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Gas to liquids technologies for natural gas reserves valorization: The Eni experience

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ABSTRACT

In recent years, most oil companies have shown a renewed interest for the Fischer–Tropsch synthesis, as a result of the current carbon scenario and the stringent regulations on sulphur level in fuels. As a matter of fact, an overview of the oil and gas reserves underlines the necessity of gas valorization to liquid fuel, especially referring to stranded gas reserves. Eni, in cooperation with IFP-Axens, has developed a new proprietary F–T process, and in this paper the catalyst design strategy and the process optimization will be discussed.

1. Introduction

Proven natural gas reserves had reached about 184 Tscm in 2006 to which 36% is stranded gas far from the final market [1]. The *International Energy Agency* is expecting natural gas to become the second energy source, ahead of coal, thanks to its affirmation in power generation. Drivers to this change are the increase in the known reserves of natural gas, the need to monetize stranded gas reserves and the environmental pressure to minimize the flaring of associated gas. All these factors play a role in the new strategic relevance of the gas-to-market technologies to transport the gas from the production area to the final market.

In the last 20 years, thanks to the technological evolution in this area, the market for the natural gas has changed its nature from regional to international, so that today it is possible to foresee a globalization of the gas and derivatives markets, similarly to the oil one.

Different technologies are today available to bring the gas on the market covering long distance: high pressure/capacity pipelines, liquefaction and re-gasification of natural gas (LNG), electric power generation and wire transportation (*Gas-to-Wire*), and finally natural gas conversion into liquid hydrocarbons, the so-called *Gas-to-Liquids* (GtL). GtL is the process of natural gas conversion into transportable liquids, characterized by an intermediate step of natural gas conversion for producing synthesis gas. The final market for LNG pipeline and wire transportation is the traditional power generation, industries and domestic heating, while for GtL technologies the final products destination is the automotive fuel market, the chemical market or the use as fuel for electricity production.

Today there are two main GtL technologies: the production of oxygenate liquid compounds (methanol and dimethylether—DME) and the Fischer–Tropsch synthesis for production of high quality middle distillates (i.e. jet, kero and diesel fuel), base-oil, or waxes. In the last decades the technical, social and economical scenario is favouring the GtL tendency to produce synthetic fuels via Fischer–Tropsch.

2. The Fischer–Tropsch process

In recent years, interest has increased significantly in using Fischer–Tropsch-based processes.

Fischer–Tropsch reaction produces hydrocarbons starting from H_2 and CO, according to the general equation:

$$n(\mathrm{CO} + 2\mathrm{H_2}) \rightarrow -(\mathrm{CH_2})_n- + n\mathrm{H_2O}, \qquad \Delta H = -167\ \mathrm{kJ/mol}$$

As a matter of fact, not only paraffins are actually produced; indeed many different reactions occur simultaneously:

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O} \qquad (\text{synthesis of paraffins})$$

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} \qquad (\text{synthesis of olefins})$$

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightarrow \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{H_2O} \quad (\textit{synthesis of oxygenates})$$

$$\mathrm{CO} + 3\mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H_2O} \quad (\textit{methanation reaction}\ (\Delta H = -206\ \mathrm{kJ/mol}))$$

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$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\textit{water gas shift reaction}\ (\Delta H = -41\ \mathrm{kJ/mol}))$$

$$2CO \rightarrow C + CO_2 \qquad (\text{Boudouard reaction}\ (\Delta H = -172\ \mathrm{kJ/mol}))$$

$$H_2 + CO \rightarrow C + H_2O \qquad (\text{coke formation}\ (\Delta H = -133\ \mathrm{kJ/mol}))$$

Discovered at the Kaiser Wilhelm Institute (Germany) in 1923 by Franz Fischer and Hans Tropsch [2,3], the process found only limited commercial application [4]. In the past, only particular geopolitical situations favoured the realization of industrial plants to produce synthetic fuels and chemicals, starting from coal. It was the case of various German companies during World War II and for Sasol in South Africa during the period of the embargo [5].

Current Fischer–Tropsch GtL technology consists of three major sections (Fig. 1) centred on *low temperature Fischer–Tropsch synthesis* (200–250 °C). Syngas generation and product upgrading technologies have extensive commercial experience; nevertheless their application to Fischer–Tropsch process needs an intensive integration activity to obtain the most cost-effective combination of these three technologies.

The low temperature Fischer–Tropsch synthesis is based on the R&D advancement for both catalyst and reactor technology. Catalyst and reactor selection influence the various characteristics of the Fischer–Tropsch process such as the thermal efficiency, heat removal, product selectivity and operating costs.

2.1. Catalyst design

Catalyst design is an optimized combination of interdependent mechanical, chemical/physical and catalytic properties: this is the so-called "triangular concept" proposed by Anderson and adapted to this reaction by Ferrauto and Bartholomew [7] (Fig. 2).

To obtain a good catalyst all the three aspects should be held in consideration since the very beginning of the work: active phase identification, reactor technology selection (consequently, catalyst shape and size) and catalyst formulation [8].

Few metals show activity on Fischer–Tropsch synthesis: the required characteristics are good H_2 adsorption, dissociative CO adsorption, and, at the same time, easy reducibility of the metal oxide. From the point of view of the mechanism, Fischer–Tropsch reaction can be conceived as a sort of polymerisation, with an adsorption step, a chain initiation, a propagation and a chain growth termination. The first hypothesis, reported in Fig. 3, was proposed by Fischer and Tropsch in 1926 [9]. They supposed the dissociative adsorption of the carbon monoxide on the metal atom, with formation of a carbide species. The insertion of the adsorbed dissociated hydrogen on this carbide generates the active CH_2-intermediate that gives rise to the propagation step. The growing alkyl chain can desorb from the metal by hydrogenation, forming paraffins, or by β-scission, forming olefins.

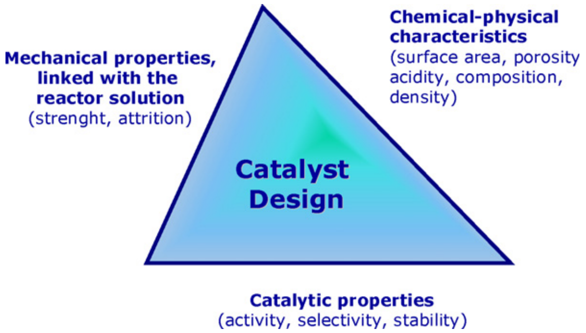

Fig. 2. The triangular concept.

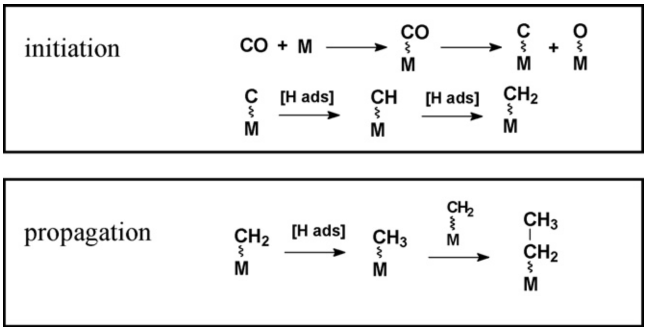

Fig. 3. Classic mechanicistic pathway.

After this first hypothesis, several different mechanicistic pathways have been elaborated, but all of them contemplate a initiation, propagation and termination step.

On the basis of these considerations, the transition metals belonging to the third, fourth, fifth and sixth group are not good catalysts for Fischer–Tropsch synthesis, because, despite of their favourable dissociative CO adsorption, they form very stable oxide that are not reducible under FT conditions. On the other hand, iridium, platinum, palladium and the metals belonging to the

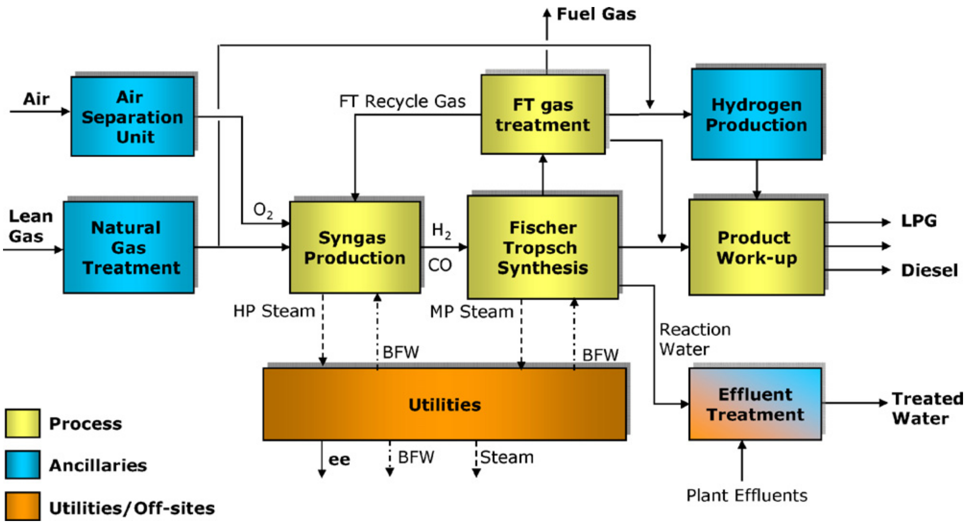

Fig. 1. GtL technology [6].

groups 11 and 12, are characterized by a non-dissociative adsorption of carbon monoxide, and for this reason they are not active in FT synthesis (Fig. 4). The best catalysts are iron, cobalt, nickel, ruthenium, osmium, while rhenium and rhodium behave in the middle [10–12].

Ruthenium is actually the most active catalyst [13], but it is too expensive and poorly available to be used to develop an industrial process. Nickel has a very high hydrogenation activity, so its selectivity to methane is too high for FT purposes. As a matter of fact, cobalt and iron are the only two metals of choice for industrial applications. Iron is economic, but has low selectivity to long chain paraffins, produces a high amount of oxygenates and olefins and is more subject to deactivation than cobalt. Cobalt is more expensive than iron, but it has a very good selectivity to long chain paraffins, low selectivity to oxygenates and olefins, and it is resistant to deactivation. So, if the target is to produce long chain paraffins, cobalt is the best choice; otherwise, to produce chemicals or olefins, iron is to be considered.

To select between cobalt and iron, an important parameter is also the carbon feedstock. Iron has a high water gas shift activity, and for this reason is particularly suitable for hydrogen-poor feedstocks, as those obtained from coal or biomasses. Cobalt performs better with an almost stoichiometric ratio of hydrogen and carbon monoxide, so it is preferred when the carbon feedstock is natural gas.

Fig. 5 correlates the H_2/CO ratio obtained from different carbon feedstocks with cobalt and iron optimum working conditions, according to Yakobson [14], Rentech Inc.

In any case, it is impossible to selectively obtain a well-defined range of products. Indeed, the product distribution of FT synthesis can be expressed by the Anderson–Schulz–Flory model [15], where the weight fraction of the single product is described with the chain growth probability parameter α, that in turn depends on the propagation and the termination rate.

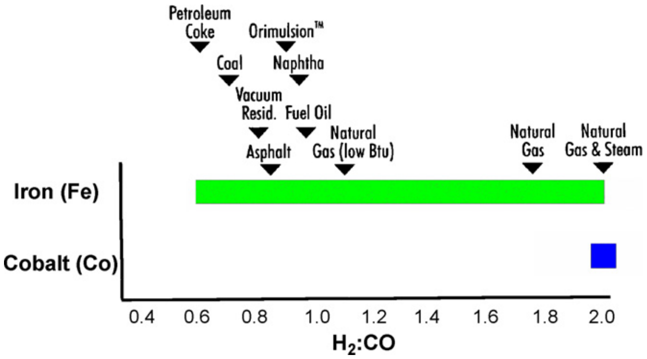

Fig. 5. H_2/CO ratio vs. carbon feedstocks [14].

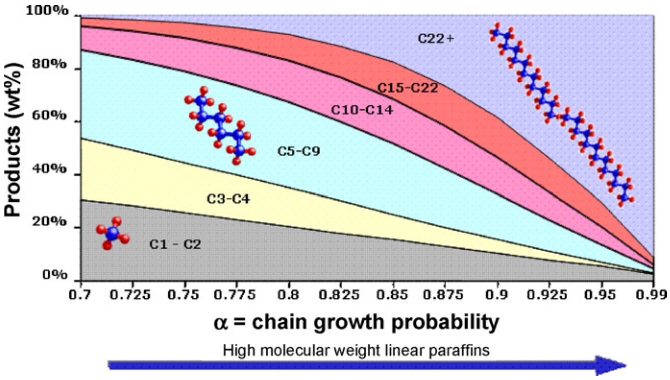

Fig. 6. ASF values sensitivity.

$$\frac{Wn}{n} = (1-\alpha)^2\alpha^{(n-1)} \quad \text{where} \quad \frac{Wn}{n} = \text{weight fraction of product with}n\text{th carbons}$$

$$\alpha = \frac{r_p}{r_p + r_t} \quad \text{where} \quad r_p = \text{propagation rate constant} \quad r_t = \text{termination rate constant}$$

According to Anderson–Schulz–Flory distribution, showed in Fig. 6, the maximum amount of C_5–C_{22} cut that can be theoretically obtained is above 50% with an α-parameter of 0.75, and it reduces considerably for very high α-parameter, i.e. 0.95. Nevertheless the correspondent gas production, particularly methane which normally is underestimated by the ASF law, decreases to few percents at very high alpha values. This is extremely important for the maximisation of the valuable middle distillates production. As a result, the best strategy is working in conditions to obtain the maximum amount of long chain linear paraffins, that can be efficiently transformed into valuable products by means of hydroprocessing steps.

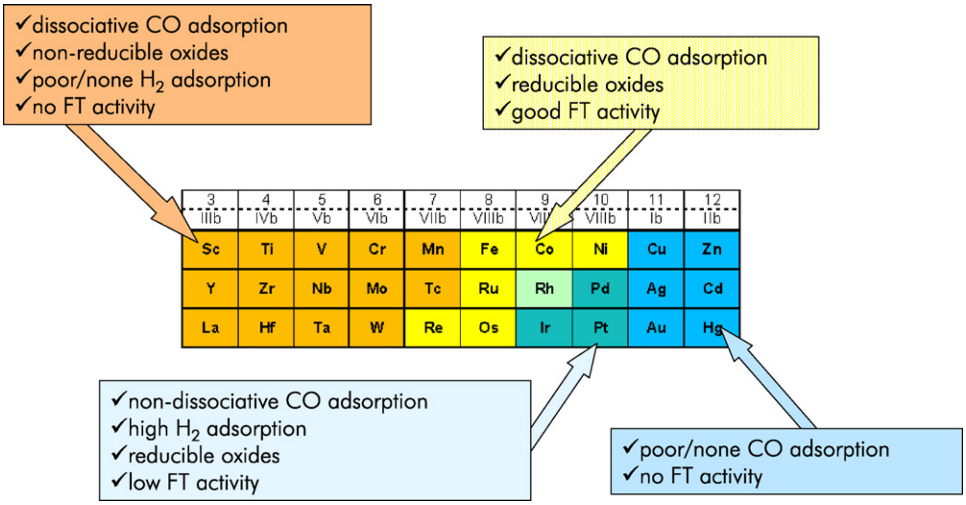

Fig. 4. Behaviour of transition metals towards FT reaction.

All these considerations drive the selection of cobalt for most of the GTL proponents, and this was also the case for Eni/IFP technology.

The second step of a catalyst design program is the reactor engineering, that strictly constrains the catalyst shape, size and mechanical resistance. From this proceeds the choice of the support that, in its turn, strongly influences the catalyst performances [16–21].

The optimum support should be chemically inert, with high surface area, good mechanical and hydrothermal resistance and low metal–support interactions. Metal–support interactions play an important role in activity and stability of the catalyst. Strong cobalt–support interactions, for example, give rise to species not easily reducible, resulting in a few amount of active metallic sites and, consequently, low activity. On the other hand, too weak support interactions are favourable for the reduction efficiency, but may cause aggregation of the metal particles during the reduction step, causing, again, low activity [22].

As a good compromise is needed, alumina is the best candidate. In comparison to other supports, alumina has good mechanical properties, high structural stability and its hydrothermal resistance can be improved by means of additives or thermal treatments. On the other hand, alumina gives rise to relatively strong metal–support interaction. To control metal–support interactions, it is important to control the metal crystallites dimension and dispersion, two parameters that are strictly connected and have high influence on the activity. High dispersion, as can be obtained by very small crystallites, means high availability of active sites, but, on the other hand, very small crystallites are easily subjected to form strong support interactions. So, also in this case, a compromise is needed. As suggested by Iglesia [22], the limit for the minimum crystallites size is 6–8 nm.

It is generally admitted that the active phase is the cobalt metal Co° [23,24], and the activation by reduction is a critical step to obtain a good catalyst. To improve the reducibility of cobalt, small amounts of promoters such as platinum, palladium, ruthenium or rhenium, are often added during the catalyst formulation [25,26]. Fig. 7 shows, as an example, the effect of the promotion with palladium: the consumption of hydrogen, during a temperature programmed reduction analysis, begins earlier in the promoted catalyst than in the unpromoted one, indicating a higher reducibility at lower temperature.

Re-oxidation of the metal can lead to a deactivation of the catalyst, especially when it is characterized by very little metal crystallites. Water is supposed to be a cause of re-oxidation because, even if bulk oxidation of Co° by water is not thermodynamically favourable, it is possible for nano-sized crystallites, probably due to the contribution of the surface energy deriving from broken bonds [27].

Sintering of the metal, encapsulation of the Co° inside the support, carbon deposition due to Boudouard reaction or formation of strong metal–support interaction during the reaction are other possible causes of deactivation.

2.2. Reactor technology

From the beginning of Fischer–Tropsch history till today different reactor typologies succeeded, with the aim to improve both capacity and efficiency [28]. Fischer–Tropsch synthesis reactions are highly exothermic, and the reactor systems must have provisions for removing this heat. Heat removal, pressure drops control, catalyst handling and reactor capacity represent the most critical factors which inevitably affect the process economics.

Fig. 8 presents an historical overview of the evolution of Fischer–Tropsch reactors in term of capacity, expressed as barrel per day (bpd), and technology. Before and during World War II, at the very beginning of the commercial application of FT synthesis, the fixed bed reactor (FBR) with different heat managements (e.g. catalyst bed with internal cooling; multi-tubular reactors; multiple adiabatic beds inter-bed cooled) was the preferred technology. The capacity of these reactors was nearly few tens bpd.

Technologies with increased potential for large scale production of synthetic fuels were developed in the period after World War II, in some cases based on concepts generated somewhat earlier: slurry, ebullating and fluidised bed reactors.

A significant improvement of capacity was obtained with the application of circulating fluid-bed reactor (CFBR), in which fine catalyst is entrained by a high velocity gas stream through a riser reactor. In 1955 at Sasolburg in South Africa the first commercial plant began operation with reactors with a capacity of 1500 bpd. In 1980 and 1982, respectively, started up in Secunda (South Africa) Sasol II and III plants with a considerably scaled-up capacity of 6500 bpd. In 1995 was installed in Secunda a fluidised fixed bed reactor (FFBR) of a new concept design, with a capacity up to 11,000 bpd [29].

All the industrial experiences so far resumed were referred to the production of synthetic fuels starting from synthesis gas obtained by coal gasification.

More recently, renewed interest in the FT process driven by the valorization of remote natural gas to liquid fuels, gave rise to several developments of more advanced reactors having very large production capacities. The first commercial large GtL unit was erected by PetroSA in Mossel Bay (South Africa) [30]. In operation since 1992, with a capacity of 22,500 bpd, the unit is based on three CFB reactors licensed by Sasol. However, this solution is only indicated for high temperature processes producing relatively light products of low α values ($\alpha < 0.7$), in order to avoid catalyst particles agglomeration due to wax deposition. For low tempera-

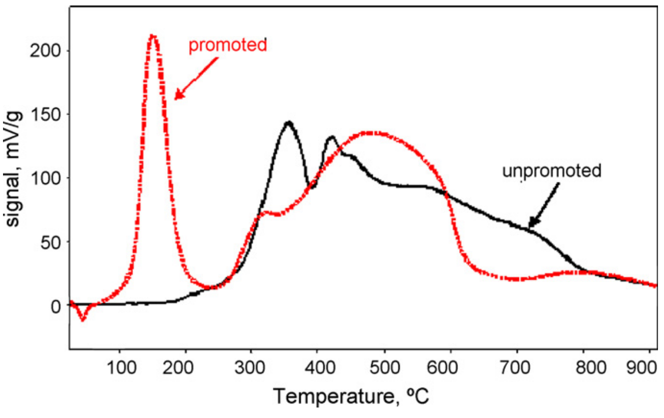

Fig. 7. TPR analysis of promoted and unpromoted cobalt catalyst.

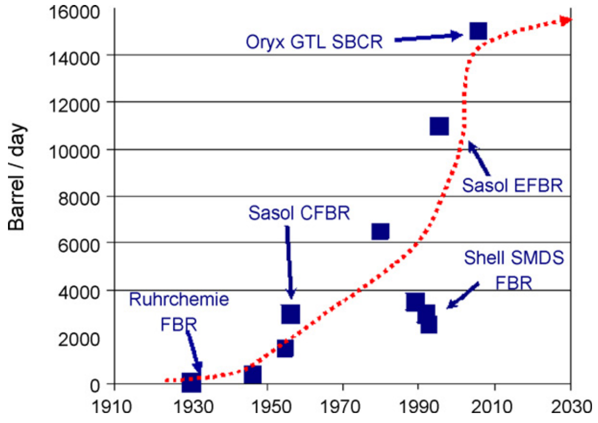

Fig. 8. Historical overview of FT reactor technology.

ture GtL processes with cobalt catalyst, where high molecular weight products are desired ($\alpha > 0.9$), it is proper the use of a multiphase reactor in which a liquid phase is present besides the gas and the solid catalyst ones. Two major types of reactors have been considered for this application: multi-tubular fixed bed reactor operating in trickle flow regime (FBR) and slurry bubble column reactor (SBCR) [28].

Multi-tubular reactors (Fig. 9) have been installed in the first Shell Middle Distillate Synthesis SMDS plant at Bintulu, Malaysia, for the today production of 14,000 bpd of synthetic hydrocarbons from natural gas starting from 1993 [31]. With a specially developed catalyst and a specific reactor design, a capacity of about 3000 bpd per reactor is attained. As an alternative to the multi-tubular fixed bed reactor, Sasol has developed an internally cooled bubble column slurry reactor (SCBR) shown schematically in Fig. 9. The Sasol slurry phase technology has undergone several development stages. The first commercial demonstration unit operated since 1993 by Sasol was based on a capacity of 3000 bpd. So far, the largest capacity up to now realized in a single reactor unit, i.e. 15–17,000 bpd, has been applied in the Oryx plant in Qatar, by Qatar Petroleum-Sasol [29]. The GtL complex with an overall capacity of 34,000 bpd was officially inaugurated in 2006.

Multi-tubular fixed bed reactor has a simple mechanical design, allows a very easy liquid/solid separation and shows high productivity. On the other hand, heat removal can be a critical factor. Depending on catalyst particle size, fixed bed reactors are subjected to high pressure drop and to limit this problem, catalysts in fixed bed reactors generally have diameters larger than 1 mm, but in this case not optimal mass transfer and intraparticle diffusion limitations can occur. At last, catalyst make-up can be a complex operation with this kind of reactor geometry [32].

In the last 20 years the trend in reactor technology applied to the Fischer–Tropsch conversion is the SBCR because of several advantages such as ideal heat removal, nearly isothermal conditions, high catalyst efficiency, simple catalyst make-up/withdrawal, low reactor pressure drops, large capacities [33]. Nevertheless successful commercialization of this reactor technology is crucially dependent on the understanding of the scaling-up principles of bubble columns, challenged by factors like catalyst mechanical stress, complex reactor hydrodynamics, slurry handling, liquid/solid separation [32]. During SBCR operation the catalyst is subjected to a high mechanical stress, which might result in production of fines generated by collision of particles among themselves and with the reactor internals. The liquid medium inside the reactor reduces the momentum of the impacting entities, but it can be severely worsened by the presence of the reaction water, depending on the chemical nature of the carrier.

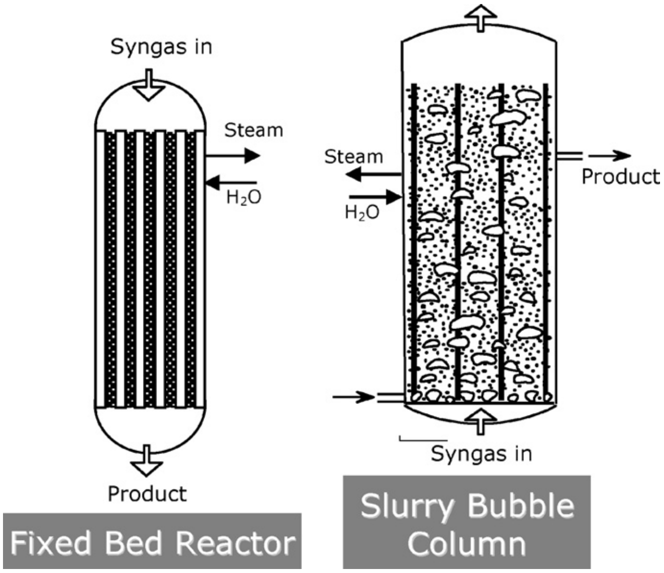

Fig. 9. FBR and SBCR reactors.

3. Fischer–Tropsch GtL project development

Several companies have been involved in intensive R&D program to develop their own GtL technology with different technological solution. Currently there are only three commercial natural gas-based Fischer–Tropsch GtL plants. As already reported, in 1992 PetroSA started up the world's first major commercial plant at Mossel Bay in South Africa. PetroSA is today in a consortium, GTL.F1, with StatoilHydro and Lurgi for the development of a GtL technology for natural gas conversion, based on a modern SBCR and cobalt catalyst technology [30].

In 1993, Shell started up a 12,500 bpd Fischer–Tropsch GtL plant at Bintulu in Malaysia for production of diesel fuel and other specialty products including lube base stock and solvents. The unit is based on the shell middle distillates synthesis process (SMDS) which uses a fixed bed reactor, operated at low temperature, and cobalt catalyst. The plant recently has increased its production capacity to 14,000 bpd due to improvements in the catalyst design [31].

In 2007 the Oryx plant, owned by state-owned Qatar Petroleum and South African chemical and fuel group Sasol, was brought on stream. Besides the extended start up period due to technical problems of high FT catalyst's fines production, the plant is the first commercial example based on the new Co-based SBCR Fischer–Tropsch technology (Oryx project) [29].

Other companies involved in GtL development are BP, ConocoPhillips, Eni/IFP, ExxonMobil, Rentech, and Syntroleum, with different process schemes, reactor and catalyst technologies.

From the early 2000's, several projects began to be developed to build world-scale GtL plants, particularly in Qatar and Nigeria. However many of these have been deferred or cancelled, with the currently active projects being only the Sasol Chevron's 34000 bpd plant in Escravos, Nigeria, and the Shell 140.000 bpd Pearl GtL plant in Qatar both in construction phase (Fig. 10).

4. The Eni/IFP-Axens GtL process development

Eni has developed a proprietary Fischer–Tropsch and Upgrading technology jointly with the Institut Français du Petrole (IFP) and its process & licensing branch Axens in a technological collaboration which started at the beginning of 1996. The GtL Eni/IFP technology has been designed according to a strategy based on three main targets:

- Development of an innovative FT/HDK technology based on tailored catalysts, proprietary FT slurry reactor design and an optimized product upgrading steps (hydrocracking).
- Minimization of scale-up risk by developing the *right tools* for scale-up.
- Engineering studies of fully integrated GtL complex, today case by case, at basic process design and FEED (front end engineering design) level.

Eni/IFP technology has adopted a dedicated development strategies before the industrialization of the cobalt FT catalyst for SBCR application, produced and licensed by Axens.

Alumina is indeed the preferred carrier for supporting cobalt because it is widely available on the market in a textural form suitable for SBCR application. However, under specific temperature and pressure conditions – typical of the Fischer–Tropsch operating

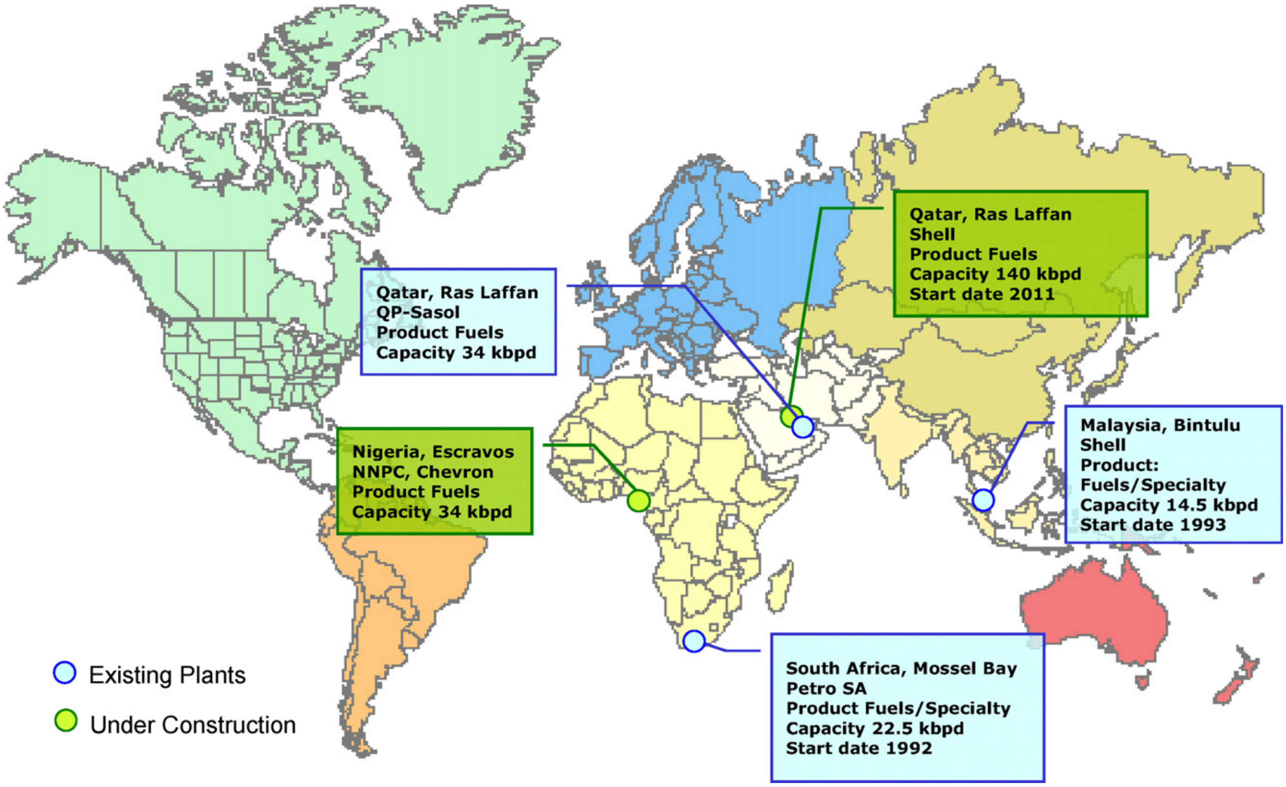

Fig. 10. Existing and under construction commercial units.

regime – alumina reacts with water evolving back to mechanically fragile hydrated forms. As a result, the intrinsic mechanical resistance of the catalyst is compromised and, when subjected to SBC regime, it could generate uncontrolled amount of fines and ultrafines ($<1\ \mu m$). Fines formation inside the SBCR can lead to several side effects as failure of the solid–liquid separation device, foam formation inside the reactor, and severe impact on the downstream upgrading section. In Fig. 11 is reported the different behaviours of two catalysts. Due to the low resistance of the first, the slurry has settling problems and plugging of the catalyst/wax separation cartridges inside the pilot reactor was evidenced (Fig. 11a). Fig. 11b shows the reaction products: after catalyst sedimentation (the black layer), waxes still appear grey because of fines suspension. A proper modification of the catalyst improved the hydrothermal stability, reducing fines production. Fig. 11c shows the reaction products obtained using an improved catalyst: in this case, no settling problems were met and waxes are white.

According to Eni/IFP experience, for an efficient scaling-up of the FT catalyst it is essential reproducing both chemical and mechanical stress of an industrial reactor. The parameters influencing a bubble column performance are related to operating conditions (pressure, temperature, and gas velocity), to the reactor geometrical characteristics (column diameter, height, internal attachments) and to the slurry properties (density, viscosity, surface tension, and catalyst concentration). It is practically impossible to study all these parameters at the same time and with the same instruments. SBC hydrodynamics is very complex and significantly influenced by the size of the column: for example, bubble characteristics and gas holdup, liquid flow pattern, interphase mass transfer are difficult to extrapolate to an industrial column starting from a lab-scale model. The hydrodynamic behaviour is strongly dependent on flow regime [34] that controls liquid mixing and interface mass transfer, and, as a consequence, affects conversion and selectivity. Numerous studies were devoted to simulation of FT slurry column, but the literature correlations give conflicting forecasts, mainly due to the fact that have been restricted to rather small diameter columns (<0.8 m), when an industrial reactor sizes on average 8–10 m [35–41].

Many theoretical models have been proposed to predict liquid recirculation and gas holdup, most of them developed by Krishna [33,42–48], and, although none of them is able to predict in a reliable way the hydrodynamic characteristics of an industrial

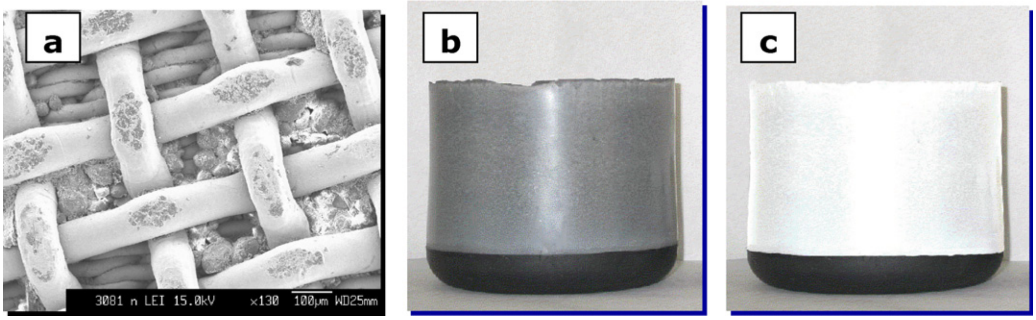

Fig. 11. Different catalysts hydrothermal behaviour.

slurry bubble column, a rational upscaling strategy to reduce the uncertainty of the extrapolation is carrying out tests both on small "hot" pilot plants and larger "cold" hydrodynamic facilities [49].

Consequently, the process was carried out performing the reaction at operating conditions as close as possible to industrial ones, on a lab-scale reactor designed on purpose, while slurry properties effects were studied in small laboratory cold columns. At the same time, unique large scale hydrodynamic facilities (cold bubble columns and loops) have been developed and operated to make reactor and ancillaries scale-up easy and reliable (Fig. 12). As an example, to study the recirculation velocity into the reactor, strictly related to the catalyst mechanical stress, a 3 m diameter column was used to study the hydrodynamics under non-reactive conditions, in order to acquire confidence on the extrapolation to a 10 m diameter industrial reactor.

As it is important to directly measure catalyst mechanical resistance also under FT conditions, computational fluidodynamic studies were used to set up a lab-scale unit with unique reactor and internal design able to assure the reproduction of very high recirculating velocity, comparable to those measurable in a 10 m diameter column.

Fig. 13. Eni/IFP FT pilot plant, Sannazzaro (Pavia, Italy).

A large scale Fischer–Tropsch pilot plant has been built and operated since 2001. The plant is located inside the Eni's Sannazzaro refinery (Pavia, IT). It reproduces at a scale of 20 bpd the overall FT synthesis section: slurry handling (loading, make-up, withdrawal), reactor configuration (internal gas recycle), and products separation units. Due to the plant size and flexibility, it was possible to assess a wide range of industrial operating conditions in order to select those that optimize catalyst performances. During the several runs carried out, different types of liquid-catalyst separation devices have been assessed and the best working one (as efficiency and long term reliability) has been adopted for the industrial scale-up. The large scale FT pilot plant is still in operation and is considered a valuable tool for trouble shooting on different parts of the technology (Fig. 13).

Premium quality fuels can be obtained by upgrading the Fischer–Tropsch waxes produced in the pilot plant. Eni/IFP developed a proprietary hydrocracking catalyst based on noble metal able to reach middle distillates yield up to 85%. Table 1 compares our GtL diesel with other grades, including high quality ones.

It is worth to note the very high cetane number and the extremely low amount of sulphur and aromatics in FT-Diesel,

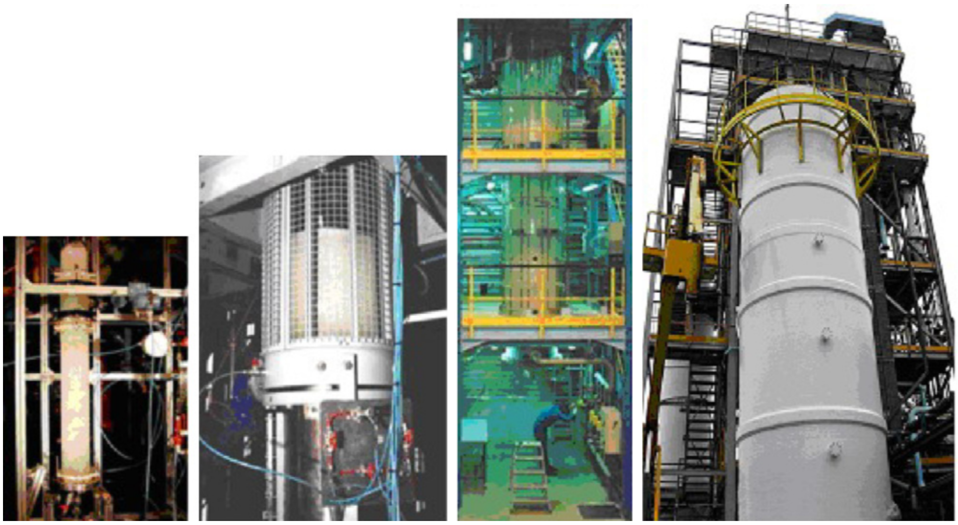

Fig. 12. Eni/IFP hydrodynamic facilities, Lyon (France) [6].

Table 1
Comparison among different diesel fuels.

	Conventional diesel	SWCL1	Blu diesel Agip	FT-diesel[a]
Boiling range (°C)	180–360	180–275	180–360	150–360
Density at 15 °C (kg/m^3)	820–845	805	835	780
Sulphur (ppm vol)	50	6	4.5	<1
Aromatics (% vol)	30	3	22	<0.1
Cetane number (CN)	>51	56	55	>70
CFPP[b] (°C)	−15	−12	−11	−20
Cloud point (°C)	0	n.d.	−1	−15

[a] Diesel from waxes produced on pilot runs.
[b] Cold filter plug point.

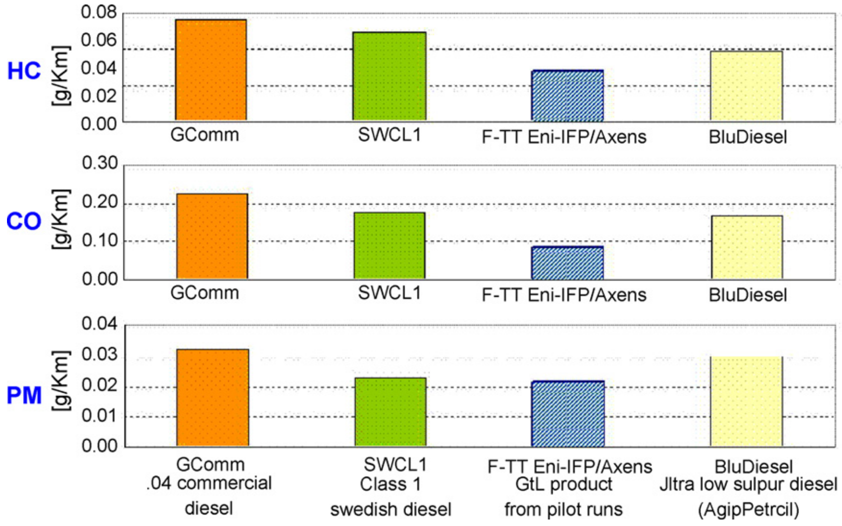

Fig. 14. Engine test on diesel fuels of different origins.

characteristics that makes this fuel particularly interesting from the point of view of the recent environmental warnings.

The emissions test carried out with different diesel fuels (Engine test, NEDC test cycle, Volkswagen Passat 1900 TDI-E3), reported in Fig. 14, also gave an excellent result.

5. Concluding remarks

Focusing on the Eni/IFP catalyst development history, we soon recognised as a critical issue the mechanical and chemical stability especially when applied in a SBCR of industrial size. The phenomena were particularly evident at pilot plant scale, when catalysts inadequately stabilized have been used.

Apart from an accurate tuning of catalyst particle size distribution, for the optimal management of the solid/liquid separation device, several stabilization routes have been identified and tested, being part today of the Eni/IFP technology know-how. In parallel we have developed protocols and tools to measure the Fischer–Tropsch catalyst performances under typical conditions of an industrial size slurry reactor. Liquid and gas velocities inside a slurry reactor grow with the reactor size. Thus, according to our catalyst scale-up strategy it is mandatory to measure the chemical–mechanical stress of the industrial reactor. For this purpose dedicated tools have been designed and constructed in the Eni and IFP laboratories. The units are able to reproduce the various mechanical and chemical stresses encountered in an industrial scale slurry reactor, operating in continuous three-phase FT reaction runs.

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