</sub> via membrane	×	
Remove CO <sub>2</sub>		×
Increase steam		×
Add shift converter		×

**Table 2.4:** Approximate variation in H<sub>2</sub>:CO ratio for natural gas feed (Karp *et al.*, 1998)

	SMR	Two-step reforming	ATR	POX
Import CO <sub>2</sub> or remove H <sub>2</sub> via membrane	<3.0	<2.5	<1.6	<1.6
Total CO <sub>2</sub> recycle	3.0	2.5	1.6	1.6
No CO <sub>2</sub> recycle	5.0	4.0	2.65	1.8
Increase steam	>5.0	>4.0	>2.65	>1.8
Add shift converter	inf	>5.0	>3.0	>2.0

volumetric flow of gas. Questions also remain about the potential for forming ammonia and other nitrogen compounds in the downstream FT conversion units (Wilhelm *et al.*, 2001).

Also problematic with air-blown operation is the low heating value of the FT tail gas. From an economic standpoint, utilising this tail gas to generate power for export sale is a potentially key contributor to the overall viability of the GTL plant. However, combustion turbine technology and commercial experience with the use of such low quality gas remains quite limited (Wilhelm *et al.*, 2001).

### 2.3.2 Syngas conversion

Conversion of natural gas to Naphtha and GTL Fuel can be achieved by means of the FT process. The FT process can be operated at low temperatures (LTFT) to produce a syncrude with a large fraction of heavy, waxy hydrocarbons or it can be operated at higher temperatures (HTFT) to produce a light syncrude and olefins (Jager, 1998). Only the low temperature Fischer-Tropsch (LTFT) reactors will be discussed in this section, because we would like to operate the FT reactor at high alpha values and produce mostly heavy, waxy hydrocarbons in the GTL process. LTFT was originally performed in the

**Table 2.5:** Estimated cost of FischerTropsch liquid (Karp *et al.*, 1998)

Manufacturing cost % of total	
Natural gas @ US\$0.50/Mscf	14.9
Operating labor	1.8
Other operating costs	19.2
Capital charges @ 20%/year	64.1
Total	100.0
Capital cost distribution	
Plant section	Percentage of total capital cost
Oxygen plant	23
Reforming	28
FischerTropsch synthesis	24
Product upgrade	13
Power recovery	12
Total	100

tubular fixed bed reactor(TFBR) (Jager & Espinoza, 1995). The TFBR is complex and expensive (Jager, 1998) and temperature control is very difficult. For this reason Sasol developed the Sasol Slurry Bed reactor (SSBR) (Jager & Espinoza, 1995). The reactor is much simpler; it is easy to operate; it has lower pressure drop; it has on-line catalyst renewal facilities and it is capable of much higher capacities (Jager & Espinoza, 1995).

### Tubular fixed bed reactor (TFBR)

Fischer-tropsch synthesis in the LTFT mode was originally practised in pre-war Germany in packed beds. This developed into tubular fixed bed. Arge reactors which were commissioned at Sasol in 1955 (Jager & Espinoza, 1995).

Heat removal for the highly exothermic synthesis reaction is achieved by generation of steam on the shell side of the reactor. Earlier reactors operated at a shell side temperature of about 220°C, and a reactor pressure of 25 bar. A reactor commissioned in 1987 operated at 45 bar. The respective capacities were about 600 and 900 bbl/day per reactor. A detailed design for a 5000 tube reactor was also produced for use at the Sasolburg (South Africa) factory but eventually not used because of the development of the SSBR (Jager & Espinoza, 1995).

The products from the LTFT as obtained from the TFBR using Fe-based catalyst vary depending on the catalyst formulation and process conditions. A typical LTFT product distribution as obtained for a TFBR and that typically obtained for high temperature

Fischer-Tropsch synthesis, is given in table 2.6. The LTFT product slate follows the Schulz-Flory distribution with a typical alpha value of 0.95 (Jager & Espinoza, 1995).

**Table 2.6:** Selectivity of Sasol processes (Jager & Espinoza, 1995)

Product	TFBR	Synthol(fluidized bed)
CH <sub>4</sub>	4	7
C <sub>2</sub> to C <sub>4</sub> olefins	4	24
C <sub>2</sub> to C <sub>4</sub> paraffins	4	6
Gasoline	18	36
Middle distillate	19	12
Heavy oils and waxes	148	9
Water soluble oxygenates	3	6

The reactor is complex and expensive. The scale-up of the reactor is mechanically difficult. The mechanical design is further complicated by the fact that the iron based catalyst has to be replaced periodically and the design has to provide for this. The replacement is cumbersome and maintenance and labour intensive; it causes considerable downtime and disturbances in plant operations. The product selectivities also change with aging of the catalyst. With a number of reactors the total selectivities can, however, be evened out by staggering the catalyst age in the reactors (Jager & Espinoza, 1995).

Axial and radial temperature profiles exist in the tubes, because of the exothermic nature of the Fischer-Tropsch reaction. Maximum average temperature is required for maximum conversion. This is, however, limited by the maximum allowable temperature peak that may not be exceeded in order to prevent carbon formation on the catalyst and the effect temperature has on product selectivities. Carbon formation causes breakup of the catalyst that in turn causes blockages and a need to replace the catalyst (Jager & Espinoza, 1995).

Product selectivities are temperature dependent and flexibility with respect to temperature control would be advantageous. The choice of temperature level is however severely curtailed by the need to avoid exceeding the maximum peak temperature (Jager & Espinoza, 1995).

Pressure drops across the TFBRs are high and may vary from 3 to 7 bar depending on the operating pressure. With relative high recycle flows, this gives rise to considerable recompression costs (Jager & Espinoza, 1995).

### Slurry bed reactor (SBR)

Most of the difficulties of the TFBR can be eliminated in a SBR. This idea was first tried out during the Second World War and up to the late 1970's by Kölbel & Ralek (1980). Sasol's own experiments on small scale started in the early 1980's. Although they could not repeat Kölbel's results, and it was difficult to obtain consistent results in the 5 cm diameter reactor used, they did show promise for the concept. It was realised that the hydrodynamics obtained from these small tubes is quite different from those expected from larger diameter reactors (Jager & Espinoza, 1995).

In 1990 a slurry bed with a diameter of about 1 m was commissioned which confirmed the original expectations. In June 1991, although the design issues had not all been resolved in detail, Sasol decided not to use existing designs for two 5000 tube TFBRs but rather use the slurry bed concept for its planned expansion of LTFT capacity. A single slurry bed reactor, 5 m in diameter, 22 m high, was commissioned in May 1993 and the process was called the Sasol Slurry Bed process (SSBP) (Jager & Espinoza, 1995).

The SSBR is much simpler than a TFBR, it is much easier to fabricate and is much cheaper. It consists of a shell with cooling coils in which steam is generated. Syngas is distributed in the bottom and rises through the slurry that consists of liquid reaction products, predominantly wax, with Fe-based catalyst particles suspended in it. The reagent gas diffuses from the gas bubbles through the liquid phase to the suspended catalyst where they react to produce hydrocarbons and water. The heavy hydrocarbons form part of the slurry phase whereas the lighter gaseous products with unreacted syngas pass through the freeboard above the bed and then to the gas outlet (Jager & Espinoza, 1995).

Because of the churning nature of the slurry-gas bubble interaction, the slurry phase is well mixed and tends to be isothermal. This gives much more flexible temperature control. Temperatures on average can be much higher than in a TFBR without the danger of carbon formation and break-up of catalyst. Better control of product selectivities become possible at higher average conversions. This makes it ideal for use with high activity catalysts where the problems with excessive radial and axial temperature gradients are much more pronounced (Jager & Espinoza, 1995).

The pressure drop across the bed is practically that of the static hydraulic head and is much lower than that for the TFBR. This translates to considerable savings in compression costs (Jager & Espinoza, 1995).

On-line catalyst removal and additions can be done without difficulty. This is an important improvement on the TFBR where the catalyst has to be replaced from time to

time. Losses due to down-time and labour intensive turn-arounds are eliminated (Jager & Espinoza, 1995).

It is thought possible that a single SBR with a capacity of about 10 000 bbl/day can be built. Full advantage is then taken of the potential for economy of scale (Jager & Espinoza, 1995).

### 2.3.3 Hydroprocessing

The current technologies in hydroprocessing will not be discussed, since only the first stage of hydroprocessing is included in this study.

## 2.4 Optimization of existing technologies

### 2.4.1 Syngas generation

Much of the forward-looking consideration of syngas production for GTL has focused on autothermal reforming. In part, this is due to the technology's basic compatibility with FT feed chemistry requirements. However, this focus also reflects the perception that ATR has other attributes-relative compactness, lower capital cost, and greater potential for economies of scale-which will contribute significantly to the economic viability of GTL plants (Wilhelm *et al.*, 2001).

Ongoing efforts to develop lower-cost syngas generation technologies include the following (Wilhelm *et al.*, 2001):

- The development and application of 'compact reformers' and of 'heat exchange reformers', in which a portion of the heat of reaction is provided by heat recovery from the reformed gas, rather than by burning fuel. Potential advantages over conventional tubular reactors include improved efficiency, smaller plant footprint, lower capital cost, and reduced emissions. Companies active in this area have included Air Products, KTI, ICI, BP/Kvaerner, Kellogg, Haldor Topsøe, Krupp Uhde, and Lurgi.
- Development and application of air-blown autothermal reformer technology, thereby eliminating the need for an oxygen plant. (Air-blown secondary reforming is well established, being commonly utilized for syngas production for ammonia plants). The chief proponent of the air-blown approach is Syntroleum.

- New reformer reactor approaches, most notably that employed by Exxon's AGC-21 process for converting natural gas to liquids. The first step in this process is syngas generation via oxygen-blown catalytic autothermal reforming in a fluidized bed reactor. The process has been demonstrated at large pilot scale of about 200 b/day.
- 'Ceramic membrane reactors', based on the use of ionic or oxygen transport membranes, which would couple air separation and partial oxidation in one unit operation, thereby eliminating the need for a conventional oxygen plant. Although being aggressively pursued by two industrial consortia, work in this area is still at a fundamental level. One consortium, led by Air Products, is being co-funded by the US Department of Energy. The participants in this effort include ARCO, Babcock and Wilcox, Chevron, Norsk Hydro and others. The second consortia, based entirely on industrial funding, involves Amoco, BP, Praxair, Statoil, Phillips Petroleum and Sasol.

According to Vosloo (2001) the thermal efficiency of the reforming section can be improved by:

1. The use of a heat exchange reformer in combination with an autothermal reformer.
2. The use of a feed/product heat exchanger to recover energy from the reformer outlet.

### Heat exchange reforming

The combination of a heat exchange reformer with an ATR is very similar to combined reforming, the major difference being that the energy to the steam reformer is not supplied by a fired heater but by the exit gas from the ATR. The potential benefits of such a reforming configuration are (Vosloo, 2001):

1. Savings of about 30% in oxygen consumption.
2. An increase of about 4 percentage points in the thermal efficiency of the plant.

One of the technical issues that must be solved is the potential problem of metal dusting in the heat exchange reformer (Vosloo, 2001).

### Feed/product heat exchange

The oxygen consumption can be decreased by about 3.5% and the production of liquid fuels can be increased by about 2.5% if a feed/product heat exchanger is used to preheat the natural gas to the reformer. As in the case of heat exchange reforming, metal dusting is also one of the major problems that would have to be solved (Vosloo, 2001).

These configurations highlight some of the design parameters of the syngas section that influence the cost and thermal efficiency of the GTL plant. They are as follow (Vosloo, 2001):

1. The preheat temperatures of oxygen and natural gas. The higher these temperatures are, the less oxygen will be used. The maximum preheat temperatures are determined by safety factors and by the need to prevent soot formation.
2. The pressure of steam generated in the waste heat reboiler. The higher the steam-pressure, the more efficient energy can be recovered from the steam, but the more costly the steam and boiler feed water treatment systems become. The optimum steam pressure will be determined by the relative cost of capital and energy.

### 2.4.2 Syngas conversion

As was already discussed under existing technologies, the slurry phase reactor is a technological breakthrough and thus the optimization of the syngas conversion process will have to look at further optimization of the catalyst. The Co catalyst can be improved as follows (Vosloo, 2001):

1. Increasing the catalyst life by making it more resistant to irreversible sulphur poisoning.
2. Changing the selectivity dependency on the  $H_2:CO$  ratio to such an extent that high diesel yields can be obtained at  $H_2:CO$  ratios similar to the usage ratio. The advantage of such a catalyst would be that, due to the increase in reaction rate at higher  $H_2:CO$  ratios, much less catalyst would be needed for the same conversion. To obtain the same conversions at a  $H_2:CO$  ratio of 1.6 than at a ratio of 2; 50% more catalyst is needed at the lower  $H_2:CO$  ratio.

### 2.4.3 Hydroprocessing

The optimization of existing technologies in hydroprocessing will not be discussed, since only the first stage of hydroprocessing is included in this study.

### 2.4.4 Integration

After an extensive search for literature on GTL process integration, it was found that not much literature was publicised on this topic. The literature that were relevant, were very secretive about what was done on integration. Hill (1998) and Vosloo (2001) gave the most information regarding this topic and the most important points were:

- Since the  $H_2:CO$  ratio of the syngas is an important design variable to maximise the production of high quality diesel, the designs of the reformer and the Fischer-Tropsch sections cannot be done in isolation. The most cost-effective design for both units can only be obtained by taking the mutual interaction between these units into account (Vosloo, 2001).
- An obvious way of improving the thermal efficiency of the process is to combine it with a power generation plant. Such a combination will create a more efficient utilization of the low pressure steam produced by the Fischer-Tropsch process (Vosloo, 2001).
- Hill (1998) also focused on the integration of the three steps together with utilities to reduce the capital cost of the GTL process. He also emphasised that heat integration is critical.

## 2.5 Exergy

### 2.5.1 The exergy concept

Thermodynamics is often used to evaluate the efficiency of a chemical process. In this evaluation, use is usually made of energy and mass balances which are based upon the first law of thermodynamics. With the first law of thermodynamics there is no difference between the quality of energy (i.e. heat or work). Thus the efficiency based upon the first law does not take different quality of energies into account (Loonen *et al.*, 2001).

To explain this in more detail, one can consider the two systems in figure 2.2. The first system has more quality of energy than the second system. The first system can still



produce work, while the second system cannot produce any work. The mass and energy in both systems are equal. Thus it can be shown that not all energy are equal (Loonen *et al.*, 2001).

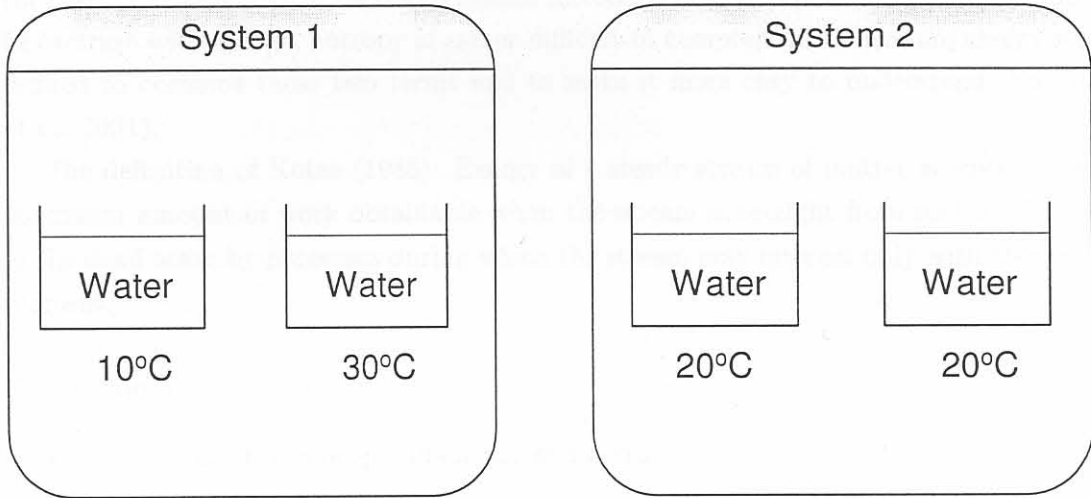


Figure 2.2: Two systems with equal energy

Except for the fact that the quality of energy and materials are not taken into account with first law thermodynamics, the internal energy losses of processes are also not taken into account. This can be seen in figure 2.3. In figure 2.3 a system is shown at three different moments in time. In this system a fuel is combusted and the combustion gases are kept within the system boundaries. Thus the total energy of the system is kept constant, but the amount of available energy to produce work decreases. This is due to the fact that the system cannot produce any work after the fuel has been combusted (Loonen *et al.*, 2001).

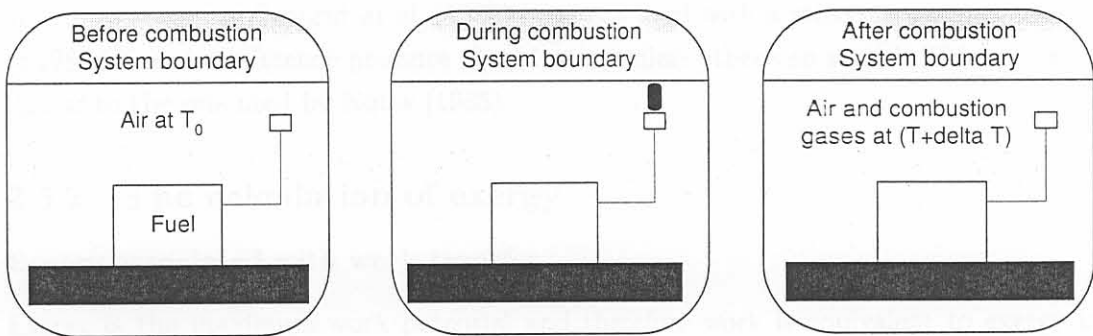


Figure 2.3: Three moments in a combustion process

It can thus be concluded that the first law of thermodynamics does not account for the quality of energy and materials. It also does not account for the internal losses of a process which would result in a higher calculated efficiency of a process than is really the case. The two laws of thermodynamics introduce two concepts: energy and entropy. In contrast with energy, entropy is rather difficult to comprehend. Therefore exergy was defined to combine these two terms and to make it more easy to understand (Loonen *et al.*, 2001).

The definition of Kotas (1985): Exergy of a steady stream of matter is equal to the maximum amount of work obtainable when the stream is brought from its initial state to the dead state by processes during which the stream may interact only with the environment.

Thus exergy is:

- derived from the concepts of energy and entropy,
- based upon the first and second laws of thermodynamics,
- referenced to the natural environment,
- a precise measure of the thermodynamic efficiency of a process.

The concept of exergy is extensively discussed in the books of Kotas (1985) and Szargut *et al.* (1988). Exergy can also be defined as the maximum work potential of a material or of a form of energy in relation to its environment that can be obtained by reversible processes. However, in reality there are only irreversible processes. For practical reasons a reference environment is considered to be so large, that its parameters are not affected by interaction with the system under consideration. In this report the reference system as stated in Szargut *et al.* (1988) has been used with a reference temperature  $T_0$  of 298.15K and a reference pressure  $P_0$  of 1 atm, unless otherwise stated. This system is similar to the one used by Kotas (1985).

## 2.5.2 The calculation of exergy

### Exergy associated with work transfer

Exergy is the maximum work potential and therefore work is equivalent to exergy in every respect (Kotas, 1985). Thus exergy transfer can be specified both in magnitude

and direction by the work transfer to which it corresponds.

$$\dot{\epsilon}^{W_x} = \dot{W}_{max} = \dot{W}_x \quad (2.7)$$

### Exergy associated with heat transfer

The exergy of heat transfer at the control surface is determined from the maximum work that could be obtained from it using the environment as a reservoir of zero-grade thermal energy (Kotas, 1985). For a heat transfer rate  $\dot{Q}_r$  and a temperature at the control surface where the heat transfer is taking place  $T_r$ , the maximum rate of conversion from thermal energy to work is:

$$\dot{W}_{max} = \dot{\epsilon}^Q = \dot{Q}_r \tau \quad (2.8)$$

where:

$$\tau = 1 - \frac{T_0}{T_r} \quad (2.9)$$

$\tau$  is called the dimensionless exergetic temperature and is equal to the Carnot efficiency for the special case when the environment, at temperature  $T_0$ , is used as the other thermal energy reservoir. The exergy associated with a heat transfer rate is called thermal exergy flow and is denoted in open system analysis, by  $\dot{\epsilon}^Q$ .

### Exergy associated with a steady stream of matter

As with energy, exergy of a stream of matter,  $\dot{\epsilon}$ , can be divided into distinct components. In the absence of nuclear effects, magnetism, electricity and surface tension,  $\dot{\epsilon}$  is:

$$\dot{\epsilon} = \dot{\epsilon}_k + \dot{\epsilon}_p + \dot{\epsilon}_{ph} + \dot{\epsilon}_0 \quad (2.10)$$

$\dot{\epsilon}_k$  and  $\dot{\epsilon}_p$  are associated with high grade energy and  $\dot{\epsilon}_{ph}$  and  $\dot{\epsilon}_0$  with low grade energy (Kotas, 1985). The kinetic and potential energies of a stream of substance are ordered forms of energy and thus fully convertible to work. Therefor, when evaluated in relation to the environmental reference datum levels, they are equal to kinetic and potential energy respectively. Thus:

$$\dot{\epsilon}_k = \dot{m} \frac{C_0^2}{2} \quad (2.11)$$

$$\dot{\epsilon}_p = \dot{m} g_E Z_0 \quad (2.12)$$

where  $\dot{m}$  is the mass flow rate of the fluid stream,  $C_0$  bulk velocity of the fluid stream relative to the surface of the earth,  $Z_0$  altitude of the stream above the sea level, and  $g_E$  gravitational acceleration (specific gravitational force), considered a constant (Kotas, 1985).

In most cases the kinetic and potential exergy can be ignored when compared with the chemical and physical components (Loonen *et al.*, 2001). It is convenient to separate physical exergy  $\dot{\epsilon}_{ph}$  and chemical exergy  $\dot{\epsilon}_0$ , enabling calculation of exergy values using standard chemical exergy tables which can be found in Kotas (1985).

Physical exergy is equal to the maximum amount of work obtainable when the stream of substances is brought from its initial state to the environmental state defined by  $P_0$  and  $T_0$  by physical processes involving only thermal interaction with the environment (Kotas, 1985)

The physical component can be derived from the first and second laws of thermodynamics. The first law states that:

$$(H_0 - H_1) = Q_0 + W_x \quad (2.13)$$

and the maximum work potential exist when the entropy production is equal to 0 and then according to the second law:

$$\Pi = 0 = (S_0 - S_1) - \frac{Q_0}{T} \quad (2.14)$$

When equation 2.13 and equation 2.14 are combined, we get the physical component that resembles the maximum work potential (Kotas, 1985):

$$\epsilon_{ph} \equiv (H - H_0) - T_0(S - S_0) \quad (2.15)$$

The physical component consists of a temperature and pressure dependent component (Kotas, 1985):

$$\epsilon_{ph} = \epsilon^{\Delta T} + \epsilon^{\Delta P} \quad (2.16)$$

The temperature dependent component of the physical component, also known as the thermal exergy component, can be calculated as follows (Kotas, 1985):

$$\epsilon^{\Delta T} = \int_{T_0}^T C_p dT - T_0 \int_{T_0}^T \frac{C_p}{T} dT \quad (2.17)$$

The chemical exergy is equal to the minimum amount of work obtainable when the substance under consideration is brought from the environmental state to the dead state by processes involving heat transfer and exchange of substances only with the environment (Kotas, 1985).

To assess the work potential (i.e. exergy) of a stream of substance by virtue of the difference between its chemical potential and that of the environment, the properties of the chemical elements comprising the stream must be referred to the properties of some corresponding suitably selected substances in the environment. One essential characteristic of these reference substances is that they must be in equilibrium with the rest of the environment. A table of these standard chemical exergies can be found in Kotas (1985).

In many important applications the working medium consists of a mixture of ideal gases, for example gaseous fuels, combustion products, etc. The expression for the chemical exergy of mixtures is:

$$\varepsilon_0 = \sum_i x_i \varepsilon_{0,i} + RT \sum_i x_i \ln x_i \quad (2.18)$$

Since the second term on the right hand side is always negative, the exergy of the mixture is always less than the sum of the exergies of the components at the pressure and temperature of the mixture.

## 2.6 Efficiency

### 2.6.1 Exergetic efficiency

Exergy efficiency and irreversibility should be used as a measure for the total resource efficiency (van Schijndel *et al.*, 2001). The efficiency of a process can be calculated in various ways by the use of the principles of thermodynamics. Traditionally the efficiency was calculated by means of mass and energy balances. But these efficiencies could not indicate the real quality of the processes. A process should be evaluated according to the second law of thermodynamics to take the quality of energy into account. This quality of energy then describes the efficiency of the process relative to the maximum work obtainable from the process. This is called exergy and takes into account the first law (energy) and second law (entropy) of thermodynamics. An exergy analysis describes all losses, internal and external to the process.

An exergy analysis describes both internal and external process 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.

Equation 2.19 describes the exergy balance and it is also illustrated in figure 2.4.

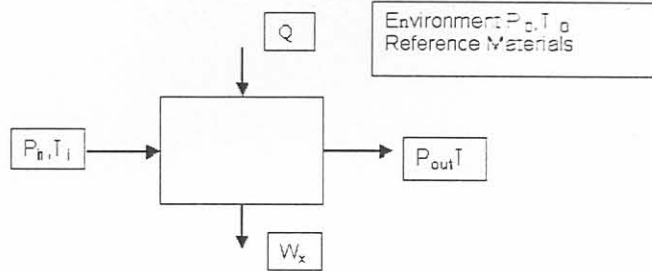


Figure 2.4: The defined system for exergy analysis

$$\dot{\epsilon}_{in} + \dot{\epsilon}^Q = \dot{\epsilon}^{W_x} + \dot{\epsilon}_{out} + \dot{I} \quad (2.19)$$

Variable	Description
$\dot{\epsilon}_{in}, \dot{\epsilon}_{out}$	in and out going exergy material streams
$\dot{\epsilon}^Q$	exergy heat stream
$\dot{\epsilon}^{W_x}$	exergy work stream
$\dot{I}$	irreversibility = $T_0 \cdot \Pi$ where $\Pi$ = entropy production

Irreversibilities are loss of exergy. Loss of exergy means loss of work potential. Lost work potential then has to be generated somewhere else in the process. This normally results in the use of primary fuel. Minimizing exergy losses is thus directly equivalent to saving primary fuel.

In this study Exercom was used to evaluate all the exergy values from the Aspen Plus model. Exercom is an add-on module to Aspen Plus.

### 2.6.2 Carbon efficiency

To examine the exergy and stoichiometry limitations of hydrocarbon production; targets have to be determined. In this study carbon efficiency (defined as the amount of carbon in the process that ends up in hydrocarbon products) and exergy efficiency (which is discussed in the exergy section) has been used as the main targets. A carbon efficiency

lower than 100% implies that carbon has to leave the system as  $\text{CO}_2$ . A carbon efficiency of higher than 100% implies that  $\text{CO}_2$  can be used as a feed to the system.

## Chapter 3

### Process design

#### 3.1 Process design objectives

##### 3.1.1 Process design objectives

The main objective of this study is to design a process for the production of...

##### 3.1.2 Design objectives

In order to meet these objectives, various process configurations were considered. The design of which the background is given in chapter 2.

#### 3.2 Assumptions

The following assumptions were made for the study:

- The efficiency of the CTL process and the CO<sub>2</sub> capture technology were assumed to be 70% and 90% respectively. The energy requirements for these processes were assumed to be 100 MJ/kg and 100 MJ/kg respectively.
- High quality natural gas (95% methane) was used as feedstock.
- An input stream of 1 tonne of water was assumed to be used in the process. The specific energy consumption of the process was assumed to be 100 MJ/kg.
- Moderate purification of the captured feed with the reformer product (RT) was assumed to be done in heat exchangers without cooling or heating duties.