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

C. Perego [a,*], R. Bortolo [a], R. Zennaro [b]

[a] Eni S.p.A., Istituto Eni-Donegani, Novara, Italy
[b] Eni S.p.A. Exploration & Production Division, San Donato Milanese, Milan, Italy

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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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[*] Corresponding author.
E-mail addresses: carlo.perego@eni.it (C. Perego), rossella.bortolo@eni.it (R. Bortolo), roberto.zennaro@eni.it (R. Zennaro).

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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.

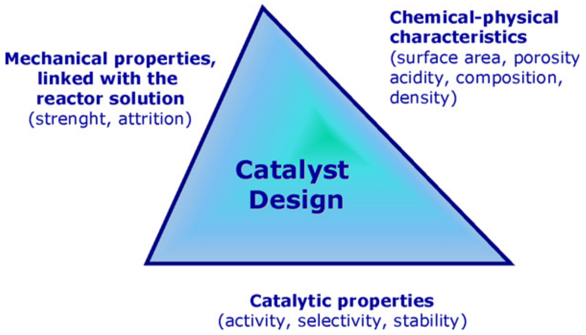

Fig. 2. The triangular concept.

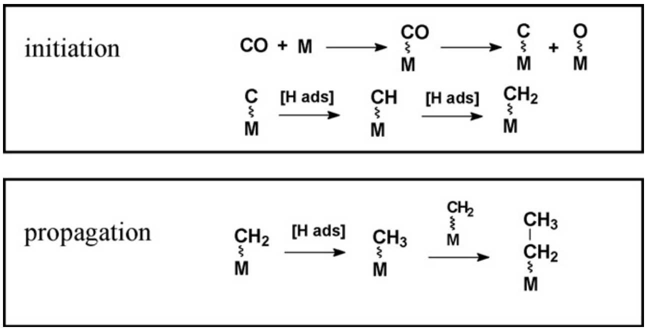

Fig. 3. Classic mechanicistic pathway.

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.

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

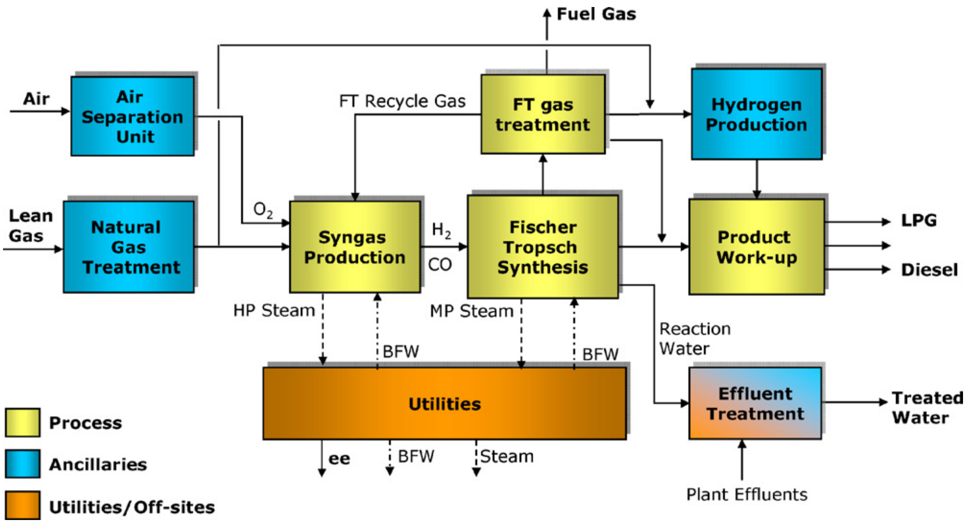

Fig. 1. GtL technology [6].