

## **Offshore gas-to-liquids: Modular solution for associated gas with variable CO<sub>2</sub> content**

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**Keywords: GTL process, Offshore GTL, natural gas conversion with variable CO<sub>2</sub> content, Extended Well Tests**

### **1) Background**

During the exploratory phase, it is Petrobras' tradition to perform extended well tests in deepwater reservoirs. Typically a six month period is required to gather information regarding reservoir behavior, damage mechanisms and flow assurance, allowing to optimize the definitive systems to be deployed in the future field. In offshore environments these extended well tests (EWT) are performed by ships designed and built for this specific purpose. These vessels are able to store the produced oil in its cargo tanks for subsequent offloading. The gas is used for power generation and the exceeding is flared, since usually no pipelines are available during EWTs. Alternative solutions for flaring are being investigated by the industry but so far none have reached technical and economical feasibility.

Brazilian legislation restricts the amount of gas burned during EWTs. In pursue of a more environmentally friendly alternative, PETROBRAS has researched Gas to Liquid (GTL), among other technologies. GTL converts natural gas into synthetic crude oil which can be mixed with the produced oil for storage and offloading.

GTL technology has been in use since the 1920s at several onshore locations. In the offshore environment however it has never been applied before, due to weight and space restrictions. It can be specially applicable to stranded or remote gas reserves, where physical, logistics or economic factors have impeded the development of the field [1,2].

The compact reactors applied in GTL process represent a breakthrough in GTL technology, because of their small footprint, lower weight, modular design and high efficiency (high conversion and selectivity by enhancing heat and mass transfer) which meet the requirements for offshore applications. The Floating Production, Storage and Offloading (FPSO) vessel designed to accommodate a GTL plant for EWT application shall consider to share the infrastructure and common utilities in order to optimize the footprint, resources and costs. An integrated and synergic control and safety philosophy for the whole FPSO shall be pursued to guarantee an overall safety and operability. The idea of combining oil and GTL production is driven by the need of complying environmental requirements and economics, since the total oil production will be increased. Besides, the synergy between the utility systems can provide a lower CAPEX, reducing the initial project investment [1].

Focusing on the offshore scenario, a joint testing agreement led Petrobras and CompactGTL to the construction and operation of a 20 bbl/d mini-channel GTL pilot plant in Petrobras' test site, in Aracaju city, Northeast of Brazil, which has been running a number of different tests since November 2010. Meanwhile, Petrobras, Velocys, Toyo Engineering and Modec signed a joint demonstration and testing agreement in 2009 to build and operate a 5–10 bbl/d micro-channel GTL demonstration plant installed in Fortaleza city, Northeast of Brazil, to evaluate this technology as well. The goal is to validate such technologies for offshore applications via long term tests under real process conditions.

Furthermore, some pre-salt fields may contain variable content of CO<sub>2</sub>. Due to this reason, PETROBRAS is particularly interested in checking the feasibility of GTL technology with natural gas feed containing CO<sub>2</sub>. Processing natural gas with CO<sub>2</sub> can make other possible technical solutions like Compressed Natural Gas (CNG), Liquefied Natural Gas (LNG) and re-injection more costly and difficult than GTL offshore.

In this paper we discuss how PETROBRAS has led an aggressive development program of a compact version of this technology for an offshore application, the Floating GTL.

## 2) Aims

Converting natural gas with CO<sub>2</sub> into syncrude is one of the key issues of the F-GTL project due to the possible adverse effects of this component in the process overall performance. Then, different cases have been simulated and analysed for a modular plant installed in a FPSO vessel. The case studies presented here consider the performance of the GTL process with 600.000 Nm<sup>3</sup>/d of natural gas feed containing from 1.6 to 35% of CO<sub>2</sub> in two independent trains of 300.000 m<sup>3</sup>/d each.

## 3) Methods

The numerical simulation was carried out considering a pre-reforming, steam methane reforming and Fischer-Tropsch synthesis section via a steady state refining process simulator called PETROX which was developed by Petrobras. The cases have considered two single trains of 300.000 Nm<sup>3</sup>/d of natural gas feed containing from 1.6 to 35% of CO<sub>2</sub>. The reaction conditions assumed in the simulations were the following:

Pre-reforming at 425 °C and 9.0 bara;  
SMR at 760 °C and 4.0 bara;  
FT reaction at 230 °C and 25 bara.

Peng-Robinson was the thermodynamic Equation of State (EOS) employed. The Gibbs reactor was used to simulate the SMR. Conversion reactor was used to simulate the FT process (chain growth probability factor: 0.86).

### 3.1) Floating GTL concept in a FPSO

This work considers a SMR process connected to a GTL section where the hydro-treatment and hydro-cracking sections, normally present in GTL onshore plants, are omitted from the Floating GTL (F-GTL) concept in a FPSO, since the goal is just to convert the natural gas into liquid hydrocarbon which will afterwards be mixed in the crude oil produced to avoid gas flaring. The process comprises two main steps. The first is the reformer where syngas is generated, and the second is the FT synthesis.

The FPSO processes reservoir fluids produced from several subsea wells tied back to the platform. Gas, oil and water separation occur on board in three stages of separation. Oil is routed to the onboard storage tanks. Water is disposed of overboard after being properly treated to remove particulates and oil. Gas is compressed for power generation and feed to the GTL plant.

The GTL Plant includes the following process units:

- Gas pre-conditioning Unit;
- Steam Methane Pre-Reforming and Reforming Unit;
- Syngas Compression Unit;
- FT Synthesis Unit;
- Final product separation, degassing and pumping;
- Water treatment;
- Utility Systems;
- Combustion air plant for SMR;
- Steam generator for start-up;
- Nitrogen plant.

### 3.2 Feed gas flow rate

The process design is based on two trains, each processing 0.3 Million Nm<sup>3</sup>/d. The total capacity installed is 0.6 Million Nm<sup>3</sup>/d. The GTL plant has a modular concept and is designed to allow adequate turndown and feed gas flexibility to absorb upstream production fluctuations. It is made possible by the number-up concept inherent to the GTL compact reactor technology.

The feed gas flow rates to the GTL plant are summarised in the Table 1.

Feed Condition	Condition	
Gas Feed Rate	Maximum	0.6 Million Nm <sup>3</sup> /d
	Minimum	0.15 Million Nm <sup>3</sup> /d

Table 1 – Feed gas flow rates in the offshore GTL plant

The syncrude production expected is 1,000 bpd per train.

### 3.3 Feed Gas Composition

The GTL plant design considers rich natural gas with three different CO<sub>2</sub> compositions, 1.6, 15 and 35% in volume, as summarised in Table 2.

Component	Case 1 (% volume)	Case 2 (% volume)	Case 3 (% volume)
Carbon Dioxide	1.6	15.0	35.0
Water	6.6	5.7	4.4
Methane	75.6	65.3	49.9
Ethane	11.7	10.3	7.8
Propane	2.2	1.8	1.4
i-Butane	0.8	0.6	0.5
n-Butane	0.7	0.6	0.5
i-Petane	0.2	0.2	0.1
n-Pentane	0.4	0.3	0.3
n-Hexane	0.2	0.2	0.1

Table 2 – Studied natural gas compositions containing different CO<sub>2</sub> contents

### 3.4 Process Description

The main process operating objectives are summarised in Table 3. The general process configuration for the offshore GTL plant and the main stream routings and unit operations are shown in Figure 1.



Process System	Objectives
Feed Gas Conditioning	The objective of this system is to reduce the impurities in the feed gas to acceptable levels. H <sub>2</sub> S removal; Mercury (Hg) removal; Mercaptan removal by hydrogenation; Chloride/salt removal; Sulphur removal.
Pre-Reforming	The pre-reformer converts heavier hydrocarbons to methane, H <sub>2</sub> , CO <sub>2</sub> and CO. The ratio of steam and carbon alters the overall reaction equilibrium.
Steam Methane Reforming (SMR)	The objective of this system is to convert methane into syngas according to the highly endothermic methane reforming reactions:  $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad (\text{Steam Methane Reforming})$ $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (\text{Water Gas Shift Reaction})$ The presence of a high CO <sub>2</sub> content makes the “dry reforming” reaction competes with the SMR reaction. $\text{CO}_2 + \text{CH}_4 \leftrightarrow 2\text{CO} + 2\text{H}_2 \quad (\text{Dry Reforming})$
Combustion Air and Fuel Gas	The objective is to provide air for the combustion to support the reforming reactions.  Desulphurised feed gas is used as fuel for normal operation.
Syngas Compression	The objective is to compress the syngas to the required pressure to feed the Fischer Tropsch reactors. Part of the compressed syngas stream is routed through a membrane unit to control the required syngas feed ratio to the Fischer Tropsch synthesis.
Fischer Tropsch Synthesis	The objective of the Fischer Tropsch synthesis is to produce predominantly long chain, paraffinic hydrocarbons from syngas  Typical FT Reaction: $n\text{CO} + (2n+1)\text{H}_2 \leftrightarrow \text{H} - (\text{CH}_2)_n - \text{H} + n\text{H}_2\text{O}$

Table 3 – Summary of the main processes and their objectives in the offshore GTL plant

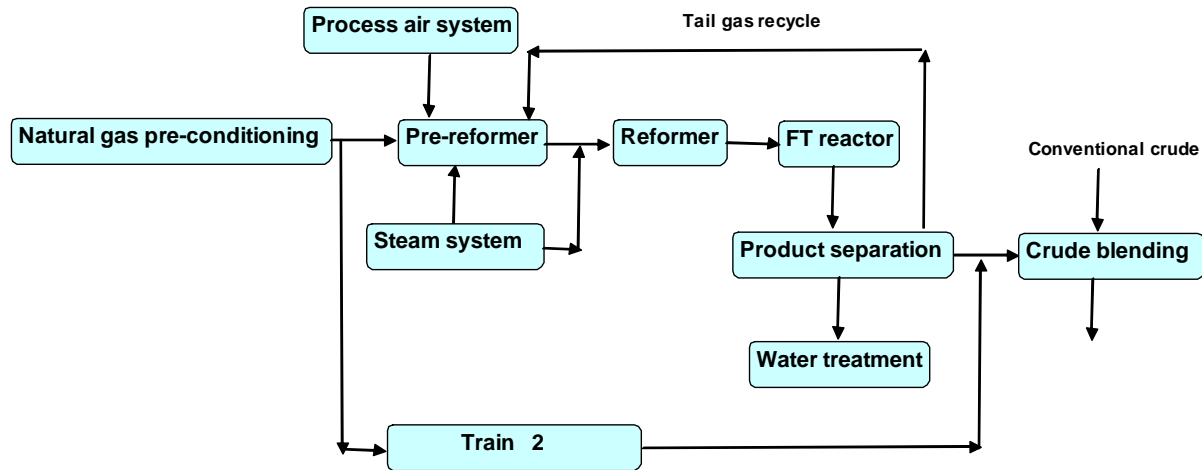


Figure 1 – Typical process block diagram for the F-GTL plant

### 3.5 Product and Discharge Specifications

The properties of the syncrude product from the GTL plant are dependent on the operating conditions of the FT reactor and on the catalyst type. The syncrude produced by the offshore GTL plant is stabilised to enable blending with the treated crude oil before storage. A typical oil required specification is summarised in Table 4.

Oil Property	Value
Reid Vapor Pressure (RVP)	<10 psia @ 37.8 °C
True Vapor Pressure (TVP)	<14.5 psia @ 55 °C
Temperature	55 °C
BS&W (% vol.)	<0,5
Salt Content	Less than 270 mg/l as NaCl
H <sub>2</sub> S	Nil

Table 4 – Typical final oil specifications for storage

### 3.6 Produced Water

The GTL produced water treatment system is designed to achieve a maximum Total Oil and Grease (TOG) value of 29 mg/liter in the discharge water. The GTL produced water from FT will be discharged to the FPSO oily water treatment facility. Use/recycle of the produced GTL water from the process steam generation is considered.

## 4) Results

### 4.1) Pre-reforming and steam methane reforming section

The produced gas from the process separator is pre-treated in the pre-conditioning unit in order to remove possible contaminants like sulphur compounds, chlorides etc. The pre-reforming section converts the higher hydrocarbons (C2+) from the mixture of natural gas and FT tail gas (recycled gas) into methane, hydrogen and carbon oxides. The pre-reforming is an adiabatic fixed bed reactor with a highly active Ni-based catalyst. The reaction 1 shows the main chemical conversion mechanism in the pre-reforming section, which is the steam reforming of high hydrocarbons to produce a mixture of CO and H<sub>2</sub>.

Typical Pre-reforming reaction:



The reaction 1 is endothermic, which is followed by the exothermic equilibrium reactions of methanation and shift, reactions 2 and 3, respectively. The overall reaction temperature will depend on the process conditions and on the gas feed composition, since it is a consequence of the energetic balance between the endothermic and exothermic reactions. Normally, the recycle stream (tail gas) is rich in CO which will result in temperature increase in the pre-reforming reactor due to the shift and methanation reactions [3].

Methanation reaction:



Water-gas-shift reaction:



The SMR was simulated considering a catalytic compact mini-channel reactor composed by stacked plates containing parallel arrays of mini-channels. The process channels (steam methane reaction) are filled with precious metal catalyst and the necessary heat for the reaction is provided by the intercalated plates containing parallel arrays of catalytic combustion channels. The conversion of methane into synthesis gas was carried out considering the water-gas-shift and steam methane equilibrium reactions (3 and 4).

Steam methane reaction:



Dry reforming reaction:



The high temperature (760 °C) and low pressure (4.5 bara) in the SMR drive the equilibrium to high methane conversion and high carbon monoxide selectivity. The effect of increasing CO<sub>2</sub> in the natural gas feed stock is illustrated in Figure 2. As the CO<sub>2</sub> content increases in the natural gas feedstock, the H<sub>2</sub>/CO ratio in the syngas produced is reduced. This happens because the equilibrium in the water-gas-shift reaction (3) is shifted to the left. The reverse water gas shift reaction leads to CO production from the reaction between CO<sub>2</sub> and H<sub>2</sub>. The volume of excess of hydrogen produced in the reformer, over the stoichiometric FT requirement (around 2:1), is reduced. This effect reduces the volume flow rate of syngas (upstream of the membrane) as the syngas ratio (H<sub>2</sub>/CO) reduces from approximately 3.1:1 in the 1.6% CO<sub>2</sub> case to about 2.4:1 in the 35%CO<sub>2</sub> case. Overall, the CO yield is improved or at least not reduced so much, despite the reduction in the proportional total hydrocarbon content in the feed, as a consequence of dry reforming (5), which is the linear combination of steam methane (4) and the reverse shift (3) reactions. Also, dry reforming extension can be increased by reducing the amount of steam employed in the reformer. This action shall be taken carefully, since it can lead to coke formation. To prevent coking, it was assumed that steam to carbon and H<sub>2</sub>/CO ratios should be higher than 1.45 and 2.40, respectively, and that the catalytic system would incorporate precious metal in its composition, which is more resistant to coke formation mechanisms.

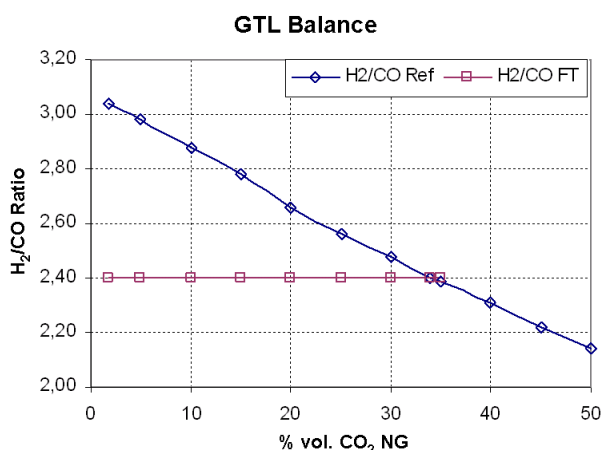


Figure 2 – Effect of CO<sub>2</sub> in the syngas H<sub>2</sub>/CO ratio

The increase of CO<sub>2</sub> in the natural feed up to 35% in volume improves methane conversion in the reforming section in 19%, compared with the base case (1,6% of CO<sub>2</sub>), which was normalised and considered as 100%, as it can be seen in Figure 3(a). It happens because the equilibrium of dry reforming reaction (5) is driven to the right side, by the raise of CO<sub>2</sub> content, increasing the extension of the reaction between CH<sub>4</sub> and CO<sub>2</sub> to produce CO and H<sub>2</sub>.

In the same way, the results represented in Figure 3(b) show the normalised CO selectivity in the reforming section considering a 1.6% volume of CO<sub>2</sub> as a base case (100%). The results have shown that the CO selectivity rose to 16% when CO<sub>2</sub> content in the feedstock was increased to 35% volume. It happens because the high amount of CO<sub>2</sub> drives the water-gas-shift reaction equilibrium to the left side, producing CO from the reaction between CO<sub>2</sub> and H<sub>2</sub>. The CO selectivity is calculated considering the conversion of CH<sub>4</sub>. So,



the selectivity number obtained in this case is higher than 100%, since part of the CO produced came from the partial CO<sub>2</sub> conversion from reverse water-gas-shift reaction.

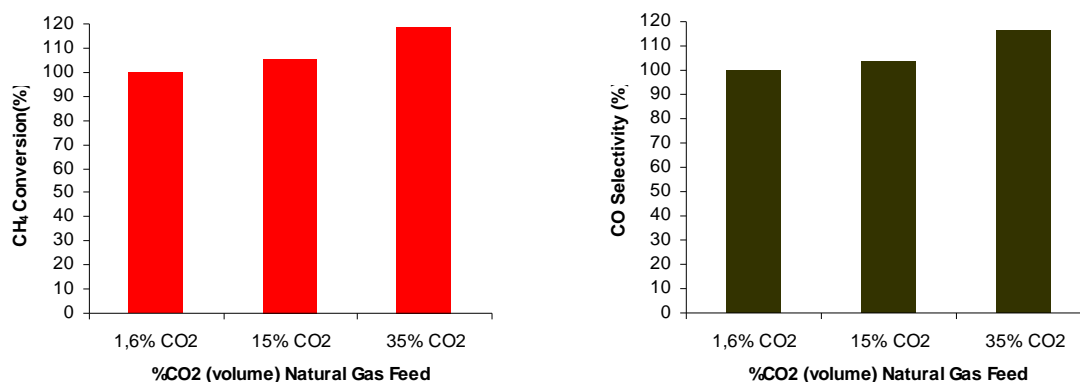


Figure 3 – (a) normalised CH<sub>4</sub> conversion in the reforming section for different CO<sub>2</sub> levels in the natural gas feed; (b) normalised CO selectivity in the reforming section for different CO<sub>2</sub> levels in the natural gas feed.

Despite the proportional reduction of hydrocarbons content in the natural feed, as a consequence of the CO<sub>2</sub> molar percentage increase, the CO yield was not reduced in the same magnitude as it can be seen in Figure 4. The increase of CO<sub>2</sub> content in the feed from 1.6% to 35% (concentration about 22 times higher) causes a CO yield reduction of about 18%. It is due to additional CO production by partial conversion of the CO<sub>2</sub> present in the natural feed as a consequence of changing the chemical equilibrium of the reverse water-gas-shift, compensating part of the lack of hydrocarbon available in the feed to be converted in CO.

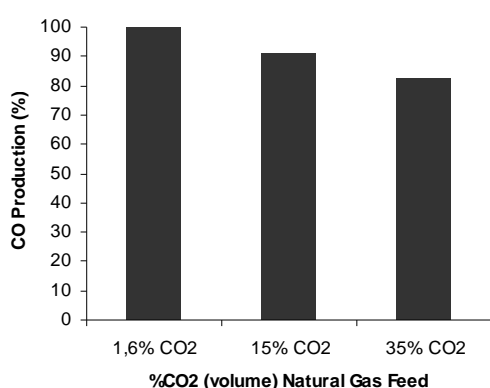


Figure 4 – Normalised CO yield

The syngas generated in the reforming process has a high CO concentration. Thus, if the syngas is submitted to temperatures between 400 and 650 °C, the Boudouard reaction (7) will be kinetic and thermodynamically favoured, driving the chemical equilibrium to the right side, forming coke and causing metal dusting corrosion in metallic

surfaces. In order to avoid such problem, the exit syngas from SMR reactor is fast cooled down from 760 °C to 250 °C via a process steam generator, which is also responsible to provide the necessary steam for the SMR reactor. The fast temperature reduction in the process steam generator avoids coke formation and metal dusting corrosion, since although the Bourdouard mechanism is thermodynamically favoured at low temperatures, the reaction is unfavoured by kinetic, so there is no time for coke grains to be formed.

Boudouard Reaction:



The higher the CO<sub>2</sub> concentration in the natural gas feed, the more Boudouard reaction (7) equilibrium is shifted to the left side, helping to block the coke formation by this mechanism in the entire system.

The exit stream from the process steam generator is submitted to a conventional treatment system to remove further contaminants (e.g.: ammonia, HCN, etc.), compressed and sent to the membrane unit in order to adjust the H<sub>2</sub>:CO ratio to 2:1, which is the suitable ratio to the FT reactor. The rich H<sub>2</sub> permeate from the membrane system can be employed as fuel for power and steam generation.

The SMR section is driven by equilibrium reactions, so it can accommodate increases in CO<sub>2</sub> content via partial conversion into CO. Then, even if the CO<sub>2</sub> levels in the natural gas change from 1.6 to 35% in volume, the syngas fed in the FT reactor, downstream of the membrane system, does not show the same order in CO<sub>2</sub> composition change, which varies from 15 to 27%, as shown in Figure 5.

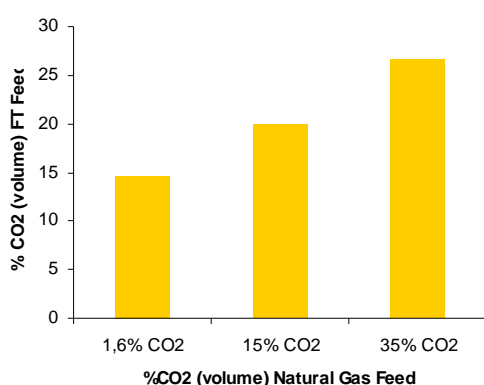


Figure 5 – CO<sub>2</sub> content in the natural gas feed effect in the CO<sub>2</sub> levels in the syngas inlet of FT reactor

## 4.2) Fischer-Tropsch section

The FT building block is comprised of stacked plates containing parallel arrays of mini-channels. The process channels (FT reaction) are filled with cobalt metal catalyst and the highly exothermic reaction produced is controlled by intercalated plates containing parallel arrays of channels filled with cooling water.

There are few discussions in the literature about the impact of CO<sub>2</sub> in the cobalt FT catalyst. However, information available about the hydrogenation mechanism, conversion, selectivity and possible deactivation or dilution is sometimes controversial [4,5]. The literature reports higher conversion levels for the CO<sub>2</sub> hydrogenation reaction to form hydrocarbons, when it is compared with CO hydrogenation reaction under the same conditions. However, its selectivity leads mainly to high methane production (around 70%) and other light compounds up to C<sub>4</sub>. The literature also shows that in presence of CO, CO<sub>2</sub> is hardly converted and seems to behave as an inert compound in some cases. It has been suggested that the competitive adsorption mechanism of CO on the active catalyst surface inhibits CO<sub>2</sub> adsorption and consequently its reactivity [4,5].

The normalised performance of the FT section is shown in Figures 6 (a) and (b). As it can be seen, the CO conversion and methane selectivity are not highly affected by high level of CO<sub>2</sub> in the plant feedstock.

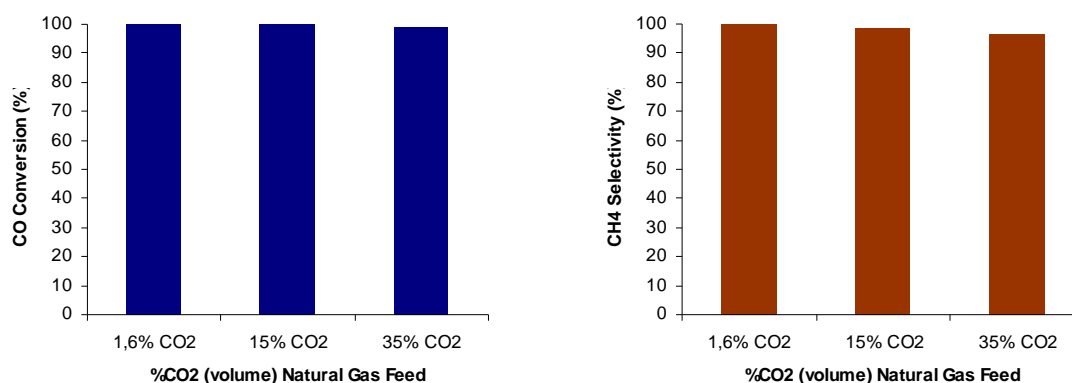


Figure 6 – (a) normalised CO conversion in the FT section; (b) normalised CH<sub>4</sub> selectivity in the FT section

Moreover, when the CO<sub>2</sub> content in the natural gas increases, more feedstock is consumed to provide energy for the SMR section, once the calorific power of the natural gas is reduced, also reducing the net natural gas available for the process and causing a reduction in the final syncrude production, as illustrated in Figure 7. This effect represents an overall reduction of less than 20% of the total syncrude production in the worst case analysed – 35% of CO<sub>2</sub> volume in the natural gas feed.

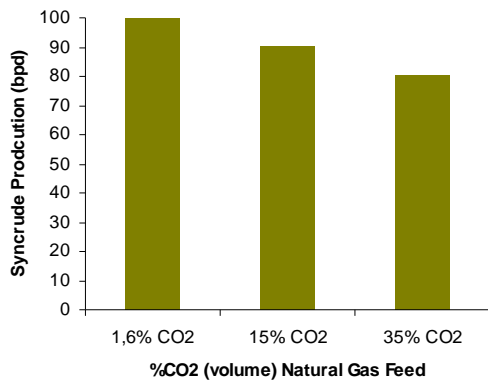


Figure 7 – Normalised syncrude production versus CO<sub>2</sub> natural gas content

Carbon Efficiency is one parameter that can be used to define the overall process performance, since it calculates the percentage of hydrocarbon carbon presented in the natural gas recovered by the GTL process as liquid hydrocarbon. Such parameter is also related to the environmental impact, operation cost and capital cost.

The Carbon Efficiency is defined as the rate of carbon contained in the final product (C5+) divided by the rate of carbon contained in the hydrocarbons compounds presented in the feedstock. The definition is presented in Formula 1 below.

$$E_C = \frac{\dot{m}_{SYN} \cdot \phi}{\sum_{j=HC,CO} (F_{j,PR} + F_{j,FUEL}) \cdot n_{C,j}} \cdot 100$$

Global Carbon Efficiency (%)

$\dot{m}_{SYN}$	Produced syncrude mass flow (kg/h)
$\phi$	Conversion factor from syncrude (kg/h) to carbon molar flow (kmol/h), considering the product as CH <sub>2</sub> ( $\phi = 0,0714$ )
$F_{j,PR}$	Molar flow of $j$ in the pre-reformer feed (kmol/h)
$F_{j,FUEL}$	Molar flow of $j$ in the SMR fuel (kmol/h)
$j$	Hydrocarbons and CO
$n_{C,j}$	Number of carbon atoms in $j$

Formula 1 – Global Carbon efficiency definition

Figure 8 shows the normalised process Carbon Efficiency for different CO<sub>2</sub> contents in the natural gas. The raise of CO<sub>2</sub> in the natural gas is responsible for an overall increase in the Carbon Efficiency due to the partial conversion of CO<sub>2</sub> into CO via reverse water-gas-shift reaction, which increases the CO available to be converted into syncrude.

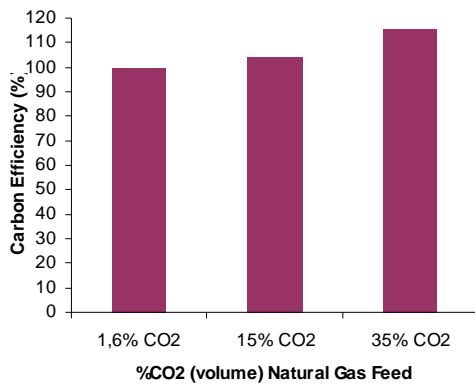


Figure 8 – Normalised overall process carbon efficiency

Related to the CO<sub>2</sub> process balance, Figure 9 shows the contribution of each section (reformer, pre-reformer and combustion) in the CO<sub>2</sub> balance in the plant. The CO<sub>2</sub> balance in the FT section was neutral (Delta CO<sub>2</sub> molar flow is null). As a consequence of the chemical equilibrium change in the steam methane and water-gas-shift-reactions due to CO<sub>2</sub> content increase in the natural gas feed, part of the CO<sub>2</sub> presented in the SMR feed is converted into CO. Due to this reason, the delta CO<sub>2</sub> flow rate is negative. Besides, it can be seen that the net CO<sub>2</sub> produced is reduced as the CO<sub>2</sub> content in the feed increases because of the new equilibriums achieved in the pre-reformer and reformer sections. On the other hand, the pre-reformer and the combustion side of the SMR reactor show a positive net CO<sub>2</sub> value. It means that there is production of this compound in those systems. As a result, the overall process is a CO<sub>2</sub> producer, since the net CO<sub>2</sub> balance is positive.

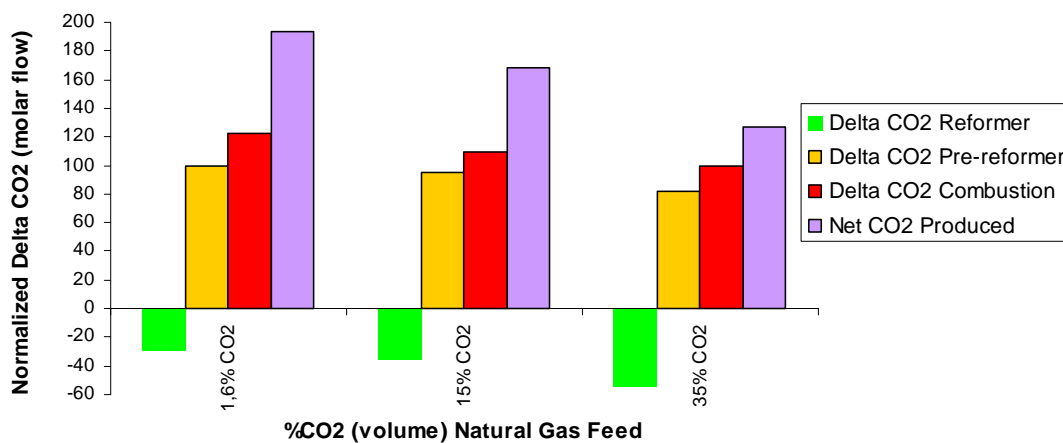


Figure 9 – CO<sub>2</sub> generated/consumed in each section and net CO<sub>2</sub> balance

## 5) Conclusion

Despite the proportional reduction of hydrocarbons content in the natural gas feed, as a consequence of the CO<sub>2</sub> molar percentage increase, the CO yield in the reformer was not reduced in the same magnitude due to the CO<sub>2</sub> partial conversion into CO, via reverse water-gas-shift reaction, which compensates part of the decrease in the syncrude production.

CO<sub>2</sub> is consumed in the steam methane reactor to form CO as a consequence of equilibrium change in the steam methane and water-gas-shift reactions. Nevertheless, the GTL overall process can not be considered a CO<sub>2</sub> sequestration process yet, since the net CO<sub>2</sub> process balance is positive. The results show that there are optimization opportunities to develop pre-reformer catalysts less selective to CO<sub>2</sub> production and reformer catalysts capable of increasing the dry reforming reaction extension with no coke formation. Besides, changes in the process can be done to replace natural gas by hydrogen in the reformer combustion to increase the overall carbon efficiency and reduce the CO<sub>2</sub> emission.

The observed reduction in the overall syncrude production with high CO<sub>2</sub> content is acceptable to the Extended Well Test scenario. It means that, for feed streams with as much as 35% of CO<sub>2</sub> in volume, there is no need of additional CO<sub>2</sub> separation facilities in the FPSO vessel.

Petrobras has been successful in the GTL modular small scale technologies studies for offshore use. Notwithstanding the contradictory discussions available in the literature about the CO<sub>2</sub> effect in the GTL process, the results obtained so far have indicated that it can accommodate high variations of CO<sub>2</sub> content in the feedstock. The process performance with CO<sub>2</sub> has been matching the forecasts.

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