International Journal of Advanced Technology in Engineering and Science www.ijates.com

Volume No.03, Special Issue No. 02, February 2015 ISSN (online): 2348 – 7550

PROCESS FOR THE UPGRADATION OF PETROLEUM RESIDUE: REVIEW

Rajesh K Gupta[1], Poonam Gera[2]

[1]*Chemical Engineering, Dr. B.R Ambedkar National Institute of Technology, Jalandhar (India)*

[2] *Associate Professor, Chemical Engineering, Dr. B.R Ambedkar National Institute of Technology, Jalandhar (India)*

ABSTRACT

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 VR and 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 CCR, Asphaltenes, sulfur, nitrogen and heavy metals. Several process technologies have been developed to upgrade these feeds through fixed-bed, moving-bed, ebullated-bed,

This paper highlights the up gradation of residue or heavy oil by visbreaking, steam cracking, fluid catalytic cracking, and coking; solvent deasphalting; hydrocracking; fixed bed catalytic ;hydroconversion;ebullated catalytic bed hydroconversion,;Nanoparticles;Biological processing of heavy fractions

Keywords: Hydrocracking, Residue, Deasphalting, Nanoparticles, Fixed Bed Catalytic

I. INTRODUCTION

World-wide fuels and petrochemicals are synthesized from coal, petroleum oil and natural gases. According to the United StatesEnergy Information Administration (EIA), total oil demand in the world is expected to growup to 123 mmbpd (million barrels per day) by 2025. In addition, the organization of petroleum exporting countries (OPEC) has estimated that production will be approximately 61 mmbpd by 2025, which is less than half of the demand.

At the same time, non-OPEC countriesare also expecting a steady increase in petroleum oil production (62 mmbpd) by 2025 [1].

As a result of this, refiners are getting burdened with heavy residues that are subsequently obtained by processing heavy crudes. Heavy crudes (≤20 ºAPI) yield large amount of residual fractions such as atmospheric residue (AR, initial boiling point, IBP > 343ºC) and vacuum residue (VR, IBP > 500ºC) as shown in Fig 1.

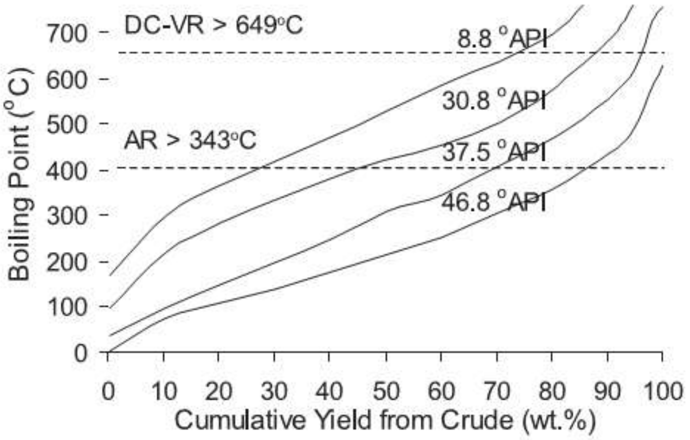


Figure 1. TBP curves for feeds with different API gravity (Boduszynski, 2002)

II. NECESSITY OF RESIDUE UPGRADING

Due to rapid population growth, the consumption of fuels, energy and petrochemical products has increased tremendously and due to this the reserves of conventional (light) crude oil are depleting and there is a gradual but sure decline in crude oil quality. Therefore, there is a dire need to fully utilize the ever-rising heavy residue of crude oil and the limited petroleum resources (Schulman et al., 1993; Bansal et al., 1994; Shen et al., 1998) .Consequently, interest is focused on diverting the crude's residual fraction from its traditional use as a heavy fuel component to processes that either convert the residue into high-value products.

Indian refiners are equally concerned about upgrading the available crude oil for refining, along with other international refiners in the area of residue upgrading, to get more light distillates required for transport fuels and also to provide the needs for the other concerned industries using petroleum products such as fertilizer and petrochemicals. The basic reason for giving extra attention to residue upgrading is that India has less options than to import crude oil with maximum percentage of residues (Sarkar, 1998).

The goals for upgradation of heavy oils and VR are to decrease viscosity and boiling point, demetallation, desulfurization, level of other impurities and increase H/C ratio with high commercial values. A number of catalysts synthesis process and technologies have been developed to upgrade heavy oils, waste materials and VR. Among all technologies for the conversion of heavy oils and VR, slurry-phase hydrocracking is the most considerable as it is applicable to upgrade high impurities feeds.

III. SOURCES OF PETROLEUM VACUUM RESIDUE AND HEAVY OIL

Heavy oils, extra-heavy oils and bitumens are found all over the world. The International Energy Agency (IEA) estimated that approximately 6 trillion ($6x10^{12}$) barrels (bbl) of heavy oils are available worldwide: $2.5x10^{12}$bbl are in Western Canada, $1.5x10^{12}$bbl are in Venezuela, $1x10^{12}$bbl are in Russia, 0.1-$0.18x10^{12}$bbl are in the United States (USA) and rest of the mass is located in other countries. The largest heavy oil reservoirs in the world are located at the north of the Orinoco River in Venezuela. Heavy oils are also located in various countries and are being produced in India, Colombia, Indonesia, China, Mexico, Brazil, Trinidad, Argentina, Eastern Europe, Ecuador, Egypt, Saudi Arabia, Oman, Kuwait, Turkey, Australia, Nigeria, Angola, the North Sea, Rumania, Iran, and Italy [2, 3].

Most of these resources are currently untapped due to high viscosity [3]. The price of heavy oil varies according to API (American petroleum institute) gravity, as shown in Fig. 2. This figure compares values that were reported in 2002 with those from 2006 [4].

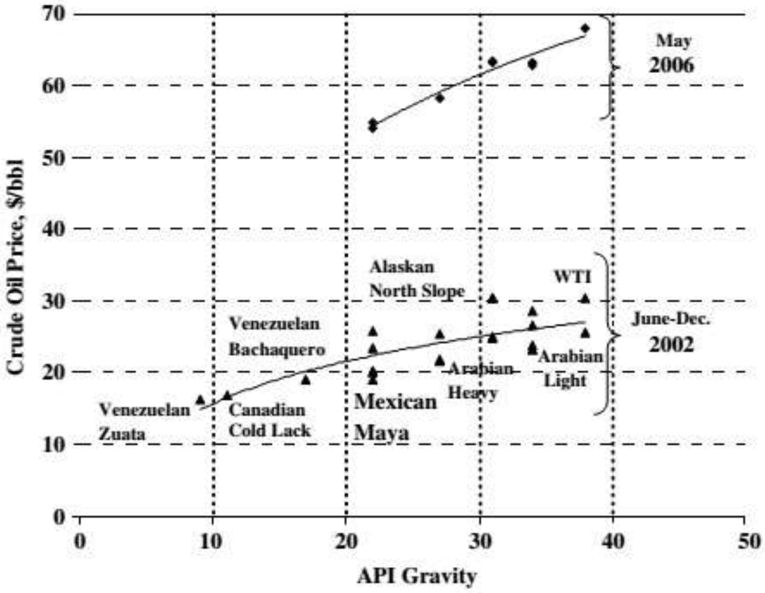


Fig.2 Relationship between Crude Oil Price and API Gravity

About 4100 million metric tons per annum (MMTPA) world-wide petroleum refiningcapacity has reached. In petroleum refining industries, two types of residues are generated. Atmospheric residues (AR,>343°C) are generated atthe bottom of an atmospheric distillation unit. AR is again treated in vacuum distillation tower. Heaviest fractions obtained at the bottom part of the vacuum distillation column tower at 0.003-0.01 MPa are called vacuum residues (VR).

Process	U. S. A.	Japan	Europe	Rest of world	Total
Thermal					
a. Cracking/Visbreaking	6.5	1	108.5	82.5	198.5
b. Coking	93	3	31.5	61	188.5
Deasphalting	13	1	0.5	5	19.5
Hydroprocessing	30.5	30.25	9	49.75	119.5
Resid FCC	31.5	12.5	10.5	37	91.5
Total	**174.5**	**47.75**	**160**	**235.25**	**617.5**

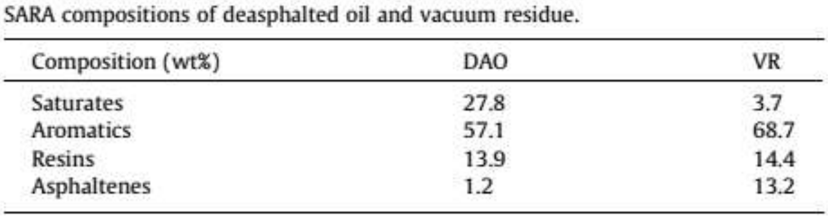
Table 1.World Residue Processing Capacity, MMTPA (Shen Et Al., 1998)

According to the report from 1998, approximately 617.5 million metric tons (MMT) of petroleum residues were upgraded or converted in various processes worldwide, as shown in Table 1. Currently, approximately 725 MMTpetroleum residues are processed through various conversion processes. Conversion of residues or heavy oil has always been aimed to refiners to obtain value-added products [5]

IV. CHARACTERISTICS OF VACUUM RESIDUE AND HEAVY OIL

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 likesaturates, aromatics, resins, and asphaltenes [6-11] are shown in Table 2.

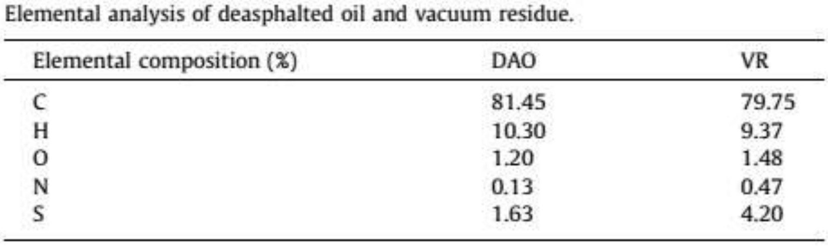
Percentages of impurities (heavy metals, nitrogen, sulfur, etc.). The properties of VR are varied according to origin (place) and synthetic route. VR can be converted into lighter oil or more value-added products using bottom of the barrel conversion processes or residue upgrading processes elemental analysis, feed compositions of various fractions and ICP analysis are provided in Table 3.



SARA compositions of deasphalted oil and vacuum residue.

Composition (wt%)	DAO	VR
Saturates	27.8	3.7
Aromatics	57.1	68.7
Resins	13.9	14.4
Asphaltenes	1.2	13.2

Table.2



Elemental analysis of deasphalted oil and vacuum residue.

Elemental composition (%)	DAO	VR
C	81.45	79.75
H	10.30	9.37
O	1.20	1.48
N	0.13	0.47
S	1.63	4.20

Table.3

Asphaltene fractions are in various color (from brown to black), non-volatile, amorphous substances which exist as colloids inthe VR or heavy oils. The asphaltenes are composed of nitrogen, oxygen, sulfur, vanadium and nickel compounds. These compounds contain a stack or cluster of naphthenic and aromatic molecules, fused ring aromatic molecules, small aliphatic side chains and polar functional groups (Fig. 3) Asphaltenes are insoluble in n-alkanes such as n-pentane and n-heptane, but soluble in benzene or toluene [12].

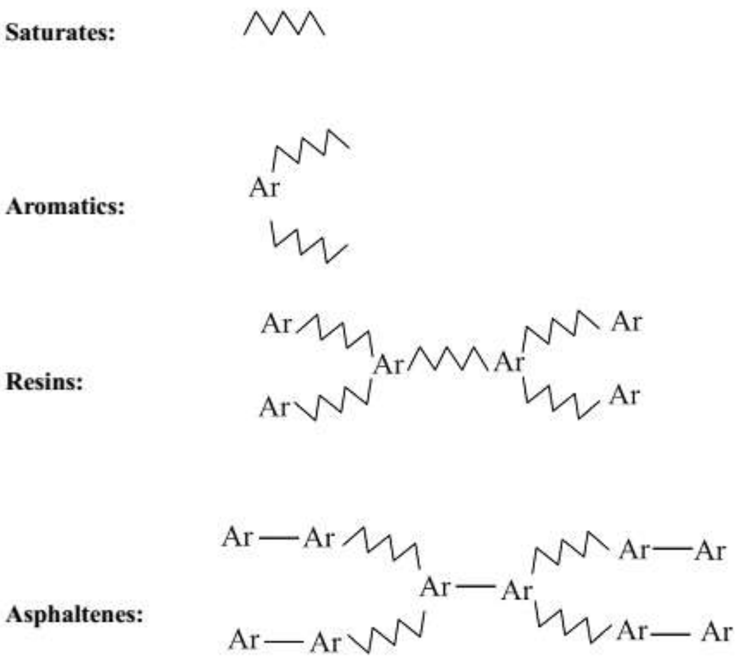


Fig. 3 Major Structural Components of the Vacuum Residue [12]

VR and heavy oils are poor in quality due to presence of asphaltenes, heavy metals and hydrocarbon, and heteroatoms [13]. Asphaltenes and resins are significant fractions in above feeds. Therefore, these feeds must be upgraded before used as fuels or chemicals.

V. DIFFERENT RESIDUE UPGRADING PROCESSES

Technologies for upgrading heavy feedstocks such as heavy oil, bitumen and residua can be broadly divided into carbon rejection and hydrogen addition processes. Carbon rejection redistributes hydrogen among the various components, resulting in fractions with increased H/C atomic ratios and fractions with lower H/C atomic ratios. On the other hand, hydrogen addition processes involve the reaction of heavy feedstock with an external source of hydrogen, which results in an overall increase in H/C ratio. Within these broad ranges, all upgrading technologies can be subdivided as follows:

1. Carbon rejection processes: 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,
4. Nanoparticles
5. Biological processing of heavy fractions.

Since 1913 carbon rejection process is used in the petroleum refining industries. In this process, the feeds (larger molecule) are heated under inert atmospheric pressure to fracture them into smaller molecules. Internal hydrogen attached to carbon molecule is redistributed among the various components such that some fractions increase their H/C atomic ratios while others decreased their H/C atomic ratios. In this processes induced carbon coke is formed. Conversely, during hydrogen addition processes, the H/C ratio of the feedstock is increased using an external hydrogen source in presence of suitable catalysts.

5.1 Carbon Rejection Processes

Thermal processes (carbon rejection) are animportant for the conversion of VR or heavy oils [14]. Generally, thermal cracking is carried out at moderatepressure; the hydrogen is transferred from larger to lighter molecules, resulting carbon orcoke. In this processes, the C/H ratio is decreased.

In gasification, feeds are heated at high temperatures (>1000ºC) in absence of air. Therefore, heated feeds are converted into major products such as gas, carbon black and ash [15, 16]. Gasification and its combination technologies are alternative efficient processes for power generation and other sectors [17, 18]. Poor selectivity and difficulty in product separation make the gasification processes is less popular than other processes.

Delayed coking has been chosen by many refiners for VR up gradation because the chemical composition of feeds can be varied. During this process, the partial conversion of a liquid product results in completely metal and carbon free products[19-21]. The product selectivity depends on the experimental conditions (temperature, pressure and reaction time). Large amounts of coke formation and low yields of liquid product make this process more expensive. Even considering these disadvantages, delayed coking is still frequently used for refiners.

Fluid coking and flexicoking are other thermal processes. In these processes coke carries heat from the burner to the reactor while serving as a reaction site for the conversion of VR into various products. The residence time of the liquid reactant in the reactor determines the coke and product formation [22]. The operating conditions and costs of thermal processes are shown in Table 4 and in Fig. 5, respectively.

Visbreaking is the oldest, cost effective option for residual up gradation. Generally, 7 wt% gas and gasoline like product is observed [23]. However, during this process, asphaltene content does not vary in the product. Therefore, stable fuel oil is obtained. This process is suitable in those areas which demanded relativelylow motor fuel. If the motor fuel demand increases in these areas and there are no other refiners, delayed coking is used [24]

A major portion (approximately 63 wt. %) of petroleum residues are up graded by thermal processes such as visbreaking and delayed coking. Depending on up grading condition and feedstock composition, various products like naphthas, middle distillates, vacuum gas oils and coke are formed. Recently, significant number of thermal cracking projects is involved to convert VR.

Thermal processing technologies[a]

Residue technology	Licenser	Operating conditions	
		Temperature (°C)	Pressure (MPa)
Delayed coking	ABB LUMMUS FOSTER Wheeler/ UOP ConocoPhillips	480–515	0.61
Visbreaking	ABB Lummus Global	450–510	0.34–2.0
Fluid coking	ExxonMobil	480–565	0.07
Flexicoking	Conoco-phillips Halliburton KBR	830–1000	
Gasification	Chevron Texaco	>1000	–

[a] Several literature based data.

Table 4 Thermal Processing Technologies and Reaction Conditions

Thermal processes and technologies based on coking have disadvantages of producing a large amount of low value by-products that required further processing. The integrated processes are expensive and time consuming. Therefore, the thermal processes are less important than catalytic upgrading processes of VR.

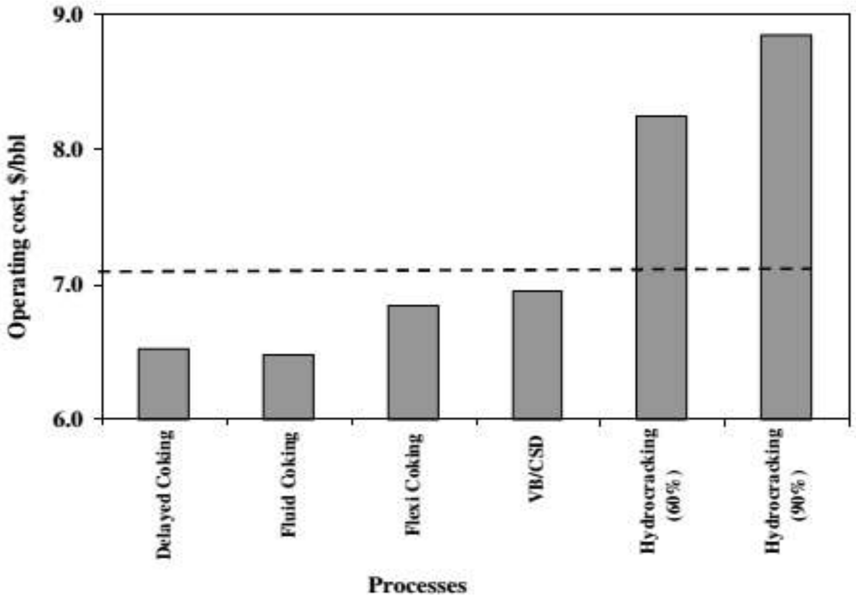


Fig. 5 Operating Costs for Various Processes

Residue fluidized catalytic cracking (RFCC) is an extension of fluidized catalytic cracking (FCC) which was developed in early1980. This method requires a vapor phase for the catalytic cracking reaction that exhibits better selectivity for gasoline and low gas yields than thermal processes. Residues (VR & AR) have high boiling point as well as high content of impurities (metals and heteroatom) which makes the feeds difficult to vaporize. At the end of the reaction, metal and coke deposits on the catalyst surface, as a result catalyst gets deactivate. To process these feedstock's, it must contain relatively low amounts of metal, sulfur, and asphaltenes, or required good quality feedstocks. Therefore, the usefulness of RFCC is limited in industrial applications [25].

5.2 Separation Processes: Solvent Deasphalting

Solvent de-asphalting and thermal (gasification, delayed coking, fluid coking, flexi coking and visbreaking) processes are non-catalytic while residue fluid catalytic cracking (RFCC) and hydro processing (fixed-bed hydro treating and hydrocracking, slurry-phase hydrocracking, ebullated-bed hydro treating and hydrocracking) are catalytic. Fig.4 illustrates the worldwide distribution of residue conversion technologies.

Solvent de-asphalting involves physical separation (metals and asphaltenes) of constituents in the feed according to their molecular weight instead of their boiling point [26-28]. The feeds are mixed with light paraffinic solvents such as propane, butane, n-pentane and n-heptane. Asphalting and other impurities are insoluble in the paraffinic oil. The insoluble portion is separated from the mixture. High energy costs, low demand for motor fuel and the limited uses of de-asphalted products are the limitations of this process. However, interest in de-asphalting is increasing. Solvent de-asphalting processes may be sufficient for residue upgrading [24]

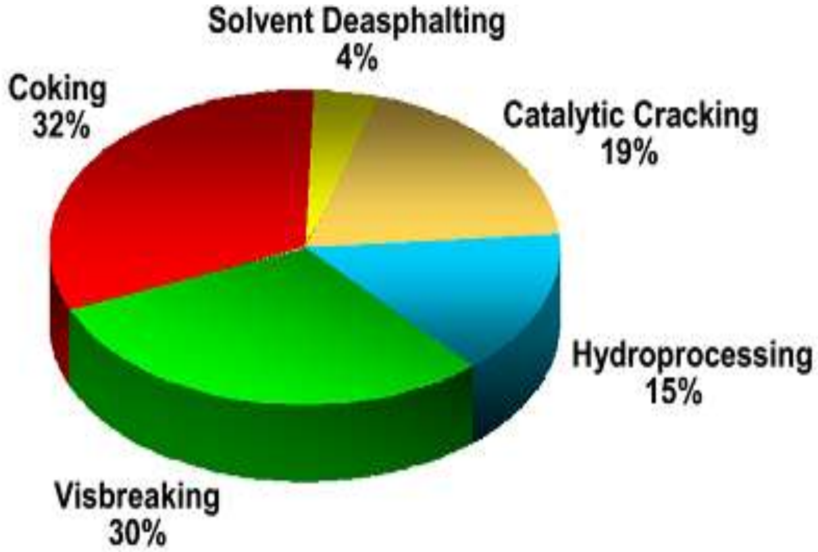
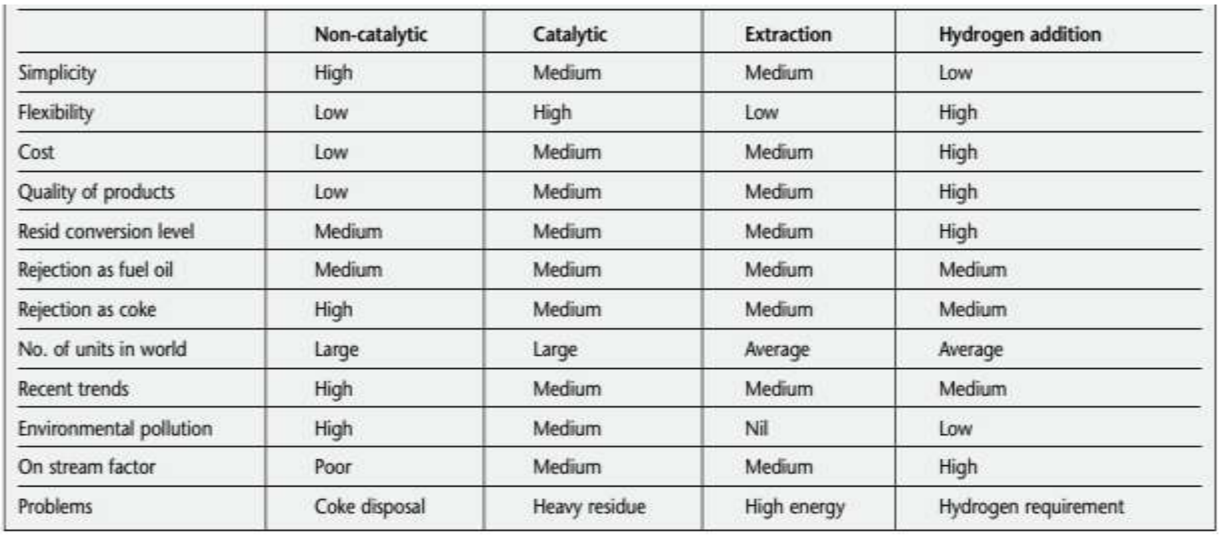


Fig. 4 Historical Worldwide Residue Conversion Selection [24]

5.3 Hydrocracking Technology

During the past three decades, hydrocracking has gained prominence in light petroleum refinery processes [29, 30]. After full industrialization of light petroleum oil hydrocracking processes are gradually applied for heavy oil and VR up gradation [31, 32]. Various hydrocracking reactor technologies suchas fixed-bed, ebullated-bed, moving-bed or slurry-phase reactors are used to upgrade heavy residues [33].

The principles of these reactor operations are almost same butdiffering with respect to some technical minutiae and tolerance of impurities [34]. InTable 5 outlines the comparison of different processes. As can be seen from Table 5, the non-catalytic carbon rejection processes score higher than other processes in simplicity and operating costs and hence have large numbers of units in the world.’]’’ In table 6 processes and their licensers are offered.



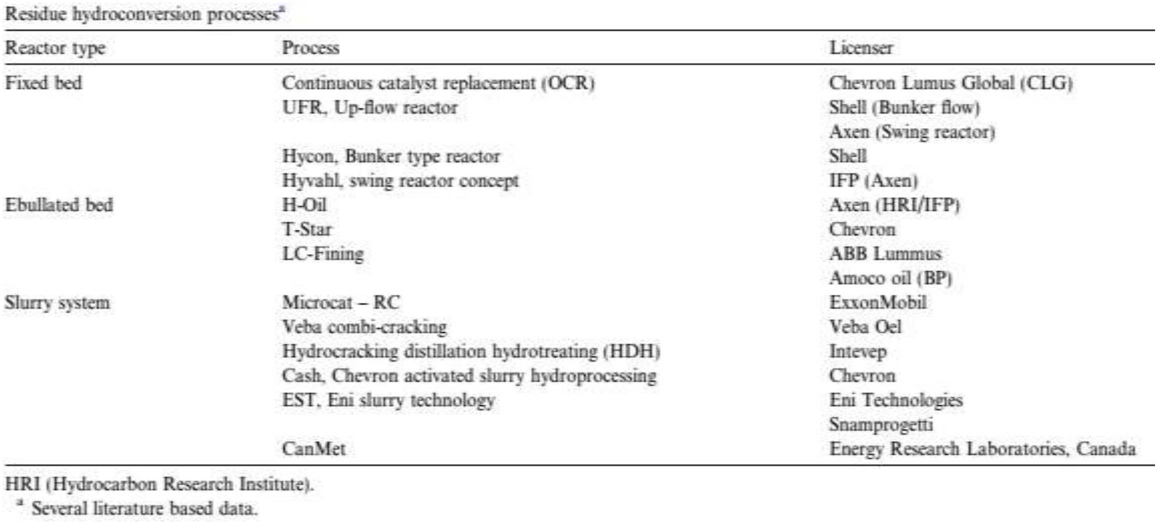
	Non-catalytic	Catalytic	Extraction	Hydrogen addition
Simplicity	High	Medium	Medium	Low
Flexibility	Low	High	Low	High
Cost	Low	Medium	Medium	High
Quality of products	Low	Medium	Medium	High
Resid conversion level	Medium	Medium	Medium	High
Rejection as fuel oil	Medium	Medium	Medium	Medium
Rejection as coke	High	Medium	Medium	Medium
No. of units in world	Large	Large	Average	Average
Recent trends	High	Medium	Medium	Medium
Environmental pollution	High	Medium	Nil	Low
On stream factor	Poor	Medium	Medium	High
Problems	Coke disposal	Heavy residue	High energy	Hydrogen requirement

Table 5.Comparison of Different Processes (Sarkar, 1998)

Product selectivity depends on catalyst properties (shape, size, active sites, chemical composition etc.) and experimental conditions. The reaction conditionsfor each technology are entirely different. Therefore,nature of the feed, use of proper reactor system and catalysts are very much important for the hydrocracking of VR. Generally, hydrotreatment of the middle distillates or a high API gravity feeds are conducted in fixed-bed reactors, while more complex feeds are used in moving-bed or ebullated-bed reactors.

A fixed-bed reactor requires continuous withdrawal of deactivated catalysts and immediate addition of fresh catalysts. In moving-bed reactors, the fresh catalyst enters at the top of the reactor, and the deactivated catalyst leaves the bottom of the reactor [35-38].

In a moving-bed reactor, the catalyst expands, and thus, the pressure drop can be reduced in some extent [39]. Generally, the hydrocracking of heavy feeds in fixed-bed reactor requires mixed or multiple beds of catalysts. Detailed catalysts syntheses and their applications in fixed-bed reactor systems have previously been reviewed [40, 41]. If the feed quality is too low for a fixed-bed reactor, moving-bed reactors in series orcombinations of ebullated-bed with fixed-bed reactors can be effective [42].



Residue hydroconversion processes[a]

Reactor type	Process	Licenser
Fixed bed	Continuous catalyst replacement (OCR)	Chevron Lumus Global (CLG)
	UFR, Up-flow reactor	Shell (Bunker flow)
		Axen (Swing reactor)
	Hycon, Bunker type reactor	Shell
	Hyvahl, swing reactor concept	IFP (Axen)
Ebullated bed	H-Oil	Axen (HRI/IFP)
	T-Star	Chevron
	LC-Fining	ABB Lummus
		Amoco oil (BP)
Slurry system	Microcat – RC	ExxonMobil
	Veba combi-cracking	Veba Oel
	Hydrocracking distillation hydrotreating (HDH)	Intevep
	Cash, Chevron activated slurry hydroprocessing	Chevron
	EST, Eni slurry technology	Eni Technologies
		Snamprogetti
	CanMet	Energy Research Laboratories, Canada

HRI (Hydrocarbon Research Institute).

[a] Several literature based data.

Table 6

5.4 Residue up Gradation 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 and sorption 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 multi-metallic nan 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.

5.4.1Hydrocracking of Vacuum Residue into Lighter Fuel Oils Using Nanosheet-Structured S_2 Catalyst

In this study, the hydrocracking of vacuum residue into lighter liquid oils using dispersed colloidal catalysts composed of nanosheet-structured WS_2materials. The vacuum residue of API gravity = 2.3was used as a reactant and hydrocracking reactions were performed in an autoclave batch reactor under 400C and the initial H_2pressure of 70 bar. Both single and multi-layer WS_2nanosheet catalysts were tested and their activities were compared with those of bulk WS_2 and MoS_2catalysts. [43]

The single-layer WS_2, which was the highest in specific surface area (97.6 m^2/g) due to its smallest particle size, showed the best performances in commercial fuel fraction yield (45.4 wt.%), C5-asphaltene conversion (75.3%),API gravity of liquid product (13.8), and metal removal activity. The fig 5 shows the graphical process description.

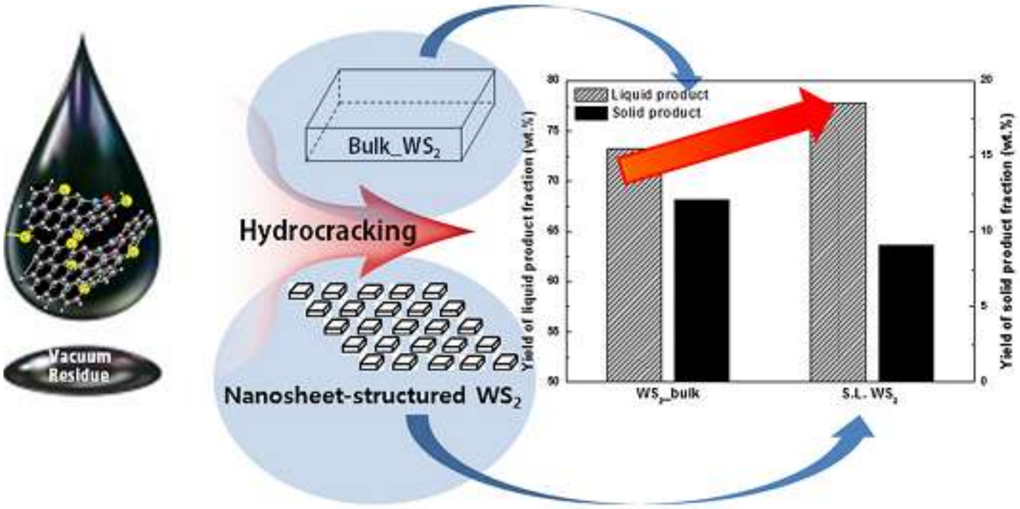


Fig.5 Graphical Process Description [43]

To characterize the physicochemical properties of catalyst, various characterization techniques were applied, including transmission electron microscope (TEM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) analysis. In addition, to assess the qualities of hydrocracking products, they carried out API gravity measurement, inductively coupled plasma-mass spectrometry (ICP-MS), and simulated distillation (SIMDIS) analysis

5.5 Biological Processing Of Heavy Fractions

Biological processing of heavy fractions of crude oils offers less severe process conditions and higher selectivity for refining. Biochemical Processes are expected to be low demand energy processes and certainly ecofriendly. Since biological processing of heavy crude oil may offer less severe processing conditions in refineries and higher selectivity to specific reactions to increase net distillates, it is proposed that the microorganisms capable to biodegrade heavy fractions of VR, could present an applicable opportunity for upgrading heavy crude oils [44-46].Bactria able to biodegrade various components of petroleum hydrocarbons such as poly-nuclear aromatic hydrocarbons (PAHs), like anthracite, monoaromatichydrocarbons such as toluene, or aliphatic hydrocarbons such asn-alkanes, are widely reported, particularly frompetroleum-contaminated sites [47,48-51]. But there are few reports on isolates that can alter several problematic petroleum components simultaneously, which are all find in VR.

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.

The result of VR chemical analysis for the percentage of alkanes, aromatics, asphaltenes and resins, usingSARA test after 20 days treatment with the bacterium in different media, is illustrated in Figure 6.The selected bacterium was able to grow in a wide rangeof pH from 5.5 to 8, salinity up to 3% and temperature from 20°C to 55°C.

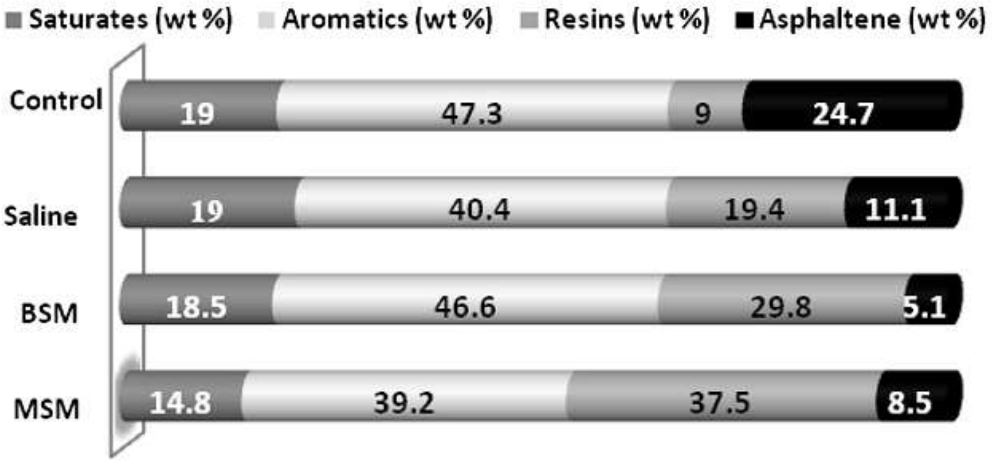


Figure 6 SARA Content Weight Percent [52]

In this process they find that Astrain of biosurfactant producing bacterium was isolated from an oil contaminated soil at Tehran refinery distillation unit. Based on selected phenotypic and genotypic characteristic including morphology, biochemical proprety, and 16 SrRNA sequencing identified as a novel strain ofBacillus cereus (JQ178332). This bacterium endures a wide range of pH, salinity and temperature. This specific strain utilizes both paraffin and anthracene as samples of aliphatic and polycyclic aromatic hydrocarbons. 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 in MSM medium. Further results with 0.9% saline showed 55% decrease in asphaltene content and 2.1% Aromatics respectively

VI. CURRENT & FUTURE DEVELOPMENTS

In next few years, crude oil will be heavier due to high contents of impurities, like nitrogen, sulfur and metal. Refineries must improve the process technology used for hydrocracking of heavy feeds into valuable environmentally friendly products. Currently, fixed-bed, moving-bed, expanded-bed or ebullated-bed reactors are available for upgrading the heavy oils and VR. Moreover, the slurry-phase hydrocracking process is attractive when combined with the existing technology and product price structure.

Heavy oil and VR contain complex molecules that pose numerousproblems during up gradation. To upgrade these feeds, the process technology, various related factors such as properties of the feeds, catalyst activity and selectivity, chemical kinetic parameters, operating conditions, and contact time are important factors for achieving a high yield of the selected product. The main challenge involves combining these aspects at reasonable capital costs. During the hydrocracking process, the catalyst should tolerate metal and other impurities possesses in feeds as well as exhibiting high performance (activity, selectivity, stability and regenerability) and being cost effective. These are the main challenges for refineries. Some integrated processes (Shell’s Hycon System, Chevron’s OCR System, and Axens/IFP’s Hyvahl System) have been developed and commercialized. However, in fixedbed processes, online catalyst replacement is preferable to a batch mode reactor, but this process cannot handle heavier oils and higher metal impurities; much improvement is needed in reactor design and operation conditions. An ebullated-bed process shows more selectivity, high conversion of feeds, high liquid yield and relatively low hydrogen consumption.

However, the back mixing of the reactants, high operating costs, high investment and low reactor efficiency are the main hurdles for hydrocracking of VR. Before slurry-phase processes commercialized, some impediments must be overcome. The main steps include optimizing the reaction conditions, lowering the reactor design cost, and using highly active and selective catalysts. The surface area, pore diameter, particle size, metal compositions and components, and metal particle distribution determine the activity and selectivity of the catalyst. The catalysts are also reasonably price having high mechanical strength and are recyclable. Hence, some attention must be paid to catalyst design. In industry, catalysts based on alumina or silica alumina must be exploited. In the near future, the VR upgrading technologies are likely to combine various hydroprocessing technologies with other processes, such as the thermal processes and solvent de-asphalting processes.

And in the field of Nanoparticle to find a proper method for catalyst recovery (or reuse) is another important subject to be dealt in the future studies. [43]

VII. CONCLUSIONS

The demand of transportation fuels and petrochemical applications are rapidly increasing. Unlike limited amount of traditional light petroleum resources, low quality heavy oils and VR are abundant. Therefore, techniques, which can upgrade heavier petroleum resources, need to be developed. One of the most efficient methods for such purpose is catalytic hydrocracking. The slurry-phase hydrocracking process is effective and is an attractive option for overcoming the limitations associated with other technologies. The main objective is to treat the heavier residue toobtain high quality products, low boiling point liquid with low viscosity.

For hydrocracking processes, coke formation can be suppressed in hydrogen rich atmosphere, and therefore, catalytic life time can be prolonged with high catalytic activity. Hydrocracking catalyst performance can be controlled by types of supports, composition, preparation procedure, and process conditions. Therefore, a strategic catalyst development is essential to obtain high activity and selectivity for hydrocracking of VR and other heavy oils. Simultaneously, deactivation caused by metal impurities and physical damages should also be considered. In addition, life span of the catalyst may be extended by changing its textural properties.

The activity of nanosheet-structured WS_2catalyst was examined for hydrocracking of extra-heavy oil (vacuum residue). A key factor in hydrocracking reaction using dispersed WS_2catalystwas the particle size of catalyst, which determines the concentration of catalyst particles per unit volume of reactant oil phase. The single-layer(S.L) WS_2catalyst, which was the smallest in size among the tested WS_2 catalysts, showed the best hydrocracking activity for vacuumresidue: It was the highest in production of liquid fuel products,especially the commercial liquid fuel fractions such as naphtha,middle distillate, and gas oil. The single-layer(S.L). WS_2catalyst was the most active in hydrocracking of the heavy fractions in vacuum residue,which led us to expect its overall good activity in hydrocracking of other kinds of extra-heavy oils. The S.L. WS_2 catalyst was also the most active for removal of metal impurities (nickel and vanadium) entrapped in the vacuum residue. [43]

The high physicochemical endurance of Bacillus cereus isolated from petroleum contaminated soil with the ability to utilize both aliphatic and complex aromatic structures of distillation residual substances as its sole sourceof carbon and energy, and the particular finding of thisresearch that revealed the remarkable ability of the bacterium to use VR as the only source of all required chemicals for growth along with surfactant production, make this bacterium a unique option for industrial use, particularly in bioremediation, bio-upgrading and bio refining processes. This bacterium with ability to biodegrade and utilize heavy fractions of vacuum distillation residue as its sole source of carbon and energy can be useful in petroleum biological processing with less severe condition to increase net distillates [52]

REFERENCES

[1] M. J. Hutzler, S. Sitzer, P. D. Holtberg, J. Conti, J. M. Kendell,A. S. Kydes, “Annual Energy Outlook 2003 with projection to 2025” The United States Energy Information Administration, US Department of Energy, Washington, DC 205, 85 (2003) 267.

[2] L. Atkins, T 3.Higgins, C .Barnes, “Heavy crude oil global analysis and outlook to 2030” Hart energy consulting report, Houston, Texas, USA, 2010.

[3] D. Vartivarian, H. Andrawis, Oil Gas J 104 (2006) 52.

[4] F. E Biasca, R. L. Dickenson, E. Chang, H. E. Johnson, R. T. Bailey, D. R. Simbeck, In upgrading heavy crude oils and residue to transportation fuel: technology economics and outlook, Phase 7, Garland R. Report Coordinator, SAF Pacific Inc. Eng. & Economic Consultant, 2003.

[5] K. E. Rose, Hydrocarbon Process. 7 (1971) 85.

[6] M. R Gray, “Upgrading petroleum residues and heavy oils” CRC Press, New York, 1994.

[7] J. G. Speight, “The chemistry and technology of petroleum” CRC Press, New York, 2006.

[8] S. Rahmani, W. McCaffrey, M. R. Gray, Energy Fuels 16 (2001)148.

[9] J. Ancheyta, G. Centeno, F. Trejo, G. Marroquín, Energy Fuels 17 (2003)1233.

[10] J. Schmidt, http:// findarticles.com/p/articles /mim3159/is12226/ 15979981, 2010.

[11] W. Kotowski, W. Fechner, B. Lucke, Przem. Chem. 2 (1999) 51.

[12] S. Sugianto, R. M. Butler, J. Can. Petrol. Technol. 29 (1990) 78

[13] R. Quann, R. A. Ware, C. W. Hung, J. Wei, Adv. Chem. Eng. 14 (1988) 95.

[14] R. L. Dickenson, F. E. Biasca, B. L. Schulman, H. E. Johnson, Hydrocarbon

[15] T. Tsujino, Fuel Energy Abstr. 37 (1996)183.

[16] R. V. Pindoria, A. Megaritis, I. N. Chatzakis, L. S. Vasanthakumar, S. F. Zhang, M. J. Lazaro, Fuel 76 (1997)

[17] O. Holopainen ,Bioresour. Technol. 46 (1993) 125.

[18] F. Gulli, Energy Policy 23(1995) 647.

[19] B. G. Houk, Fuel Energy 37 (1996) 176.

[20] A. Tokarska, Fuel 75 (1996)1094.

[21] F. R. Reinoso, P. Santana, E. R.Palazon, M. A. Diez, H. Marsh. Carbon 36 (1998)105.

[22] E. Furimsky, Fuel Process Technol. 67(2000) 205.

[23] B. I. Zuba, Hydrocarbon Process.10 (1998)132.

[24] A. Billon, F. Morel, J. P. Peries, "Use of solvent deasphalting process in Residues Conversion schemes" 15th World Petroleum Congress, Beijing, China, 1997.

[25] H. Shen, Z. Ding, R. Li, "Thermal Conversion-An Efficient Way for Heavy Residue Processing" in Proc. 15th World Petroleum Congress, 2 pp. 907-913, Beijing, China, 1998.

[26] S. L. Chen, S. S. Jia, Y. H. Luo, S. Q. Zhao. Fuel 73 (1994)439

[27] V. A. Adewusi, B. Ademodi, T. Oshinowo. Fuel Process. Technol. 27 (1991) 21.

[28] C. W. Curtis, K. J.Tsai , J. A. Guin. Fuel Process Technol.16 (1987) 71.

[29] J. W. Scott, A. G. Bridge, Advan. Them. Ser. No. 103 (1971)113.

[30] J. W. Scott, N. J. Patterson, Proc. 7th Wld. Petrol. Congr. 4 (1967) 97.

[31] G. L. Farrar, Oil Gas J. 71 (1973) 25.

[32] D. H. Stormont, Oil Gas J. 66 (1968) 104.

[33] J. Cherzer, A. J. Gruia, "Hydrocracking Science and Technology" Marcel Dekker, New York, 1996.

[34] E. Furimsky, Appl. Catal. A 46 (1988) 177. [35] G. N. Sarkar, "Advanced Petroleum Refining" Khanna Publishers, New Delhi, 1st Ed., 1998

[36] J. W. Gosselink, Cattech 2 (1998) 127.

[37] S. Kressmann, F. Morel, V. Harle, S. Kasztelan, Catal. Today 43 (1998) 203.

[38] B. E. Reynolds, R. W. Bachtel, K. Yagi, "Chevron's on stream catalyst replacement (OCRTM) provides enhanced flexibility to residue hydrotreaters" Presented at the 1992 NPRA Annual Meeting, New Orleans, LA, 1992.

[39] J. Ancheyta, J. G. Speight, "Reactors for Hydroprocessing of Heavy Oil and Residua" Chapter 6, Eds., Taylor and Francis, New York, 2007.

[40] E. Furimsky, F. E. Massoth, Catal. Today 52 (1999) 381.

[41] L. E. Gardner, S. G. Kukes, "Hydrofining employing a support material for fixed beds" US 4828683, 1989.

[42] J. Ramirez, M. S. Rana, J. Ancheyta, J. G. Speight, “Characteristics of heavy oil hydroprocessing catalysts” Chapter 6, Eds., Taylor and Francis, New York, 2007.

[43] Y.G. Hur et al. / Fuel 137 (2014) 237–244.

[44]. Sood N, Lal B: Isolation and characterization of a potential paraffin-waxdegradingthermophilic bacterial strainGeobacilluskaustophilusTERINSMfor application in oil wells with paraffin deposition problems.Chemosphere2008, 70:14451451.

[45]. Vazquez-Duhalt R, Quintero-Ramirez R: Prospects for biological upgrading ofheavy oils and asphaltenes, Petroleum Biotechnology: Developments andPerspectives.4th edition. The Netherlands: ELSEVIER B.V; 2004:113143.

[46]. Wang XB, Chi CQ, Nie Y, Tang YQ, Tan Y, Wu G, Wu XL:Degradationofpetroleum hydrocarbons (C6-C40) and crude oil by a novelDietziastrain.Bioresource Technol2011,102(17):7755–61.

[47] Liu W, Luo Y, Teng Y, Li ZQ, Ma L: Bioremediation of oily sludgecontaminated soil by stimulating indigenous microbes.EnvironGeochemHealth2010, 32(1):23–29

[48]. Karimi A, Golbabaei F, Neghab M, Reza PM, Nikpey A, Mohammad K,MehrniaMR:Biodegradation of high concentrations of benzene vaporsin a two phase partition stirred tank bioreactor. Iranian J Environ HealthSci Eng2013, 10:10.

[49]. Kim IS, Park J, Kim KW:Enhanced biodegradation of polycyclic aromatichydrocarbons using nonionic surfactants in soil slurry.Appl Geochem2001,16:1419–1428.

[50]. Östberg TL, Jonsson AP, LundströmUS:Enhanced degradation of n-hexadecanein diesel fuel contaminated soil by the addition of fermented whey.Soil Sediment Contamination2007,16(2):221–232.

[51]. Whyte IG, Bourbonniere I, Greer CW:Biodegradation of petroleumhydrocarbons by psychrotrophicpseudomonasstrains possessing bothalkane (alk) and naphthalene (nah) catabolic pathways.Appl EnvironMicrobiol1997,63(9):3719–3723

[52] Tabatabaee and MazaheriAssadi Journal of Environmental Health Sciences & Engineering2013, 11:18