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BOTTOM OF THE BARREL, AN IMPORTANT CHALLENGE OF THE PETROLEUM REFINING INDUSTRY

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Abstract

The most important concerns of the petroleum refining Industry in the near future are: meeting the growing market of cleaner fuels, gradual substitution of scarce light low - sulfur refinery feeds by heavy high - sulfur ones, and the decreasing demand for heavy fuel oil .One solution of the above problems is using residue upgrading processes. Furthermore, economic and strategic reasons promote the exploitation of refining residua and also considerable reserves of very heavy crude oils.
Accordingly, the selection of proper processes is an important challenge of the petroleum refiners. The present article – considering the aforementioned problems – discusses the most appropriate ones.

Key words: Bottom of the Barrel; Heavy Crude Oil; High Sulfur Crude Oil.

1. Introduction

Due to the recently imposed restrictions of : meeting the growing market of cleaner fuels, gradual substitution of light low - sulfur refinery feed (due to its scarcity) by heavy high - sulfur one, and the decreasing demand for heavy fuel oil , serious challenges have been raised in the petroleum refining industry. This fact necessitates using processes, for conversion of heavy high – sulfur refining residues into lighter low – sulfur products (generally called residue upgrading processes).

The final product slate, the refining product values and the price difference between light and heavy crude oils are three major factors in the selection of these processes .By recent high crude oil prices, the later two factors are significantly increased, and the investment profitability of residue upgrading plants has been promoted.

The significant economic growth of the Eastern Asia region and the subsequent export potential is also another important concern of such a process selection.

Considering the above points, residue upgrading processes should carefully be selected.

2. Description

During the recent 150 years, the easy and cheap access to the light crude oil (with higher than 20 API Gravity) has been the guarantor and support of the economic growth of many countries.

Studies show that about 830 billion barrels of crude oil has globally been produced More than 70 % of this amount has come from 300 large oil fields, containing about 500 billion barrels of crude oil. But, their future economic production depends on new technologies and comprehensive studies.

The petroleum products global demand has grown during the recent 15 years .The recent *Global Petroleum Market Outlook* study by Purvin and Gertz (Fig.1) shows a 1.7 % per year rate of its growth, which is expected to continue, up to 2015.

Their study also implies that the petroleum supplies growth from 60 million barrels per day in 1990 to 75 million barrels per day in 2005, will continue up to 95 million barrels per day in 2020.Figure 2 shows the expected crude mix quality for the refiners during that period of time [1].

Up to the year 2015, the global crude oil production will reach to its maximum value of 30 billion barrels per year and will then follow a descending trend. On the year 2030, the global consumption and production of crude oil will be 38 and less than 24 billion barrels per year (by the existing technologies), respectively. Therefore, this gap should be filled through increased production of non-traditional hydrocarbon deposits (natural gas, heavy and very heavy oils, gas hydrates, gas bearing sand, coal bed methane gas, tar sands, gas shales, nuclear energy and renewable energies).

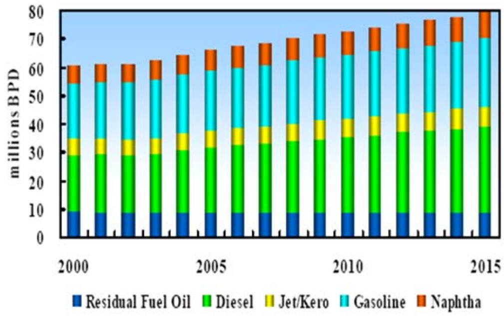

Fig. 1 Global demand for refined products [1]

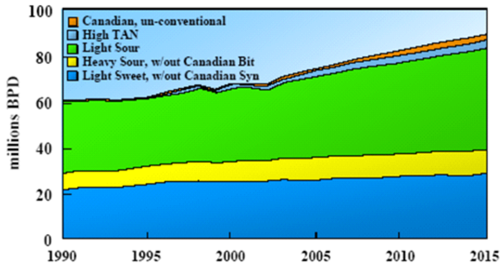

Fig. 2 World crude supply prediction [1]

These deposits are considered non-traditional as they cannot be transported via pipeline due to low API gravity, high viscosity or high pour point. The producers of these non-traditional deposits must solve the pipeline issues at a cost that will still produce a positive return. Synthetic crude oil from non-traditional supplies has an important role in the world total market, due to the scarcity of light- sweet petroleum resources [1].

Unpredicted and sever fluctuation of crude oil price and its refining margin is an indication of the intense effect of light and medium sweet crude oil starvation in the near future (Fig. 3,4,5).

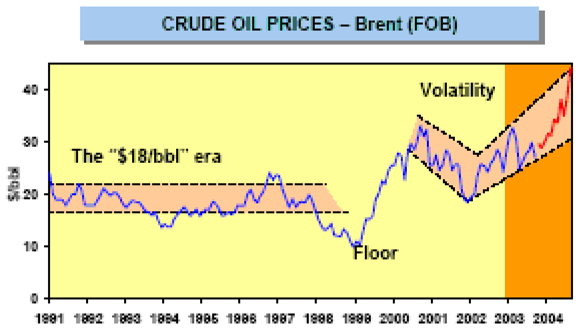

Fig. 3 Crude oil price volatility has been driven by external forces [16]

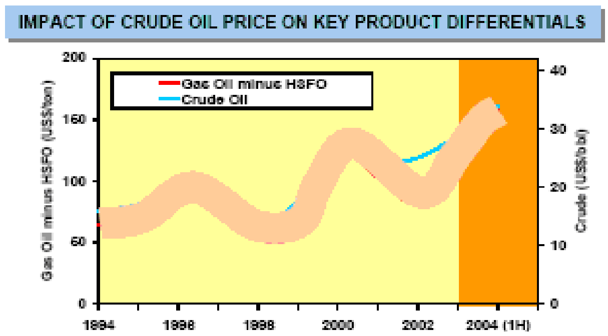

Fig.4 Key product price relationships have tracked crude oil price movements [16]

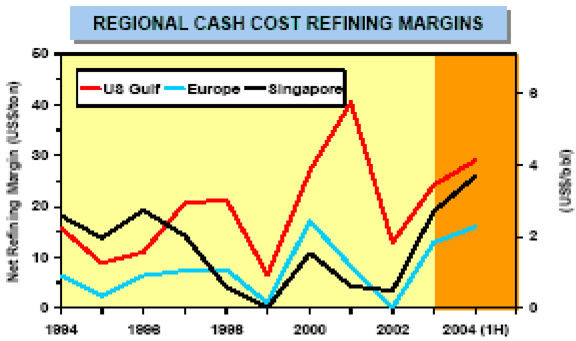

Fig. 5 Global upturn in refining margins [16]

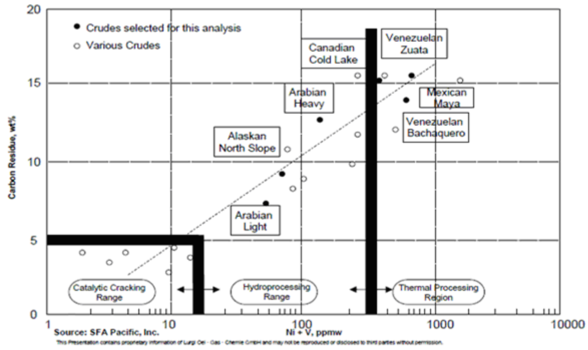

Fig. 6 Properties of 343°C+Boiling Point Residues [20]

Heavy crude oil is one which has an API Gravity of 25(Specific Gravity of 0.904) or less, and a viscosity of up to few thousand centi-poises (Table 1). Heavy crude oil(due to its abundance and ease of upgrading methods, in comparison with other aforementioned energy sources) is a better alternative to the light one .Its huge resources have been discovered in Canada, Venezuela, Russia, Middle East, etc. Concerning the prospect of energy situation, after light crude oil and natural gas, only heavy crude oil can supply the future global energy requirements.

The long time and globally growing production of light and medium crude oils (even up to the secondary recovery stage), has decreased their reserves. Also, by continued production of each oilfield (even those containing light ones), its sulfur, nitrogen, metals, salts and Asphaltenes contents will gradually increase. Therefore, heavy or very heavy crude oil will compose the majority of refineries feeds, in the near future. By now, the heavy residue conversion technologies have been indebted by the price difference between light and

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heavy crude oils, light petroleum products and fuel oil, and finally fuel oil consumption restrictions due to the environment conservation.

Table 1 The light to very heavy crude oils definition

	Very Heavy	Sour Heavy	Sweet Heavy	Sour Light	Sweet Light
Degree (API)	<=10	10-30	10-30	30-40	30-40
Sulfur(%wt.)	>3.0	1.0-3.0	<0.5	0.5-1.5	<0.5
Metals (ppm)	High	Low to High	Low to High	Low	Low
Acidity	Variable	Variable	Variable	Variable	Variable
Nitrogen (ppm)	High	Variable	Up to 50	Variable	Up to 20

3. The refining products consumption trend

3.1.Gasoline

All of the North American gasoline shortage cannot be compensated by Europe .By now, Europe has been the gasoline requirement regulator. But, by 2015, this role will be played by the Middle-East. Up to the end of this decade, this region will become stand alone in gasoline supply [2].

3.2. Middle-distillates

Up to 2015, a middle- distillates deficiency will be confronted in Asia and Europe. The Middle Eastern (& African) countries will compensate it by diesel fuel, gas oil and jet fuel [2]. Due to the specifications change of Jet Fuel, a portion of Kerosene will be added to the diesel fuels and the jet fuel scarcity will become worse. The Middle- Eastern capacities for Sulfur refining and GTL products supply will increase, and considerable amounts of middle distillates will be exported to Europe. The Asia continent middle-distillates shortage, seem to become worse and reach about 650'000 barrels per day, up to 2015. But, during the next decade, this situation in Asia will become better.

The fuel oil price will not economically be acceptable, in comparison with the crude oil prices.

At the same time, the heavy crude demand is decreasing because:

- Heavy crude oil requires special methods of transportation, affecting its profitability.
- Heavy crude oil refining produces residue, 2-3 times as much as the light or middle ones. This residue is used as fuel or bitumen.
- Heavy fuels contain a lot of sulfur and nitrogen, producing SOx and NOx on combustion. Due to costly emission penalties of these acid rain producing gases, heavy fuels consumption is declining.
- Heavy fuels produce heavy metals and CO emissions, which are dangerous environmental pollutants.
- Heavy fuels produce more CO_2 (the green house effect gas), have lower thermal efficiency and lower service lives in the equipment, consuming them.

The total global reserve of heavy and very heavy crude oils is estimated to be about 4000-5000 billion barrels [2].Even if, only 20% of this reserve is produced (about 1000 billion barrels), this will be equal to the existing global crude oil reserve. The main difficulty in the heavy crude oil production is its high viscosity. Therefore, the injection of gas, chemicals, hot water, steam and in–situ combustion, are indentified as the most useful ways of its production [3].

Due to having a high viscosity, the heavy crude oil transportation requires methods like: Asphaltenic compounds elimination, dilution by hydrocarbon solvents or using heated pipelines. These methods prevent heavy compounds precipitation and pipeline plugging.

If these methods are not economical, the heavy crude oil transportation problems can be solved via the construction of the refinery in the vicinity of the heavy crude oil field [2].

Therefore, even for petroleum exporting countries, this shows the importance of processes, for conversion of low value – high sulfur heavy residue, into clean – valuable light fuels This is a significant step in crude oil preservation .To achieve this goal, the refiners should use one or both of the following process categories:

I. Breaking heavy molecules into lighter ones (carbon rejection processes) , which are (usually) non-catalytic thermal and low pressure processes , in which Poly-Nuclear Aromatics (PNA) form coke . Coking, residue fluid catalytic cracking (RFCC) and advanced visbreaking are some examples of these processes. Their main feature is" feedstock flexibility". They can accept feeds (Atmospheric Residue) with up to 20%

Conradson Carbon and 10,000 ppm metal content (Ni + V). The capital and operating costs of these processes are low, but their light products yields are also low [4].

II. Adding hydrogen to light molecules (hydrogen addition technologies), which are high pressure catalytic processes (more than 150 Bars), and consume a lot of hydrogen. Hydro-cracking and hydro-visbreaking are examples of such processes. Their main feature is the "product quality". Some of their innovative types can accept feeds (Atmospheric Residue) with up to 38% Conradson Carbon and about 4000 ppm metal content (Ni + V). Their capital and operating costs are high, but their light products yields are also high [4]. Coking, solvent extraction, residue fluid catalytic cracking (RFCC), hydro-cracking, advanced visbreaking, gasification and finally residue hydro-cracking are dominant residue conversion processes. Combinations of them also become increasingly attractive for large volume applications.

As it can be clearly observed in figure 6, hydro-processing is the best solution in case of heavy metals content feeds.

Gasification: Gasification is a conversion by a partial oxidation of a carbon containing gas, liquid or solid into the synthesis gas, in which the major components are hydrogen and carbon monoxide. In the past, its main applications were in the petrochemical industry, for the ammonia, methanol and hydrogen production. But, today it has been widely used in petroleum refineries and integrated combined cycle power generation plants (IGCC). Its wide spectrum feed (from natural gas to heaviest high metals and sulfur content petroleum or coal derived pitches) can even contain agricultural residua, worn out automotive tires , un-recyclable polymer wastes, sewage sludge ,biomass , municipal garbage ,etc. . Therefore, a major economic advantage of destroying waste material, plus a lot of steam and electricity can be gained by gasification, which is now very important for many municipalities. All the sulfur content of the feed(s) is also converted into H_2S, which can easily be separated by the well-known Amine treating process .This advantage is very important, because the main factor of heavy residue price reduction is its sulfur content, mainly due to the environmental regulations .In other words, by using IGCC, there is no need for expensive refining of heavy fuels. A key benefit of IGCC is the lowest SO_x and NO_x emission of any liquid/solid feed power generation technology. Table 2 expresses well this fact [5,6]. Also, IGCC represents the most promising technology for CO_2 capture (sequestration). Each ton of gasification feed requires one ton of oxygen, which requires an air separation plant construction. But, nitrogen and rare gases are its other valuable and saleable products, which compensate for a large fraction of its costs. The produced Syngas, can be used for the production of : power and steam (30% of global capacity), petrochemical products ammonia ,ammonium nitrate, urea (fertilizer), methanol , ethanol , Di -Methyl Ether(DME),acetic acid , etc. (45% of cumulative global capacity) , transportation fuels(via Fischer - Tropsch reaction- now 25% of global capacity) and even hydrogen [5]. Rarely, a feed with a price higher than 10 $/barrel is used for gasification.

Residue Hydro-cracking: Heavy residue is refined under high temperature and pressure, by using a robust catalyst to remove sulfur, nitrogen, metals, olefins, condensed aromatic, oxygen, etc., and is converted into high quality lighter fuels. Good quality products make this family of processes, one of the best options for residue upgrading, however higher crude prices (e.g., 30 $ / barrel) improves its economy .Feed Conradson Carbon (which comprises asphaltenes, metals and minerals) under 30 % is usually suitable for it. The feed conversion is relatively high (50 to 75 %) [5,7].

Table 2 Air Emissions (mg/Nm3) [5]

	Typical IGCC	European Standards for Conventional Power Station
SOx	10	130
NOx	30	150
Particulates	10	16

All Fixed Bed units designed for vacuum residue processing, now run on lighter feed or atmospheric residue for FCC feed .This is due to the short catalyst life (6 months or less) of fixed-bed designs; on the contrary to the large catalyst volumes used (LHSV typically between 0.5 to 1.5). Although some licensors have tried to conquer it by some innovative developments. However, the refining industry has remained cautious about these processes, such that by now, only about 17.5 % of the residue upgrading global capacity belongs to them [4,5].

Ebullated Bed technologies were first introduced in the 1960's to overcome problems of catalyst ageing and mal-distribution in fixed – bed designs .In this design , feed and hydrogen enter at the reactor bottom , thus expanding the catalyst bed .Even though the catalyst performance can be kept constant by replacing it continuously , de-sulfurization and hydro-conversion are lower than obtainable in the fixed-bed design , due to the back mixing effect of ebullation .Today, most commercial ebullated bed units operate in the 70 to 85 % de-sulfurization and 50 to 70 % volume conversion of non- distillables (538^{+} ^{o}C).

By R&D, some improvements in catalyst and reactor have been made. Now, this technology is well developed with 12 commercial plants in service [7].

Before the application of the ebullated bed technologies , the hydro-processing upper limit of metal contaminants were taken as 200 ppm .But this technology increased that limit to 460 ppm. The asphaltene upper limit increased from 12 – 19 % to 28 %, as well [8].

Recently, for residua with up to 4000 ppm metals(Ni + V) content and about 38 wt.% asphaltenes , a new process is developed by several companies, which is slurry hydro-cracking .This route can have a very high feed conversion(more than 95 % with recycle) (Table 2).

HRH (Heavy Residue Hydroconversion) process is slurry hydro-cracking, for converting heavy crude oils with less than 10 API gravities, to a light crude oil with more than 30 API gravity, and also converting heavy residues to middle distillate products.

The most important advantages of this technology are categorized as the following items [9]:

- Having more appropriate operating conditions than other existing processes (60-70 bar pressure and 400-500 ° C temperature)
- High products yield (90-95%)
- Applicable to a variety of feeds with large sulfur and heavy metal contents
- Complete elimination of heavy metals
- Reduction of sulfur content by 60-80%
- Negligible coke formation (less than 1%)
- No polymerization reaction
- Catalyst recovery of more than 95 %

In table 3 and 4, The Performance of Ebullated Bed and Slurry Hydro-cracking processes and the product slate of slurry hydro-cracking are presented respectively. In other words, this process demonstrates feedstock flexibility, together with almost complete conversion.

Table 3 The performance of ebullated bed and slurry hydro-cracking processes [8, 21]

	Hydro-De-Sulfurization Performance	Hydro-De-Metallization Performance	Hydro-De-Nitrification Performance	% Conradson Carbon Reduction	% Conversion
Ebullated Bed	60 to 95	70 to 98	n. a.	40 to 75	40 to 92 (525^{+} ^{o}C)
Slurry Hydrocracking	> 82	> 99	> 41	> 95	> 99

Table 4 The product slate of slurry hydro-cracking (wt. %) [8]

Gas ($HC+H_2S$)	Naphtha (C_5 to 170^{o} C)	Gas Oil (170 to 350^{o}C)	Vacuum Gas Oil (350 to 500^{o}C)	DAO (500^{+} ^{o}C)
9.9 to 15.1	4.9 to 14.0	26.9 to 39.1	23.3 to 34.9	8.5 to 24.4

Slurry hydro-cracking vacuum gas oil and DAO products are suitable feed stocks for conventional FCCU and hydro-cracker [8]. For obtaining maximum yield of transportation fuels, the hydro-cracking /delayed coking scheme should be used [5].

The Research Institute of Petroleum Industry (RIPI) also has developed a slurry hydro-cracking process, with a 90 to 95 % conversion. It recovers its catalyst and also can be used to convert a heavy, high-sulfur, low-price crude oil (Deg. API < 7 to 20) into a light, low-sulfur , high-price one (Deg. API < 30 to 35), with trace metals content.

Useful data and features of different upgrading methods are summarized in table 5.

4. Economic issues

A brief economic comparison between six residue conversion technologies is presented in figure 7. As is observed, HRH type processes are also economically favorable.

5. Discussion and results

The projected global demand of refined products shows an appropriate situation for the residue conversion processes construction, especially for hydro-processing ones (Fig.8).

It should be considered that in the figure 9, the relative share % of gasoline is declining in the total demand, not the absolute gasoline demand. The trend of global heavy oil hydro-processing and residue FCC capacity growth are shown in the figures 10,11.

There is a promising future for middle distillates and gasoline producing upgrading processes , specially for hydro-cracking .However , there is a stability limit for the high conversion region of the ebullated bed hydro-cracking process (Fig. 12) [10]. Likewise, due to the increasing natural gas prices , hydrogen production from residue , via gasification can be economical .With such a processing scheme , there is a balance point between the hydrogen consumption and production , which limits the residue conversion level (to e.g. 83 % - as in Fig.13) [11].

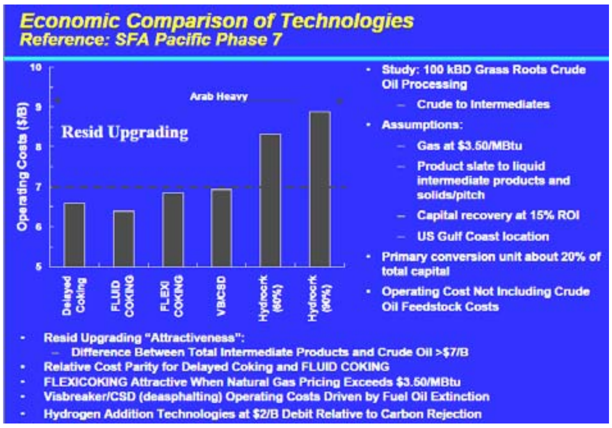

Fig.7 The economic comparison of conversion technologies [19]

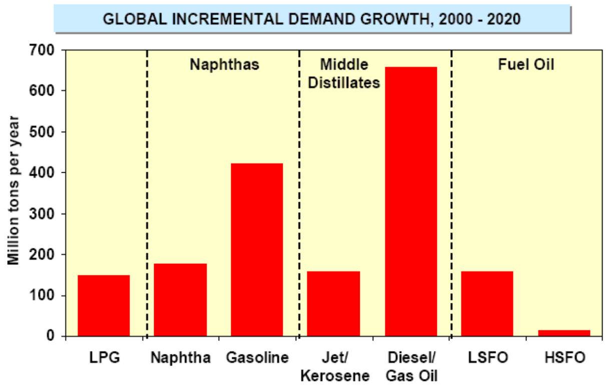

Fig. 8 Asia is the Primary Region for Demand Growth [16]

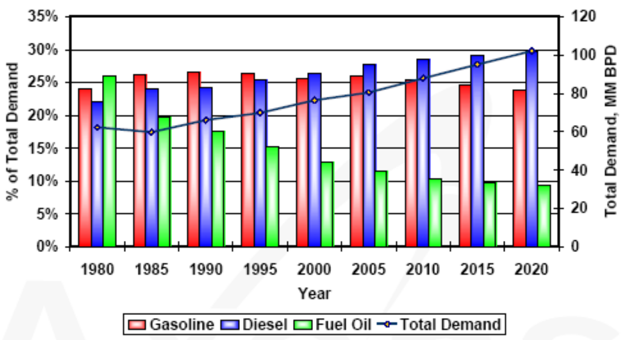

Fig. 9 Global Market Demand for Refining Products [10]

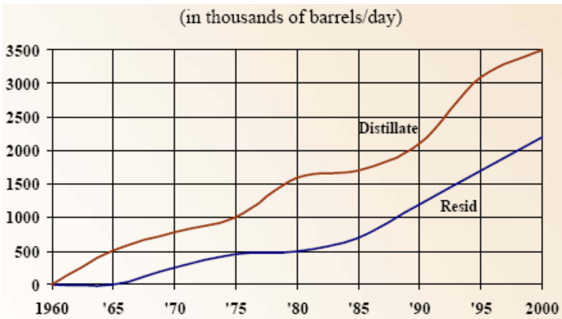

Fig.10 The trend of global heavy oil hydro-processing [17]

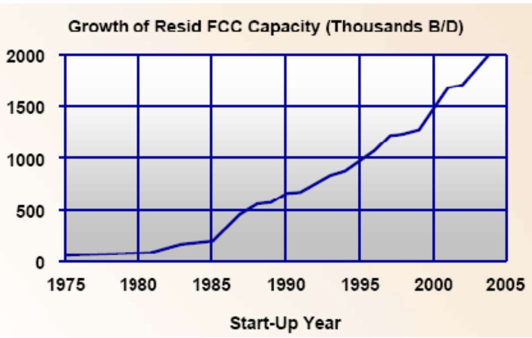

Fig.11 The worldwide residue FCC capacity growth [17]

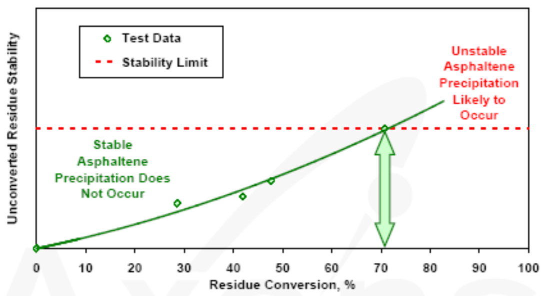

Fig.12 The stability limit for the ebullated bed hydro-cracking conversion level [10, 6]

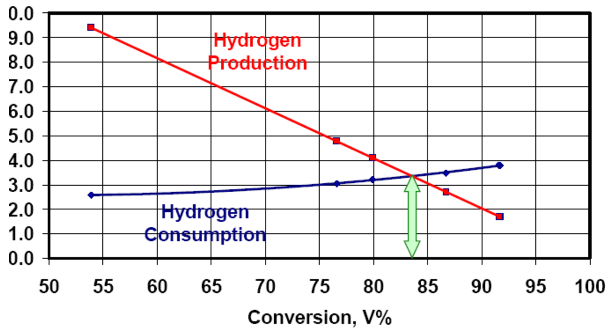

Fig. 13 Hydrogen Balance Point [6, 11]

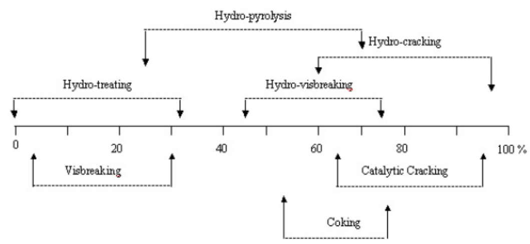

Fig. 14 Extent of feedstock conversion in various processes [18, 6]

Therefore, this promotes the slurry hydro-cracking processes.

From the feed conversion extent point of view, figure 14 shows the relative place of each residue upgrading scheme.

Considering the above various economic cases (albeit using their own assumptions and conditions), the following results can be realized:

- Delayed coking is a non-expensive (capital & operating costs), relatively high conversion process, and for refineries with coke export capabilities can be an interesting route However, the gradually tightening regulations for the environmental protection dictates progressively cleaner fuels, and the related costs may affect the economic feasibility of this process in the future.
- Integrated gasification and combined cycle (IGCC) is becoming cheaper and can be a good final solution for refining heavy residues .Besides all other benefits , it neatly destructs industrial, agricultural and municipal wastes and can be a very economical – yet clean – heavy residue upgrading method.
- Both RFCCU and hydro-cracking processes seem to have a promising future, but slurry hydro-crackers can be the best one in the coming decade .This should be considered by refineries which are to construct new hydro-cracking plants.
- Of course, RFCCU is a lower cost one .The main RFCCU product – which is gasoline – contains aromatics, olefins (and sometimes di-olefins), which produce Ozone in the vehicles exhaust gas. But, they cannot be neglected due to their high octane numbers, and as a practical solution, their concentrations in gasoline are specified and limited As an example, in California state of the United States, the standard olefin volume percent in motor gasoline was decreased from 9.5 % to 6% from 1995 on [12, 13, 14, 15].

On the other hand, the reduction of olefins in gasoline will increase its volatile organic compounds (VOC) pollution, mainly due to the aromatics increase necessity, to compensate for the high octane numbers of olefins.

In other words, there should be an environmentally safe blending constituent to substitute olefins .Such a valuable and useful compound is the branched paraffin (iso - paraffin) , which is mainly produced via the Alkylation or Light Naphtha Isomerization processes. Today, alkylation is done by sulfuric acid or solid boron triflourides catalysts. Also, by hydrogenation of dimerized (oligomerized) butylenes (producing iso- octene or polymer gasoline), iso -paraffin can be produced.

An interesting alternate for the FCCU or RFCCU plants product slates, is the ability of future shifting to polymer – grade olefins .This can economically be very interesting. Even in the gasoline producing units, propylene recovery is economical.

The naphtha isomerization process (as mentioned above) should also be considered and helps to maximize gasoline octane number in an environmental-friendly manner. The light straight-run Gasoline stream is this process feed.

Due to the low conversion of Visbreaking units and limited future market for fuel oil, it is appropriate to convert them into Delayed Coking or Hydro- Visbreaking plants.

Even the combination of the latter processes, would have a still better result, with a relatively low cost.

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Table 5 The comparison table of different upgrading methods

	Process	Type	Catalyst	General product	Feed/Product treating requirement	Conversion	Features
1	Delayed coking	Semi batch thermal cracking	no	Light gas, Naphtha, Light Gasoil, Heavy Gasoil	Feed demetalization, Product treatment: HDS, olefin/Aromatic Saturation	54-76%	• Low capital cost and feed flexibility • 33% of installed upgrading plants in the world • Industrial coke as byproduct
2	Fluid coking	Continuous thermal cracking	no	Light gas, Naphtha, Light Gasoil, Heavy Gasoil	Feed demetalization, Product treatment: HDS, olefin/Aromatic Saturation	54-76%	• Low capital cost and feed flexibility • 33% of installed upgrading plants in the world • Industrial coke as byproduct
3	Solvent De Asphalting (SDA)	Solvent	no	De asphalted oil	no	35-75%	• Complete asphaltenic separation
4	Visbreaker	Mild thermal cracking	no	Light gas, Naphtha, Gasoil	no	4-30%	• 26% of installed upgrading plants in the world • Fuel oil by-product
5	Hydro Visbreaker	Mild thermal cracking	no	Light gas, Naphtha, Gasoil	no	44-74%	• Lower coke formation • More stable products than visbreaker • Fuel oil by-product
6	High conversion Soaker Cracking (HSC)	Thermal cracking	no	Light gas, gasoline, middle distillate	Product HDS	30-60%	• Relative Simplicity • Low hydrogen consumption
7	Heavy Oil Cat cracking (HOC)	Catalytic cracking	Regenerable	Light gas, gasoline, light and heavy cycle oil	Feed Demetalization, Product treatment: HDS, olefin/Aromatic Saturation)		
8	Catalytic cracking (RFCC)	Catalytic cracking	Regenerable	Light gas, Diesel, gasoline, fuel oil	Feed or Product hydro treating , and Product treatment: olefin/Aromatic Saturation	63-95%	• 24% of installed upgrading plants in the world • Olefin as by-product • Capable to 12ppm metal tolerable catalyst, and 7% Conradson carbon tolerable
9	H-Oil	Catalytic in presence of Hydrogen	Regenerable	Light gas, Naphtha, Kerosene, diesel fuel, vacuum gasoil, fuel oil	Product amine treating		• High pressure process
10	L.C. Fining	Catalytic in presence of hydrogen	Regenerable	Light gas, Naphtha, Kerosene, diesel fuel, vacuum gasoil, fuel oil	Product amine treating		• High pressure process
11	HRH	Catalytic in presence of hydrogen	Regenerable	Light gas, Naphtha, Kerosene, diesel	Product amine treating	95%	• Low capital cost and feed flexibility • Complete elimination of heavy metals • Low pressure process • Catalyst recovery of more than 95 %