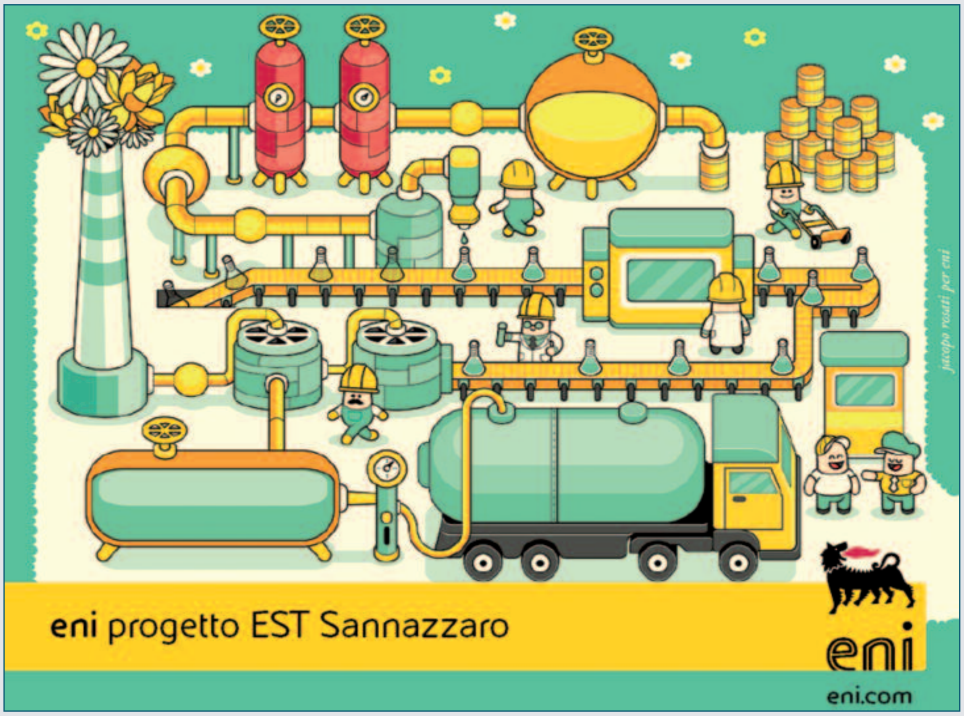

Giacomo Rispoli, Francesco Misuraca, Giuseppe Bellussi
eni SpA Refining & Marketing Division
San Donato Milanese (MI)
giuseppe.bellussi@eni.com

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CONVERTING HEAVY OILS TO GOOD QUALITY FUEL GRADE DISTILLATES: ENI SLURRY TECHNOLOGY (EST)

About a hundred years ago extensive studies were conducted in Germany for the hydrogenation of various molecules at high pressures and temperatures. The related R&D activities gave way to historical results such as the Haber process for the synthesis of ammonia and the Bergius process for the hydrogenation of liquids from coal to gasoline and other distillates. These results led to the awarding of the Nobel Prize to Fritz Haber in 1918 and to Carl Bosch and Friedrich Bergius in 1931. Today, after a century, a new technology arises on the worldwide scenario, that starting from these results and from the subsequent work of eminent scientists such as Matthias Pier, Mario G. Levi, Giacomo Fauser and others, is leading to the creation of an advanced process for converting heavy oil to light products of good quality, substantially avoiding the side production of coke and fuel oil. This technology will efficiently convert heavy residues and non-conventional oil reserves widening the availability of fossil energy sources.

The efficient conversion of refinery heavy residues and heavy and unconventional crude oils is becoming more and more important. For example, last April 13th, during a presentation to a Bridge Forum Dialogue, held in Luxembourg, Nobuo Tanaka, the executive director of the International Energy Agency (IEA) has launched the message that according to a scenario proposed by the IEA, the "New Policy Scenario", around the year 2035 there will be the need to replace three-quarters of oil production from existing wells with new reserves (www.iea.org /index_info.asp?ID=1928).
This argument raises the urgency for the development of efficient technologies for the conversion of residues and non-conventional crude

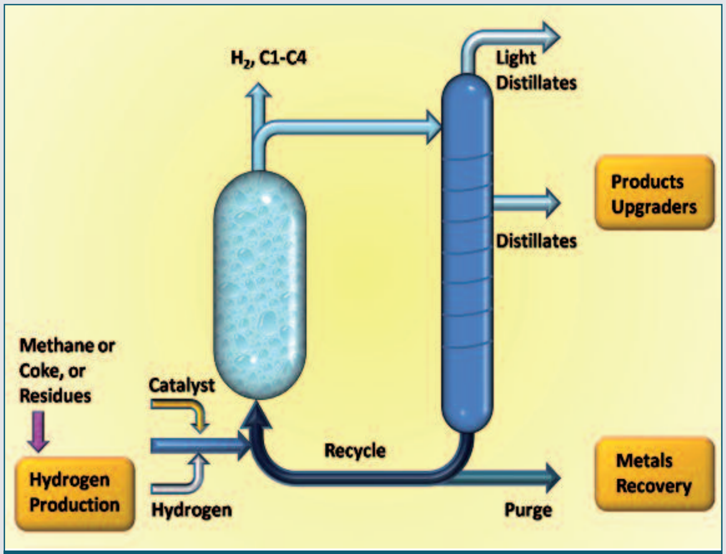

Fig. 1 - Simplified scheme of the EST process

oils, whose availability is at least equivalent to that of known oil reserves. Today there are already technologies that can convert heavy fractions by thermal or catalytic processes through “carbon rejection” or “hydrogen addiction”, but all the available processes produce large quantities of by-products that in the near future will be less desirable, such as coal or fuel-oil.

Therefore it appears important to have in the coming years, the availability of efficient processes to convert heavy fractions to distillates of good quality with almost total conversion. To achieve full conversion there are limitations due to the quality of the feedstock. The carbon rejection processes are thermal processes that produce two main fractions: one lighter having a H_2/C ratio greater than the feedstock and one heavier having a H_2/C ratio lower than the feedstock and constituted by pitch/bitumen or coke. So the nature of these processes inevitably lead to the side production of fatal heavy fractions with low environmental value. The hydrogen addiction processes, are catalytic processes operated at high pressures of hydrogen to promote the hydrogenation of the feedstock. There are technologies based on the use of fixed bed reactors or ebullated bed reactors. In both cases, the catalyst used consists of a millimeter-sized ceramic material. Many reactions are occurring in these processes: hydrogenation of double bonds and aromatic rings, cracking, isomerization, hydrogenolysis. It is not possible to reach the full conversion of the feed to gasoline and diesel in a single step because of the multiplicity and diversity of molecules which are present in the reactor. In fact the cracking of the heavy molecules occurs through the progressive and sequential hydrogenation and demolition of large components such as asphaltenes in a series of consecutive reactions. To achieve the full conversion, a residence time sufficiently long to allow the heavier molecules to be reduced below the maximum acceptable size must be used, but in doing so many of the smaller and more reactive molecules are converted to light fractions of little value such as the mixtures of C1-C4, or to heavier fractions, such as the coke. The only way to achieve the total conversion is to realize only a partial conversion of the feedstock during a single pass and then recycle to the reactor the heavier unconverted fraction, so that only this fraction can remain in the reactor for a longer residence time. With the existing technologies this is not possible, because the recycling of heavier fractions leads to a rapid poisoning of conventional cracking catalysts, due to metal deposition and accumulation of coke, making this operation not convenient from the economic point of view. The hydrocracking slurry technology, can overcome the problems of recycling through the use of a catalyst which is inherently stable towards the poisoning. This property allows the recycling of the heavy fraction and hence the total conversion of the feedstock.

The hydrocracking process with a slurry reactor

The simplified scheme of the EST process is shown in Fig. 1. The precursor of the catalyst is added to the feedstock as a oleo-soluble molybdenum salt. Inside the reactor, in the presence of H_2S and hydrogen, a layered molybdenum sulfide phase is formed. Under appropriate conditions is possible to drive the formation of MoS_2 towards single layer particles, with an average diameter of 5-6 nanometers. These particles are, for the purposes of fluid dynamics modeling, almost indistinguishable from the liquid phase. The main catalyst function is the activation of mol-

Fig. 2 - A) EST pilot plant at San Donato Milanese research center; B) EST demonstration plant at Taranto refinery

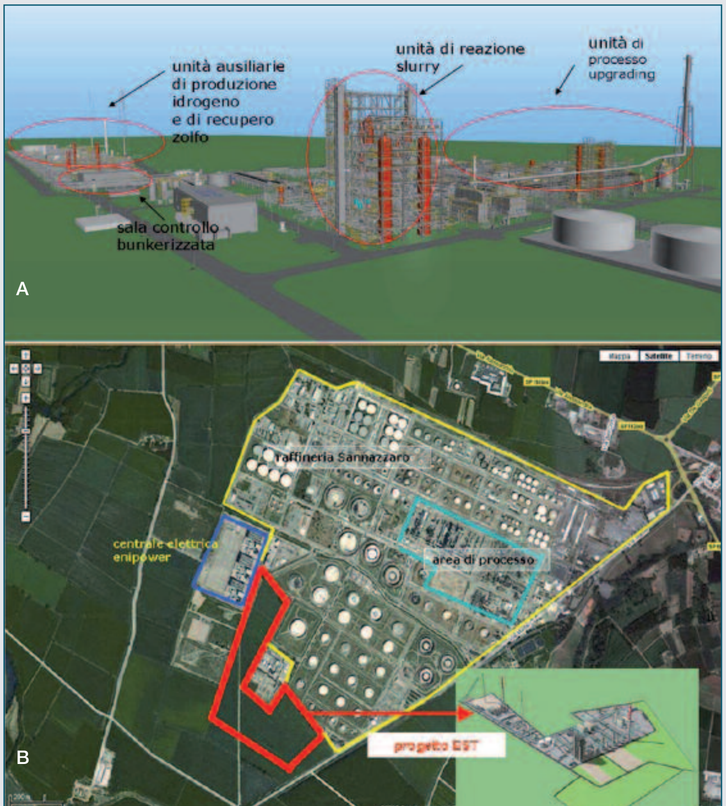

Fig. 3 - A) Plant lay-out; B) Plant location within the refinery

ecular hydrogen, producing species which are very active in hydrodesulfurization, hydro-dearomatization and hydrogenolysis, whereas the cracking activity is mainly of thermal origin. The presence of active hydrogen reduces the formation of coke in the reaction conditions. The reactor outcome is separated in a fractionation system from which the heavier compounds are recycled back to the reactor. This recycle permit the total conversion. The catalyst is concentrated in the heavier fractions, and therefore it can be entirely recycled back to the reactor. The organometallic complexes of nickel and vanadium, which are normally present in crude oils and are concentrated in the heavy residues, under the process conditions are rapidly transformed to the correspondent sulfides. Even these sulfides are recycled with the heavy residues and inevitably they tend to accumulate in the process fluids. For this reason it is necessary to purge the heavier process stream before to recycle it to the reactor, in order to maintain the concentration of these solids constant. A bleeding rate of 1-3% by weight with respect to the fresh feed, keeps the system at equilibrium. The pitch drained, can be used as fuel for the steel or cement industries, or it can be sent to a processing system that enables the recovery of the metals. Because of the levy due to bleeding, it is necessary to replace the catalyst by adding a few parts per million of molybdenum salts with the fresh feed.

There are several theories that explain in part the mechanism of action of molybdenum sulfide particles in these reactions, although there are still knowledge gaps and questions of interpretation. The catalytic activity is performed mainly near the rim of the MoS_2 lamellae, where there are electronic situations that can promote the hydrogen activation. The inner flat surface of the catalyst particles has a much lower catalytic activity than the rim, if any. The peculiar structure of the single layer MoS_2 allows the catalyst to survive in the reaction medium without being deactivated by metals or by coke deposition. Even the interaction of the molybdenum sulfide with the others nickel and vanadium rich inorganic species causes no deactivation or poisoning, probably because at the reaction conditions the different metals tend to forms single metallic phase sulfides rather than mixed phases. The discovery that the catalyst could be, under certain conditions, fully recycled to the reactor maintaining its catalytic activity, was the most important achievement for the development of this new technology. The development project, which lasted more than ten years, has included the construction and operation of half barrel/day capacity pilot plant in the laboratories of San Donato Milanese and a demonstration plant of 1,250 barrels/day capacity at the refinery of Taranto in the south of Italy (Fig. 2).

The industrial project

The first industrial scale project is under construction at the Eni refinery of Sannazzaro de' Burgondi in Northern Italy.

The project includes an EST plant of 23,000 bbl/d capacity, plus relevant utilities and two auxiliaries equipments, a 100,000 Nm^3/h steam reforming plant, which will provide the hydrogen required for the slurry reaction starting from natural gas, and two 80 t/d capacity sulphur recovery units.

The tar vacuum produced in the refinery will be the main feedstock to the EST plant. The main output will be constituted by gasoil, naphtha and kerosene, without any production of fuel oil.

All utilities needed for plant operations are part of the project, while the 50 MW power required by EST will be provided by the existing Eni refinery power plant, adjacent to project area.

All operations of the new plant will be remotely executed from a new bunker control room that will be built within the project.

Innovative equipments and devices will be installed because of the special needs of the process, such as spiral heat exchangers, slurry 3-way valves, nuclear density gauges patented on purpose for the project.

Sannazzaro EST plant is a grass-root project which extends on a 50 hectares area; its total investment cost is around 1.1 billion euro. The project has employed 1.3 million hours of detailed engineering, more than 300 purchase orders and about 30 contracts for construction have

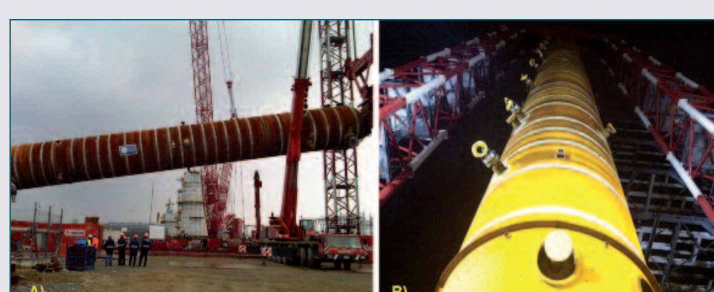

Fig. 4. - A) The reactor lift; B) The reactor in vertical position

Fig. 5 - The EST yard: A) Slurry Structure Prefabrication; B) The heaters prefabrication; C) The Construction Site

been issued, construction will require 6 million man-hours, with a peak of more than 2,000 direct workers. Some further project metrics are:

- foundations: 50,000 m^3
- steel structure: 20,000 t
- piping: 16,000 t
- equipment: 25,000 t
- electrical & instrumentation cables: 2,000 km.

In other words, with such figures, the first EST industrial project can be certainly considered in the ranking of the mega-projects worldwide (Fig. 3 A,B - Plant Lay Out).

The engineering activities had been started in mid 2008, so that the procurement of the two slurry reactors, core of the process and main long lead equipment, could be initiated in 2009. The reactors have been fabricated along more than two years and, because of logistics due to the inland location of the site, a dedicated assembling yard has been constructed at site, where all welding, thermal treatments and tests have been carried out. Presently, the two reactors have been successfully completed and just erected on foundations. Heavy lift operations have been performed with tower lifts to erect each of the 2,000 tons, reactors (Fig. 4 A,B - Slurry Reactor Lift).

Innovation has been also implemented in construction methodologies, as the extensive use of pre-fabrication, with the objective to maximize safety and minimize time of construction. In fact, lot of concrete works, such as foundations, have been pre-fabricated in dedicated yards, but also entire equipments (n. 5 process heaters) and heavy structures (the main plant structure, 2,200 t weight and 55 m high) have been pre-assembled at ground in dedicated areas, and then moved onto their final foundations (Fig. 5 A,B,C - Structure and Heaters prefabrication, Construction Site).

Construction of the plant, presently at 20% progress, is planned to be completed by the end of 2012, when the new plant will be ready for start-up. Particular care is given to recruitment and training of personnel who will have to operate the plant; Eni is not only the owner of the plant and the contractor of the project, but also the licensor of the technology, so that all training of the future operating people, the operating manuals and procedures have been prepared by Eni itself, taking into account the experiences done in the demonstrative plant in operation at Eni Taranto refinery. The project management is done by an integrated team composed by owner and main contractor, Saipem, one of the most reputable engineering & construction company in the world controlled by Eni company (Fig. 6 - EST Project Team).

Utmost importance is attributed to safety at work, as the project is managed in accordance with the highest safety standard recognized worldwide. Before starting construction works, Eni has called all construction contractors to a formal agreement for safety (Fig. 7 - Agreement for Safety); that agreement, a completely new initiative, represents a symbolic act aimed at making tangible and apparent the commitment of everybody to prevention, safety and the environmental protection.

The project is being carried out with the aim of Zero Accident. A safety management system has been implemented during construction, which implies ranking of the contractors in terms of their safety performance, a system based on points to penalize or incentive each worker

Fig. 6 - The EST Project team

Fig. 7 - The pact for safety

for his safe behaviour, daily, weekly, monthly and on purpose safety meetings, safety walks, etc.

The project applies all the best available technologies in terms of environmental protection: all emissions are largely compensated by countermeasures taken in the refinery process to reduce SOx, NOx and particulate emissions; no further liquid effluents are generated, as the project includes a water reuse plant; all new tanks are provided with double seal at their bottom, the sewer system is done by fibreglass piping, no earth has been moved outside during the site preparation, but all reused to erect all around the plant small green hills aimed at improving the landscape compatibility of the plant.

Other initiatives related to the project, aimed at improving the environment quality for the surrounding community, are the implantation of a 15 hectares forest, a pedestrian-bicycle path all around the industrial area connecting green areas and historical places, investments in photovoltaic energy to the benefit of the local community.

Conclusions

The heavy feedstocks hydrocracking technology with slurry reactor allows the conversion of non-conventional heavy crude oils and heavy refinery fractions into gasoline and diesel, avoiding the formation of undesired products such as coke and fuel oil. The upgrading process is the result of hydrogenation and cracking of the original feed. When hydrogen is produced from natural gas, much of the high-quality energy from natural gas is transferred to liquid fuels products. The results obtained through more than ten years of research activities dedicated to the development of EST technology, have supported the first industrial initiative. The first industrial plant in the world, which is a mega grass root project under construction at the Eni refinery of Sannazzaro de' Burgondi (Pavia-Italy), will be ready for start up at end 2012. The spread of this technology will allow the efficient use of the large reserves of unconventional fossil resources, thereby increasing the time available to complete the transition towards a totally renewable energy supply system.

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[1] D.W. Breck, Zeolite Molecular Sieves, J. Wiley, New York, 1974, 320.

[2] R.D. Shannon, *Acta Crystallogr.,* 1976, **32**, 751.

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