KUALA LUMPUR 2012 WORLD GAS CONFERENCE

25th world gas conference

"Gas: Sustaining Future Global Growth"

Offshore Gas-to-Liquids: modular solution for associated gas with variable CO_2 content

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Venue: Kuala Lumpur

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Topics

1) What is Gas-to-Liquid (GTL)?
2) Why Offshore GTL?
3) Brazilian Pre-Salt Province Formation
4) Modular GTL Technologies and Principles
5) Offshore GTL Process
6) Results with variable CO_2 levels
7) Conclusions

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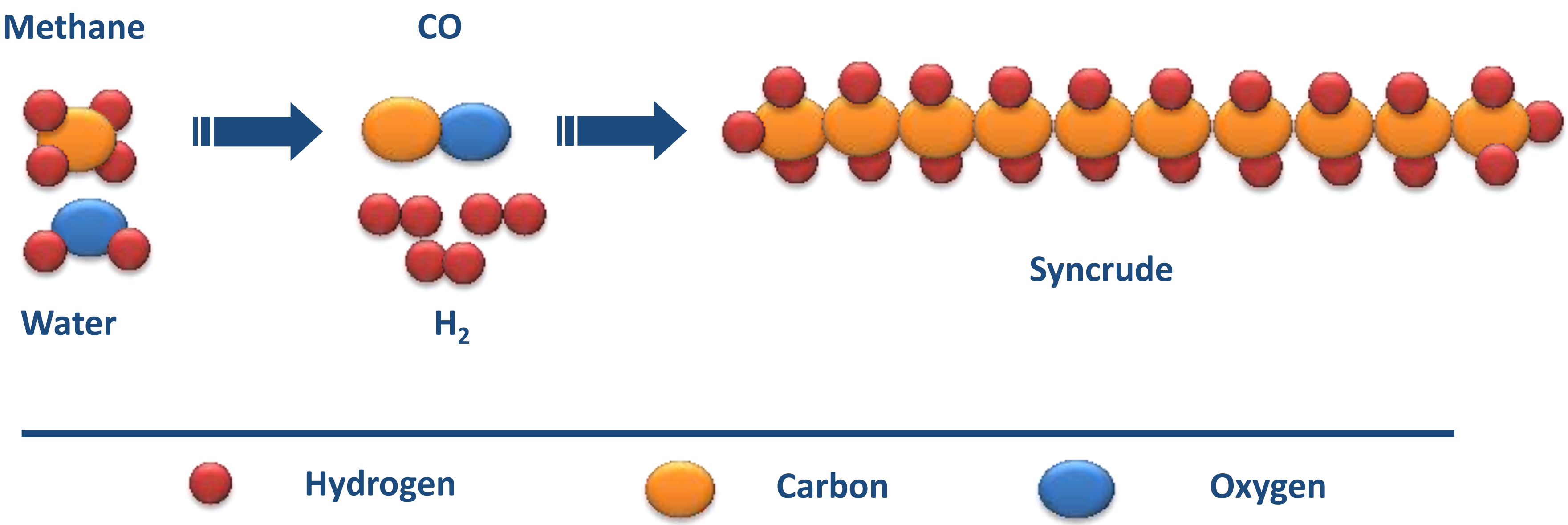
Gas-to-Liquids (GTL)



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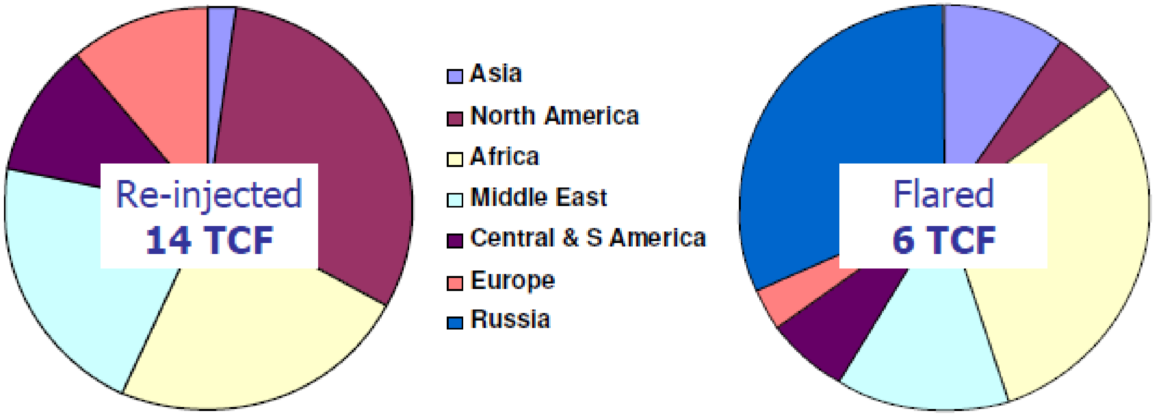
Flaring associated gas is a big global problem



~4 TCF
Not used to enhance oil recovery

= 27%
of annual US gas consumption !

> 10 TCF (= 4.6 mmboe per day)

Source: International Energy Annual 2005 World Bank GGFR 2006,2007

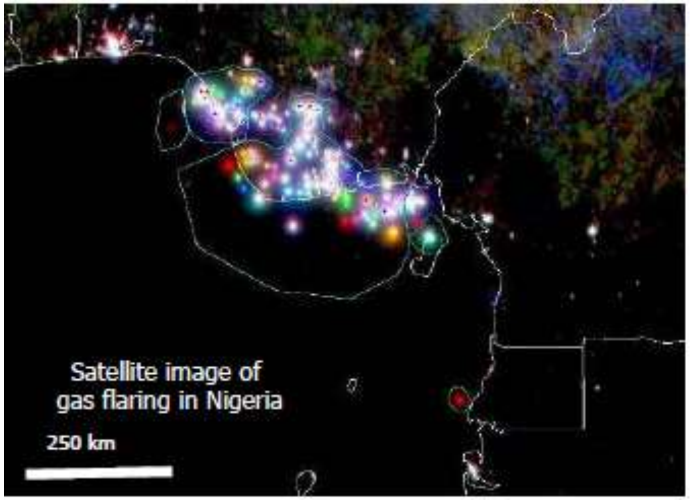
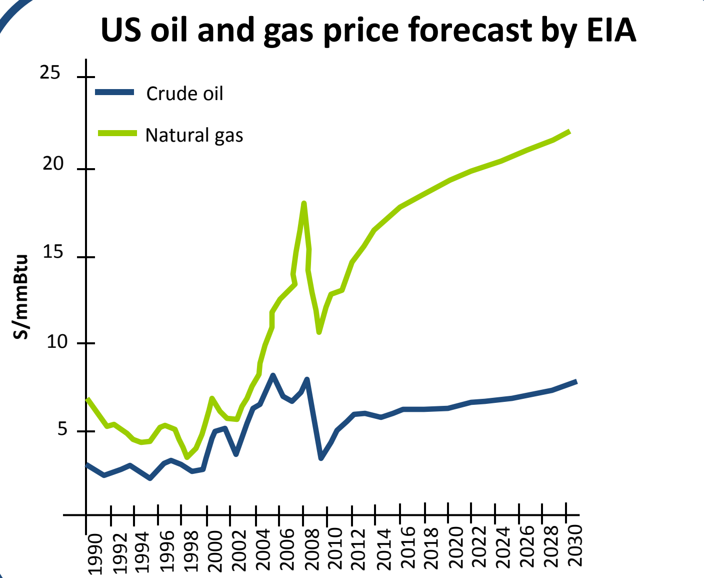


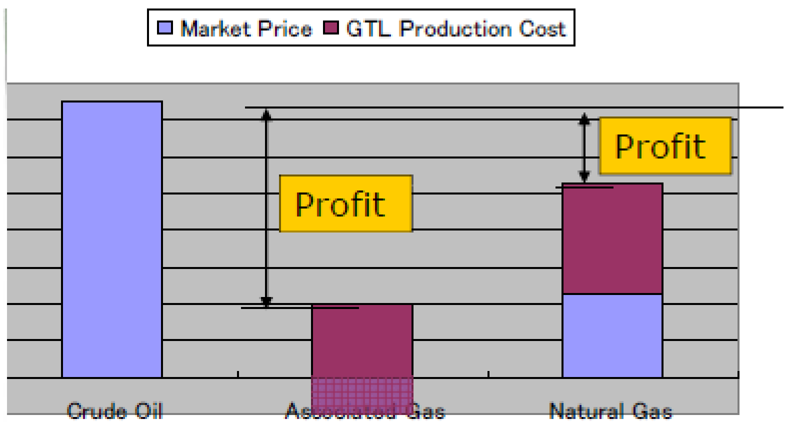
Image courtesy of Chris Elvidge, National Geophysical Data Centre, Bouder, CO, USA

Why GTL?

- Large spread between crude oil and natural gas princes
- Converting crude 1 bbl at 5.8 million btu:
  - Crude price @ $100/bbl corresponds to $17/million btu;
  - Current US gas price (Henry-rub) is $4/million btu;
- Crude oil have a premium value ($13/million btu) over the gas since it is liquid



Source: IEA



Source: Toyo Engineering Corporation, 2011

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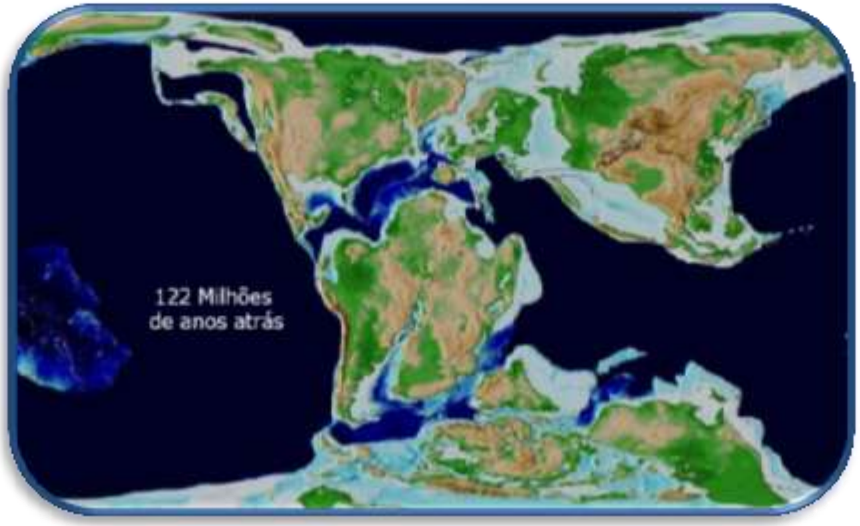
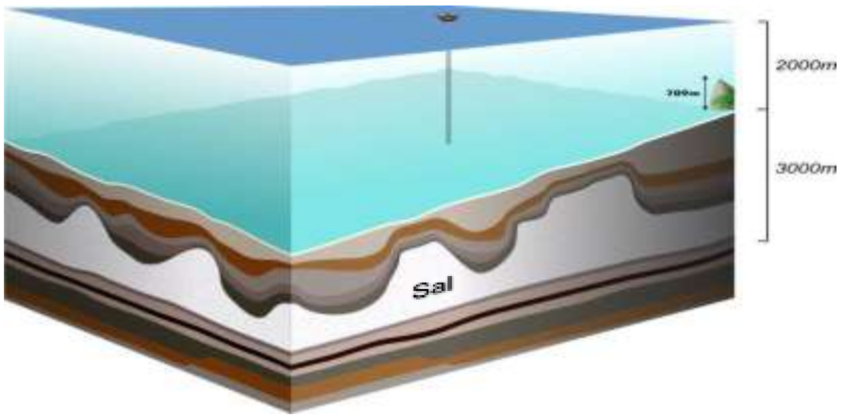
Pre-Salt Province Formation



- Reservoir pre-salt formation when Latin American e African continents were separated;

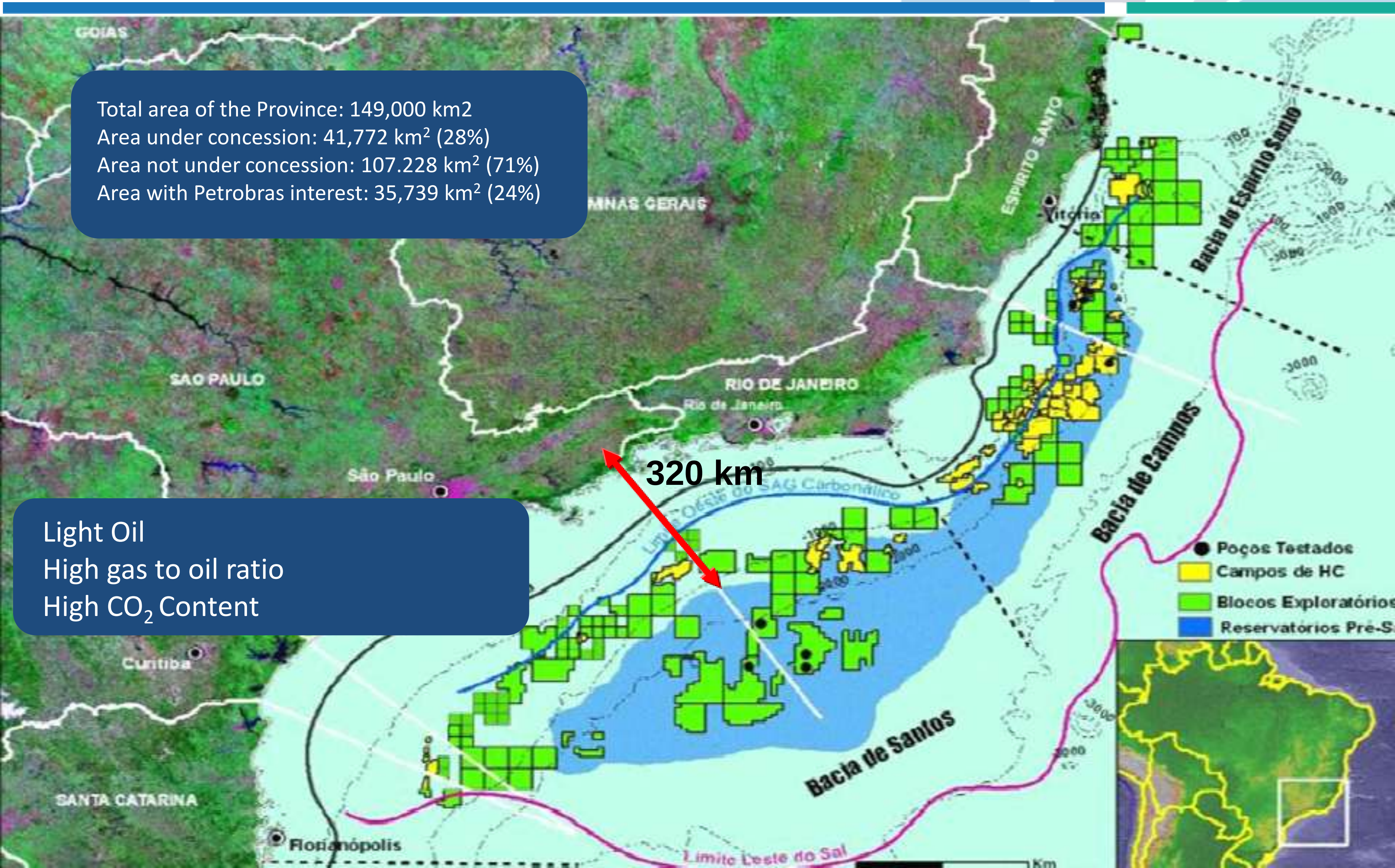
- Huge oil and natural gas reserves;
- Reservoirs located between 5,000 and 7,000 m under sea level;
- Deep Water (more than 2,000 m);
- Under Salt layer (may present more than 2,000 depth).



Brazilian Pre-Salt Province in Numbers

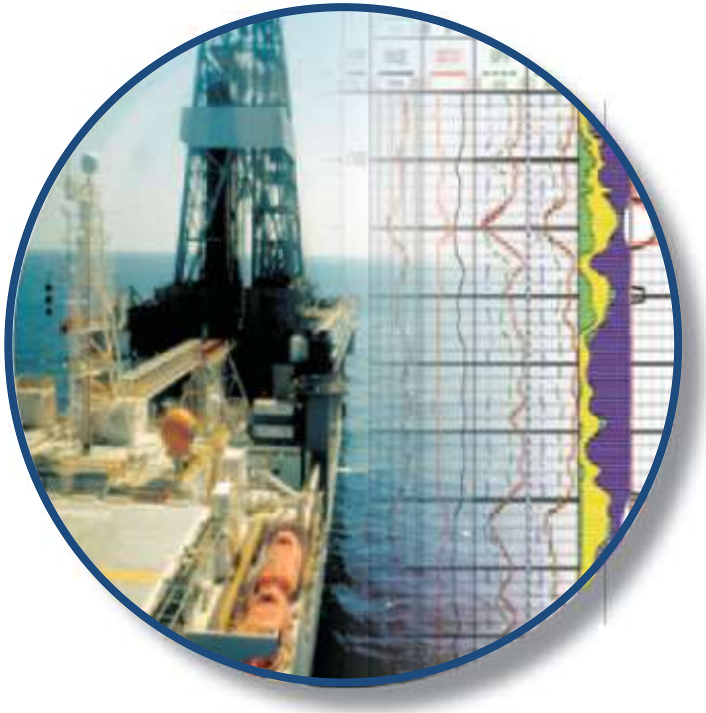
Total area of the Province: 149,000 km2
Area under concession: 41,772 km^2 (28%)
Area not under concession: 107.228 km^2 (71%)
Area with Petrobras interest: 35,739 km^2 (24%)

- Light Oil
- High gas to oil ratio
- High CO_2 Content



Pre-Salt Challenges

- New Exploratory Frontier
- Extended Well Tests (EWT)
  - Reducing technical and geological risks
  - 6 to 12 months duration
  - Powerful tool to character the reservoir
    - Reservoir Production along the time
    - Checking Damage mechanisms and reservoir hydraulic communications
    - Sampling rocks and fluids
    - Flow assurance
    - economic potential
- Long Distances from the cost
- Fields located in deep and ultra-deep water
- No access to infrastructure for associated natural gas re-injection or transportation during EWT
- Avoid flaring the associated natural gas (legal and environmental constrains)
- Processing natural gas with high CO_2 contents



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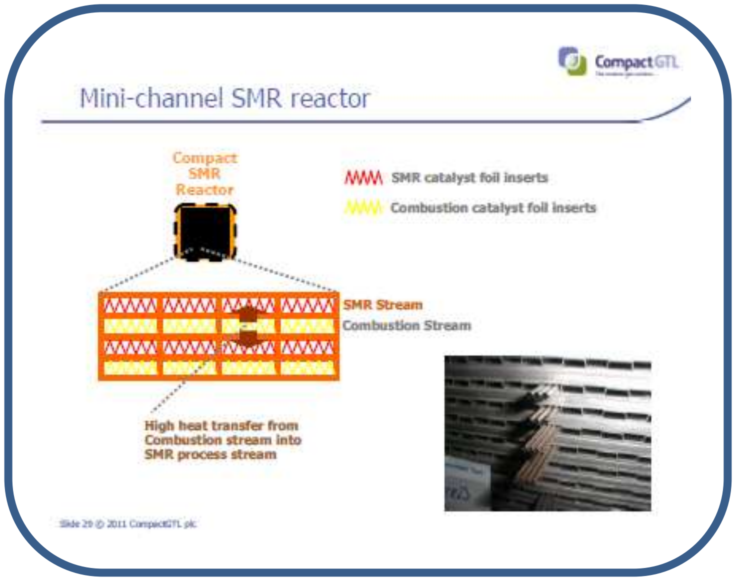
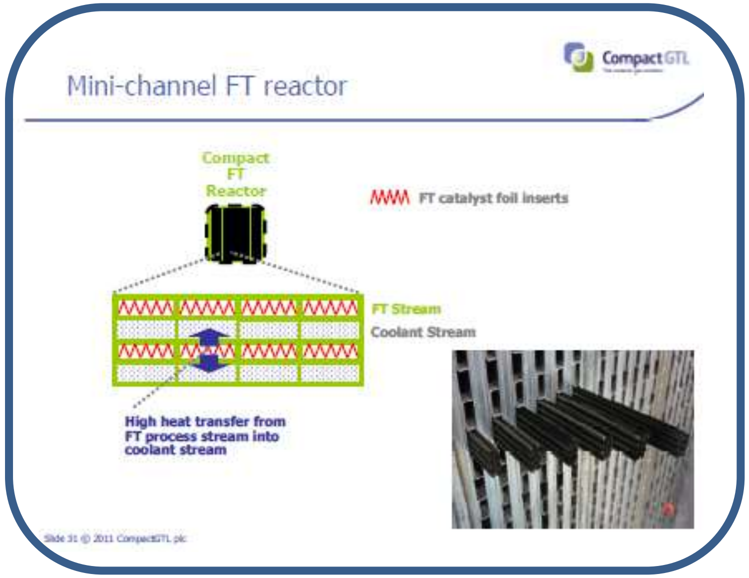
Modular GTL Demonstration Plant Aracaju/SE (CompactGTL Technology)

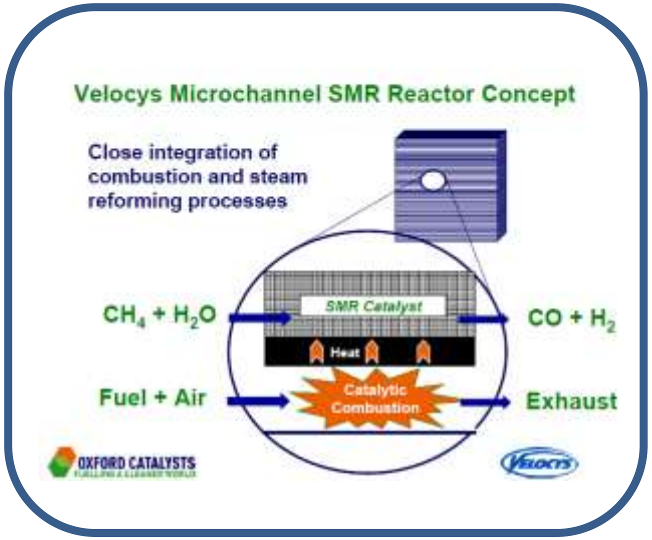


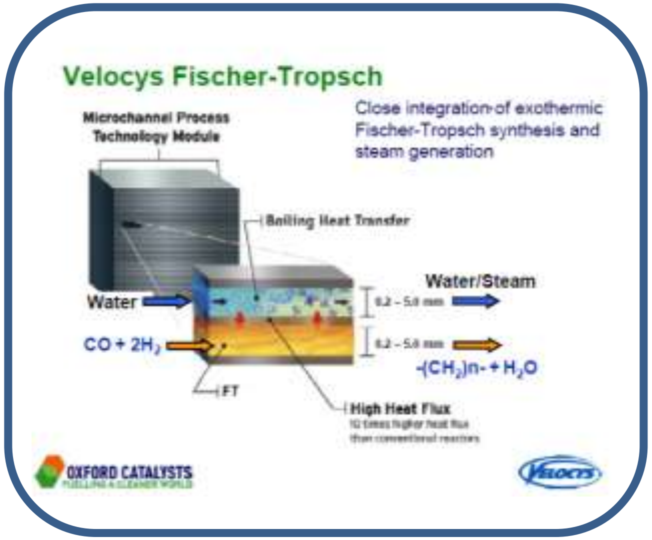


Source: CompactGTL Plc.

- Dec/2010 – Final comissioning;
- Jan/2011 – First syncrude;
- Nov/2011 – Tests with high CO_2 content and Technology Qualified;

Modular GTL Demonstration Plant Fortaleza/CE (Velocys Technology)



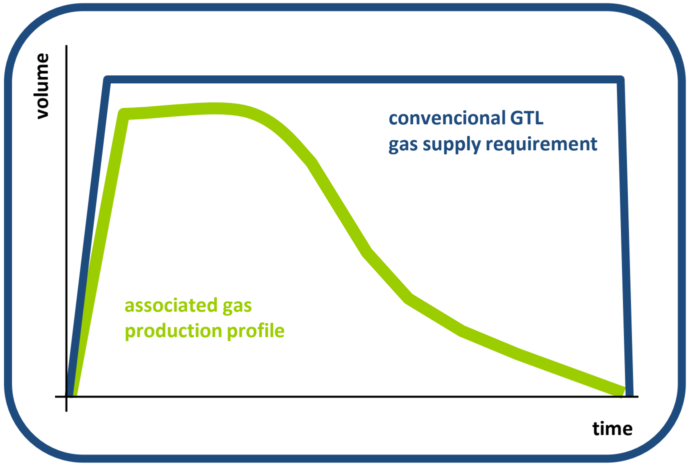


Source: Velocys, Zeus 2011 Modular GTL Seminar

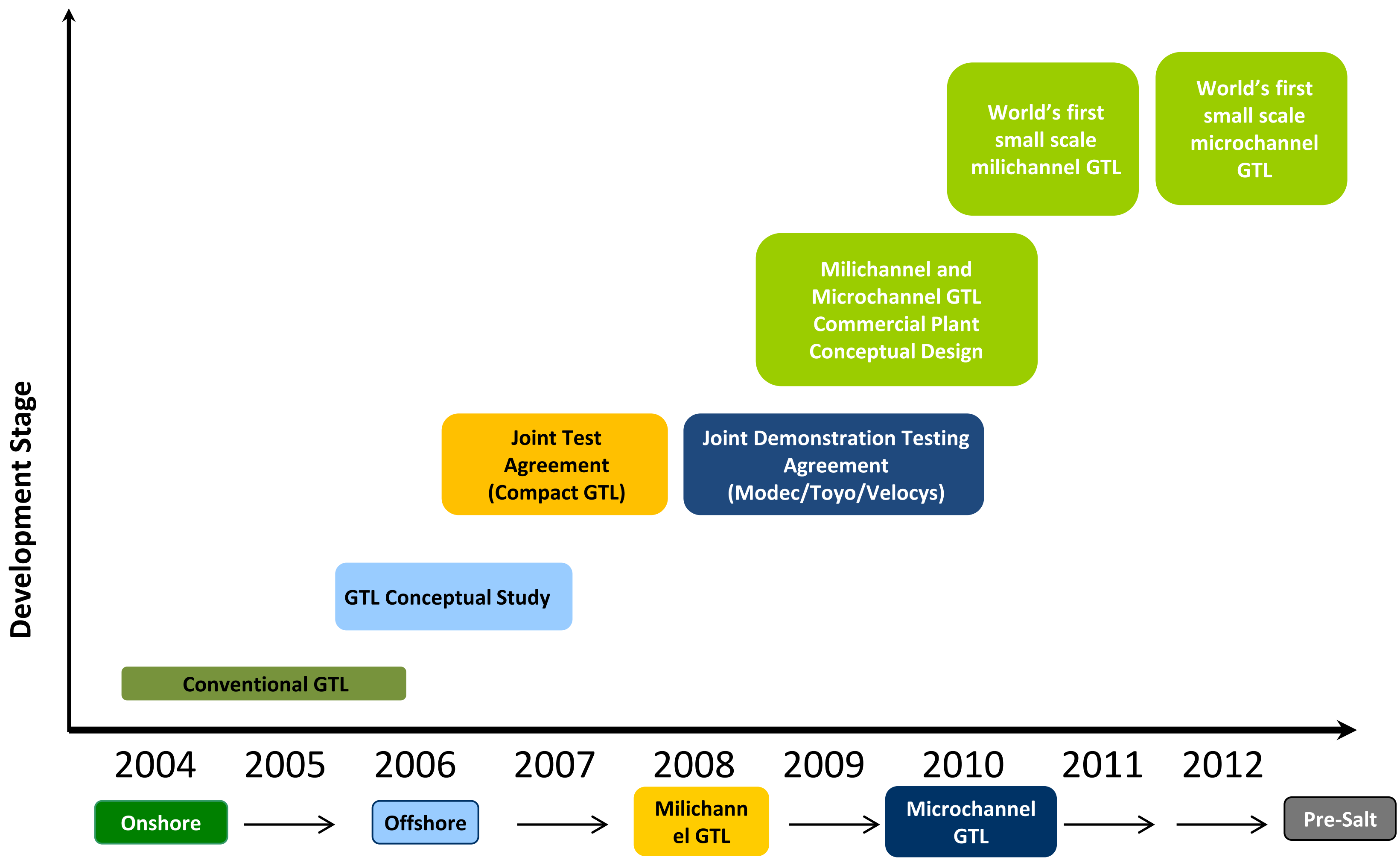
» **Under Qualification**

Why Compact and Modular Reactors Use?

- Limitation of space and weight in an offshore production facility
- Needing of intensified processes of mass and heat transfer
- Production of natural gas falls along the time
- Modules can be removed as production falls
- Modules can go on-line and off-line to accommodate production variability (turndown flexibility)



Roadmap Toward Modular GTL Plant



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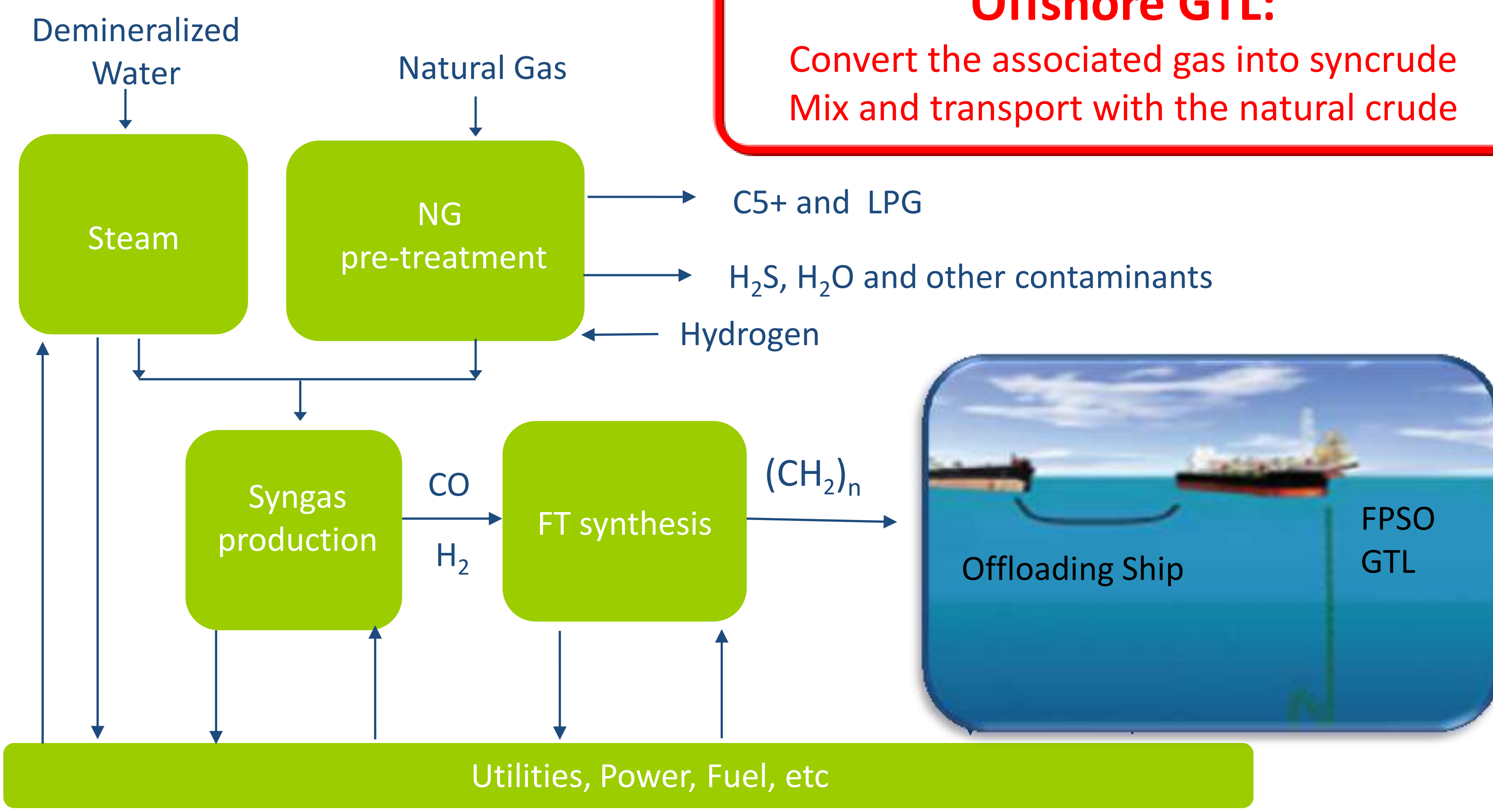
Offshore GTL Process

Offshore GTL:

Convert the associated gas into syncrude
Mix and transport with the natural crude



Modular GTL Concepts

Source: CompactGTL and SBM

Source: MODEC, Toyo and Velocys

Main Reactions

- **Steam Methane Reforming**

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ (Steam Methane Reforming)

$CO + H_2O \leftrightarrow CO_2 + H_2$ (Water Gas Shift Reaction)

CO_2 content makes the "dry reforming" reaction compete with the SMR reaction.

$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2$ (Dry Reforming)

- **Fischer-Tropsch Synthesis**

$nCO + (2n+1)H_2 \leftrightarrow H - (CH_2)n - H + nH_2O$

  - Polymerization of H_2 and CO into alkanes
  - Exothermic ($\Delta H-$)
  - Requires efficient temperature control

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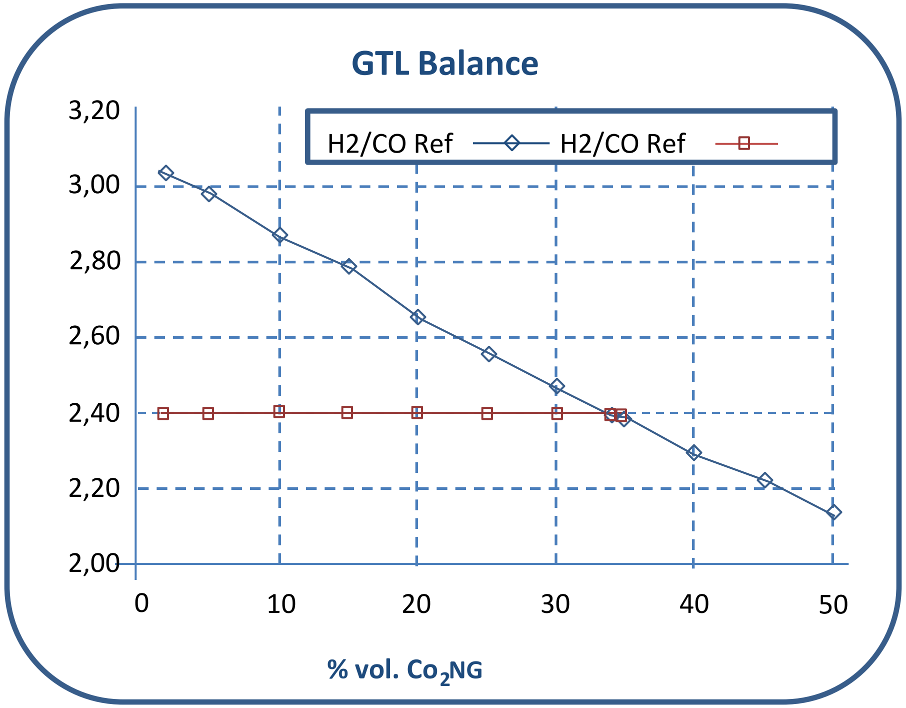
Results – Steam Methane Reformer



- The raise of CO_2 in the natural gas feedstock leads to a reduction in the H_2 / CO ratio due to RWGS reaction.

Prevent coking via:

- Steam / carbon $\geq$ 1.5
- H_2 / CO $\geq$ 2.40

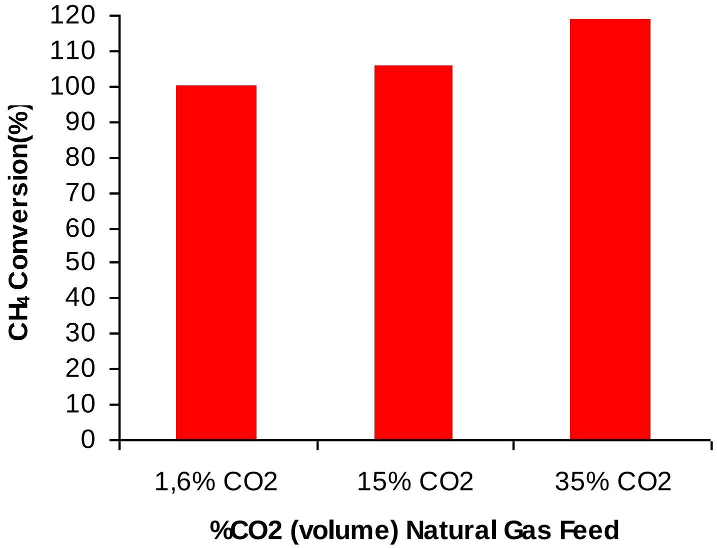
$CH_4 + H_2O \leftrightarrow CO + 3H_2$ (Steam Methane Reforming)

$CO + H_2O \leftrightarrow CO_2 + H_2$ (Water Gas Shift Reaction)

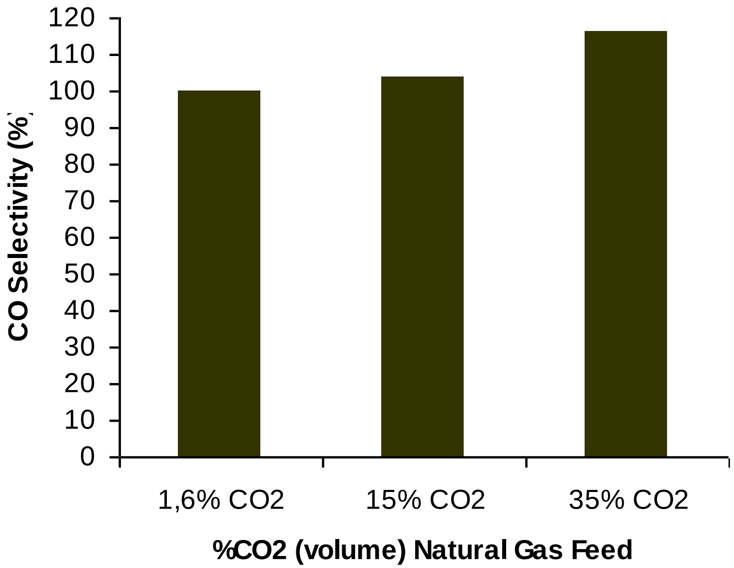
$H_2 + CO_2 \leftrightarrow CO + H_2O$ (Reverse Water Gas Shift - RWGS)

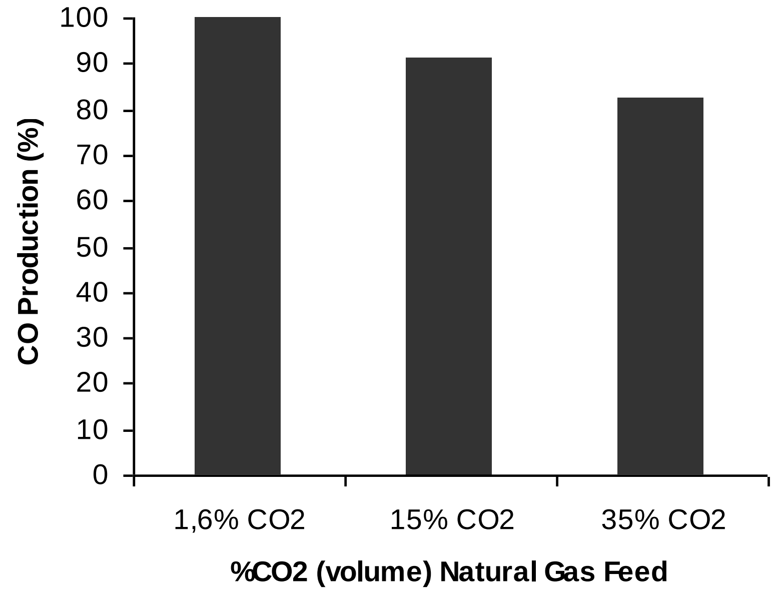
$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2$ (Dry Reforming)

Results – Steam Methane Reformer

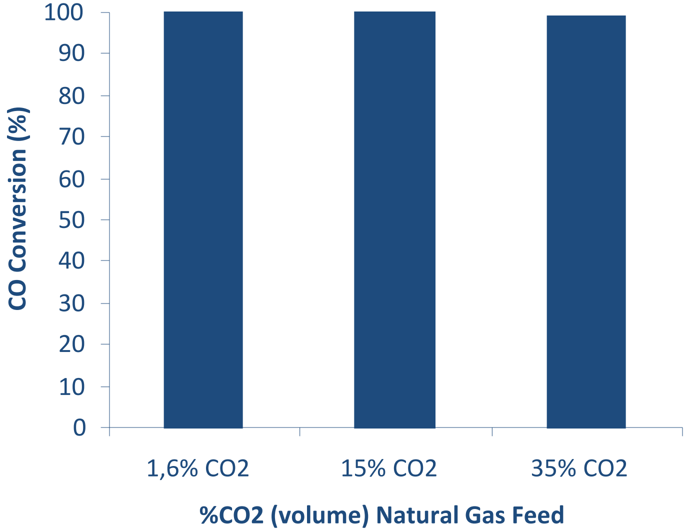


- Improving CH_4 conversion and CO selectivity
- Reduction of hydrocarbons content in the natural fe as a consequence of the CO_2 raise, does not reduce yield in the same magnitude
- Partial conversion of the CO_2 into CO (RWGS)

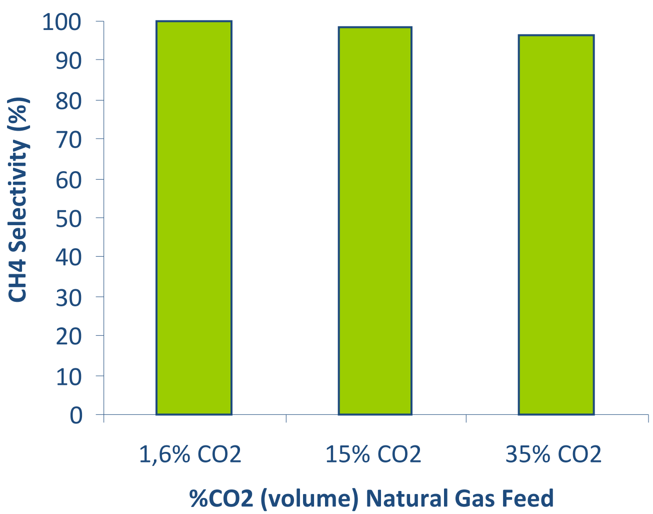


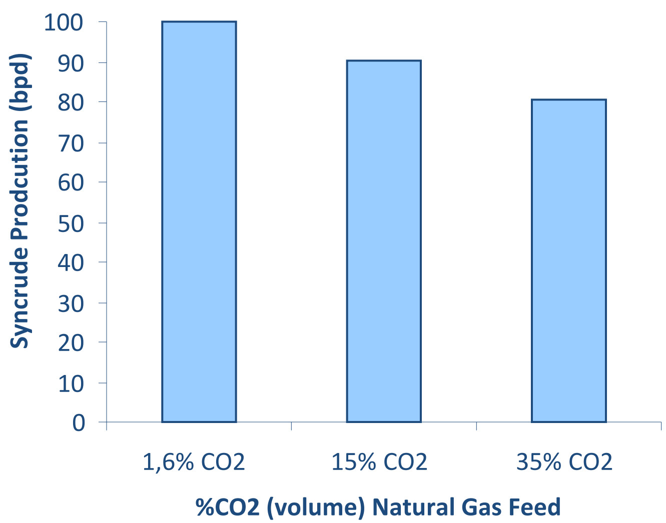


Results – Fischer-Tropsch



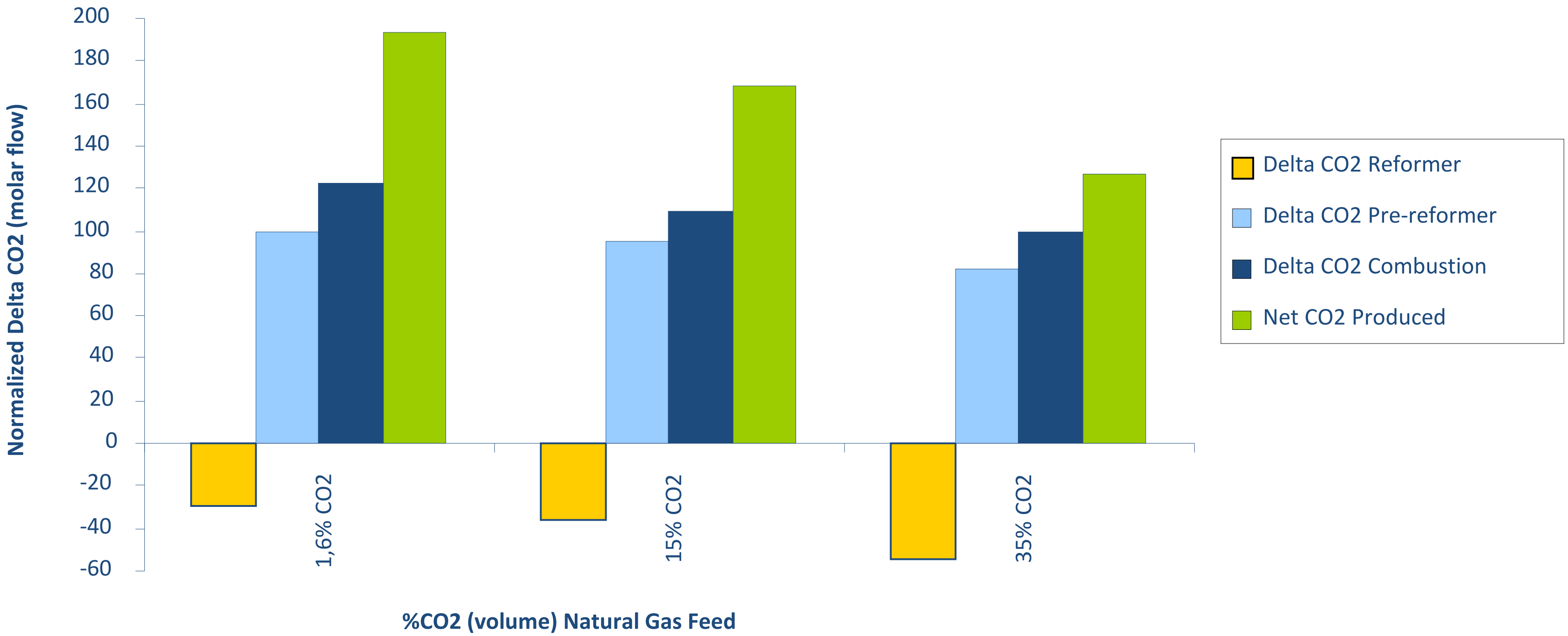
- The CO conversion and methane selectivity are not highly affected by the CO_2
- Negative impact on the overall production due to lower CO yield in the SMR



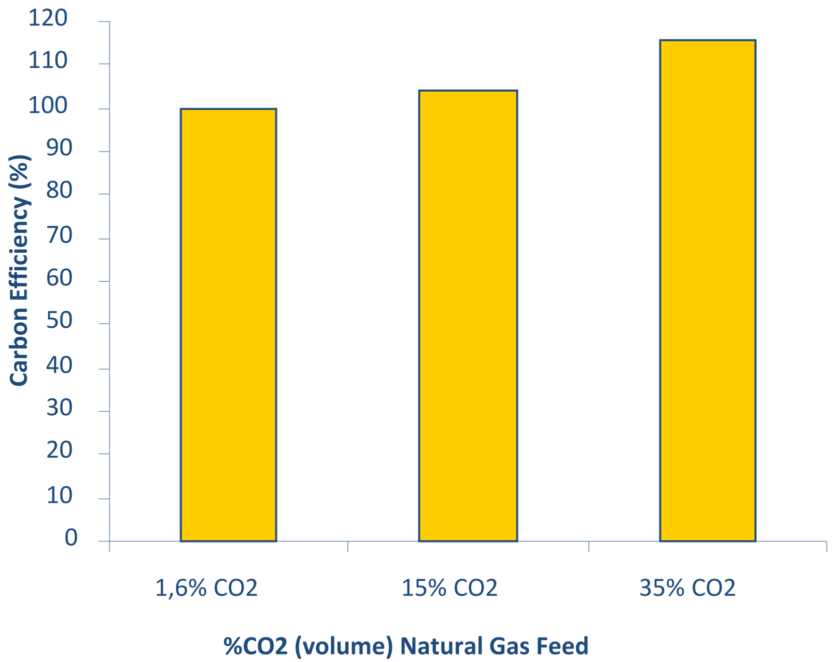


Results – CO_2 Balance

- The FT section shows a neutral behavior
- The SMR section is a CO_2 consumer due to the RWGS reaction
- The pre-reformer and catalytic combustion are CO_2 producers
- The overall process is a CO_2 producer
- Opportunity to optimize pre-reformer and SMR catalytical combustion



Results – Carbon Efficiency



- Carbon Efficiency takes into consideration the rate of hydrocarbon in the feed
- The raise of CO_2 in the natural gas causes an increasing in the Carbon Efficiency due to the partial conversion of CO_2 into CO via RWGS reaction

Global Carbon Efficiency (%)

$$E_c = \frac{m_{SYN} \cdot \Phi}{\sum_{j=HC.CO} \left(F_{j.PR} + F_{j.FUEL}\right) . n_{C_j}} \cdot 100$$

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Conclusions

- The GTL process can accommodate variable CO_2 content in the natural gas feed stock (tested in demonstration plant up to 35% mol). It did not reduce the process efficiency

- CO_2 is consumed in the steam methane reactor to form CO as a consequence of an equilibrium change in the steam methane and water-gas-shift reactions. Nevertheless, the GTL overall process cannot be considered a CO_2 sequestration process, since the net CO_2 process balance is positive

- The results show that there are optimization opportunities to develop more efficient catalyst to improve the process in order to increase the overall carbon efficiency and reduce CO_2 emission

- Petrobras has been successful in the GTL modular small scale technologies qualification tests and studies for offshore use

Conclusions

It is time to unlock the full potential of Natural Gas!

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The Challenge is our Energy!

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