Eni Slurry Technology: A new process for heavy oil upgrading

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Abstract

EST (Eni Slurry Technology) represents a significant technological innovation in residue conversion and unconventional oil upgrading and will mark a step change in the treatment of the heavy end of the barrel. This new technology, internally developed by Eni, allows the total conversion of the heaviest fraction of the barrel into useful products, mainly transportation fuels, with a great major impact on the economic and environmental valorisation of hydrocarbon resources.

EST employs nano-sized hydrogenation catalysts and an original process scheme which allow complete feedstock conversion to valuable distillates or its upgrading to synthetic crude oil with a substantial API gravity gain, avoiding the production of residual by-products, such as pet-coke or heavy fuel oil.

Since the 1990's, the technology has been successfully tested on both laboratory and pilot scales. Following the positive results obtained at this scale, Eni decided to build a 1200 bpd Commercial Demonstration Plant (CDP) within its Taranto refinery. The plant was completed and successfully started up in the third quarter of 2005.

Since then, the CDP unit operation has allowed the successful test of EST performance on heavy feedstocks from around the world (Russia, Venezuela, Mexico, Middle East and Canada), confirming the great flexibility of the process.

The peculiar characteristics of EST in terms of yield, products quality, absence of undesired by-products and feedstock flexibility constitute its superior economic and environmental attractiveness. EST can offer additional margins in the range of 3-5 $/bbl of feedstock over current conversion technologies, which can be crucial for the exploitation of unconventional oil reserves.

The positive results obtained to date have encouraged the decision to host the first full scale industrial plant based on this new technology at Eni's Sannazzaro refinery.

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1. Introduction

In the last few years, energy policies have adapted to a changing context and it is therefore appropriate to consider or reconsider a number of topics with a view to increase the importance of the *unconventional hydrocarbons* resources /1-2/. Definitely, technologies for the optimum use of residues and extra-heavy crude are among these topics for at least two reasons:
to exploit our oil resources efficiently in an environmentally sustainable way;
to increase the profitability of the refining system by increasing their flexibility.
With regard to the first point, we know that oil is a finite and scarce resource and it should therefore be used to the maximum extent possible to produce the high value "light" products for which it is still irreplaceable. But today's world refining industry, still produces by-products, such as pet-coke or High Sulphur Fuel Oil (HSFO) at an average level of about 15 to 20 percent of the crude oil feedstock /3/. This material has long been used for applications as diverse as generating electricity and powering ships, but in the future the tendency is towards the use of more environmentally acceptable fuels (less sulphur, less metals and possibly higher hydrogen content such as natural gas). On the other hand, as a cogeneration feedstock in Integrated Gasification Combined Cycles (IGCC) applications, the HSFO must compete with low price fuels such as coal and pet-coke.
Speaking about the raw material supply, bitumen and extra heavy oils constitute the largest component of unconventional oil resources that we can expect to add to the so called conventional ones in the coming decades. The estimated oil in place for these fossil fuels amounts to around 4.3 trillion barrels /4/. Considering that the technically recoverable fraction is in the range 15-20%, it is evident that we are talking about enormous quantities if one takes into account that the whole Middle East has resources of about 2,000 billion bbl, of which 743 are considered to be recoverable /5/. The greatest part of these unconventional reserves is concentrated in Canada, in the province of Alberta (tar sands), and in Venezuela in the so called Orinoco Belt. A third country which is rich in non-conventional oil is Russia, even though in this case the deposits are scattered so that the recoverable portions are not quantitatively as large as in the other two countries; other important deposit are in many other countries such as USA, Brazil, Mexico, China, Saudi Arabia, etc. (Figure 1).
These oils vary widely in quality and correspondingly, require different solutions to be upgraded and economically transformed into valuable distillates. Most of them have API gravity lower than 10, high viscosity and an unusual concentration of poisons such as sulphur, metals and asphaltenes. Poisons are even more concentrated in residues from distillation and primary conversion processes, posing a serious challenge to currently available refining technologies that can not afford complete conversion and upgrading of these residues into distillates. Once again, the main problem is the huge production of polluted by-products, particularly pet-coke, whose market is shrinking so that it is usually buried or stockpiled resulting in severe environmental impact.
In this scenario, Eni has decided to develop a novel hydrocracking process (**EST: Eni Slurry Technology**) which is particularly well-suited for the total conversion to distillates of a variety of black oil materials, such as conventional vacuum residues, visbroken and thermal tars, as well as residues from unconventional oils /6/.

2. Process Description

EST is a process for converting petroleum residues from different origin into an upgraded, bottomless syncrude with an API gravity gain higher than 20. From the technological point of view, EST can be classified as a hydrocracking process, while the peculiar characteristics concern: *i)* the use of dispersed catalysts and, *ii)* an original process scheme for the catalyst handling, that allow the almost total feedstock conversion as well as high upgrading performance.

The heart of the process is a slurry reactor in which the heavy feed is hydrocracked to lighter products in the presence of thousands ppm of nano-sized molybdenum based catalyst. The feedstock conversion is initiated thermally, breaking the C-C bonds and generating free radicals that are suddenly quenched via H-uptake reactions preventing the free radical recombination that could evolve to coke formation. The H-uptake is promoted by the presence of a very active Mo-based catalyst such as molybdenum-sulphide that is produced *in-situ* by the decomposition of an oil-soluble precursor. As a matter of fact, this reaction gives rise to a nano-sized dispersion of very active, not supported isolated layers of molybdenite (MoS_2), i.e. a very active hydrogenation catalyst.

The use of unsupported slurry catalysts is particularly useful in case of feedstock containing high concentration of pollutants, particularly metals and asphaltenes. As a matter of fact, contrary to the conventional supported catalysts utilized in fixed and ebullating bed reactors, the dispersed molybdenite do not suffer for the plugging problems due to the metals and coke deposits on the porous supports.

The upgraded oil withdrawn from the reactor is sent to a separation system to recover gas, naphtha, middle and vacuum distillates, while the unconverted material, as well as the dispersed catalyst, are recycled back to the reactor. Depending on the feedstock, we select the process severity (reaction time and temperature) in order to generate a residue at the limit of stability avoiding the phenomenon of asphaltene precipitation that could generate coke and foul the process equipments. The operation of recycling and blending the partially converted residue with an aromatic stream such as the fresh feed, allows the recycle stream to recover stability so that it can be reprocessed to get almost total conversion. After repeated cycles, the system reaches a sort of “steady-state” situation so that the net result is the total conversion of the feedstock to valuable products. A small purge is necessary to sweep-away the metals (Ni and V) entering with the feed.

In this way, EST can process heavy black oil materials assuring very high conversion to distillates because does not generate by-product, such as coke or heavy fuel oil.

One of the main characteristics of the EST process is the excellent feedstock flexibility. In several years, we have processed a variety of different feedstock (conventional petroleum residues, extra-heavy oils and bitumen); in all cases we have demonstrated the possibility to get the total conversion of the residue to light, medium and heavy distillates with minimum purge. Moreover, in all cases the process assures a complete metal removal (HDM), an excellent Conradson Carbon Residue and sulphur reduction (HDCCR and HDS) and a fairly good denitrogenation (HDN).

Another peculiar characteristic of the EST is the production of a high quality Vacuum Gas Oil (VGO) with low sulphur and low aromatic content that can be further converted into transportation fuels (diesel or gasoline) via hydrocracking (HDC) or Fluid Catalytic Cracking (FCC) as a function of the market requirements, assuring the product flexibility.

3. Commercial Demonstration Plant

After an intensive R&D activity carried out at laboratory level and therefore at pilot plant scale, the EST outstanding upgrading performance has been recently demonstrated in test runs carried out at 1,200 BPSD Commercial Demonstration Plant (CDP) successfully operating in the Eni'Taranto refinery since 2005 /7/.
The first test with a vacuum residue (VR) from Ural crude was mainly addressed to confirm the process performance already obtained at pilot plant scale as well as the fluid-dynamics of the in-house developed and designed slurry bubble column reactors and gas distributors. Slurry reactors resulted very well mixed as demonstrated by the almost isothermal axial and radial temperatures profiles.
The second five months long experimental campaign with a vacuum residue from Athabasca bitumen was completed in 4Q 2006.
After a major turndown in which most of the equipments and piping were inspected for fouling and corrosion, the third run with a VR of a Middle East heavy crude oil was started in spring 2007. Eventually, the fourth test run with visbroken tar, the ultimate refining bottom product, was successfully completed in February 2008. All these tests were focused to optimize the operating conditions in order to reduce Capex and Opex of the EST process.
More than 160.000 bbl of black feed were processed (Figure 2). Purge at steady-state condition set at 2 %wt or lower, while the liquid volume yield always exceeded 100 %.
Table 1 show the typical yield structure and the main upgrading performances for each feedstock tested.

	Ural VR	Athabasca Bitumen VR	Basrah VR	VB Tar
Origin	Russia	Canada	Iraq	
API gravity	7.9	4.3	5.3	-0.2
Sulphur (wt.%)	3.0	5.3	5.1	6.0
Nitrogen (ppm)	5000	3800	3800	4900
Ni & V (ppm)	90 - 280	90 - 240	35 - 115	60 - 116
CCR & Asf. C5 (wt.%)	21 - 13	17 - 18	19 - 14	27 - 22
Upgrading performance				
SCO API gravity	30.6	29.6	24.7	23.6
HDS (%)	74	82	71	80
HDN (%)	43	28	32	46
HDM (%)	99.7	> 99	> 99	> 99.9
HDCCR (%)	96.7	98.2	98.3	99.7

Table 1: Chemical composition of selected residues processed in the CDP & main upgrading performance.

The EST/CDP runs also allowed:

1) training operation and maintenance personnel;
2) training process engineers;
3) to develop and test operating procedures for steady-state operation and emergency conditions;
4) to develop and tune process simulation models;
5) to evaluate the performance of selected materials against corrosion in harsh environment;
6) to evaluate the performance of different kind of instrumentation in harsh environment with heavy, fouling fluids.

4. Economics

Based on these results, we were able to update the economic analysis carried out to evaluate the benefits deriving from the application of EST process for the upgrading of Athabasca oil sands.
The merit of implementing an upgrading complex of 200,000 bpd capacity of bitumen has been investigated by conducting a "Cash Flow Analysis" and by calculating the inherent profitability indexes.
A customized Basic Design Package has been developed by SAIPEM/Snamprogetti for a location of the EST unit in Alberta Province. Quotations from the market have been obtained for the critical items, whereas the cost for the balance of equipments, for the bulk material and for construction have been evaluated from Data Base relevant to projects implemented in Canada. The typical capital expenditure for an EST-based upgrading complex is represented in Figure 3.
Cash Flow projections have been carried out in current US$ (inflation 2.0 %/y) and unlevered terms (100% Equity Funding) considering an oil price scenario with Brent crude oil ranging from 45 to 55 US$/bbl at year 2012. The Athabasca bitumen (7.4 °API, 4.78 wt.% sulphur) has been valued on a netback basis from the market price at Edmonton of the SynBit and diluent. The resulting prices are respectively: 24.1 and 31 US$/bbl at year 2012 for the two Brent price scenarios, while the natural gas price has been valued respectively at 5.4 and 6.9 US$/MMBtu.

Figure 4 shows the block-flow diagram of the upgrading complex comprising:

a) Pre-fractionation system to separate the naphtha used for the bitumen transportation and the straight-run distillates in order to generate the vacuum residue (about 50% of the original bitumen) that is send to the EST upgrading unit;
b) EST upgrader for the total conversion of the residue into distillates that are blended with the original distillates to generate the upgraded Synthetic Crude Oil (SCO) as shown in Table 2;
c) Hydrogen production via Steam Methane Reforming.

Starting from 200,000 bpd of bitumen, the upgrading complex produces about 216,000 bpd of SCO. The API gravity increases from 7 to about 30 and the oil results deeply upgraded, with 80% sulphur reduction, 60% nitrogen reduction, 100% metal removal, no asphaltenes and a very low CCR.

	H2S	Gases	LPG	Naphtha	Atm. GO	Heavy GO	SCO*
Yield (wt.%)	4.6	5.0	5.2	11.8	32.9	40.5	
API gravity				60.0	31.7	17.4	29.7
S (wt.%)				0.14	0.75	1.40	1.72
N (wt.%)				728	3133	2780	0.16
CCR (wt.%)						0.84	0.24
Ni-V (ppm)						< 1	< 1

(*) Synthetic Crude Oil

Table 2: Product yield & quality from CDP test with Athabasca bitumen.

The economic analysis shows that within a conservative crude oil price scenario (Brent price within 45 and 55 US$/bbl @ 2012), the upgrading complex based on EST process assures a very interesting Internal Rate of Return, from 15 to 20% before tax, that means a bitumen upgrading margin ranging from 11 to 16 $/bbl (Table 3), that is to say from 5 to 8 US$/bbl higher than that obtainable by state-of-the-art technologies, and in particular by the Delayed Coking (DC) process.

Reference Scenario	Brent @ 45 $/bbl	Brent @ 55 $/bbl
Upgraded feed value	57.8	71.5
less:		
Opex	*8.6*	*10.1*
Capex (@ 8%)	*10.2*	*10.2*
Fixed Costs	*4.0*	*4.0*
Netback crude price	35.0	47.2
less:		
Base crude price	*24.1*	*31.0*
UPGRADING MARGIN (@ 8%/y)	10.9	16.2

Table 3: Economics for a 200.000 bpd upgrading complex based on EST process.

5. Conclusions

EST (Eni Slurry Technology) is a novel technology to fully convert black oil materials (extra-heavy oils, tar sands bitumen and petroleum residues) into distillates, so that may represent the solution for the profitable exploitation of the huge reserves of unconventional oils, ensuring the availability of additional strategic reserves.
The EST advantages include:

- total feedstock conversion to high quality products (no production of either heavy fuel oil or coke);
- high product slate and feedstock flexibility;
- high products upgrading, with total metals removal and excellent HDS, HDN and CCR reduction;
- lower environmental impact compared to thermal cracking technologies.

The EST outstanding performance has been demonstrated in test runs with different heavy feedstock carried out in the 1200 BPSD Commercial Demonstration Plant successfully operating for more than 2 years in the Taranto refinery, since December 2005.
The positive results obtained to date have encouraged the decision to host the first full scale industrial plant (20,000 BPSD) based on this new technology at Eni's Sannazzaro refinery (start-up scheduled for the 2Q 2012). Reactors of maximum size in terms of internal diameter and weight will be installed to establish a sound reference in view enhancing major industrial initiatives. As a matter of fact, Eni is interested to deploy EST in large integrated projects (upstream-downstream) worldwide.

5. References

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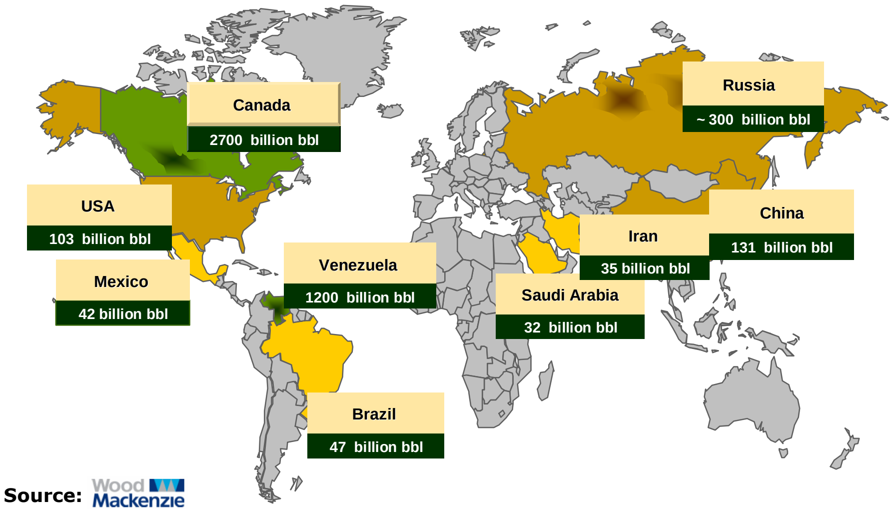

Figure 1: Unconventional oils main deposits.

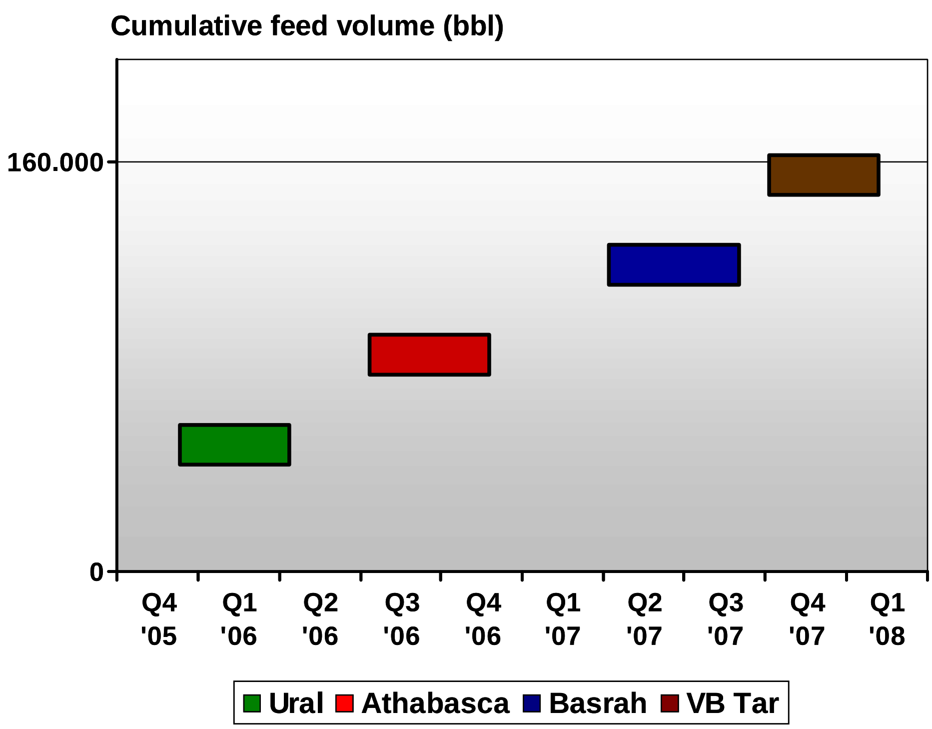

Figure 2: Test runs carried out in the EST-CDP unit since December 2005.

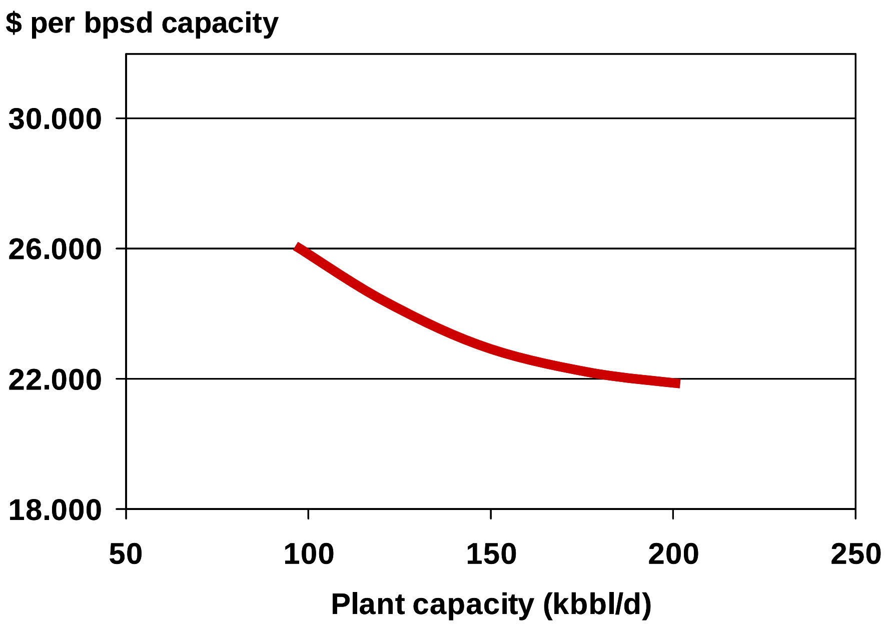

Figure 3: EST capital expenditure at graduated processing capacity.

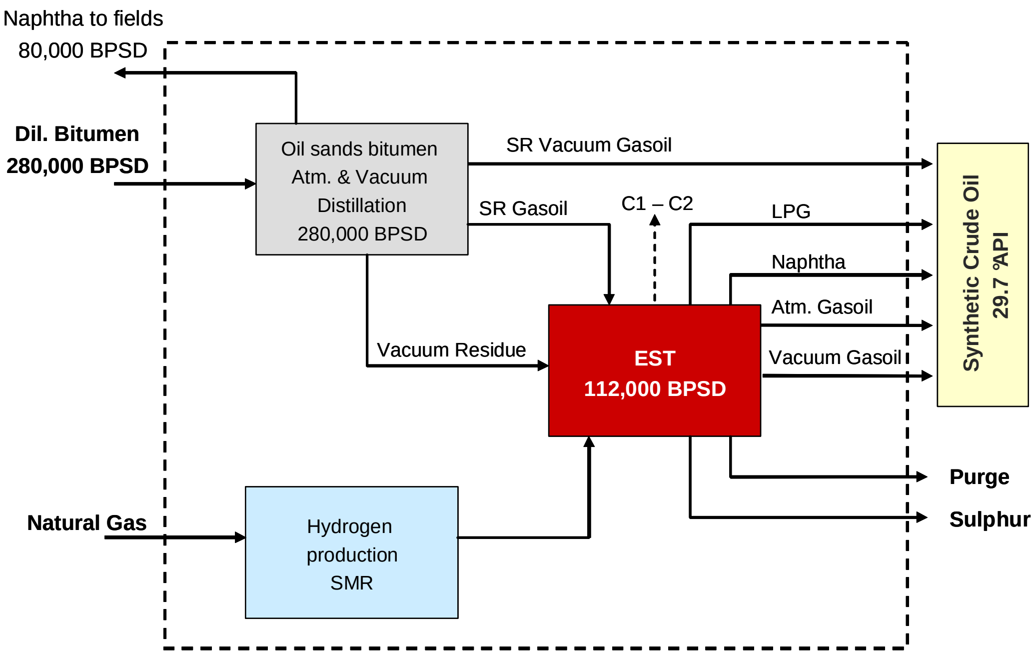

Figure 4: EST-based upgrading complex block-flow diagram.