Conversion of syngas to diesel

An overview of Fischer-Tropsch technologies for the production of diesel from syngas using a variety of feedstocks. Process technology, reactor design and catalyst requirements to achieve a successful industrial scale-up are discussed

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Fischer-Tropsch (FT)-based XtL options (gas, coal, petroleum coke or biomass to liquids) represent viable routes for the production of non-crude oil-based ultra-high-performance motor fuels and speciality products. Improvements in catalyst and reactor technology, coupled with optimised integration and economies of scale, have allowed gas-to-liquids (GtL) complexes to be competitive with LNG and pipeline projects. Most major oil and gas companies are closely following XtL developments. Currently, several large GtL industrial projects have been realised (Oryx in Qatar) or are under construction (Pearl in Qatar, Escravos in Nigeria).

Eni and IFP (French Institute of petroleum) have developed proprietary FT and upgrading technologies in a close collaboration between the two groups. These technologies are based on proprietary catalysts and reactor designs resulting from scale-up criteria developed over 12 years of common research and development. Large-scale hydrodynamic facilities (slurry bubble columns), dedicated bench-scale pilot units and a large-scale FT pilot plant have been developed and operated to minimise reactor and ancillary unit scale-up risks.

A large-scale FT pilot plant has been built and operated since 2001. The plant, located within the Eni refinery in Sannazzaro, Italy, is fully integrated with the refinery utilities and network. The 20 bpd FT synthesis section has been used to optimise slurry handling (loading, make-up and withdrawal), reactor configuration and product separation units. Large-size scale-up has been accomplished through the implementation of several specifically designed scale-up tools to assess the catalyst's stability under industrial conditions, and study fluid dynamics and liquid-solid separation.

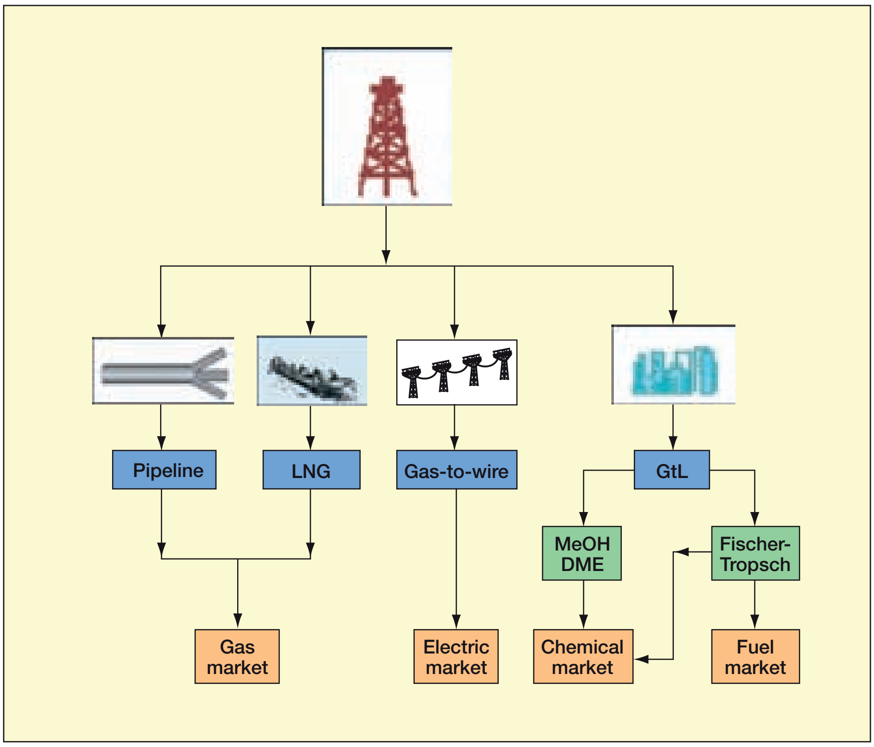

Figure 1 *Gas to market options*

Fuel diversification: from GtL to XtL

The estimated amount of natural gas reserves has continuously increased over the past ten years, moving from the 1997 estimation of 152.2 Tcm to 181.5 Tcm in 2007, with a reserve/production ratio of around 63 years, higher than oil of 38 years.[1] It is thus quite logical to envisage using natural gas (or coal with its R/P ratio above 140 years) as a source of liquid transportation fuels, through natural gas conversion into liquid hydrocarbons, the so-called GtL, which is characterised by an intermediate step of natural gas conversion for producing synthesis gas (hydrogen and carbon monoxide). This production can be divided into two main value chains:

— Production of methanol and methanol-derived products (including acetic acid, DME and so on)

— FT synthesis for production of high-quality middle distillates (ie, kerosene and diesel fuel), pure paraffinic naphtha, lube bases, waxes and, in some cases, olefins and speciality chemicals.

While the final market for LNG, pipeline and wire transportation is the traditional natural gas one, GtL technologies open up new markets (automotive fuel, chemicals) to natural gas producers (Figure 1).

Increasing global demand for ever-cleaner fuels, particularly middle distillates, such as in Europe, should favour the FT GtL route, which answers market needs.[2]

A relatively recent requirement, but fundamental for decades to come, is that automotive fuels must not only be cleaner, but the impact of their well-to-wheel lifecycle on the greenhouse effect (ie, overall CO_2 emissions from production through consumption of the liquid fuel, including biomass CO_2 absorption [in the case of biomass]) must be as low as possible.

This general requirement will be translated into different regional targets.

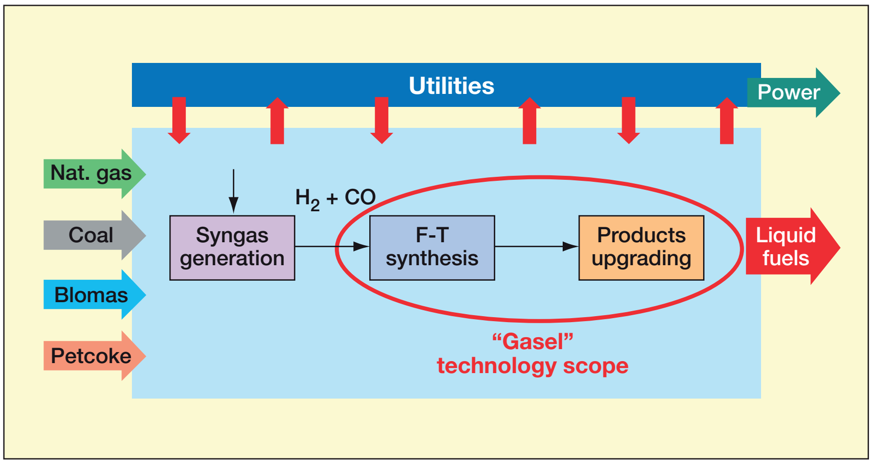

***Figure 2** Gasel technology scope*

As an example, the European Council stated on 8–9 March 2007: "a 10% binding minimum target to be achieved by all Member States for the share of biofuels in overall EU transport petrol and diesel consumption by 2020." As it is commonly agreed that the first generation of biofuels (using vegetable oils and sugars) will not be sufficient, the so-called second-generation biofuels will have to come into force. And the most promising technology to achieve this target is BtL-FT (biomass-to-liquid through Fischer-Tropsch: production of FT diesel from a syngas generated by the gasification of biomass), which allows for a decrease in the equivalent CO_2 emissions per km down to 90% compared to a conventional diesel.[3] Biomass may also be mixed with petroleum residues or coke in order to take advantage of refinery infrastructures and operating experience.

All these XtL options (ie, gas, coal, petroleum coke or residue, biomass-to-liquids, or a mixture of some of them) will allow diversifying fuel sources, producing cleaner fuels and limiting overall GHG emissions. They all require a reliable technology package to transform clean syngas from whatever source into ultra-clean liquid fuels, and this is the scope of the Gasel technology suite (Figure 2).

Fischer-Tropsch technologies: industrial applications

FT technologies can be characterised/differentiated by four parameters:

— FT catalyst: two main types:
  – Iron-based catalysts
  – Cobalt-based catalysts.

— FT reactor: three main types of reactor:
  – Fixed bed (the catalyst is located inside tubes)
  – Fluidised bed (the catalyst is maintained in suspension by the syngas)
  – Slurry bubble column (three-phase reactor with synthesis gas, waxes, liquid products and solid catalyst).

— Operating temperature:
  – HT-FT: High-temperature Fischer-Tropsch (around 350°C and above)
  – LT-FT: Low-temperature Fischer-Tropsch (220–240°C).

— Final products obtained (after FT upgrading):
  – Middle distillates (diesel): paraffinic naphtha (also in some cases waxes or lube base)
  – Gasoline: olefins and chemicals specialities.

However, it must be noted that these four parameters are not independent of each other, and only three combinations are feasible and have been developed so far, as illustrated in Figure 3.

These three combinations or categories include:

— HT-FT on iron catalyst in fluidised-bed reactor for gasoline, olefins and speciality chemicals production

— LT-FT on cobalt catalyst in fixed-bed reactor for middle distillates (kero, diesel), naphtha and waxes production

— LT-FT on cobalt catalyst in slurry bubble column reactor (SBCR) for middle distillates (kero, diesel), naphtha and waxes production.

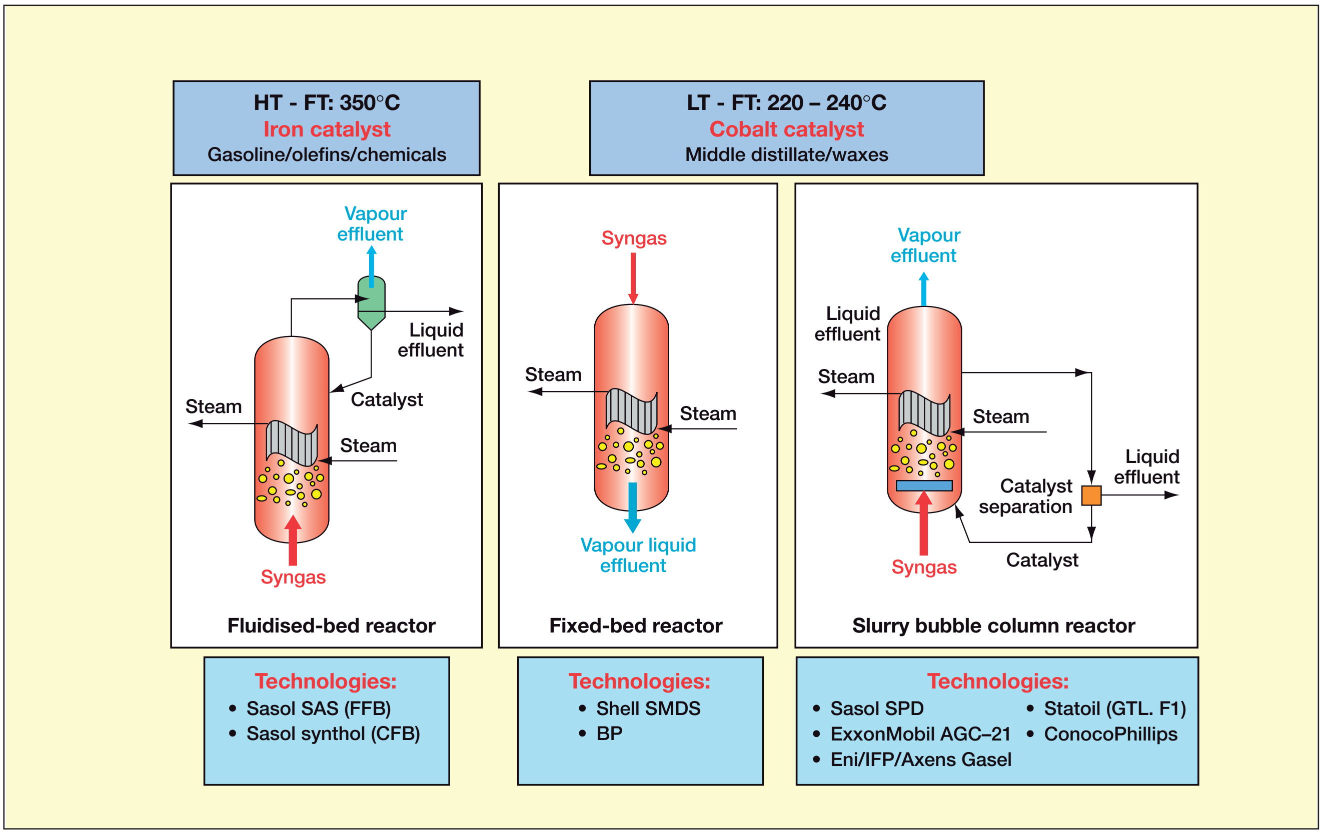

***Figure 3** The three main families of FT technologies*

Each of these three categories has its own unique background and strengths:

Category 1: In the operation of a fluidised bed reactor, where solid catalyst is kept in suspension by synthesis gas (and gaseous products), liquid production must be limited or avoided. That is why this type of reactor can only be accommodated with HT-FT (above 350°C) with iron catalysts (cobalt catalyst selectivity towards methane is too detrimental at these temperatures).

The corresponding catalyst selectivity (characterised by the Schultz-Flory [SF] coefficient for paraffins distribution: $\alpha = C_{n+1}/C_n$, with C_n being the number of moles of paraffins formed with *n* atoms of carbon) is in the order of 0.7, leading to more than 50 wt% production of C_1–C_4 and less than 20 wt% of diesel and above (Figure 4). This technology requires a heavy work-up of the raw FT products to obtain valuable products like a relatively limited yield of gasoline, as well as olefins and speciality chemicals.

Category 2: The LT-FT on cobalt catalyst in fixed bed reactor technology for middle distillates (kero, diesel), naphtha and waxes production was primarily developed by Shell back in 1970. The catalyst is placed inside tubes. The syngas passes through the tubes and the vapour-liquid products are recovered at the bottom of the reactor. The α-paraffins' SF coefficient of around 0.9 and above leads to a good final yield (after product upgrading) of ultra-clean-FT diesel or middle distillates, with the possibility of producing lube base and waxes (Figure 4).

This fixed-bed technology has two important advantages:

— The scale-up to industrial reactors is theoretically simple (multiplying the number of tubes)

— There is normally no problem with liquid-solid separation, as the catalyst is fixed inside the tubes.

Certain mechanical constraints in the reactor design should be noted with this technology (ie, temperature gradient along the tubes, limitations in the thickness of the main tubesheets), and transfer limitations between the gas-liquid phase and the solid catalyst can lead to a limited capacity per single train: from 3000–6000 bpd per reactor of 7–8 m diameter. Also, catalyst continuous make-up is not feasible. For example, in the case of catalyst deactivation, the reactor must be shut down, tubes emptied and refilled (estimated time by Shell is about two weeks).[4] This issue is particularly critical when the risk of having impurities/poisons in the syngas is higher (coal, biomass). This is also why this type of technology is not combined with iron catalysts, which are known to deactivate much faster than cobalt-based catalysts.

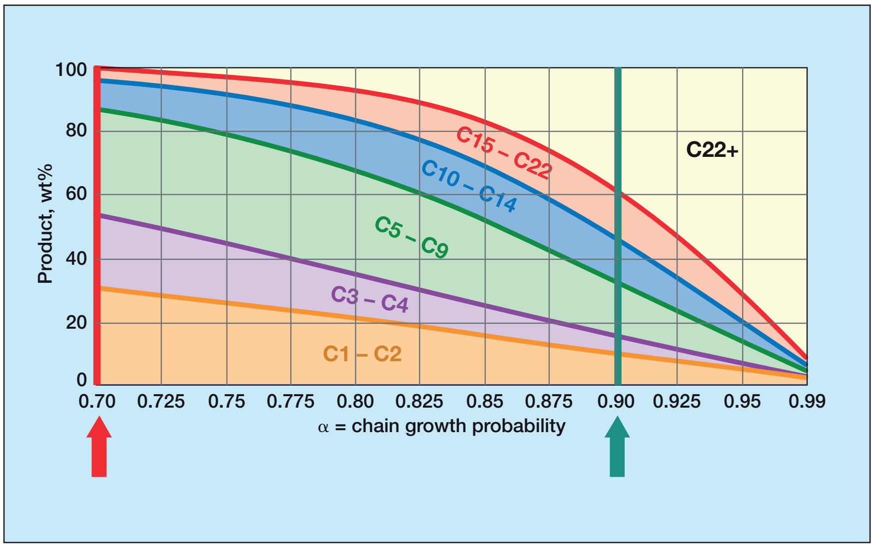

Figure 4 *Distribution of raw FT product as a function of the Schultz-Flory (SF) selectivity coefficient*

Main FT industrial applications in the world

HT-FT in fluidised bed with iron catalyst: Sasol CFB and FFB in South Africa	
	GTL
South Africa (Petro SA & Sasol)	Main products
Capacity: 200 000 bpd	Olefins specialities
Last start-up: 1993	Liquid fuels
LT-FT in fixed bed with cobalt catalyst: Shell SMDS in Malaysia	
	GTL
Malaysia (Shell)	Main products
Capacity: 14 500 bpd	Diesel
Last start-up: 1993	Naphtha/waxes
LT-FT in slurry bubble column with cobalt catalyst: Sasol SPD in Qatar	
	GTL
Qatar (QP/Sasol)	Main products
Capacity: 33 000 bpd	Diesel
Last start-up: 2007	Naphtha

Table 1

Category 3: The LT-FT on cobalt catalyst in slurry bubble column reactor (SBCR) technology for middle distillates (kero, diesel), naphtha and waxes has been developed over the past 20 years. It is the most promising in terms of catalyst productivity, capacity per train and operational flexibility. The reaction takes place in a three-phase slurry bubble column reactor, where the syngas is contacted with solid catalyst mixed in the produced waxes. The obtained products are the same as in the fixed bed case (mainly ultra-clean FT diesel). Compared to the fixed-bed technology, the SBCR has the following advantages:

— Higher capacity per train: at least 15 000 bpd per FT train (with reactors of up to 10 m diameter)

— Easy isothermal operation in the reactor

— Possibility of continuous catalyst make-up/withdrawal, allowing for a constant production to be maintained in case of catalyst deactivation or partial poisoning.

But some important challenges must be solved:

— Catalyst mechanical stress in a large SBCR

— Liquid-solid separation.

Table 1 summarises the main industrial applications. Today, only two companies can claim to have brought their FT technology up to industrial scale: Shell and Sasol.

XtL technology for conversion of syngas to diesel

The proprietary Gasel FT and upgrading technologies have been developed by Eni and IFP in close collaboration, which began in early 1996. At an early stage, Axens became associated with the project to optimise the basic engineering design, the operability of the chain of processes, and to develop the

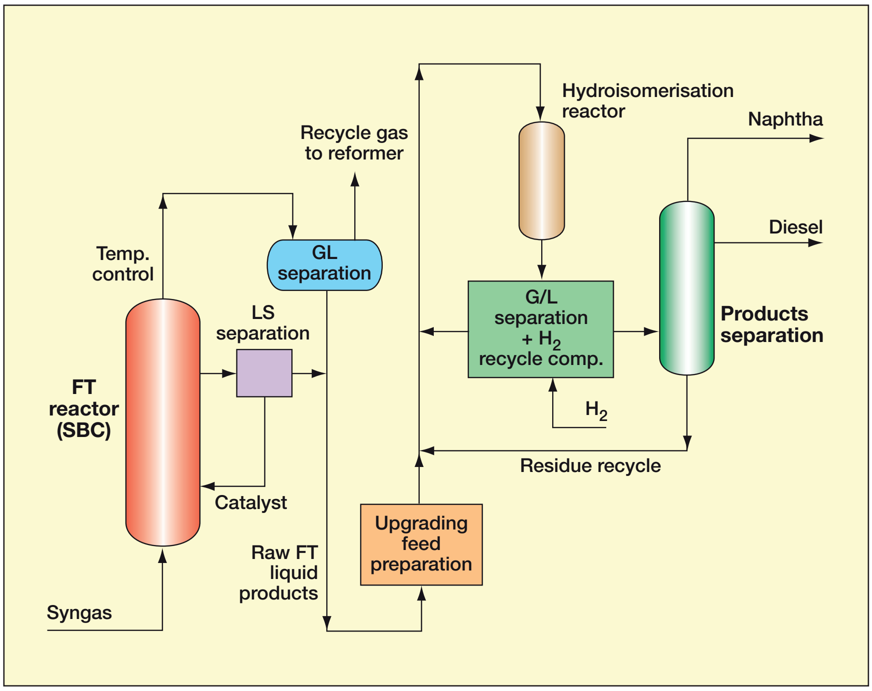

Figure 5 *Gasel simplified process flow diagram*

Figure 6 *Eni/IFP/Axens FT pilot plant, Sannazzaro, Italy*

preparation and production of the associated proprietary catalysts at industrial scale. The Eni and IFP technologies have been developed according to the following strategy:

— Development of FT technology based on a tailored cobalt-based catalyst and a proprietary FT SBC reactor design

— Development of specific upgrading catalysts (mild hydrocracking and isomerisation) to be adapted with the industrially referenced Axens hydrocracking technology

— Focusing on the reduction of the scale-up risk, developing in parallel a complete FT pilot plant and necessary complementary tools to assess the catalyst mechanical stability under reactive and hydrodynamic conditions representative of a large SBCR

— Engineering studies of fully integrated GTL complexes, up to front-end engineering design, including detailed operating instructions.

Process description

Gasel is a complete technology suite for the conversion of a purified syngas originating from various sources (natural gas, coal, biomass, petroleum residue or coke) into ultra-clean liquid fuels. The technology, as shown in Figure 5, consists of:

— **FT synthesis:** LT-FT conversion of syngas in a SBCR on a cobalt-based catalyst. The liquid products are recovered after gas/liquid and liquid/solid separations and sent to the upgrading section. The liquid/solid separation takes place outside the reactor in an external slurry loop for a safer operation and easier maintenance (internal L/S separation is feasible but considered today too risky)

— **FT products upgrading:** After a preparation step, which includes the condensate stabilisation and hydrotreatment of light olefins, the pretreated raw FT product is hydrocracked and isomerised. The fully converted product is separated into approximately 70% of an ultra-clean FT-diesel (no sulphur, no aromatics) having a high cetane number (> 70) and excellent cold flow properties (CFPP<-20°C), and 30% of a pure paraffinic naphtha — an ideal feedstock for petrochemical production. Instead of recycling the residue from the fractionator bottom, one can also envisage recovering it and using it as a lube base after further dewaxing.

The technology suite is based on proprietary catalysts manufactured and guaranteed by Axens:

— FT synthesis (cobalt-based on an oxide carrier)

— Product upgrading (specified catalyst combinations to provide specific product yields and properties).

The catalysts and the technology have been developed and optimised from several dedicated facilities available and still in operation:

— Large-scale hydrodynamic facilities (cold mock-up columns, diameter up to an equivalent 2500 bpd FT unit) have been developed and operated to ensure low-risk and easy reactor and ancillaries scale-up. Hydrodynamics, as well as mass and heat transfer, thermodynamics and kinetics have been merged in a detailed reactor model. The model was first used for the design of the FT pilot plant, and is now used to design the industrial-scale reactors (up to 10 m diameter). The reactor model, combined with process simulator software, reproduces the whole plant equipment and provides material and heat balances

— A large-scale Fischer-Tropsch pilot plant has been built and operated since 2001 (Figure 6). The plant is located inside the Eni refinery of Sannazzaro, Italy, and is completely linked to the refinery utilities. It reproduces at a large pilot scale (20 bpd) the overall FT synthesis section: catalyst and slurry handling (loading, make-up and withdrawal), FT reactor, gas/liquid and liquid/solid separation. Due to the size of the plant, it was possible to assess a wide range of industrial operating conditions in order to select those that optimise catalyst performances. During the several runs carried out, different types of liquid-solid separation devices were assessed and the best working device (in terms of efficiency and long-term reliability) was adopted for the industrial complex. Significant operating

experience has been achieved and operating instructions consolidated for the industrial unit. The DCS platform of the pilot plant can be used as a dynamic training simulator, to reproduce critical operations, offsets, emergencies, and so on. The large-scale FT pilot plant is still in operation and is considered a valuable tool for troubleshooting of different aspects of the technology
— Special laboratory equipment for FT catalyst scale-up has been designed in order to assess the FT catalyst mechanical stability under reactive and hydrodynamics conditions representative of a large SBC reactor. Indeed, this issue has been identified early in the development as critical. This task has been achieved from knowledge acquired in the development of slurry bubble column hydrodynamics. A proper stabilisation of the FT catalyst, as well as the ability to assess this stability through the right tools and tests assures FT catalyst performance on an industrial scale
— A hydrocracking pilot plant unit at the IFP R&D centre of Solaize, France, where the raw FT products from the FT pilot plant have been transformed into diesel and naphtha with the dedicated upgrading catalyst, allows for the testing of the final products' characteristics and quality
— Axens has developed facilities at its catalyst manufacturing plant of Salindres in the south of France for the production of the FT catalyst (full line from oxide precursor preparation up to catalyst activation) on a semi-industrial scale —around 100 kg/d, in particular to produce the catalyst for the FT pilot plant. The catalyst manufacturing lines for industrial production (1–5000 tons/year) have already been designed, and will be a simple scale-up of the semi-industrial facilities already existing, with the same process and operation sequence, so the scale-up risk for catalyst manufacturing has also been reduced to a minimum. During operation of the industrial GtL or XtL plant, Axens will manage the entire lifecycle of the FT catalyst, including manufacturing, transport, activation, recovery of used catalyst, recycle and cobalt recovery with specialised companies, and use of the recovered cobalt for new catalyst manufacturing.

Conclusion

The scale-up basis has been completed and the technology is ready for industrial deployment. It has recently been proposed for several GtL and BtL initiatives and is currently looking for its first commercial implementation. The licensing package, available on an unrestricted basis, includes:
— Transfer of the FT and Upgrading technologies
— Basic design package for the FT and Upgrading units—Assistance during detailed engineering and unit start-up
— Manufacturing and supply of the associated catalysts
— Guarantee of the process and catalyst performances.

Axens' licensing package, including the Eni and IFP proprietary FT+Upgrading technologies (and associated catalysts), is under the Gasel trademark.

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