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INVESTIGATION ON EFFECTIVENESS PARAMETERS IN RESIDUE UPGRADING METHODS

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Abstract

In recent decade, the residue upgrading processes are developed for producing light cuts because the demand of heavy fuel oil is decreasing in world.
This paper presents the effectiveness parameters on heavy residue upgrading methods to select the optimum condition for various feedstock specifications.

Key words: Residue upgrading; 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 by heavy high-sulfur one (due to its scarcity), and the decreasing demand for heavy fuel oil , serious challenges have raised in the petroleum refining industry.

Therefore, it is currently developed ways to upgrade heavy oil or residue to light product to add value so that necessitates using processes for conversion of heavy high-sulfur refining residues into (mostly) lighter low-sulfur products , which are generally called as residue upgrading processes. The final product slate requirement, 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 International Energy Agency (IEA) has predicted 70% growth in worldwide demand for primary sources of energy by 2030. The IEA expects 88% of this increased demand to be met by oil, natural gas, and coal. While production from other renewable sources is expected to almost double, these sources will still meet only 2.5% of overall demand. Oil will consequently remain a dominant factor in energy through this century.

There has been an extended substitution program of petroleum-derived fuels by natural gas; therefore, the future refining schemes in some of refineries should be revised.

2. Upgrading processes

It‘s developed upgrading methods for conversion of low value-high sulfur heavy residue to clean-valuable light fuels as following.

2.1 Breaking heavy molecules into lighter ones (carbon rejection processes),

such methods 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. They have flexibility for feedstock specification like 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.

2.2. Adding hydrogen to light molecules (hydrogen addition technologies),

which are catalytically processes, hydrocracking and hydro-visbreaking is the examples of these processes. Their main feature is "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 [2]. Coking, solvent extraction, residue fluid catalytic cracking (RFCC), hydrocracking, advanced visbreaking, gasification and finally residue hydrocracking are the dominant residue conversion processes. Combinations of them are also becoming increasingly attractive for large volume applications. Some of the relevant processes are briefly reviewed [1-2].

2.2.1 Delayed coking

Delayed coking process completely converts the residues into gas oil, distillates, lighter hydrocarbons and coke. This process can handle residues of heaviest, contaminated crude oils, and has the lowest capital cost among high conversion processes; besides has suitable flexibility. Nowadays, about one-third of installed residue upgrading plants all over the world are by delayed coking. It is noteworthy to mention that some of the liquid fuels produced by delayed coking should be intensely hydrotreated, which have their own costs [3-5].

2.2.2 Solvent de-asphalting (SDA)

In this process a paraffinic solvent (C_3 , C_4 , C_5 or a mixture of them) is used to separate (physically) the vacuum residue feed, into a De- Asphalted Oil (DAO) (usually 35-75 vol.%) and a De-Oiled Asphalt (DOA). The first stream is a higher value product and is normally used as a hydrocracker feed, an FCCU feed or a lube oil blending agent .DOA is a low value asphalthene rich pitch stream ,and contains most of the contaminants (i.e., Conradson carbon) and can be used as a heavy fuel constituent , a delayed coking feed or a gasification feed [3-4].

Recently, another version of this process is developed (Critical Solvent De-asphalting), which uses critical state solvents for the best separation of lighter liquid products from all kinds of heavy residues (supercritical extraction), specially with coking or gasification for the elimination of SDA pitch [5].

This method has a considerable energy conservation. The integrated processing of delayed coking and solvent de-asphalting is also proposed [6]. Generally speaking, it is usually advised to select heavy residue which are as paraffinic as possible and with less contaminant (impurities).

2.2.3 Residue fluidized catalytic cracking (RFCC)

This process is a version of FCCU, which can handle heavy residue as its feed. Its products slate may be focused on: gasoline, gasoline/diesel, propylene or petrochemicals. Around 24% of the global residue upgrading capacity belongs to this process. It can accept feeds (Atmospheric Residue) with up to 7% Conradson carbon and about 12 ppm metal content (Ni+V) [2-4]. In other words, to some extents it is driven by sweet crude oil availability. Recently, some catalyst manufacturers have claimed to produce catalysts which can tolerate up to about 8500 ppm metal contents (Ni+V) and have better product slates [7].

2.2.4 Visbreaking

This is a mild thermal cracking process, in which the residue's viscosity is reduced and the residue is partially converted into lighter hydrocarbons and coke [1]. About 26 % of the global residue upgrading capacity is occupied by this process. There is also a version of this process called Deep Thermal Conversion, which produces a very heavy residue (bitumen blowing unit feed) and a lot of heavy to light liquid fuels, instead of fuel oil product of traditional visbreaking unit [8]. Recently, the conversion of Visbreaker units into delayed coking ones is also suggested. For a one million metric ton per year (approximately 23,000 barrels per day) visbreaker unit; 68 million $ installed cost (instead of 84 million $ for a grassroots one of similar capacity) was required to be converted into a coking unit. 60 % of the existing equipment was re-used. The incremental cost was 112 million$ and the simple payback period was very attractive (about seven months) [9]. Another non-catalytic version of visbreaking (called Hydro-visbreaking) exists, which is done under 100 to 260 bar hydrogen pressure and about 430°C temperature. Due to its lower coke formation and more stable products, higher conversions than straight visbreaking can be achieved.

2.2.5 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 in the production of ammonia, methanol and hydrogen. But 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 petroleum or coal derived pitches) can even contain agricultural residues, 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 our 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 their sulfur content, mainly due to the environmental regulations .In other words, by using IGCC, there is no need to 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-1 expresses this fact well:

Table 1 Air emissions (mg/Nm^3) [4]

	Typical IGCC	European Standards for conventional power station
SO_x	10	130
NO_x	30	150
Particulates	10	16

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. 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, dimethylether (DME), acetic acid, etc. -45% of cumulative global capacity], transportation fuels(via Fischer-Tropsch reaction- now 25% of global capacity) and even hydrogen [4]. Rarely, a feed with a price higher than 10 $/barrel is used for gasification.

2.2.6 Residue hydrocracking

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 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 asphalthenes, metals and minerals) under 30 % is usually suitable for it .The feed conversion is relatively high (50 to 75 %) [4-5].

From the reactor design point of view the following categories are usually observed:

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 [2, 4].

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. Due to the back mixing effect of ebullation desulfurisation and hydro-conversion are lower obtainable in the fixed-bed design. Nowadays, most commercial ebullated bed units operate in the 70 to 85 % desulfurisation and 50-70 % volume conversion of non-distillable (+538°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 [5]. 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 [3].

Novel technology, recently, for residues 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 hydrocracking. This route can have a very high feed conversion(more than 95 % with recycle) (Table 2).

Table 2 Performance of ebullated bed and slurry hydrocracking processes [11-12]

	HDS Performance	HDM Performance	HDN Performance	CCS Reduction %	Conversion%
Ebullated bed	60 - 95	70 - 98	N.A.	40 - 75	40- 92
Slurry HC	> 82	> 99	> 41	> 95	> 99

In other words, this process demonstrates feedstock flexibility, together with almost complete conversion.

Table 3 Product slate of slurry hydrocracking (wt. %) [11]

Gas ($HC+H_2S$)	Naphtha (C_5 - 170°C)	Gas Oil (170 - 350°C)	Vacuum Gas Oil (350 - 500°C)	DAO (+500°C)
9.9 - 15.1	4.9 - 14.0	26.9 - 39.1	23.3 - 34.9	8.5 - 24.4

Slurry hydrocracking vacuum gas oil and DAO products are suitable feedstocks for conventional FCCU and hydrocracker [11]. For obtaining maximum yield of transportation fuels, the hydrocracking /delayed coking scheme should be used [4].

3. Economic analysis

The fluctuation of crude oil and refinery products price is a key parameter in economic investigation of upgrading processes.

The crude oil price is increased more than 60 $ / barrel, therefore, it's very important to consider world demand and also new marketing for refined products.

However there is no unique for the residue upgrading and it should be considered all concepts for each case to select suitable upgrading method.

In below, it's presented some cases to describe various conditions:

Case I.

For a U.S. Gulf coast location with midyear 1998 construction, total fixed cost increases in the order: delayed coking **<** RFCC **<** residue hydrocracking. Plant profitability is a strong function of product values. Return on investment (ROI) for each of the three processes ranges from less than 10%/yr to 24%/yr based on midyear 1998 product and feedstock values (crude oil around $14/b). ROI's improve to the 30-38 %/yr for each process based on November 1999 values (crude oil about $25/b) [10].

Case II.

It's demonstrated a comparison of three carbon rejection processes in following example [4]. The capital cost of residue upgrading schemes based on gasification continues to decrease steadily. The capital cost of gasification for power generation Integrated Gasification Combined Cycle (IGCC), is now reported to be in the range of 850-950 $/kW, compared to 1500-2500 $/kW, about the period 1987-1992. Gasification application has an approximately 10% grow rate per year, based on the syngas production [4].

Plant 1 Delayed coking on an FCC-based refinery

In this plant, vacuum bottom is upgraded into transportation fuels (naphtha and middle distillates), FCCU feed gas oil and (fuel grade) coke.

Plant 2 Integrated gasification combined cycle (IGCC) on an FCC-based refinery

In this plant, vacuum residue and FCCU slurry are consumed for power generation (usually in the range of 987 to 1,836 MWe), without any appreciable amount of pollutants emission. Besides, there are many cases of petrochemicals, transportation fuels or hydrogen production in this option .It is noteworthy to remind that even in natural gas abundant areas, this process is a good choice.

Plant 3 RFCCU with atmospheric residue hydro-treatment

The entire atmospheric residue is hydro-treated and sent to an RFCCU (without any vacuum distillation). Hydro-treatment removes metal content (30-40 ppm wt maximum economic limit), reduces the products sulfur content and improves the RFCCU yield.

To obtain more transportation fuels rather than electricity, RFCCU or delayed coking should be used. The choice between the two depends on many site-specific factors. RFCCU has also the advantage of using unsaturated LPG's by Alkylation, MTBE or DIPE (Di-Isopropyl Ether) processes.

3.1.Capital investment and operating costs

In each plant, 220,000 Barrels per day has been taken .The crude oil price is assumed between 16 to 24 $ / barrel .The coke price is taken conservatively as Zero $/ton (by using the current trade price of 20 $/ton, the Delayed coking option IRR is improved by 3%).The analysis includes the primary residue upgrading plant, plus the plant required to refine its products (for example additional FCCU capacity). The power price is taken as 5 cents/ KW.

IGCC has the largest capital cost, $ 800 Million of which is due to the power generation train. The annual operating cost is also the highest ($ 150 Million). But the product revenue is also high (Table 4).

Table 4 - Three carbon rejection residue upgrading schemes [4]

	Delayed coking	IGCC	AR HDS / RFCCU
Capital cost ($ million)	485 - 623*	1,353 - 2,103*	703 - 705*
Operating cost ($ million per year)	40 - 50*	138 - 230*	91- 100*
Operating Cost ($ /barrel AR feed)	1.1	3.7 - 5.0*	2.4 - 2.7*
Product Revenue, ($ million per year)	861 - 932*	1,079 - 1,404*	987 -1,020*

* *Depending on the crude oil heaviness*

By the assumptions made , all the three above options have positive rates of return (IRR) between 7 to 20%(AR HDS has the higher IRR, then IGCC and delayed coking) .For cheaper , heavier crude slates , the delayed coking and IGCC become more economically attractive , and also more operationally flexible from the crude selection point of view .The IRR is very sensitive to the atmospheric residue price, and each 1$ / barrel change of its price can change IRR by 2% to 8%(for delayed coking). IRR values are pre-tax ones and do not include the owner's costs [4].

Case III.

There is another case study by a different reference [11], which compares four residue upgrading schemes (Table 5); obviously by its own assumptions.

Table 5 - Comparison of four Residue Upgrading Schemes [11]

Technology	NPV (Million US$ @10%/Yr)	IRR (%/Y)	NPV Ratio (@10%/Yr)
Gasification	-2	8.5	-0.10
Ebullated bed	-253	N.A.	-1.40
Delayed coking	-1	9.8	-0.01
Hydro-conversion	112	75.1	6.20

Case IV.

This reference [2] (Table 6) has the following assumptions:

- 100,000 barrels per day grass roots crude oil processing (Arabian Heavy) in each of the plants studied.
- 3.50 $ / M Btu gas price
- product slate to liquid intermediate products and solids / pitch
- capital recovery at 15 % ROI
- US Gulf Coast location
- primary conversion unit about 20 % of total capital
- operating cost not including crude oil feedstock costs

Table 6 - Comparison of some residue upgrading schemes [2]

Process	Operating Cost ($ / Barrel)
Delayed coking	6.6
Visbreaking/Critical solvent Deas-phalting	6.98
Hydrocracking, (60 % Conversion)	8.3
Hydrocracking, (90 % Conversion)	8.85

4. 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.1).

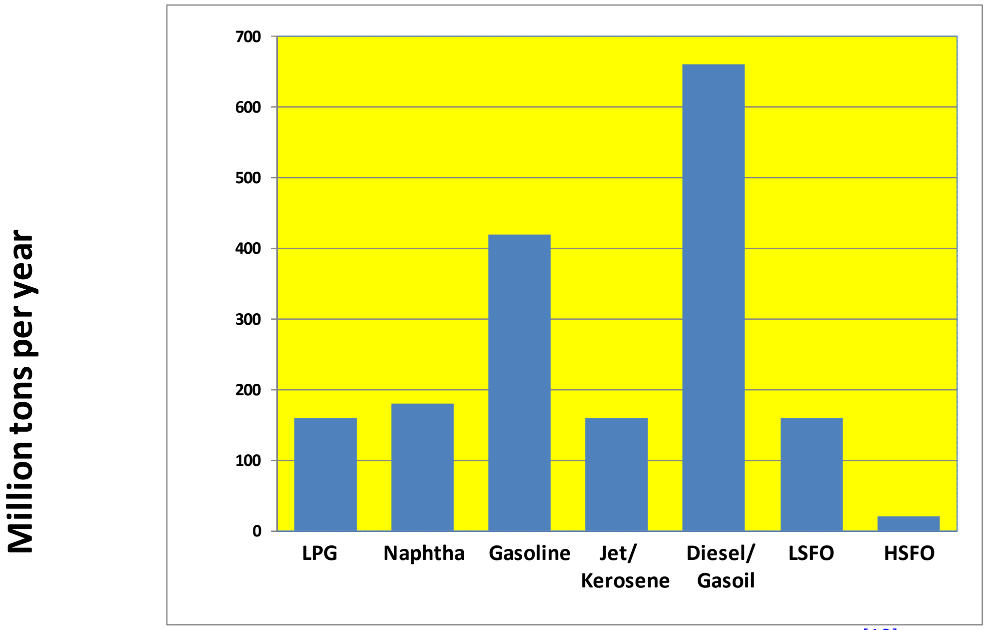

Figure 1 Global Incremental Demand Growth [13]

There is a promising future for middle distillates and gasoline producing upgrading processes. However, there is a stability limit for the high conversion region of the ebullated bed hydrocracking process (Fig. 2) [14]. 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.3). Therefore, this promotes the slurry hydrocracking processes.

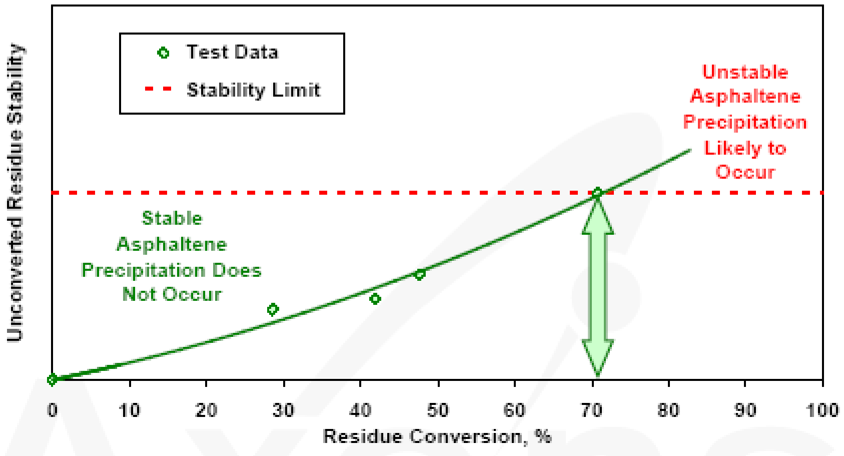

Figure 2 Stability Limit for ebullated bed hydrocracking conversion level [14]

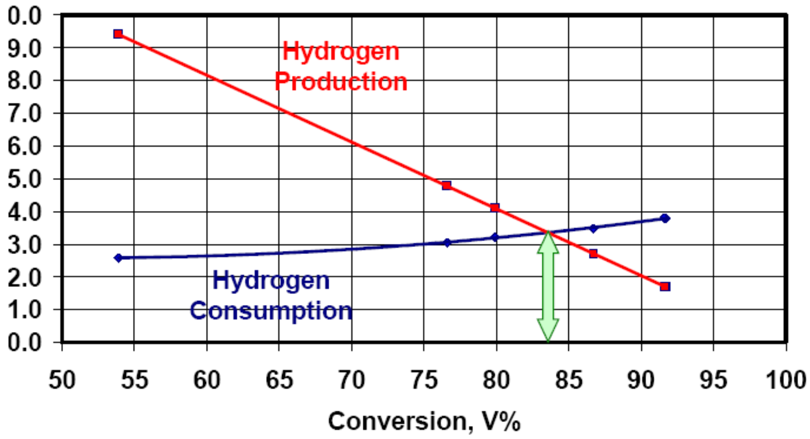

Figure 3 Hydrogen balance point [14]

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 be a very economical-yet clean-heavy residue upgrading method.
- Both RFCCU and hydrocracking processes seem to have a promising future, but slurry hydrocrackers can be the best one in the coming decade .This should be considered by refineries which are constructed new hydrocracking plants. Of course, RFCCU is a lower cost one .The main RFCCU product which is gasoline contains aromatics, olefins (and sometimes di-olefins), that produce ozone in the vehicles exhaust gas .But due to their high octane numbers, they cannot be neglected. Therefore, their concentration in gasoline is specified and limited .As an example, in California State of United States, the standard olefin volume percent in motor gasoline was decreased from 9.5 % to 6%. On the other hand, the reduction of olefins in gasoline will increase its Volatile Organic Compounds (VOC) pollution, (most probably) due to the aromatics increase necessity, to compensate for the high octane number 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) Isomerisation processes. Today, Alkylation is done by sulfuric acid or solid boron flourides catalysts. Also, hydrogenation of dimerized (oligomerized) butylenes (iso-octene or polymer gasoline) can be used.

- Visbreaking units
  - Due to the low conversion of this process and limited future market for fuel oil, it is appropriate to convert them into Delayed Coking or Hydro-Visbreaking plants.
  - Combining these latter two processes with the aforementioned ones, would have a still better result, with a relatively low cost.

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