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SOLVENT DEASPHALTING OF VACUUM RESIDUE IN A BENCH-SCALE UNIT

M. Sattarin[1], H. Modarresi[2]*,H. Talachi[1], M. Teymori[1]

[1]Petroleum Refining Division, Research Institute of Petroleum Industry, Tehran, Iran, [2]CAPEC, Department of Chemical Engineering, Technical University of Denmark, DK-2800 Lyngby, Denmark,*Corresponding author.
Tel.:+45-4525-2986, Fax: +45-45932906. Email: ham@kt.dtu.dk

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Abstract
The introduction of solvent deasphalting (SDA), on different refining schemes, bring to the refineries a very promising solution for desulfurization problems and/or catalytic cracking processes in recent years. In this work, some effective parameters of SDA process such as temperature and solvent and residues nature have been studied on the different residues of an Iranian crude oil mixture (ºAPI 19.5) in a bench unit. All produced deasphalted oils (DAOs) were almost free of asphaltene (<0.5 wt%) apart from the feed nature. SDA by means of pentane as solvent reduced the heavy metal content of the feeds up to 85%, sulfur content up to 20% and CCR (Carbon Conradson Residue) content up to 50%, where SDA with butane results in 93% reduction of heavy metals content, 20% reduction of sulfur content and 66% reduction of CCR.

Keywords: oil upgrading; extraction; deasphalted oil; pitch.

1. Introduction

Direct hydro-desulfurization followed by hydrocracking of crude oil heavy cuts and vacuum residues is one of the best methods of heavy residue upgrading in refining industry. But, problem emerges when metal and asphaltene contents of residue are high. In fact, the presence of these compounds adversely influences the activities of the hydro-desulfurization and hydrocracking catalysts.

The solvent deasphalting process (SDA) which is based on liquid–liquid extraction by using paraffinic solvents (C_4–C_7) is one of the most efficient approaches to reduce metal and asphaltene contents of heavy oil cuts before sending them to hydro-desulfurization and hydrocracking units.

A number of deasphalting process parameters are to be considered, amongst which the DAO process yield and the levels of demetalization and deasphalting could be noted. The important factors influencing the mentioned parameters are solvent composition and ratio of the solvent to the feed, temperature, pressure and the type of extractor equipment.

Increasing the solvents molecular weight increases the yield of recovered DAO by allowing more of the heavier, more – resinous components of the feed stock to remain in the DAO. At the same time, however, the quality of the DAO decreases because these heavier materials have higher contaminant levels. Consequently, proper solvent selection involves balancing increased product yield and decreased product quality. The precipitation increases substantially as the solvent/feed ratio increases up to 10 folds. Beyond this value, precipitation increases by very small amounts[1].

Contrary to the liquids solving behavior, DAO yield is reduced by rising the temperature. This is due to the solvent density reduction with increasing the temperature. The solvent density reduction with temperature rise, leads to the reduction of solvent tendency to dissolve heavier compounds and improves DAO quality at the expense of reduced DAO yield. Extraction temperature must be maintained below the critical temperature of the solvent, however, because at higher temperatures no portion of the residue is soluble in the solvent and no separation occurs[2]. In industrial plants, increasing the solvent to feed ratio compensates for the DAO yield reduction with temperature rise. In consequence, the extraction process selectivity for paraffinic oils escalates and eventually the extracted oil will have an improved quality due to the reduction of undesirable components.

Extraction pressure which is chosen to ensure that the SDA extractors solvent–residue mixture is maintained in a liquid state, is related to the critical pressure of the solvent used. During normal operation, when both pressure rise results in the solvent density increase and therefore DAO yield increases. This effect gets even more pronounced near the critical point caused by the sharp variation of density versus pressure. Nevertheless, due to the process and mechanical restrictions, changing the extraction operational pressure to regulate DAO yield, is not an industrial common practice [3].

The main aim of this study was to investigate some key factors influencing SDA process. Therefore, the residues of a typical Iranian heavy crude oil (i.e. 450^+, 470^+, 500^+, and 520^+ °C) are deasphalted, by using of pentane and butane solvents. In addition, different operational temperatures in SDA process (i.e. 35, 50 and 80°C) have been studied.

2. Bench Scale SDA Operation

The set of equipment employed in the bench unit (Fig. 1) comprises a jacket vessel equipped with a mixer (as an extractor), inlet and outlet for the materials in accordance with extraction operation and utilities such as warm and cold fluid suppliers, outlet DAO condenser and products collection facilities.

The operation is batch–wise and in each batch after being pre-diluted with the solvent, some of the residue is introduced to a high-pressure extractor. The solvent is introduced to the extractor ten-folds the amount of the feed. After the temperature is kept constant for a certain period of time, mixing and precipitation operations are performed. Afterwards, DAO was withdrawn from the extractor by means of a pipe dipped into it. After passing a condenser, DAO was collected. When DAO was completely evacuated from the extractor, extraction residue was drawn out from the extractor bottom. The extracted DAO phase was sent to the next step for solvent evaporation and regeneration.

As the pitch content is small in bench scale studies, solvent regeneration step was waived. But the solvent carried along with the DAO was regenerated, primarily by being introduced to an atmospheric evaporation vessel and then to a vacuum rotary evaporator. Eventually, the DAO and the dried pitch were sent to the laboratory for further analysis.

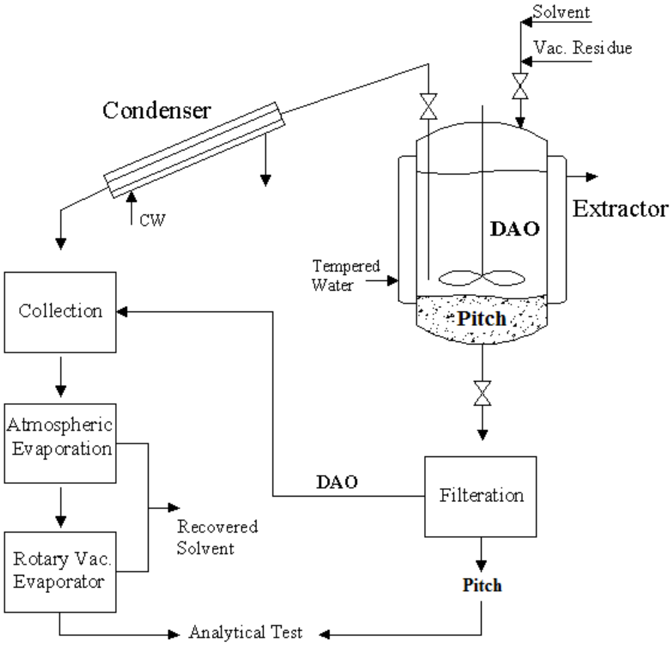

Fig. 1: A schematic diagram of the bench scale SDA unit (CW: Cooling Water)

3. Results and Discussion

The results of tests, with butane and pentane solvents, are presented in Table 1 for different vacuum residues. The effective parameters of SDA process, included in this table, are specific gravity, asphaltene content, Conradson carbon residue (CCR) content, metals content and sulfur content, test results. Tests with pentane solvent are carried out at 50 and 80 ºC.

To further clarification of SDA process parameters, the test results are presented in the form of graphs. Figure (2) shows mean variation of extraction yield (DAO yield) for each solvent versus the type of vacuum residue (SDA feed). This figure clearly shows that extraction yield increases as the solvent molecular weight increases and, decreases as feed mean molecular weight increases. Figure (2) shows that for vacuum residues heavier than 500^+, extraction yield does not change significantly. The reason is that oil and light resin contents of vacuum residue are reduced when its mean molecular weight (or boiling point) increases and after the 500^+, this amount tends to trivial. Additionally, the SDA process temperature variation does not have a pronounced effect on extraction yield for cuts heavier than 500^+. It should be noted that extraction yield increases directly with temperature, but here, the results are contrary to this fact. This could be explained by referring to the concept of macro-fluid. According to Kolmogrov's relationship for macro-fluid, mean size of a coalescent aggregate of a same fluid in a semi-immiscible liquid mixture can be estimated by equation (1) :

$$\lambda = (\gamma^3 / \varepsilon)^{1/4} \qquad (1)$$

where λ is the aggregate size [m], γ is kinematic viscosity [m^2/s], and ε is mixing power per mass unit [W/kg]. For mixture of the vacuum residue (VR) (450^+) and pentane, with a fairly high mixing power of 1 W/kg, the order of magnitude of the aggregate size (μm) can be roughly varied between 100 for low temperature (close to ambient temperature) and 1 for temperature as high as 150 °C. Big aggregates can hold almost large quantity of DAO, therefore, it can be considered another mechanism for solving of VR in solvent. According to Figure (3), for low temperatures (close to ambient temperature), solubility of DAO is controlled with size of aggregates, so it increases as temperature rises up. For high temperatures, which are estimated higher than 120 ºC (for pentane solvent), aggregate sizes are quite small where they cannot hold much DAO. Therefore, solubility is controlled by density variation of solvent and it decreases as temperature rises up.

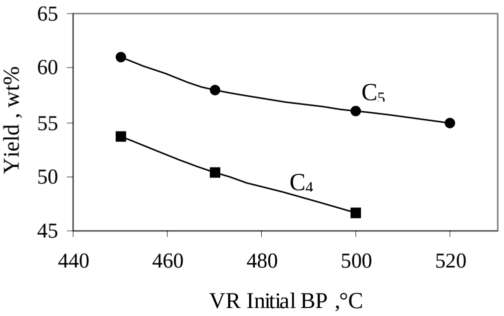

Fig. 2: DAO Yield of SDA with butane (C_4) and pentane (C_5)

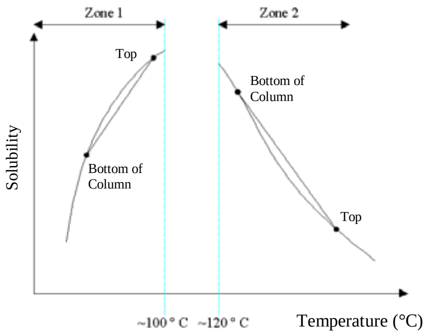

Fig. 3: Qualitative solubility of DAO in a parafinic solvent

Table 1: Some results of bench operation @ T=50 ºC for pentane solvent and T=35 ºC for butane solvent.

	450^+			470^+			500^+		
		DAO			DAO			DAO	
	VR	C_4	C_5	VR	C_4	C_5	VR	C_4	C_5
Sp.Gr 15.56°C	1.0458	0.9912	1.0038	1.0525	0.9985	1.0096	1.0646	1.0003	1.0007
Asphaltene,wt%	17.2	<0.5	<0.5	18.3	<0.5	<0.5	20.0	<0.5	<0.5
CCR., wt%	19.42	6.59	9.65	20.5	6.99	10.07	21.45	6.99	11.88
Sulfur , wt%	4.70	3.79	3.96	4.79	3.72	3.92	4.88	3.99	4.15
Vanadium, ppm	215.0	14.0	28.0	240.0	16.3	33.0	265.0	19.0	50.0
Nickel, ppm	55.0	3.9	7.2	70.0	4.2	8.8	73.0	4.6	12.0

Figure (4) shows the heavy metal content (Vanadium +Nickel) variations of DAO in SDA process according to the type of feed used. This figure shows, when the initial boiling point of vacuum residue increases, the DAO metal content increases accordingly. Also, raising the process temperature results in a better purified DAO. CCR content variations of DAO shown in figure (6) are similar to the heavy metal variations. The DAO sulfur content)S) variation is shown in figure (7), which is almost similar to CCR and heavy metal content graphs.

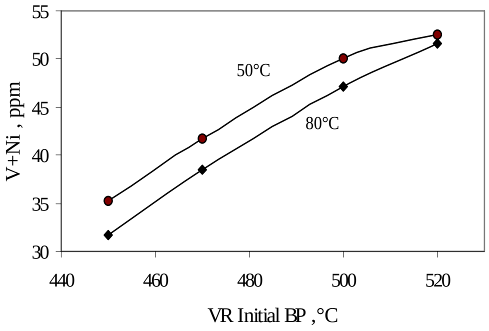

Fig. 4: Metal (V+Ni) content variation of DAO, SDA with pentane

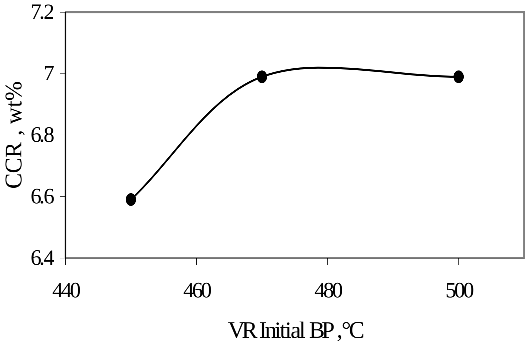

Fig. 5: CCR content variation of DAO, SDA with pentane

For all the tests, the DAOs produced were free of asphaltene (<0.5 wt%), regardless of the feed type. Table (2) presents the amount of the vacuum residue impurities reduction after the SDA process with pentane. According to this Table, extraction with pentane will reduce the heavy metal content of vacuum residue up to 85%, its sulfur content up to 20% and its CCR content up to 50%. As expected, because of the uniform distribution of sulfur compounds in different crude oils, no significant reduction in DAO sulfur content comparing to the vacuum residues is detected. Schematic graph of Figure (7) could be an understandable representation of how impurities in a vacuum residue are distributed.

Table 2: Reduction of Impurities in the SDA Process with Pentane

Parameter	Impurity Reduction (%)	Vacuum residue
Vanadium	87.7	**450⁺**
Nickel	87.4	
Sulfur	18.3	
CCR	50.8	
Vanadium	86.9	**470⁺**
Nickel	87.6	
Sulfur	21.5	
CCR	51.8	
Vanadium	85.5	**500⁺**
Nickel	85.9	
Sulfur	18.6	
CCR	50.4	
Vanadium	85.0	**520⁺**
Nickel	84.8	
Sulfur	21.5	
CCR	52.6	

Figures (8) and (9) depict metal and CCR content variations of the DAO product with butane solvent. Comparing these two figures with Figures (4) and (5) reveals that the DAO produced by extraction with butane is more purified than the DAO produced by extraction with pentane. SDA with butane results in 93% reduction of heavy metals content and 66% reduction of CCR content of the vacuum residue while for pentane as the solvent, these figures are 85 and 50%, respectively.

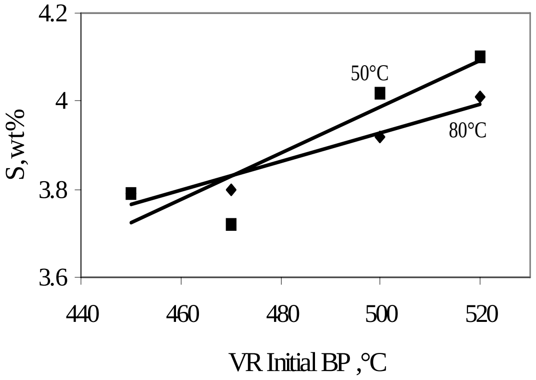

Fig. 6: Sulfur content variation of DAO, SDA with pentane

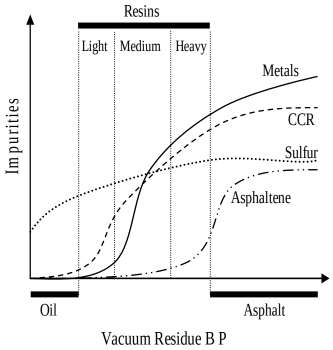

Fig. 7: Qualitative variation of impurities of vacuum residue among its constituents

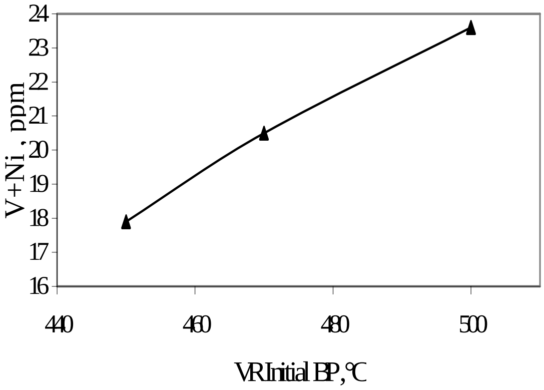

Fig. 8: Metal (Vanadium+ Nickel) content variation of DAO, SDA with butane

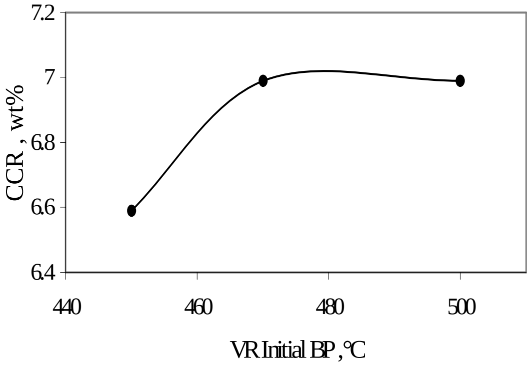

Fig 9: CCR content variation of DAO, SDA with butane

4. Conclusion

In this study, SDA bench-scale tests have been carried out on vacuum residues 450^+, 470^+, 500^+ and 520^+ using butane and pentane solvents. It should be noted that prior to the design of an industrial plant, more studies have to be performed. In the other words, in order to design an industrial scale extractor, design data from similar equipment in a pilot-plant scale are required. Having said that, the results of the present work can be referred to as a good measure for selection the feed, solvent, and somewhat, for the process operational conditions.

The extract and raffinate phases were fully separated in all tests, which is not common in an industrial scale. In the other words, full separation of the two phases is hardly practicable in industrial scale plants as it will be very costly, therefore, it can be concluded that the yields reported here are almost the highest possible amounts.

In real industrial process conditions, part of oil and light resins enter the pitch. Nonetheless, the result of tests carried out on back-blending of oil-resin cuts with pitch (the tests are performed in a way close to industrial conditions), do not show any improvement in the quality of the pitch for industrial production of commercial bitumen. Except for SDA units specifically designed to produce roofing or paving asphalt, the asphalt product is normally considered a law - value by-product. Partial oxidation of pitch can be produced synthesis - gas for manufacturing power, steam, methanol and many other products, aquaform for pelletizing asphaltene from solvent deasphalters is a new technology. It is low – cost, high capacity, continuous process for producing uniform, solid asphaltene pellets. The pellets produced are resistant to dusting and can be easily handled, stored, and transported[4]. The asphaltene pellets have a higher heating value and improved fuel properties versus petroleum coke and thus represent improved fuel value.

References

[1] Gonzalez, E. B., C. L. Galeana, A. G. Villegas, J. Wu, AIChE Journal, vol. 50, No.10, Oct. 2004, p. 2552
[2] Meyers, R. A., Handbook of Petroleum Refining Processes, 10th ed., McGraw-Hill, 2003.
[3] Ditman, J.G., Van Hook, J.P.: ACS Meeting, Atlanta, April 1981.
[4] Subramanian, M., Moretta, J., Bloom, R., Martin, M.: PTQ J., 2000, Summer, p.17