# Improving Yield of High Added Value Derivative of Crude Oil: a review

**[1]Ashwini Thokal, [2]Kedar Salunkhe,**

**[1]Assistant Professor,[2]B.E. Chemical,**
**[1]Department of Chemical Engineering,**
**[1]Bharati Vidyapeeth College of Engineering, Navi Mumbai, Maharashtra, India.**

***Abstract :*** *Entrance gate of crude oil in refineries is crude oil distillation unit, that aims to separate crude into process streams under atmospheric crude oil distillation unit . Bottom stream still contains some recoverable products. This can be converted into high added value derivative. To avoid thermal cracking vacuum distillation column is used. High value of metal content and residual carbon concentration in feedstock leads to quickly deactivation of catalyst used and raise the operational cost. To avoid this add a withdraw line of stream in treatment of heavy or light gasoil. Which removes the metal content? And to improve the yield of highly added derivative of crude oil vacuum distillation normally directed to asphalt production or in refineries with high conversion capacity to bottom barrel conversion unit like delayed cocking and solvent desulphating , it gives high added value derivative.*

***Keywords: - Atmospheric crude distillation unit , vacuum distillation unit , carbon concentration , deactivation of catalyst , desulphating , high added value derivative.***

## I. INTRODUCTION

Rising demand of transportation fuels, petrochemicals and the ever-rising heavy residue of crude oil have resulted in a renewed interest in the processing of this heavy residue to generate useful lighter fuels and chemicals. Non-conventional feeds such as heavy oils have shown an alternate source for the production of high value transportation fuels, as it is abundantly available. These feeds are of low quality due to presence of impurities like ( carbon concentration in residue ) CCR, Asphaltenes, sulfur, nitrogen and heavy metals. Several process technologies have been developed to upgrade these feeds through fixed-bed, moving bed, ebullated-bed. Up gradation of residue or heavy oil by visbreaking, steam cracking, fluid catalytic cracking, and coking; solvent desulphating; hydrocracking; fixed bed catalytic hydroconversion, ebullated catalytic bed hydroconversion, Nanoparticles, Biological processing of heavy fractions. Heavy crude oils normally have a high Sulphur content and are usually very viscous. Heavy oil, or VR, is complex, black in color, highly dense, and extremely viscous in nature with API gravity between 10-20°. It is also high molecular weight, low hydrogen to carbon (H/C) ratio, highly viscous (at room temperature) materials. These materials contain impurities such as nickel, vanadium, iron, calcium, and silica, compounds of nitrogen, oxygen, and sulfur. Based on polarity difference, these materials can be classified into4 organic fractions like saturates, aromatics, resins, and asphaltenes Entrance gate of crude oil in refineries is crude oil distillation unit that aims to separate crude into process streams under atmospheric crude oil distillation unit . Bottom stream still contains some recoverable products. This can be converted into high added value derivative. To avoid thermal cracking vacuum distillation column is used. The heavy and light gasoil streams are normally directed to conversion units like hydrocracking or fluid catalytic cracking (FCC), according to the adopted refining scheme. High value of metal content and residual carbon concentration in feedstock leads to quickly deactivation of catalyst used and raise the operational cost. When the crude oil presents high metals content, it's possible to include a withdraw of fraction heavier than the heavy gasoil called residual gasoil or slop cut, this additional cut concentrates the metals in this stream and reduce the residual carbon in the heavy gasoil, minimizing the deactivation process of the conversion processes catalysts as aforementioned. This removes the metal content.

## II. DESCRIPTION

### A. Most commonly used crude oil processing methods:

1) Carbon rejection process- visbreaking, steam cracking, fluid catalytic cracking, and coking.
2) Separation processes: solvent deasphalting
3) Hydrogen addition processes: hydrocracking, fixed bed catalytic hydroconversion, ebullated catalytic bed hydroconversion, hydrovisbreaking, hydropyrolysis.

### B. Different residue upgrading processes:

**1) Desulfurization of heavy crude oil by microwave irradiation:**

Desulphurization process of Arabian heavy sour crude oil was studied by a novel method of microwave irradiation. The heat transfer characteristics of various mineral additives were studied for use as microwavesensitizers. Crude oil samples containing various combinations of hydrogen donor additives, catalysts, and microwave sensitizers were studied. The samples were exposed to different irradiation periods at different power levels in a modified domestic microwave oven. The results indicate that crude oil microwave absorption characteristics can be improved fourfold with charcoal and doubled with polar solvents, but they showed negligible change with serpentine, due to poor heat transfer properties. The sulfur content of the original crude oil was reduced by 2.3% with $H_2$ at 20 atmosphere pressure and 5 minutes irradiation period; and by 33.8% with ethanolamine as the hydrogen donor and 25 minutes irradiation period. For the crude oil fractions, the sulfur reductions were up to 48% and 10% for lighter and heavier fractions respectively [3].

**2) Heavy crude oil upgrading using homogeneous Nano catalyst:**

This research is related to the preparation of heavy crude oil upgrading homogenous nano catalyst. The present research is directed to reduce the operational temperature of catalytic hydrocracking of heavy crude oil and also to increase the yield of process by utilizing the lower concentration of the synthesized nano catalyst. successfully prepared kerosene from heavy crude oil during a hydrocracking reaction in the presence of the as-prepared oil soluble homogenous nano catalyst. In this reaction, liquid product yield is more and the reaction temperature is less than the other previous similar researches. Firstly, $MoO_3$ nanoparticles with average particle size about 50 nm were prepared with spray pyrolysis method. Secondly, the as-prepared $MoO_3$ nanoparticles were converted to the $MoS_2$ nanoparticles with average particle size about 70 nm via gas-phase reaction in the presence of $H_2/N_2$ as reducing gas and $H_2S$ as sulfidizing gas at high temperature. In the third step, the exfoliated $MoS_2$ nano catalyst was prepared by reaction of the $MoS_2$ nanoparticles with n-buthyl Lithium/n-Hexane under $N_2$-atmosphere and washing with water, 2-Propanol and Decaline, respectively. In the forth step, the hydrocracking reaction and upgrading of Soroush heavy crude oil was performed at different temperatures, $H_2$ gas pressures and nano catalyst amounts and optimum amount for each parameter was obtained.

**Experimental process :**

a) Preparation of $MoO_3$ nanoparticles:

Typically 1.6 g ammonium hepta molybdate was dissolved in 100 ml distilled water. 2.6 g Sorbitol was added as fuel additive. The solution was sprayed to the vertical tubular furnace at 600° C by using air as carrier gas.

b) Preparation of $MoS_2$ nanoparticles:

Gas phase reaction was performed by using the as-prepared $MoO_3$ nanoparticles as precursor in the presence of H2/He as reducing gas and $H_2S$ as sulfurizing gas at 800° C for 2 h in the horizontal tubular furnace.

c) Preparation of oil soluble homogenous nano catalyst: The as-prepared $MoS_2$ nanoparticles were exfoliated with n-buthyl lithium/n-Hexane under $N_2$-atmosphere. The product was washed with water, 2-propanol and Decaline (decahydronaphthalene), respectively.

d) Hydrocracking reaction for upgrading of heavy crude oil:

The suitable amount of the as-prepared exfoliated $MoS_2$ homogenous nano catalyst was added to about 100 g of Soroush heavy crude oil at 70–80° C with vigorous mechanical mixing. prepared mixture pressurized with $H_2$ gas; then, it was heated at a rate of 5° C/min to the desired reaction temperature. The hydrocracking reaction was performed in different temperatures, hydrogen gas pressures and nano catalyst amounts.[7]

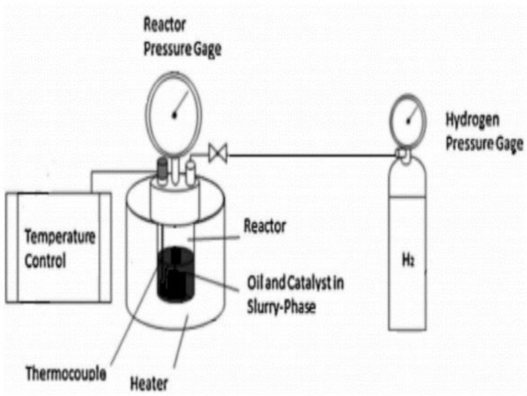


**Fig1.** Slurry-phase reactor used in this research for hydrocracking reaction

**3) Biological processing of heavy oil:**

Biological processing of heavy crudes may provide an eco-friendly alternative or complementary process with less severe process conditions and higher selectivity to specific reactions to upgrade heavy crude oil. it is proposed that the microorganisms capable to biodegrade heavy fractions of VR, could present an applicable opportunity for 18 upgrading heavy crude oils Bactria able to biodegrade various components of petroleum hydrocarbons such as poly-nuclear aromatic hydrocarbons (PAHs), like anthracite, monoaromatic hydrocarbons such as toluene, or aliphatic hydrocarbons such as n-alkanes, are widely reported, particularly from petroleum-contaminated sites. The microbial decontamination of petroleum-polluted soils seems to be an efficient, economic, and versatile alternative to physicochemical treatments. Several abiotic and biotic parameters including the conditions for microbial degradation activity (e.g., presence of nutrients,oxygen, pH, and temperature), the quality, quantity, and bioavailability of the contaminants (e.g., particle size distribution), and the soil characteristics, which are hardly to be controlled in the in situ condition, affect the rate of microbial degradation of hydrocarbons in soils. Therefore the bacteria with high physicochemical endurance and degradation ability could be a proper choice not only in bioremediation but also in other aspects of oil industry, like heavy oil bio-upgrading or microbial enhanced oil recovery.[1]

**4) Residue upgradation by nanoparticle :**

Nanotechnology has emerged as an alternative technology for in-situ heavy oil upgrading and recovery enhancement. Nanoparticle catalysts (Nano catalysts) are one of the important examples on nanotechnology applications. Nan catalysts portray unique catalytic andsorption properties due to their exceptionally high surface area-to-volume ratio and active surface sites. In-situ catalytic conversion or upgrading of heavy oil with the aid of multimetallic nano catalysts is a promising cost effective and environmentally friendly technology for production of high quality oils that meet pipeline and refinery specifications. Further, nanoparticles could be employed as inhibitors for preventing or delaying asphalting precipitation and subsequently enhance oil recovery.[1]

**5) Heavy crude oil upgrading using nanoparticles by applying electromagnetic technique:**

Nanoparticle catalysts (nanoparticles) are among the new technologies that are being used today in upgrading and even increasing production from heavy oil reservoirs, focusing on viscosity reduction and wettability alteration. The use of microwave (MW) technology in the process of upgrading heavy and extra heavy oil is one of the new processes that are being considered. As the heating rate in terms of time can be very important in the conventional upgrade process.

**Experimental process :**

150 g of the Azadegan oil sample from an oilfield in Southwest Iran was exposed to MW radiation under the Fischer Assay apparatus. A schematic of the Fischer Assay extended to microwave radiation can be seen in MW heating was carried out at 2450 MHz frequency and 600 W power. First, all parts of the device were filled with helium gas so that the heating was carried out without the presence of oxygen and other gases. The oil sample, with 4 wt% of nanoparticle, was heated inside the Fischer Assay at time intervals of 2, 4, 6, 8 and 10 min. The gas extracted by heating the sample of oil was stored inside the gas meter. The output condensate from the oil sample was collected by heating after cooling by a condenser inside the receiving flask. The condenser used cold-water flow for cooling. The heated oil sample was cooled for 1 day at the ambient temperature to reach stability. Because intervals of 2 min were selected, there was no significant change between the steps in the 1-min intervals. The heating interval was chosen to extend up to 10 min because the variations were almost constant after that time. After the MW radiation, the oil sample and the nanoparticles were centrifuged for 20 min at 6000 rpm to remove the upgraded oil from the nanoparticles.[8]

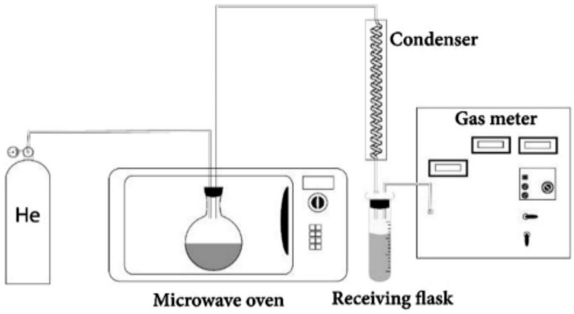


**Fig2.** Schematic of microwave Fischer oven.

**6) Upgrading and visbreaking of super heavy oil by catalytic aqua-thermolysis with aromatic sulphonic copper :**

To upgrade and visbreak a kind of super-heavy oil, a new type of catalyst aromatic sulfonic copper is synthesized to process it. The experimental results show that, using 0.2 wt.% catalyst and 25.0 wt.% water at 280 °C for 24 h, the viscosity of oil sample could be decreased by 95.5%, with 13.72% in the conversion of heavy content to light content. Synthesis and characterisation of catalyst: During the synthesis, 0.025 mol copper (II) sulfate was dissolved in 30 mL of distilled water and stirred for 5 min to form a clear blue solution. Then 1.0 mol/L NaOH aqueous solution was added dropwise under stirring until the pH value of the mixture was adjusted to about 7, and formed a pale blue slurry. Besides, 0.100 mol aromatic sulfonic acid was placed in a beaker and placed in 100 °C oil-bath for 30 min to preheat the acid. Then the pale blue slurry was added into the beaker under stirring, and heated subsequently at 100 °C for 2 h, then air cooled to room temperature. Lastly, the pale blue gelatin (aromatic sulfonic copper) was collected and dried in vacuum at 60 °C for 24 h, and characterized by Fourier transform infrared spectroscopy (FT-IR, Nicolet 5700). The synthesis experiments were repeated 6 times, and all of the productivities are more than 80%.[9]

## III. CONCLUSION

From the above review we can conclude that we have studied six different residue upgrading methods.

Each method gives us different alternatives for treatment crude oil residue in order to increase it's efficiency.

1. From the microwave irradiation technique we observe that the sulfur contents of the light distillates were reduced to 39% and 48%, while those of heavy distillates were reduced to 0.9% and 10%. The results showed approximately 50% desulphurization can be achieved in the lighter fractions.
2. From the Heavy crude oil upgradation using homogeneous Nano catalyst we observe Optimum condition is T= 350$^o$ C, P = 80 bar, Nano catalyst amount = 200 ppm. reaction temperature and liquid product yield are 350$^o$ C and 80%, respectively. reaction temperature is lower and the reaction yield is higher than the similar previous researches.

3. The selected bacterium was able to grow in a wide range of pH from 5.5 to 8, salinity up to 3% and temperature from 20°C to 55°C. The ability of this bacterium to acquire all its energy and chemical requirements from Vacuum Distillation Residue (VR), as a net sample of problematic hydrocarbons in refineries, was studied. SARA test ASTM D4124-01 revealed 65.5% decrease in asphaltenic, 22.1% in aliphatics and 30.3% in Aromatics content of the VR.
4. Residue upgradation bynanoparticle, we see that nanoparticles could be employed as inhibitors for preventing or delaying asphalting precipitation and subsequently enhance oil recovery.
5. By applying electromagnetic technique the production of heavy oil can be increased.
6. From the aqua thermolysis method we use 0.2 wt.% catalyst at 280 °C for 24 h, the experimental results show that the viscosity of heavy oil could be decreased by 95.5%, with 13.72% in the conversion of heavy content to light content.

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