

EDOARDO MELLONI

Offshore Gas to Liquids Technology

São Paulo
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RESUMO

As reservas não econômicas estimadas de gás natural no mundo são da ordem de 3.000 trilhões de pés cúbicos. As principais razões que impedem uma exploração economicamente adequada são a quantidade relativa de gás no reservatório e as questões tecnológicas para seu transporte das áreas remotas no qual são extraídos para o local onde será tratado. De fato, o foco deste trabalho de revisão será sobre o gás associado offshore, que está localizado muito longe para ser comprimido e transportado por dutos e nem sempre pode ser liquefeito e enviado. Até poucos anos atrás, uma solução popular era a queima do gás associado. Esta solução está se tornando cada vez mais impopular devido à perda de uma valiosa fonte e as restrições ambientais, cada vez mais rigorosas a cada ano. A tecnologia para a produção de combustíveis líquidos a partir do gás natural (GTL) permite a conversão do gás natural em hidrocarbonetos de cadeias longas que podem ser posteriormente tratados para a obtenção de um diesel de alta qualidade. O processo é composto por uma conversão inicial do gás natural em gás de síntese (uma mistura de monóxido de carbono e hidrogênio, denominado syngas) seguido pelo processo Fischer-Tropsch, que converte a mistura do syngas em hidrocarbonetos. O grande desafio é elaboração de um processo que historicamente é realizado na maior planta química do mundo, capaz de operar em condições desfavoráveis como nos campos offshore. As restrições são evidentes: segurança, espaço, escala do processo e econômica. Uma das tecnologias mais promissoras é o sistema flutuante de produção, armazenamento e transferência (FPSO): um navio que contém todas as utilidades e equipamentos necessários para execução da síntese GTL, sendo também capaz de estocar os produtos de reação.

Palavras-chave: Gás para Líquidos; Fischer-Tropsch; Gás associado offshore; FPSO; Gás de síntese

ABSTRACT

The uneconomic natural gas reserves estimated in the world are approximately 3,000 trillion cubic feet. The principal reasons that impede an economically convenient exploitation are the relative quantity of the gas in the reservoir and the technological issues to its transport from the remote areas in which it is extracted, to a treatment center. In fact, the focus of this review will be on the offshore associated gas, which is located too far to be compressed and transported by pipelines and cannot always be liquefied and shipped. Until a few years ago, a popular solution was to flare the associated gas. This solution is becoming more and more unpopular due to the loss of a valuable resource and to the environmental constraints, which are becoming every year more stringent.

The Gas to Liquid (GTL) technology permits the conversion of the natural gas into long chain hydrocarbons that can be further treated to give a high quality diesel. The process is composed by a first conversion of the natural gas to synthetic gas (a mixture of carbon monoxide and hydrogen), followed by the Fischer-Tropsch process, which converts the syngas mixture into hydrocarbons. The great challenge is to design such a process, which historically is driven in the biggest chemical plant in the world, capable to operate under unfavorable conditions such as offshore fields. The constraints are evident: safety, space, process scale and economical.

One of the most promising technologies is the Floating Production, Storage and Off-Loading (FPSO) system: a vessel that contains all the utilities and the equipment necessary to perform the GTL synthesis, being also capable to store the reaction products.

Key-words: Gas to Liquid. Fischer-Tropsch. Offshore associated gas. FPSO. Syngas.

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Chapter 1. Introduction

Stranded gas reserves are those that are not economic to be developed due to a variety of reasons. By 2002, the discovered but undeveloped gas reserves were of approximately 2,000 trillion cubic feet worldwide (THACKERAY; LECKIE, 2002); actually the estimation raised to 3,000 trillion cubic feet. Among the principal reasons that turn a gas reserve not economic to be exploited one can find the field dimensions, too small to justify the investment in the infrastructure for its exploitation and the distance from the potential market, too far thus making the transportation costs prohibitive (CASTELO BRANCO; SZKLO; SCHAEFFER, 2010).

The associated gas reserves, if not economically exploited, are burned (gas flaring), released into the atmosphere or reinjected in the reservoir. The gas flaring and the ventilation are becoming more and more unpopular due to the loss of an economic resource and to the environmental constraints, which are becoming every year more stringent. Nevertheless, it is important to emphasize the fact that especially the oil-producers developing countries are continuing to flare and ventilate the associated gas (WORLD BANK GROUP, 2003).

One possible solution to valorize this precious resource is the Gas to Liquid (GTL) technology, which firstly converts the natural gas into a mixture of carbon monoxide and hydrogen (called syngas), and secondly converts the syngas into linear hydrocarbon molecules, precursors of a high quality diesel, by the Fischer-Tropsch reaction. One of the principal advantages of this technology is the possibility to exploit the existing infrastructure for the storage and the transportation of the GTL technology products, which avoids the high investment costs to create a new infrastructure. In fact, the syncrude (the final product of the GTL technology) can be transported together with the oil produced in the field (DE KLERK, 2008).

Besides the advantages of this technology, many critical factors must be considered when thinking about the GTL in an offshore context. Among them, the production of the syngas with correct specification for the Fischer-Tropsch (FT) reaction and the compaction of the FT process itself, which historically presents chemical plants among the biggest in the world.

Chapter 2. Synthesis gas: Production and Treatments

The synthesis gas, or syngas, is a gas mixture consisting principally of hydrogen and carbon monoxide in various ratios (MOULIJN; MAKKEE; VAN DIEPEN, 2013). The term syngas does not define a specific mixture since a nitrogen/hydrogen mixture for the ammonia production can also be referred to as syngas. From now on, syngas will indicate a mixture of H_2/CO and, eventually, other elements such as carbon dioxide.

The importance of the syngas lies in its uses as a feed for further chemical processes and for its importance in the energy industry. In fact, massive worldwide produced chemicals such as ammonia and methanol use the syngas as a feed. Moreover, the petroleum industry relies on hydrogen for various refinery treatments such as hydrocracking and hydrodesulfurisation. In addition, the H_2/CO mixture is also used in the synthetic petroleum production (gas to liquids process) via the Fischer-Tropsch synthesis, converting the syngas into higher hydrocarbons, which can be used as fuels in diesel engines or as lubricants. Finally, hydrogen can be exploited as a relatively clean fuel in the fuel cells and can also be burnt producing only, ideally, water.

Syngas can be produced from any carbon source such as natural gas, heavy oils, coal or biomasses but because of many factors such as world reserves and global yield, natural gas is the principal feedstock for this process.

Moreover, for a global gas-to-liquid process with a Fischer-Tropsch plant, the investment costs for the syngas production section account for 60% of the total investment costs (DANTAS RAMOS et al., 2011). For this reason a general overview of the syngas industrial production will be given, with a focus exclusively on processes that use natural gas as a raw material.

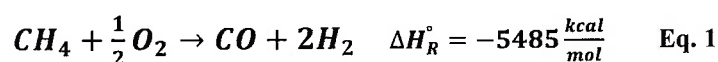
2.1. Industrial processes

The syngas can be produced starting from a wide range of raw materials: natural gas, virgin naphtha, heavy oils, carbon and biomass. Depending on the feedstock used, the principal processes for the production of the syngas are:

- Non-catalytic partial oxidation
- Steam reforming
- Autothermal catalytic reforming
- Carbon gasification

2.1.1. Non catalytic partial oxidation

The process can use natural gas, virgin naphtha or heavy hydrocarbons as a feedstock. The principal reaction of the process is:



The typical reaction conditions are a temperature of 1200-1300 °C and a pressure of 30-40 atm. For the total conversion of the hydrocarbon, the theoretical quantity of oxygen is 0.5 kmol for every kmol of carbon. Nevertheless, the reaction is driven with a slight lack of oxygen in order to inhibit the total combustion reaction, producing CO_2 and H_2O . Moreover,

another byproduct of the reaction is soot, impure carbon particles deriving from the incomplete combustion of the hydrocarbons.

The Francis diagram shows the free Gibbs molar energy of formation divided by the number of carbon atoms in the molecule. The diagram is useful to compare the relative stability of a compound with respect to another, based on thermodynamics considerations. Some hypothesis can be done:

- The thermodynamic equilibrium of the reaction is reached, due to the high temperature, which involves fast kinetics.
- The oxygen consumption is total since it is fed with a slight lack compare to the correct stoichiometry.
- The system is free of hydrocarbons other than methane since, from Figure 2.1, it is possible to see how at the operating conditions the methane is the most stable compound with respect to the pyrolysis reaction $C_xH_y \rightarrow xC + \frac{y}{2}H_2$.

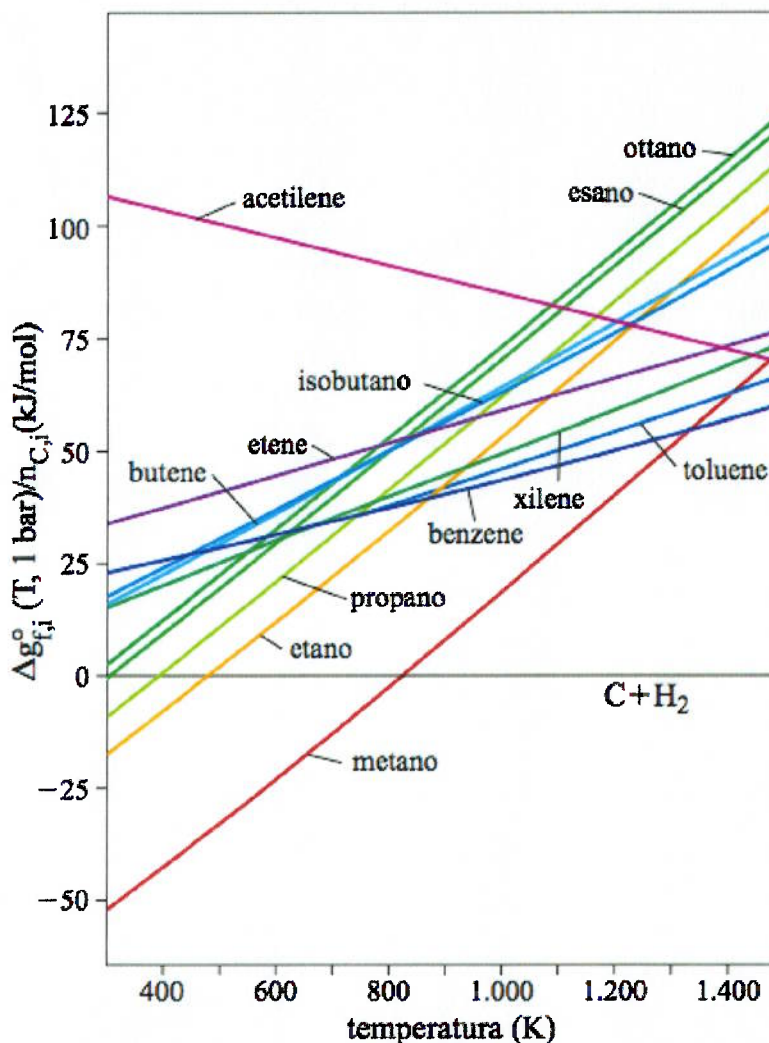


Figure 2.1 Francis diagram for some hydrocarbons (ROTA, 2005).

Mayland and Hays (1949) studied the reaction driven at adiabatic conditions in order to exploit the high exothermicity of the reaction to pre-heat the feed of the reactor. The results are shown in Figure 2.2.

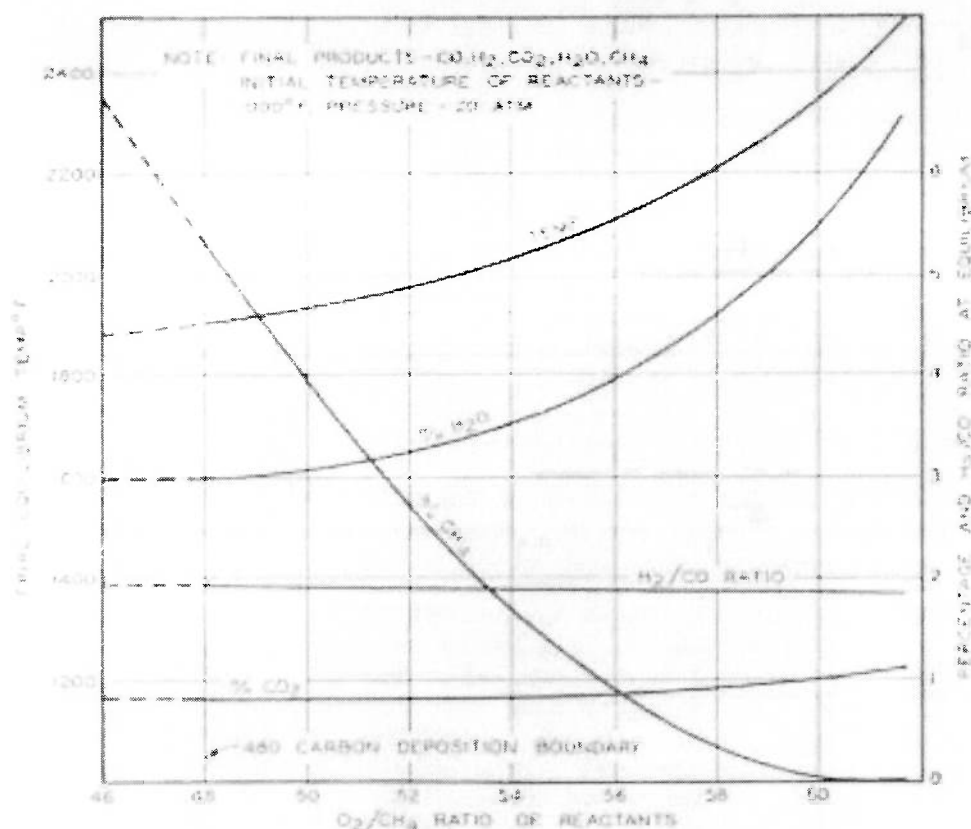


Figure 2.2 Equilibrium conditions for the adiabatic reaction between CH₄ and O₂. Pre-heating temperature of 540°C, pressure 20 atm (MAYLAND; HAYS, 1949).

From Figure 2.2 some important deductions can be made:

- It is convenient to use $\frac{O_2}{CH_4}$ ratios close to 0.6 in order to reduce the methane percentage exiting from the reactor. Higher ratios would decrease the reaction selectivity to H₂ and CO.
- The pre-heated reactants temperature cannot pass 500 °C in order to avoid CH₄ cracking and oxygen corrosion of the heat exchanger material.
- The outlet temperature of the stream leaving the reactor is comprised between 1200 °C and 1300 °C.

The effect of the pressure rise on the equilibrium composition is negative because of Le Chatelier's principle but, as it is possible to see from Figure 2.3, at the process temperatures the effects of the pressure are almost negligible. For this reason the industrial process operates at 30-40 atm in order to reduce the equipment volumes and consequently the plant investment costs.

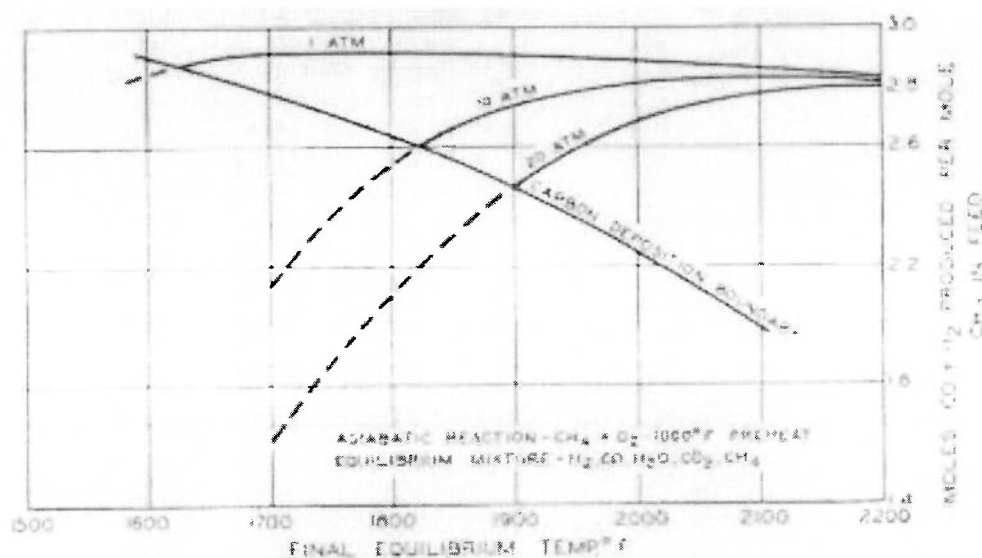


Figure 2.3 CO and H₂ yield with respect to the CH₄ fed to the reactor. Adiabatic reaction, pre-heating temperature 540 °C (MAYLAND; HAYS, 1949).

Because of the very high temperatures of the process, there is no need for a catalyst and consequently the feed does not need a preventive desulfurization process.

Moreover, Figure 2.3 shows the operating conditions at which the reactor should operate to avoid soot formation. When the outlet stream exits the reactor it is necessary to quench it fast to avoid soot formation which is thermodynamically favorite at low temperatures. In practice, after the reactor, the gases are quenched in contact with water whose purpose is also to retain the soot produced during the reaction.

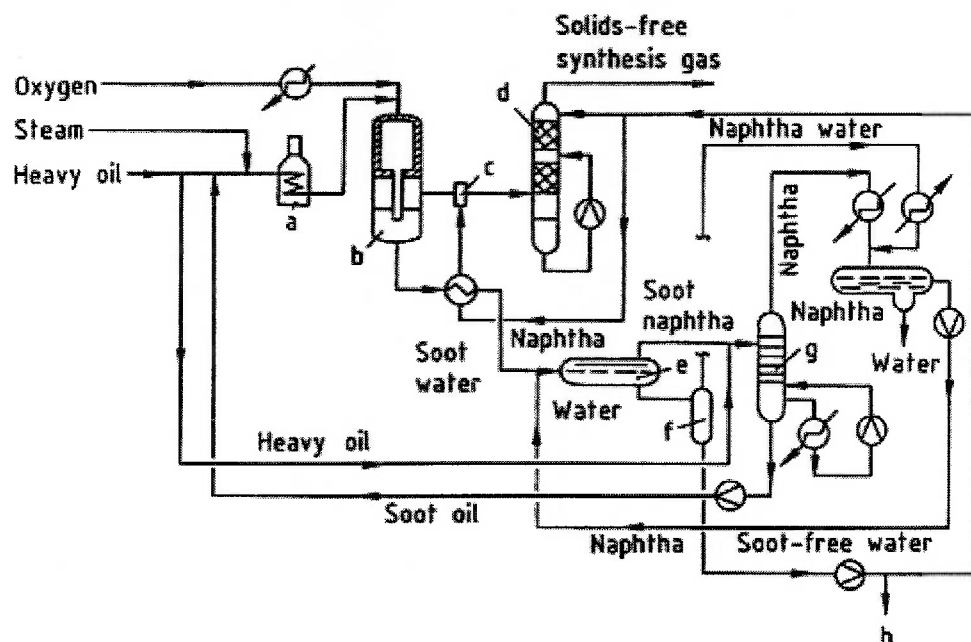
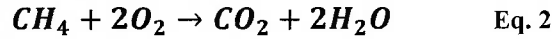
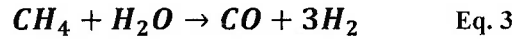


Figure 2.4 Texaco gasification process; a) Preheater; b) Reactor; c) Venturi scrubbing section; d) Soot scrubber; e) Decanter; f) Flash distillation; g) Naphtha column; h) Water clarification

From Figure 2.4 it is interesting to highlight the fact that the larger section of the plant is dedicated for the soot removal and recycling. Soot formation is prevented guarantying a perfect mixing in the flame so that methane can react with the total oxidation products, CO₂ and H₂O. To understand why the mixing is so important, let us write the reaction that happens in the burner:



The oxygen is completely consumed by the methane (in excess) with the exothermic total combustion.

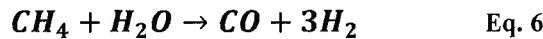


The methane can then react following these reactions. If a perfect mixing is not guaranteed, the methane will crack to hydrogen and soot. Consequently, the project of the burners is a critical step. Using natural gas as feedstock, however, prevent the soot formation resulting in a much simpler plant.

2.1.2. Steam Reforming

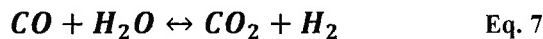
The steam reforming is a process that involves a catalytic endothermic reaction which uses as feedstock natural gas or vaporizable liquid hydrocarbons.

The desired reaction is endothermic and represented by:



$$\Delta H_R^\circ = 53 \frac{\text{kcal}}{\text{mol}}; \Delta G_R^\circ = 0 @ 700^\circ\text{C}$$

From the Gibbs free energy of the reaction it is possible say that the reactions products are favored at high temperatures so, in order to have reasonable yields, it is convenient to operate the reactor above 700 °C. The water gas shift reaction (WGS) may happen in the system:



$$\Delta G_R^\circ = -8514 + 7.71 * T \frac{\text{cal}}{\text{mol}}; \Delta G_R^\circ = 0 @ 800^\circ\text{C}$$

The WGS reaction is exothermic and penalized at high temperatures.

Supposing that the reactive system reaches the thermodynamic equilibrium at the reactor's exit, the outlet composition can be calculated. The result is shown in Figure 2.5.

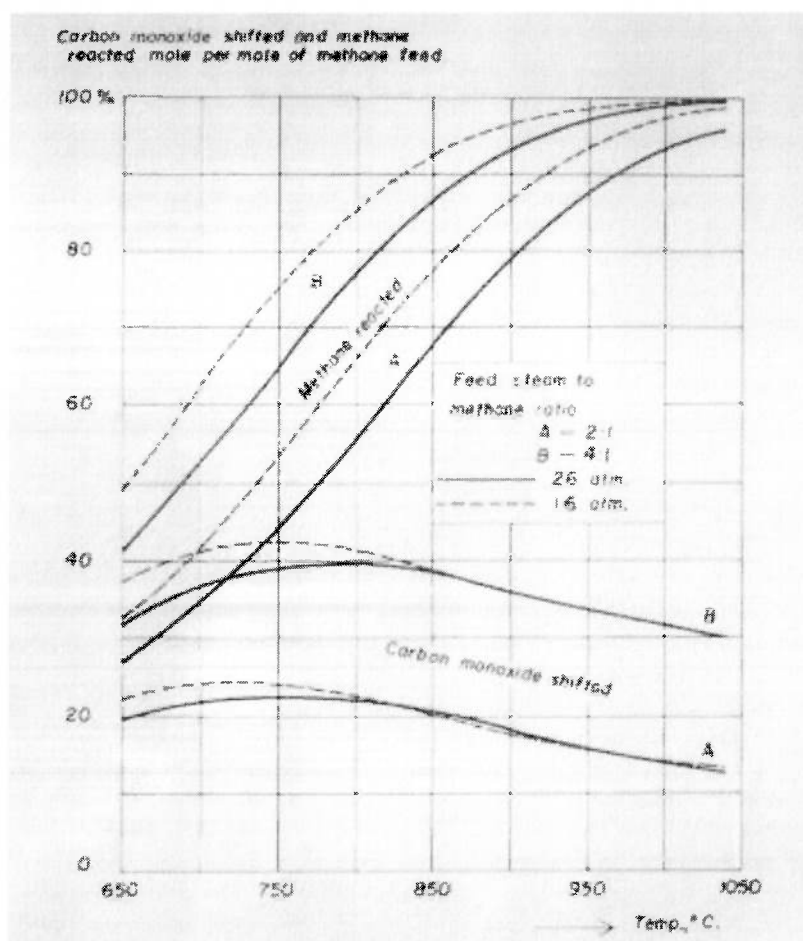


Figure 2.5 Equilibrium composition for the methane steam reforming reaction.

With an industrial-scale focus, it is not necessary to try to reach complete methane conversion during the steam reforming reaction; if necessary, the process is combined with a secondary reforming section that will be studied in the next chapter. Since the reaction is endothermic, heat must be supplied externally: this is made thanks to a heat exchange through a wall. Some basic considerations with respect to the heat exchange phenomenon lead to the conclusion that, if the gas temperature should be between 700 and 800 °C, the wall temperature will be less than 900-1000 °C. With such operating conditions there are several technological constraints on the materials to be used in the reaction section, even more if the process is under pressure.

Even if the reaction temperature is high, due to the great stability of methane a catalyst is still required to accelerate the reaction. The catalyst is contained inside the tubes, placed in the furnace that is heated by combustion of fuel. The composition of the catalyst is Nickel supported by Aluminum oxide ($\text{Ni}/\alpha\text{-Al}_2\text{O}_3$) or Magnesium aluminate ($\text{Ni}/\alpha\text{-MgAl}_2\text{O}_4$). Such catalyst is deactivated by sulphurated compound so that the feed must be sulphur-free. This purification is made passing the feed through a Zinc oxide packed bed at 400 °C whose role is to retain the most common sulphurated compounds such as H_2S , COS and mercaptans RSH. Organic cyclic compounds like thiophene are hydrogenated over Molybdenum-Cobalt catalysts forming H_2S which is sent over the Zinc oxide packed bed.

Carbon formation must be prevented for two principal reasons. Firstly, coke deposition on the active sites of the catalyst causes fouling, increases the pressure drops of the tubes and deactivates the catalyst. Secondly, the growth of a carbon deposit can create hot spots in the tube. Hot spots are areas in which the temperature increases anomalously,

threatening the resistance of the materials. The prevention of carbon formation is made by regulating the steam/methane ratio in the feed: a higher ratio guarantees not only the reduction of coke formation but it also enhances the methane conversion due to the lower partial pressure of the hydrocarbon. Industrially, the reformer operates with a steam-to-carbon ratio between 2.5 and 4.5.

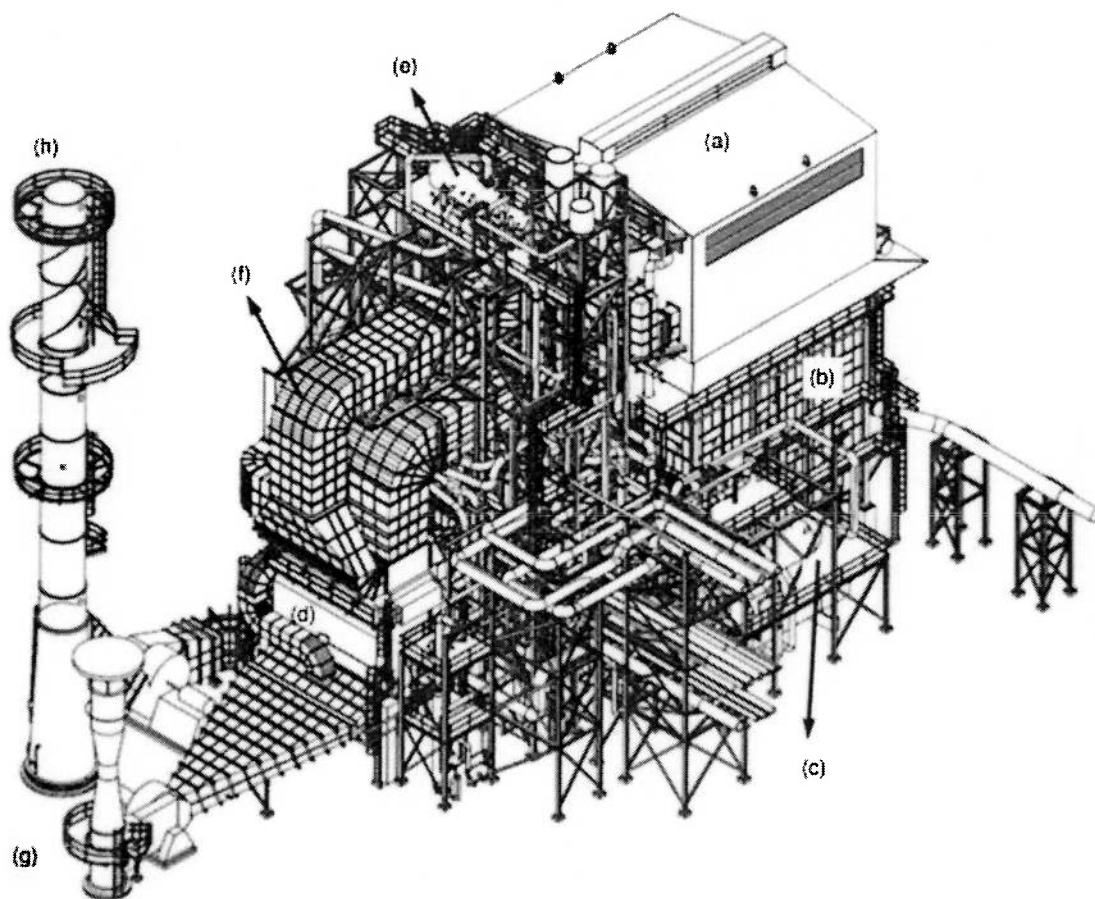


Figure 2.6 General arrangement of a steam reformer. (a) Distribution systems for feed, fuel and combustion air; (b) reformer radiant box; (c) cooling section of the reformer effluent (cooled to 350 °C); (d) combustion air preheater; (e) steam drum to provide water to boilers; (f) convection section for heat recovery; (g) combustion air fan with air intake; (h) discharge of flue gases. (Courtesy of van Uffelen, Technip Benelux B. V.)

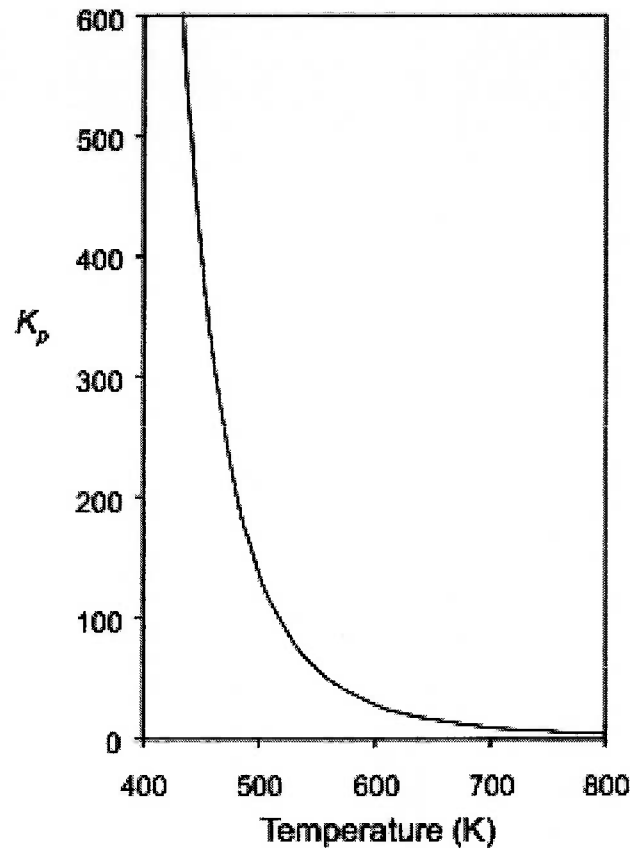


Figure 2.8 Water gas shift equilibrium constant (MOULIJN; MAKKEE; VAN DIEPEN, 2013).

The majority of the catalysts developed for this reaction were active at temperatures above 600 K. More active catalysts require extremely pure gases because of their extreme sensitivity to poisoning. For practical purposes the reaction is carried out in two adiabatic reactors with an intermediate cooling, as reported in Figure 2.9.

In the high temperature shift reactor, most of the carbon monoxide is converted. The catalyst is a compound made of $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-MgO}$, active between 630 K and 800 K. Below this temperature range the catalyst is poorly active and above 800 K sintering happens, modifying the physical structure of the catalyst.

The low temperature shift reactor converts the remaining carbon monoxide with a more active catalyst made of $\text{Cu-ZnO-Al}_2\text{O}_3$, active between 480 K and 540 K. At lower temperatures the risk to reach the dew point is high and the water deriving from the vapor condensation can damage the catalyst, above 540 K the copper starts to recrystallize, losing its catalytic activity. The amount of catalyst in the low temperature shift reactor is much larger than the amount needed to convert the remaining carbon monoxide. The extra catalyst is included to guarantee a continuous plant operation for at least two or three years before stopping the reactors to change the catalyst.

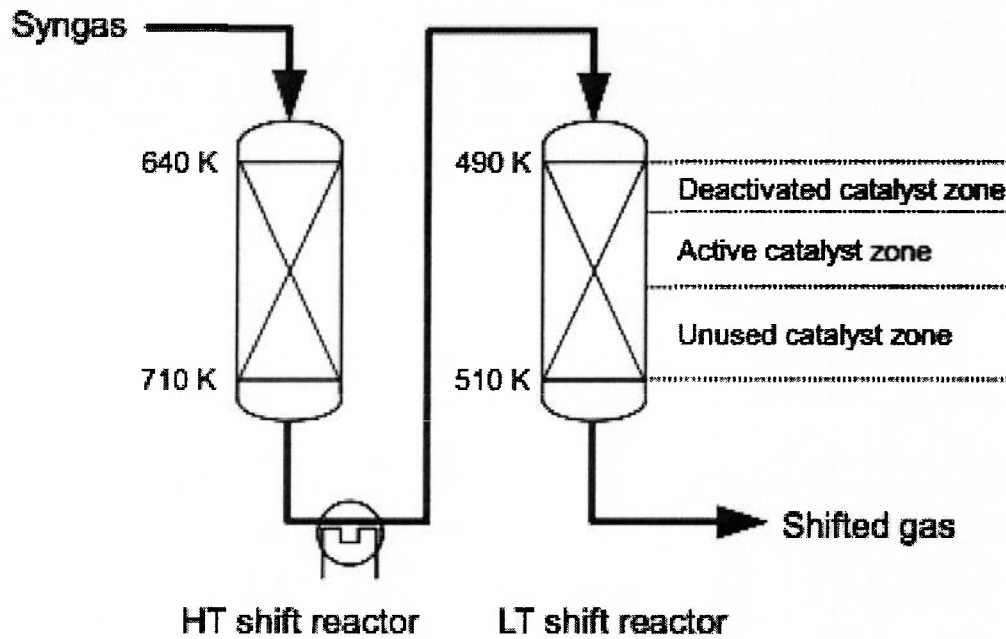


Figure 2.9 Water gas shift reactor configuration (MOULIJN; MAKKEE; VAN DIEPEN, 2013).

2.1.3. Autothermal Reforming

This process is the combination of steam reforming and partial oxidation in a single unit operation. Heat is produced in the reactor thanks to the combustion of a part of the feed with oxygen in the higher part of the reactor vessel. In the lower part, the steam reforming zone, the rest of the hydrocarbon is reformed to hydrogen and carbon monoxide with the CO_2 and H_2O produced in the combustion zone.

According to Moulijn, Makkee and Van Diepen (2013), this solution is not frequent when the feedstock is composed by light hydrocarbons or natural gas because of its very high investment costs due to the need of an air separation unit.

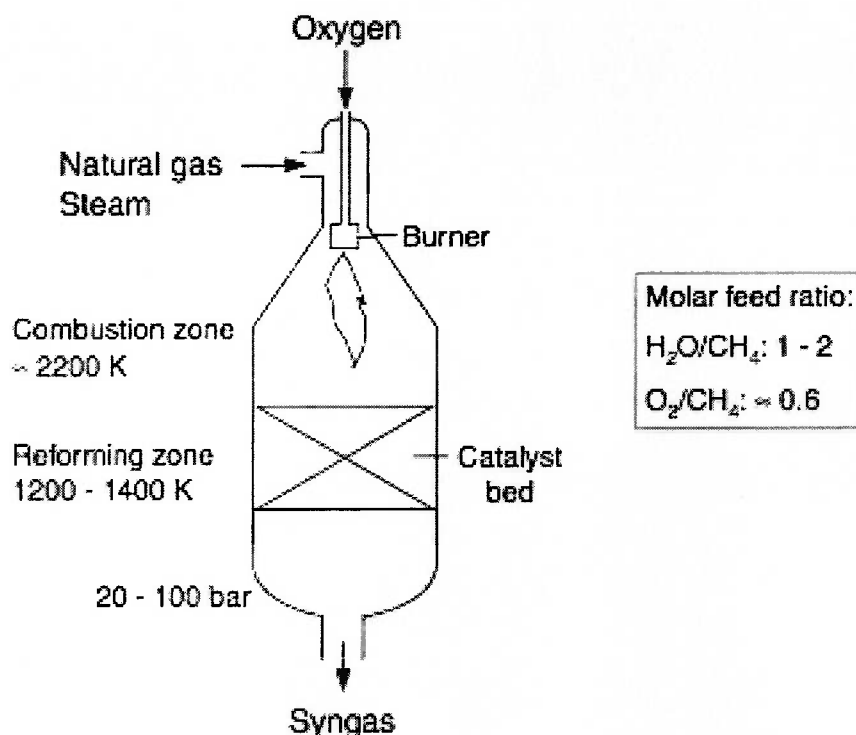


Figure 2.10 Schematic of an autothermal reformer (MOULIJN; MAKKEE; VAN DIEPEN, 2013).

2.2. Off-shore syngas production

According to Lahn et al. (2002) half of the world's proven natural gas reserves are in remote areas, far from sizeable markets and apparently unsuitable for an exploitation economically advantageous. Besides the pipelines transportation and the liquefied natural gas shipping, which are not always feasible due to technological and, above all, economical constraints, there are other applications for the gas associated with crude oil deposits. Among the most popular options it is possible to detach the methanol production and the gas to liquid technology (GTL). Methanol production is increasing due to its important role in the synthesis of many other chemicals like acetic acid, methyl methacrylate, methyl tert-butyl ether, dimethyl terephthalate (CROCCO, 1992). The GTL technology produces a syncrude, which can be further treated and sold as a conventional fuel.

Regardless of the final use of the natural gas, the syngas production is an intermediate step common to all the processes. The choice of the syngas generating technology is not simple and needs to be investigated. It is possible to summarize the processes discussed in section 2.1: steam reforming is increasingly being combined with a secondary reforming in an autothermal process while partial oxidation is an exothermic alternative to the endothermic steam reforming. The partial oxidation offers the possibility to exploit the generated heat in an energy integration of the process, producing steam which can be used in other utilities of the process or in the power generation. However, besides the energetic efficiencies of the various processes, the composition of the product is still the most important parameter to consider when choosing a chemical process. The hydrogen-to-carbon monoxide ratio for a Fischer-Tropsch synthesis is 2:1 which, from Eq. 1, is obtainable from a partial oxidation process. Despite this, the steam reforming process (Eq. 6) provides extra hydrogen that can be used in the hydro-treating of the Fischer-Tropsch syncrude. From another point of view, since CO₂ emissions are getting more and more taxed and limited a steam reforming combined with an

autothermal reformer appears to be the right choice. In conclusion, since the autothermal reformer needs pure oxygen in the feed, a new problem appears to be the off-shore oxygen supply.

Considering the dimensions of an off-shore platform, conceive an all-in-platform production is prohibitive due primarily to space constraints. For this reason, Floating Production, Storage and Off-Loading (FPSO) applications are becoming more popular (WHITE; CHAFEE; DESAI, 1994). An offshore vessel poses new problems to the plant design in addition to those already existing.

2.2.1. FPSO technology

The development of the FPSO technology started in 1974. Actually, the FPSO technology is becoming more and more popular, as it can be seen in Figure 2.11.

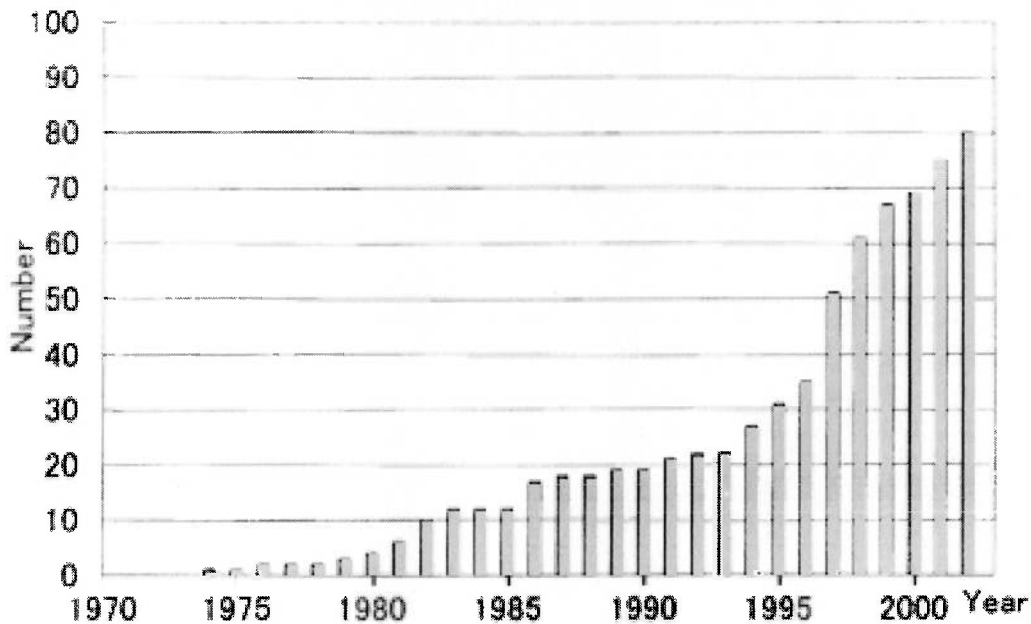


Figure 2.11 Growth in the use of FPSO systems (SHIMAMURA, 2002)

The further developments of the technology, as shown in Figure 2.12, aimed to reach the offshore oil reservoirs in ultra-deep water (3000 m), as an alternative of the conventional platforms. As a matter of fact, mooring an FPSO system in ultra-deep water costs less than mooring a conventional fixed structure or a tension leg platform (SHIMAMURA, 2002). Others advantages offered by this technology are the possibility to move and relocate the FPSO system and to combine it with other facilities such as offshore platforms, characteristic that will be extremely useful when studying the syngas and the GTL offshore production.

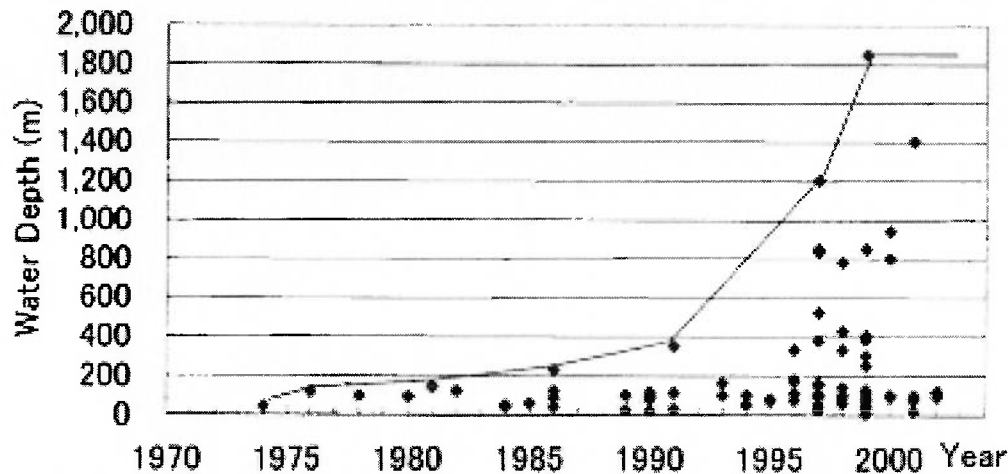


Figure 2.12 Changes in the water depth in which FPSO systems are used (SHIMAMURA, 2002)

In fact, nowadays the new frontiers in the FPSO systems are focused in the development of the offshore gas fields, including the associated gas in oil reservoirs. The major issues related to these projects are safety, isolation of the storage tank and facilities positioning (SHIMAMURA, 2002).

2.2.2. Off-shore oxygen production

A syngas production plant can satisfy its oxygen needs using air. However, this solution presents two problems due to the large volume of nitrogen (WHITE; CHAFEE; DESAI, 1994):

1. The Fischer-Tropsch process is driven under pressure so, if air were used, all the inert N_2 would need to be compressed to the final pressure. The plant energy demand would be too high as well as the equipment size. Moreover, the GTL process would need to work with high recycling rates and purges.
2. A partial oxidation driven with air would critically reduce the adiabatic temperature rise of the reactor. The equilibrium of the reaction would shift from products to reactants, having more CH_4 and CO_2 at the reactor's exit and consequently, more inert inside the Fischer-Tropsch reactor.

The traditional air separation process uses cryogenic distillation and obtains highly pure oxygen (>99%); it is the most economical approach for large-scale production of approximately 1000 tonne/day (THOROGOOD, 1991) occupying an estimated area of 1000 m^2 . When the high purity is not required, the vacuum swing adsorption technology offers the possibility to produce oxygen with purity between 90 and 98%. The maximum capacity of a single unit does not exceed 150 tonne/day (the limit is due to the vacuum pumps which cannot bear a higher productivity). A 1000 tonne/day plant would occupy an estimated area of 6720 m^2 (THOROGOOD, 1991). The membrane separation technology does not give a high purity of oxygen without a great energy demand (WRIGHT; COPELAND, 1990). A single stage separation plant produces a low pressure product containing 30-40% oxygen thus, to produce highly pure oxygen, multiple stages need to be arranged in series with an inter-stage recompression and consequently a high capital investment with a great energy demand.

Moreover, when producing off-shore syngas many other limitations applies to the plant such as safety issues. Gaseous oxygen would need to be compressed before entering in the syngas reactors; this is not recommended because compressors do leaks, threatening the safety of the whole process (BROWN et al., 1998).

The traditional cryogenic distillation produces low pressure liquid oxygen which can be pumped much more safely than compressed gaseous oxygen. For this reason it is considered the most suitable process for the FPSO application.

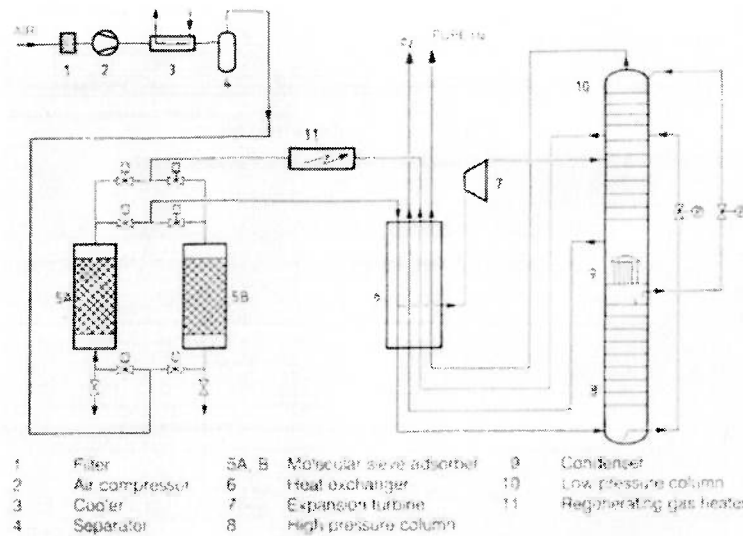


Figure 2.13 Air separation plant with upstream molecular sieve station

Air is filtered, compressed, cleaned and cooled to cryogenic temperatures. It is then distilled in a double column arrangement in order to produce low pressure oxygen.

The distillation column should be a packed column and not a trays column. Using trays would affect the column efficiency in terms of tray maldistribution caused by the swaying motion of the ship. A packed bed works with very thin liquid films which would not be affected.

Chapter 3. Fischer-Tropsch Synthesis

Due to a desire of finding ways to economically exploit remote natural gas, its conversion to hydrocarbons is one of the most promising topics in the energy industry. Franz Fischer and Hans Tropsch discovered the conversion of the syngas to hydrocarbons in 1923 (FISCHER; TROPSCHE, 1925). They observed that the carbon monoxide hydrogenation was possible over iron, cobalt and nickel catalysts resulting in a mixture of linear hydrocarbons. The principal reaction products are n-paraffins (linear alkanes) and α -olefins (linear alkenes with a double bond at the primary position). The fuel produced in this process is sulphur-free and consequently does not produce sulphur oxides when burned. Moreover, due to the high linearity of the products (almost no ramified or aromatic compounds are produced) the diesel fuel synthesized has a high cetane number¹.

At ambient conditions, the products are distributed among three different phases:

- Gaseous (methane, GPL)
- Liquid (kerosene, fuels)
- Solid (waxes)

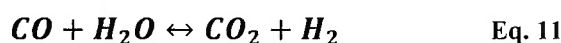
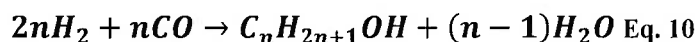
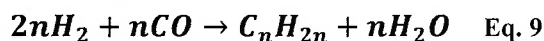
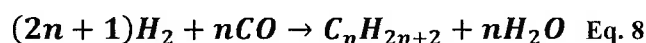
Nevertheless, the principal product of the reaction is water.

The Fischer-Tropsch process is strongly related to its upstream process: the syngas production. In plant consisting of syngas production, Fischer-Tropsch synthesis and product upgrading (refining area), the estimated costs for the production of the syngas are approximately 66% of the total on-site capital costs (CHOI; KRAMER; TAM, 1997). In an offshore production overview, one can imagine the refining and upgrading step separately from the syngas synthesis and its conversion to liquid fuels; this turns the estimated costs for the syngas production being approximately 75% of the total on-site capital costs.

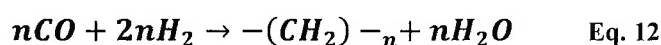
Therefore, the syngas must be transformed into hydrocarbons as much efficiently and completely as possible. Efficiency and completely are two adjectives directly related to conversion and selectivity: high conversions are desired together with high selectivity, in order to minimize the production of undesired products such as oxygenated products and methane.

3.1. Chemistry of the Fischer-Tropsch synthesis

The Fischer-Tropsch reaction can be seen as a polymerization process driven by a variety of reactions:



The principal reaction can be summarized by:

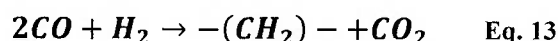


¹ The cetane number (NC) indicates the fuel's ignition delay between the start of injection and the first pressure increase during the combustion of the fuel. It is a measure of the quality of a diesel fuel but it is not the only parameter indicating diesel's quality. It is an equivalence of the octane rating of gasoline. The references are cetane (C₁₆H₃₄): NC=100 ; methylnaphthalene (C₁₁H₁₀) NC=0.

The reaction is strongly exothermic, with a reaction enthalpy of approximately $\Delta H_{\text{rxn}} = -40 \frac{\text{kcal}}{\text{mol}_{\text{CO}}}$.

3.1.1. Stoichiometry

The stoichiometric study of the reaction is an important step since it determines the ideal composition of the feed (i.e. the composition of the syngas to be produced). In the Fischer-Tropsch process, the stoichiometry is principally related to the ratio of consumption of H_2 and CO . Sometimes, the CO_2 may be involved if acting as a reactant. Depending on the catalyst, the WGS reaction may affect or not the usage ratio of the reactants. When using cobalt catalysts the WGS reaction is negligible and consequently the H_2 to CO usage ratio is determined principally by Eq. 12, being included between 2.06 and 2.16. At the opposite side, when the iron-based catalysts are employed, the WGS reaction may approach the equilibrium and the usage ratio will be much more affected by the composition of the feed gas (DRY, 2004). Dividing Eq. 12 by n and adding it to Eq. 11 one obtains:



This indicates a H_2 to CO usage ratio of 0.5. Unlike cobalt catalysts, when dealing with iron catalyst, the H_2 to CO usage ratio is different from the stoichiometric ratio. Adding the reverse WGS reaction to Eq. 12 divided by n leads to:



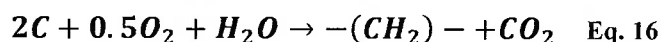
Here, carbon dioxide acts as a reactant and both Eq. 12 and Eq. 14 must be considered to determine the stoichiometry. Finally, two hydrogen molecules are consumed by each molecule of CO and three hydrogen molecules are consumed by each molecule of CO_2 .

The Ribblett ratio expresses the hydrogen to carbon monoxide and carbon dioxide ratio and is equal to one when the reactants are in stoichiometric balance:

$$\frac{\text{H}_2}{2\text{CO} + 3\text{CO}_2} \quad \text{Eq. 15}$$

Summarizing, when using cobalt catalysts the usage ratio is approximately 2.15, when iron-based catalysts are used, the usage ratio is typically 1.7 if the process is driven at low temperatures. If using high temperatures coupled to iron catalysts, the WGS reaction rapidly goes to equilibrium and allows the CO_2 to be converted to FT products (DRY, 2002).

Considering the ideal case in which carbon is gasified to produce syngas which is afterwards used to produce heavy hydrocarbons, the overall reaction is:



This shows how the maximum theoretical carbon efficiency when converting carbon to hydrocarbon is 50%.

3.2. Fischer-Tropsch product distribution

Using the Anderson-Schultz-Flory theory it is possible to describe the product distribution of the Fischer-Tropsch reaction. Chemically, the process can be seen as a step-growth polymerization (PUSKAS; HURLBUT, 2003). Introducing a parameter α related to

the chain growth probability, one can describe the probability of obtaining a species having length n , thus the probability that $n-1$ additions happened:

$$P_n = \alpha^{n-1}(1 - \alpha) \quad \text{Eq. 17}$$

Where $(1 - \alpha)$ indicates the probability the, reached the length $n-1$ the chain termination occurs. Note that this theory assumes that there is no correlation between the chain-length reached by the hydrocarbon and its probability of growth. This probability corresponds to the molar fraction of the hydrocarbon and it is used to write the mass fractions:

$$W_n = AP_n n \quad \text{Eq. 18}$$

Where A is a parameter used to fit the molar fraction to the mass fractions. To determine this parameter the normalization condition is imposed:

$$\int_0^{\infty} W_n dn = 1$$

Which implies:

$$A = \frac{\alpha \ln^2 \alpha}{1 - \alpha} \quad \text{Eq. 19}$$

Inserting Eq. 19 into Eq. 18 give the weight fraction:

$$W_n = n \alpha^n \ln^2 \alpha \quad \text{Eq. 20}$$

The weight fractions can be plotted in a logarithmic diagram (ANDERSON, 1984):

$$\ln \left(\frac{W_n}{n} \right) = \ln(\ln^2 \alpha) + n \ln(\alpha) \quad \text{Eq. 21}$$

This plot is called the Anderson-Schultz-Flory (ASF) diagram and it can be seen in Figure 3.1.

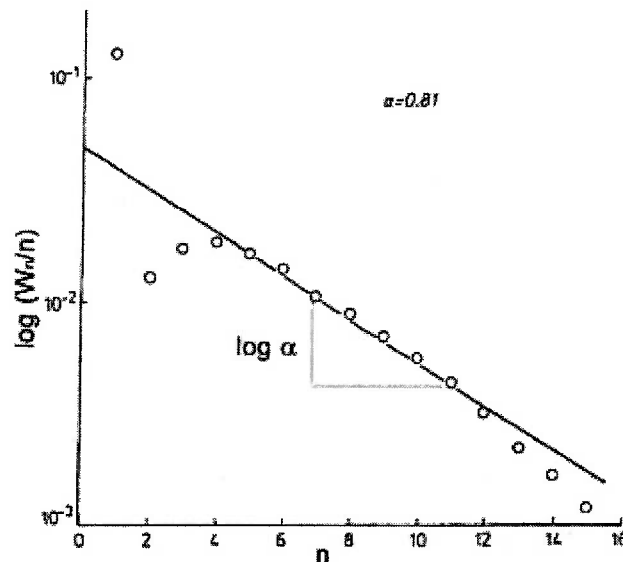


Figure 3.1 Anderson-Schultz-Flory diagram for the Fischer-Tropsch reaction product distribution

According to Eq. 21, the plot of Figure 3.1 should give a straight line. However, there are some deviation from this line that have been observed experimentally:

- Methane is typically more than predicted due to the fact that the molecule has a different mechanism of formation, being produced from the hydrogenolytic cleavage of the α -olefins in secondary reactions (PUSKAS; HURLBUT, 2003). For this reason, methane formation should be treated separately.
- C_2 and C_3 fractions are much less than predicted due to a different chemical reactivity. In fact, these molecules have the predisposition to incorporate into polymeric molecules by initiating a new chain. It is assumed that at the beginning of the reaction the C_2 and C_3 fractions are formed in the amounts predicted by the ASF distribution (EIDUS, 1967).

3.3. Off-Shore Fischer-Tropsch synthesis

To compact a process such as the Fischer-Tropsch one is a great challenge: at the industrial scale it involves probably the largest chemical plant in the world. To have an idea of how big a Fischer-Tropsch plant can be, the largest GTL plant in the world, the Shell Pearl GTL located in Qatar can be taken as an example.

The project of the plant cost 5 million american dollars (EVANS, 2008) and its construction 24 billion \$ (WORLD GAS INTELLIGENCE, 2009); it covers an area of 2.5 km² and 52,000 workers were employed to build it. The cores of the GTL section are 24 reactors each one weighing 1,200 t and each filled with 5,000 t of catalyst (BORDEN, 2014). The plant can treat 1.6 billion cubic feet per day of natural gas coming from 22 wells, producing 140,000 barrels per day of GTL products and 120,000 barrels per day of natural gas liquids such as ethane, propane, normal butane, isobutane and pentanes (SHELL GLOBAL, 2011). Recalling that the principal product of the Fischer-Tropsch reaction is water, the Pearl GTL is equipped with the largest water processing plant, having a capacity of 280,000 barrels per day, comparable to that for a city of 140,000 people.



Figure 3.2 Shell's GTL Pearl plant in Qatar under construction (SHELL GLOBAL, 2011)



Figure 3.3 Overview of the Shell's GTL plant in Qatar (SHELL GLOBAL, 2011)

Reducing such a plant into one having reasonable dimensions to allow an off-shore use is a real challenge that many oil and gas companies have accepted.

There are several advantages related to the scale reduction. Besides the possibility to be constructed at remote locations and the possibility to integrate them with existing facilities, one can emphasize the risks reduction: commercial risks, project risks and safety risks (LLOYD, 2013). In fact, the low initial investment compared to the conventional GTL plants guarantees, together with the shorter schedules and the opportunity for early production, a lower commercial risk. From the modular nature of the reduced scale plant, the projects can be conceived to allow a phased production, starting to generate revenue prior to the completion of the plant (ENERGY GLOBAL, 2013). Moreover, the technical risks of a small scale GTL plant have been eliminated by the company CompactGTL that has conceived the plant as a group of modules (BOWE et al., 2010), mass produced in a production line which manufactures identical Fischer-Tropsch and Steam Methane Reforming modules (ENERGY GLOBAL, 2013).

The Brazilian oil and gas company Petrobras is facing a double problem caused by the increasingly stringent regulations on the gas flaring procedure. The National Petroleum Agency (ANP) announced that they are “keen to put an end to flaring in Brazil, and there is some frustration within the agency about how much this practice has persisted”. In fact, this is disturbing the Petrobras’ extended well tests in the Lula Central area located in the Santos basin pre-salt, capping the production to 17,600 bpd even though the Dynamic Producer FPSO employed could easily reach 30,000 bpd (CHETWYND; LISKEY, 2013).

3.3.1. CompactGTL and Petrobras

With a partnership with the brazilian company Petrobras, CompactGTL installed the world’s only small scale fully integrated technology that has been tested by Petrobras for 2

years and 6 month (at January 2014). It is a 45 million \$ project consisting of a 20 bpd pilot production plant located at Aracaju, Sergipe. CompactGTL followed up the pilot project with a commercial development agreement with SBM Offshore (CHETWYND; LISKEY, 2013). The idea is a FPSO application centered on a modular GTL plant having a production capacity of 2,000 bpd, weighting approximately 4,000 tonnes and whose maximum size should occupy one-third of the deck space of a Suezmax size tanker².

A patent registered by Bowe et al. (2010) shows a commercial application of modular, low-scale GTL plant for off-shore gas treatment on an FPSO. Ideally, there will be a single FPSO unit which comprises the oil extraction and pre-treatment section connected to one or more separate wells in the same field (up to twenty wells, depending on the relative productivity) and the compact modules of the GTL section. The integration of the extraction and gas treatment section is likely to reduce the overall plant costs. In the specific case, the GTL section is convenient for facilities having gas to oil ratios between 35 and 350 m³/m³ but can be adapted to match the operating conditions for wells producing with a gas to oil ratio as low as 15 m³/m³. Smaller ratios turn the process uneconomical because of the lack of raw material which, in this case, is the natural gas. Such values perfectly match with the Brazilian pre-salt condition which presents gas to oil ratios between 200 and 350 m³/m³ in the Lula and Cernambi field, located in the Santos basin (ESTRELLA, 2011; BELTRÃO et al., 2009) and between 60 and 240 m³/m³ in the Albacora field, located in the Campos basin (PORTAL BRASIL - AGÊNCIA PETROBRAS, 2011).



Figure 3.4 CompactGTL's plant at the Petrobras research center in Aracaju

² Naval architecture term referring to the largest ship measurements (basically draft and height) capable of transiting the Suez Canal.

3.3.2. Chevron Research and others

Besides CompactGTL and Petrobras, other companies are working on a compact solution for the GTL technology, demonstrating the worldwide interest in this field. Chevron Research, Technology Company, Air Products and Chemicals Inc. and other partners are working together with the U.S. Department of Energy to evaluate a Fischer-Tropsch process on a FPSO vessel.

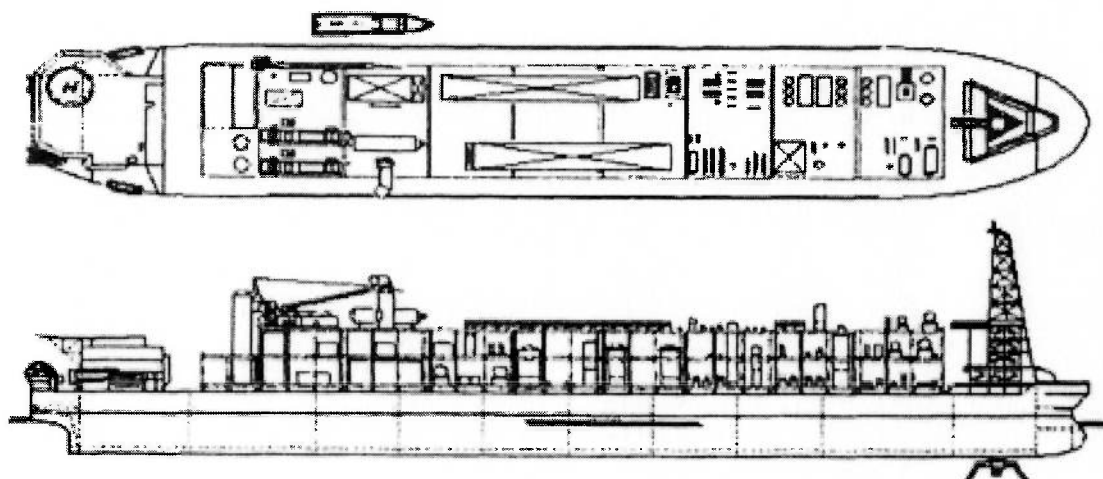


Figure 3.5 GTL FPSO plan and side views (LOWE e GERDES, 2001)

They determined the technical feasibility of an offshore GTL plant capable to handle associated gas; they estimated the cost of the facility and examined different syngas synthesis (LOWE; GERDES, 2001). The field considered produces 50,000 barrel per day of crude and has an associated gas production of 100 million SCFD, entirely fed to the GTL plant. The different configurations for the generation of the syngas were: air-blown autothermal reforming, oxygen-blown autothermal reforming and ion transport membrane reforming. The principal differences between the air-blown and the oxygen-blown autothermal reforming are the presence of high quantities of nitrogen in the former and the presence of an air separation plant and a pre-reformer to convert the C_{2+} hydrocarbons into H_2 and CO in the latter. The ion transport membrane reforming, shown in Figure 3.6, is an unconventional route for the syngas generation studied by the same group of companies in association with the U.S. Department of Energy. The principal idea is to use a compact ceramic membrane reactor, which separates the oxygen from an air stream and uses the separated oxygen for an oxygen-blown steam reforming. The principal advantage of the process is the absence of an air separation unit in the plant and the lower pressures in the whole process (CHEN et al., 2001).

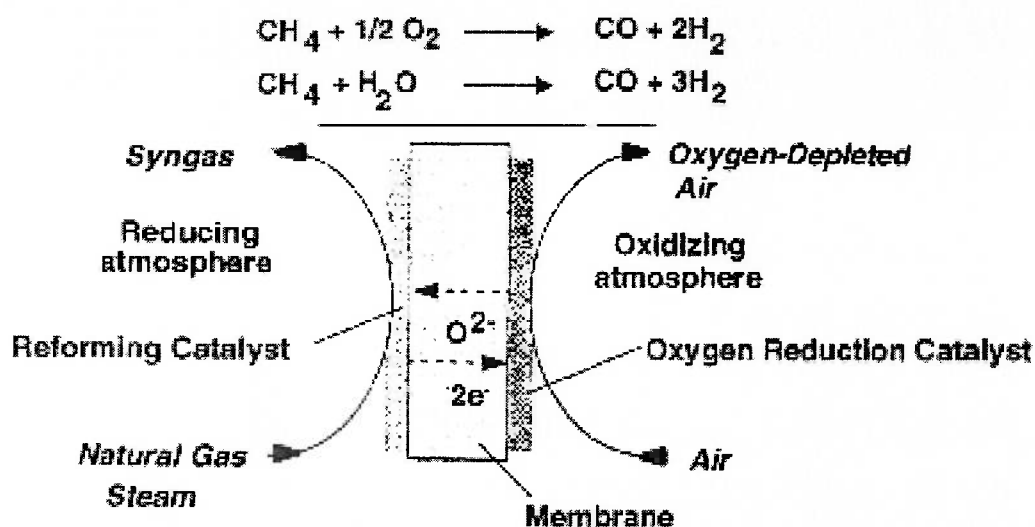


Figure 3.6 Conceptual ion transport membrane syngas technology (CHEN et al., 2001)

Due to the high nitrogen content, the air-blown process cannot include a recycle stream: for recycling to the reactor a small quantity of unconverted syngas, one must recycle great quantities of inert gas thus increasing the volume of the reactors. For this reason, the air-blown process uses a series of reactors while the oxygen-blown process and the ITM process use a single stage reactor with off-gas recycle (LOWE; GERDES, 2001).

It is important to notice how the ITM process and the oxygen-blown process had a favorable Fischer-Tropsch product yield distribution compared to the air-blown process.

	Air-blown process	Oxygen-blown process
C1/C2	18	12
C3/C4	11	7
C5-C11	34	29
C12-C18	19	23
C19+	18	29
Total	100	100

Table 1 Fischer-Tropsch yield distribution³, wt.% (LOWE; GERDES, 2001)

In fact, considering the C₁₂₊ range, which is the most interesting and more valuable range of products, the overall yield for the air-blown process is 37% while the oxygen-blown yield is 52%. An explanation to this is given by Van Berge and Everson (1997) that studied the effects of the reactant pressure on yield, for a Fischer-Tropsch synthesis based on cobalt catalysts. What the authors observed was that increasing the reactant partial pressure increased α , the probability to produce longer hydrocarbons. Consequently, the air-blown process is much more oriented to low value light products due to the dilution effect of the nitrogen.

³ Due to proprietary and development nature of the ITM syngas technology, the detailed results were not included in the work.

	Air-blown process	Oxygen-blown process
Hull length [m]	275	300
Hull width [m]	50	53
No. of decks	3	3
No. of process modules	7	8.7
Total deck space [m ²]	17,100	22,100
FPSO size [t]	156,000	215,000
Storage capacity [bbls]	873,000	1,239,000

Table 2 Deck and Hull requirements (LOWE; GERDES, 2001)

Table 2 shows the FPSO system dimensions for the air based and the oxygen based processes. Notice that, because of the absence of the air separation unit, the FPSO system based on the air-blown process weight much less and requires less space. In both cases the minimum acceptable storage capacity of 500,000 bbls was widely met.

The total operating costs were 39.9 million\$/year for the air-blown process and 45.1 million\$/year for the oxygen-blown process; this difference in the capital costs is due to the presence of the air separation unit in the oxygen based process. The highest contribution for the total operating costs is given by maintenance and operating manpower.

The capital costs were almost the same for the two processes: 750 million\$. In fact, the extra costs given by the air separation unit in the oxygen based process were balanced by lower costs in the utilities, being that there is no need to compress the air and to remove the heat. The ITM based process presented the lowest capital investment: besides the absence of the air separation unit it also saved capital in the utilities, thus combining the advantages of the air-blown and the oxygen-blown processes.

	Air-blown process	Oxygen-blown process
Raw crude [bpd]	50,000	50,000
Syncrude [bpd]	8,400	10,800
Total [bpd]	58,400	60,800
CapEx \$/bpd	61,000	47,500

Table 3 Production rates/Unit capital cost (LOWE; GERDES, 2001)

The difference in the syncrude produced by the oxygen-blown process is principally due to the effects of the reactant partial pressure (LOWE; GERDES, 2001). Dividing the CapEx costs related to the GTL section (approximately 68% of the total CapEx) one obtains the dollars of capital costs per barrel of product. In 2001 the industry target was to reach a CapEx per barrel included between 20,000\$/bpd and 25,000\$/bpd. Despite the high costs of the project, the FPSO GTL technology is a real alternative for the production of both crude oil and associated gas. Technological evolutions on the syngas generation (such as the ITM technology) and oil price evolution may turn the process economically advantageous.

In fact, according to the market in 2013, the Oryx GTL plant (operating in Qatar, onshore) has a CapEx per barrel in the range of 35,000 \$/bpd and 44,000 \$/bpd (SALEHI; NEL; SAVE, 2013). The Pearl GTL plant described in the introduction of section 3.3 has a CapEx per barrel of 77,000 \$/bpd. These two plants are actually producing and the payback

for the Pearl GTL was estimated in around 4 years, based on a 50 \$/bbl oil price, which gives a 4.5 billion\$/yr income (DONOVAN, 2008). Considering now the consumer price index, which describes the inflation in the United States of America, the inflation factor between 2001 and 2014 is 34.12% (with an average of 2.28% per year). Thus, a CapEx per barrel of 47,500 \$/bpd in 2001 could be roughly translated into a CapEx per barrel of 63,000 \$/bpd in 2014, which is perfectly included between the Capex per barrel of the Oryx GTL plant and the Pearl GTL plant.

Chapter 4. Conclusions

The offshore GTL technology has been studied under various aspects. First of all, a summary of the different chemical routes to produce the syngas starting from natural gas as feedstock has been presented and, subsequently, a special focus was given to the offshore syngas production. Notwithstanding the advantages presented by the partial oxidation reaction, especially in terms of energy integration of the process, the best way to produce was the autothermal reformer, coupling a steam reforming to a partial oxidation process. The oxygen supply for the partial oxidation section of the autothermal reformer is a critical step since pure oxygen must be obtained offshore. A FPSO system appeared to be the best solution to accomplish the air fractioning offshore; the traditional cryogenic distillation process was the best solution in terms of safety, capital investments and space occupation.

With respect to the GTL overall process (thus including the Fischer-Tropsch section), many companies are orienting their efforts on the FPSO systems, which can guarantee not only the process itself but also the storage of the products of the reaction and, eventually, the storage of the reservoir production. It appeared that the technology is evolving into identical modular reactors that can be used to perform indistinctly the steam reforming reaction or the Fischer-Tropsch reaction, occupying a small space and reducing the global investment costs for the plant.

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