

Effects of aromatic cycle oils on performance of residue hydrotreating

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Abstract—Hydrotreating, as an important pretreatment process of residue catalytic cracking, is used to eliminate metals, S and N contaminants and partly process asphaltene from streams so that the products can be efficiently processed in downstream conversion units. We investigated the effects of aromatic additives on residue hydrotreating (RHT) by adding various types and contents of high aromatic cycle oils into atmosphere residue (AR). The aromatic additives modify the colloidal structure of asphaltene in AR and improve the liberation of heteroatomic compounds bound in nucleus. Therefore, the amount of carbon residue in blending oils decreases and the removal efficiency of Ni, V, S and N increases obviously. The increase of conversion is greater for nitrogen than for sulfur, and hydrodevanadium reveals a distinct advantage over hydrodenickel. However, excessive amount of light cycle oil (more than 20% wt) is not helpful for removing the Ni and V since a little of metalloporphyrins stubbornly bond with the superstructure of nucleus.

Key words: Residue Hydrotreating, Cycle Oil, Asphaltene, Colloidal Structure

INTRODUCTION

The increasing consumption of fuels and the availability of heavy petroleum have compelled refiners to process not only a larger amount of oil but also increasing amounts of heavy crude, in order to fulfill the demand for gasoline and diesel. This fact, therefore, increases the level of hydrotreating of the high molecular weight residue. These residues contain large amounts of several polluting agents, such as sulfur, nitrogen and metals. Among the metals, the most abundant and problematic ones, without any doubt, are vanadium and nickel. Specifically, vanadium and nickel compounds cause severe problems in the hydrodesulfurization and catalytic cracking reactors. In the hydrotreating units, these metals accumulate on the catalyst as metal sulfides. The metal deposits poison the active sites, obstruct the pores entrance and also shorten the lifetime for the catalyst [1].

Coke deposition on hydrotreating catalyst is another problem that confronts researchers [2]. As is well known, the problem is mainly caused by asphaltenes which are the most complex molecules present in petroleum and consist of condensed polynuclear aromatics carrying alkyl, cycloalkyl, and heteroatom constituents. Much work is still being devoted to unravelling the relations between coke deposition and the chemical nature and properties of asphaltenes. Seki and Kumata [3] have reported that asphaltene quality rather than quantity plays a key role in coke deactivation. Matsushita et al. [4] concluded that the quality and quantity of coke on the spent catalysts were affected by the relative solubility index, namely coke decreased with the improvement of solubility of asphaltenes in oils.

The colloidal nature of residua and asphaltenes was first propounded by Nellensteyn [5] in 1924. From then on, a series of physical models depicting the true icons of asphaltene have been elaborated conceptually by Mack [6] and Yen [7], and diagrammatically by Pfeiffer and Saal [8]. Of these, the most vivid conceptual represen-

tation of the physical structure of residue and its construction modes should be attributed to the Pfeiffer model and Yen model. The former is popular for elaborating the sol-gel property, solubility, stability, dispersion and viscosity of asphaltenes in oils and solvents [4,9,10]; the latter is obtained from X-ray diffraction analysis and quantitatively describes the aromaticity, single sheet size, and diameters of micelle, cluster and aggregate. It is more favorable to explain the micro chemical structures and properties of asphaltenes [11]. However, all of these theories imply that the colloidal structure of asphaltene can be modified. Therefore, several papers have attempted to introduce some additives, such as tetrahydronaphthalene, phenol and tetralin [12,13], to inhibit formation of coke during cracking and coking of heavy oils. As early as 1992, Oboho [14] pointed out that the extract from phenol purification as an aromatic addition into catalytic cracking feed decreases coke formation on the catalyst by 50 to 70% and increases the yield and octane number by about two units of gasoline. Mizutani et al. [15] then reported the effect of several solvents on residue hydrodesulfurization activity in the order of light cycle oil>tetralin>none (base)>1-methylnaphthalene>phenol. The authors suggested that enhancement of asphaltene desorption reduces coke formation on the catalyst, whereas hydrogenation conversion of solvents with sulfur species in AR may indicate competitive occupation on the active sites.

Moreover, some researchers considered the aromatic distillates from petroleum as additives to improve the heavy oil hydroprocessing. Kubo et al. [16] presented that a highly aromatic heavy fraction from petroleum and its hydrogenated product were effective for the inhibition of coke formation. They supposed these additives as hydrogen transfer medium from the vapor phase to the oil, which reduced the hydrogen consumption and coke formation. Niu [17] investigated the effects of coke gas oil, vacuum gas oil and paraffin wax (mixed into vacuum residua) on residue hydrotreating reactions. The results indicated that high aromaticity distillates can help depress the coke formation and improve the hydrodesulfurization and hydrodemetallization.

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Table 1. Properties of atmosphere residue

S (% wt)	N (v wt)	Ni (wppm)	V (wppm)
3.52±0.15	0.21±0.01	21.40±0.65	49.80±0.52
MAC (% wt)			CCR (% wt)
Maltene	Asphaltene	Coke	
96.27±0.83	3.17±0.21	0.56±0.03	10.27±0.45

However, few studies discuss the effects of the high aromatic distillates on the colloidal nature and properties of asphaltene, although asphaltene plays an more important role for removal of heteroatoms (such as S, N, Ni and V) and coke formation during residue hydrotreating. We investigated the effects of aromatic additives on RHT by adding light cycle oil (LCO) and heavy cycle oil (HCO) into AR. The purpose was to reveal the modification of aromatic additives on the colloidal nature of asphaltene and the improvement in performance of RHT and to explore the physico-chemical mechanism.

EXPERIMENTAL

1. Materials

A commercial NiMo/ γ -Al₂O₃ RHT catalyst was employed in all experiments. AR of Kuwait crude derived is characterized in Table 1. Two highly aromatic products of residue fluid catalytic cracking (RFCC), LCO and HCO, were used as additives. Polycyclic aromatic hydrocarbons in HCO are more than that in LCO.

2. Hydrotreating Experiments

Hydrotreating tests were performed with addition of LCO (5, 10, 20, 50%wt) and HCO (20%wt), using a batch autoclave that was inserted into an electric furnace, to evaluate the effects of additives on performance of RHT. 25 g of feedstock was charged with 5 g of presulfided catalyst sample into autoclave, the inner volume of which was 150 ml. The autoclave was pressurized under a hydrogen atmosphere of 8 MPa at room temperature and was then heated to 350 °C for reaction 2 or 5 hr.

Heating tube tests were conducted at the same conditions to estimate the effect of additives on coking trend of AR during hydrotreating. The identical autoclave was employed without catalyst.

3. Characterization of Feeds and Products

The concentration of Ni and V in feeds and products was determined by inductively coupled plasma mass spectrometry (IPC-MS, SPS 1700HVR). Approximately 200 mg of each sample was placed in a digestion vessels (Berghof microwave oven), and a mixture of fluorhydric acid (40%) and azotic acid (69.5%) was added prior to ICP-MS analysis. Bi-element, matrix-matched standards were used for the quantitative determinations. Instrument conditions were as follows: principal argon flow rate, 16 L/min; coolant, 0.2 L/min; nebulizer, 0.7 L/min. The final results are the average of three replicates.

Nitrogen analyzer model Antek 9,000 N (Antek Instruments, Inc., USA) was used for high temperature oxidative combustion of samples and quantitative determination of the total, chemically bounded nitrogen by chemiluminescence detection. Nitrogen in the sample is converted into nitric oxide in the oxidative furnace at 1,050 °C; then the nitric oxide reacts with ozone to emits light. The light is measured with a chemiluminescence detector that correlates to nitro-

gen amount in the sample.

X-ray fluorescence analysis (Oxford Model 3000 XRF) was performed for sulfur content with a 1800H sulfur analyzer, using 20 mm i.d. PTFE cells with 7 μ m Mylar film windows. Acquisition time was 300 s, and measurements were in triplicate.

The weight percent CCR was determined using the ASTM D-189 method. The sample mass used for the experiments varied from 5 to 10 g depending on the CCR content of the sample. A weighed quantity of the sample was first placed in a crucible and subjected to destructive distillation powered by a blowtorch at atmospheric pressure; thus the heavy oil underwent cracking and carbonization due to severe heating. Then the crucible containing the resultant carbonaceous material was cooled and weighed to determine CCR content.

Separation of crude oils into MAC fractions was achieved by precipitation and column chromatogram using the ASTM D4124 method. Diluting the crude oil with 40 volumes of *n*-hexane separated the asphaltene and coke fractions of oils. The mixture was shaken for 1 h and stored overnight in the dark. Filtration of this mixture was the next step to obtain hexane soluble (Maltene) and hexane insoluble (HI). Then the HI was dissolved by 40 volumes of toluene and filtrated to separate the asphaltene (toluene soluble) and coke (toluene insoluble). The asphaltene and coke fractions were dried in an oven for 6 hr under a helium atmosphere.

RESULTS AND DISCUSSION

1. Effect of Additives on Asphaltene and Coke Formation during RHT

In petroleum refinery processes, coking has a major impact on catalyst deactivation, equipment fouling and pipe clogging. Running the refinery units under severe operating conditions to achieve higher conversion levels and using heavier feedstocks has led to even more fouling problems [18,19]. Carbon residue is an important indicator of coke deposit during RHT [20]. To evaluate the coking trend, feeds and products of hydrotreating tests were evaporated, pyrolyzed and burned at the prescriptive conditions of ASTM D189 to get the value of CCR (see Table 2). Addition of LCO and HCO (20%wt) decreases the content of CCR and improves the conversion of CCR.

To further evaluate the effect of additives on coke formation, heating tube tests were carried out. The results (shown in Table 3) demonstrate that the coke formation of blending oils is inhibited by adding additives.

It's well-known that coke formation during heat treatment of AR is mainly derived from asphaltene; therefore, dissolving asphaltene or inhibiting its agglomeration by additives helps to reduce coke. As Table 3 shows, the content of asphaltenes in blending oils is de-

Table 2. CCR of feeds and products of hydrotreating tests

	Feeds	Products	
	CCR (% wt)	CCR (% wt)	Conversion of CCR (%)
AR	10.27±0.45	8.97±0.40	12.66±0.48
AR-LCO	8.09±0.30	6.55±0.22	19.04±0.45
AR-HCO	8.15±0.32	6.65±0.25	18.40±0.57

Table 3. MAC of feeds and products of heating tube tests

	Samples	Maltene (% wt)	Asphaltene (% wt)	Coke (% wt)
Feeds	AR	96.27±0.83	3.17±0.21	0.56±0.03
	AR-HCO	97.41±0.47	2.22±0.17	0.37±0.02
	AR-LCO	97.52±0.72	2.14±0.05	0.34±0.02
Products	AR	95.35±0.86	3.67±0.22	0.98±0.05
	AR-HCO	96.82±0.65	2.69±0.20	0.49±0.03
	AR-LCO	97.02±0.72	2.55±0.11	0.43±0.02

Table 4. MAC of AR and blending oils

	Maltene (% wt)	Asphaltene (% wt)	Coke (% wt)
AR	96.27±0.83	3.17±0.21	0.56±0.03
AR-HCO	97.41±0.47	2.22(2.54)*±0.17	0.37(0.45)±0.02
AR-LCO	97.52±0.72	2.14(2.54)±0.05	0.34(0.45)±0.02

*The data in brackets eliminate LCO or HCO fraction in calculation

creased by LCO and HCO. The data in Table 4 imply the same result, regardless of excluding the effect of dilution by LCO and HCO.

Petroleum and its fractions are capable of acquiring the properties of a colloidal system [21,22]. The dispersed phase of such a system is made up of complex structural units, comprising a nucleus and a solvate shell. The nucleus is a supermolecule structure, the composition of which can include asphaltenes and resins as well as intermediate substances which are not easily separated from the nucleus. The solvate shell surrounds the nucleus and comprises hydrocarbons of a lesser degree of aromaticity and lower molar mass. The dispersion medium is a mixture of low molar mass hydrocarbons without intermolecular interactions (marked as OIL in Fig. 1).

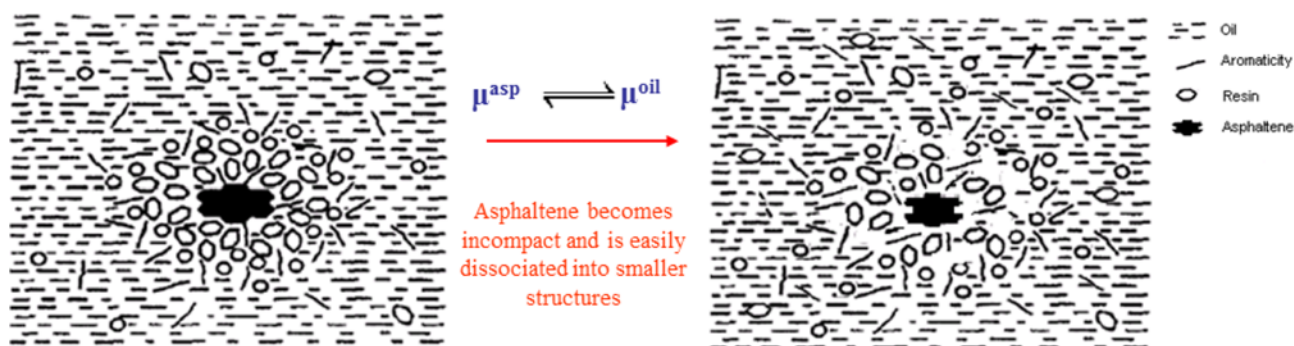
When aromatic additive is inducted, a dissolution equilibrium

between nucleus and oil should be considered. It is hypothesized that the chemical potentials of aromatic compounds in them should be equal ($\mu^{asp} = \mu^{oil}$) to maintain the balance. Addition of high aromatic additives increases the solubility of aromatic compounds in oil (μ^{oil} reduces); therefore, resins in asphaltene are apt to transfer into oil. Asphaltene becomes incompact and is easily dissociated into smaller structures under some special conditions (see Fig. 1). With the presence of high aromatic additives, some polycyclic aromatic hydrocarbon sheets in the core of asphaltenes may even be dissolved under high temperature. This conclusion may help to explain the mentioned order of solvents improving residue hydrodesulfurization activity in Mizutani's report [15].

2. Effect of Additives on Performance of RHT

Hydrotreating tests of AR and blending oils with LCO or HCO (20%wt) were carried out for reaction 2 hr. The results shown in Table 5 demonstrate that additives enhance the removal efficiency of metals, S and N in feeds. Furthermore, the increase of conversion is greater for nitrogen than for sulfur, and hydrodevanadium reveals a distinct advantage over hydrodenickel. As a whole, improvement of LCO on RHT is better than that of HCO.

Most of the heteroatomic compounds containing Ni, V, S and N of AR, mainly metals porphyrins, benzothiophene with steric hindrance and pyrrole, concentrate in asphaltene by chelating with condensed aromatic rings [23]. As mentioned above, additives can dissolve asphaltene to some extent. With the presence of additive and hydrogen at hydrotreating conditions, asphaltene becomes incompact and is easily dissociated into small molecule secondary structures, while the heteroatomic compounds bound in the nucleus of asphaltene could be released into oil. Therefore, the removal efficiency of metals, S and N is improved, and the secondary structures are easier to crack in the downstream process (see Fig. 2). As is known, vanadium and nickel in asphaltene are mainly complexed in porphyrins. The vanadium appears in the V=O (+4) state, and nickel exclusively in the +2 valence state. Unlike nickel atom being

**Fig. 1. Colloidal structure and dissociation of asphaltene.****Table 5. Effect of additives on performance of RHT**

Feeds	Conversion (%)				
	Ni	V	Ni and V	S	N
AR	21.50±0.66	38.15±0.78	33.15±0.70	18.47±0.55	4.76±0.21
AR-HCO	22.23±0.50	54.09±0.80	44.09±0.65	19.51±0.27	13.64±0.22
AR-LCO	27.98±0.61	50.87±0.60	44.13±0.60	24.22±0.30	15.00±0.34

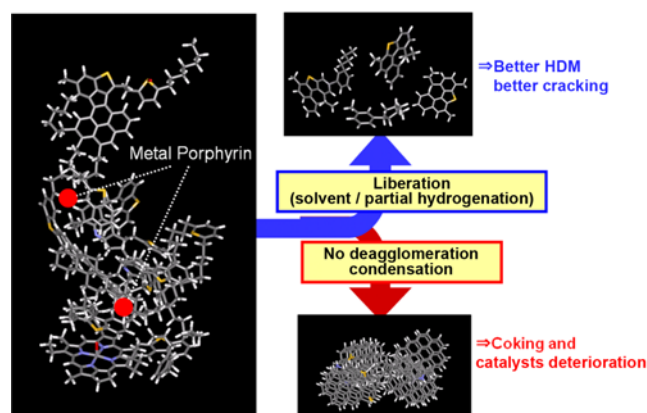


Fig. 2. Superstructure and Deagglomeration of Asphaltene.

locked in the center of pyrrole rings, vanadium bulges upwards about 0.53×10^{-10} m to the basal plane, and the V=O bond in porphyrin macrocycle is always distorted in asphaltene [24]. This structure results in that vanadium porphyrins, especially which are liberated from the nucleus of asphaltene, more easily adsorb on the surface of hydrodemetallization catalyst to be removed. Similarly, compared with sulfide compounds, nitride compounds tend to chelate with complicated superstructure of nucleus, but nitride compounds will more quickly adsorb on catalyst and react as long as they are free from shackle.

On the contrary, some macromolecule polycyclic aromatic hydrocarbons without deagglomeration are condensed, which coke and deteriorate the catalysts during hydrotreating.

3. Effect of LCO Contents on Performance of RHT

A series of hydrotreating tests with adding various contents of LCO for reaction 5 hr were conducted to evaluate the effect trend. As Fig. 3 shows, the conversion curves of sulfur and nitrogen go steadily up with increasing the amount of LCO in feeds. It implies that the component of LCO is more miscible with aromatic part of sulfide and nitride compounds in order to persistently extract them from asphaltene. For the reason noted above, although the conversion is better for sulfur than for nitrogen, the curve slope of the latter is higher. However, peaks of curves of hydrodenickel and hydrode-

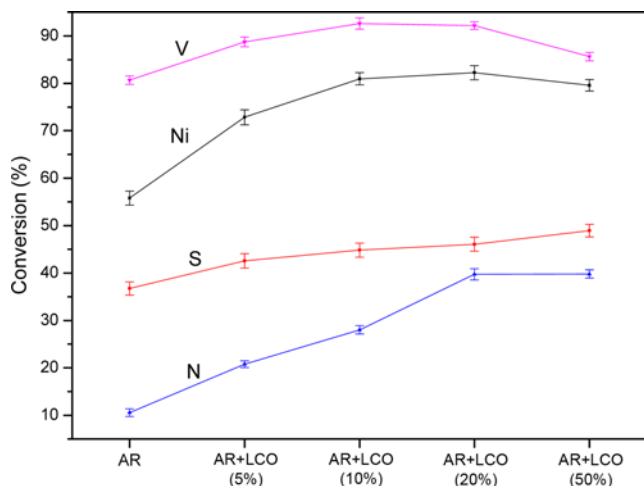


Fig. 3. Effect of various contents of LCO on performance of RHT.

vanadium in Fig. 3 suggest that a limitation of additive is present since a little of the metalloporphyrins bond with the superstructure of nucleus or are encased throughly.

In the conventional RHT-RFCC combined process, HCO and LCO are cycled to RFCC unit itself and the high content of condensed aromatic in them leads to a high yield of coke and a low yield of light oil [25]. However, based on the above discussions, if the aromatic cycle oils are cycled to a hydrotreating unit and mixed into feed AR (or VR), which will enhance the performance of RHT and improve the quality of RFCC feed, the more profit should be achieved obviously. Further research is being conducted by the present authors.

CONCLUSIONS

The world demand for light and middle distillates continually increases, while the available crude oil becomes heavier. Refining processes converting heavy residual oils (eg. AR) into more valuable products are therefore vital to a refinery. However, These residues contain high amounts of several polluting agents, such as asphaltene, metals, sulfur and nitrogen, problems which have annoyed researchers. Thus, the effects of aromatic cycle oils on residue hydrotreating were investigated by adding aromatic cycle oils into AR. Asphaltene as a colloidal system is composed of a nucleus and a solvate shell with a dissolution equilibrium. Aromatic additives increase the solubility of aromatic compounds in shell and help to dissociate asphaltene into small molecule secondary structures. Therefore, the removal efficiency of heteroatomic compounds (containing Ni, V, S and N) bound in nucleus of asphaltene increases obviously, while the amount of CCR of blending oils decreases. However, excessive amount of LCO (more than 20% wt) isn't helpful for removing the Ni and V since a little of metalloporphyrins stubbornly bond with the superstructure of the nucleus. Furthermore, due to the different structures of heteroatomic compounds, the increase of conversion is greater for nitrogen than for sulfur, and hydrodevanadium reveals a distinct advantage over hydrodenickel.

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