INTEGRATION OF EXTRACTION AND RESS FOR SOLVENT

RECOVERY FROM ASPHALTENE

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Abstract   A continuous three-stage supercritical extraction process with capacity of 1.0 kg/hr was setup to extract petroleum residue by pentane to obtain more oil for further upgrading. A problem how to recover solvent remained in asphaltene was encountered when very high oil yield is aimed. As is well known, asphaltene is very complicated mixtures with high molecular weight up to ten thousands or higher, having a very high melting points (Softening Point) and being thermally liable, solvent in it can't be recovered by furnace heating without risk of coking. To solve this problem, a spray system integrated to the bottom of extractor was used to spray asphaltene phase. By RESS process, rapid expansion of supercritical or subcritical asphaltene solution, the asphaltene was sprayed and cooled into solid particles and solvent was recovered as gas. The influence of operating conditions on the yield and quality of extracts, i.e., deasphalted oil (DAO) and resin were searched in the range of temperature 150-220？, pressure of 4.0-6.0MPa and solvent to feed ratio (S/F) 2.5-5.0(wt/wt). The particles distribution, apparent forms and the packing density, which vary as spray nozzle size and operating pressure, were measured. The particle structures by SEM were observed as well. With this innovation to conventional processes, furnace can be eliminated for solvent recovery from asphaltene, thus reducing energy consumption.
Key words: spray, particle, RESS, solvent, recovery, asphaltene

Introduction

Solvent deasphalting processes, as successful supercritical extraction applications, have been commercialized for many years. Commonly used solvents are propane, butane, pentane and their mixture. The objective of heavy solvent deasphalting by butane and pentane is to concentrate most of the contaminants such as metals and asphaltene in petroleum residua to the asphalt stream and produce a clean DAO that can be fed to further upgrading processes such as fluid catalytic cracking and hydrocracking. There are many licensed commercial processes including ROSE, Demex, LEDA and Solvahl [1]. However, there is no distinct difference among these processes, except for minor variations in equipment design. The operating principle is similar to the propane deasphalting process, in which liquid-liquid extraction is carried out followed by supercritical solvent recovery. The latest development is the supercritical fluid extraction (SFE) deasphalting process developed by the State Key Laboratory of Heavy Oil Processing at the University of Petroleum, China. In the SFE deasphalting process, the extraction step occurs under supercritical or near-critical condition

of the solvent, followed by supercritical solvent recovery. The SFE deasphalting enhances DAO yield and selectivity [2] and provides a cleaner separation. Heavier solvent could help getting more deasphalted oil (DAO) for further upgrading to produce more gasoline and diesel. But DAO yield is limited by properties of unextractable asphaltene. Higher yield DAO will result in very hard asphaltene. As is well known, asphaltene is very complicated mixtures with high molecular weight up to ten thousands or higher, having a very high melting points (Softening Point) and being thermally liable. In conventional processes when softening point of asphaltene is not very high, say below 100? , solvent remained in asphaltene phase can be recovered by furnace heating and then flashing and stripping by high temperature steam . But to separate solvent from asphaltene with softening point over 150 ？ is a very difficult task because overheating will cause risk of coking and plugging in furnace tube.

Rapid expansion of supercritical solution (RESS) has been widely searched as tools to make fine particles [3]. Common procedure is to solve organics in supercritical carbon dioxide and spray the solution into atmospheric pressure through a thin nozzle. Fine particles could be separated from gas carbon dioxide under proper conditions. Inspired by this conception, RESS of the asphaltene phase was thought could be a choice for solvent recovery since it contains solvent under subcritical or supercritical conditions. A few aspects were emphasized in this work. One is that pentane must be gas state that it can be easily separated from particles. Secondly is that asphaltene phase contains much less solvent [4] than in conventional RESS process and is very viscous. As well most important things are extraction and separation conditions must be coupled to obtain high enough DAO yield and at the same time get particles with good fluidity that it can be discharged easily. Experiments were carried out to verify the idea and a method for low temperature solvent recovery from asphaltene was established successful [5].

1. Experiments

A continuous three-stage supercritical extraction process with capacity of 1.0 kg/hr was setup to extract petroleum residue by pentane to obtain more oil for further upgrading. Showing in figure 1 is the schematic flowsheet of the process. The solvent and feed are heated and pumped and then mixed under given conditions, the mixture then is fed into the extractor, where the extract and the bottom phase are separated. The extract is further separated into two fractions in resin separator by heating, getting one light phase of DAO and one heavy of Resin. In solvent recovery tower DAO is separated from solvent which is then recycled back to the solvent cylinder. The bottom phase is further extracted in the extractor by auxiliary solvent. A spray system integrated to the bottom of extractor was used to spray asphaltene and cool it into solid particles while solvent was recovered as gas. The particle distribution is analyzed by Malvern ？K (Malvern Instruments Ltd), SEM was carried out on a S250 MK3 (Cambridge, British) and the packing density was measured by standard method.

2. Results and Discussion

At first the influence of operating conditions on the yield and quality of extracts were searched in the range of temperature 150 to 220? , pressure of 4.0 to 6.0MPa and solvent

to feed ratio (S/F) of 2.5 to5.0(wt/wt). The feed is vacuum residue of domestic Dagang crude oil. The operating conditions were optimized based on following rules. The separation must be clean, i.e., the contaminants such as carbon residue (CCR) which is coking precentor and heavy metals which are poisons to catalysts for further upgrading processes should be enriched in asphaltene. Experiments showed that the total yield of DAO plus resin should be kept below 85wt% otherwise resin quality would become much worse. Thus the operative conditions range is as following: Extraction temperature 160-170 ? , Resin separator temperature 165-185? , pressure 4.0-5.0MPa and solvent to feed ratio 4.0-4.5(wt/wt). As well the supercritical conditions for solvent recovery are pressure 4.0- 4.5MPa and temperature 200-220? .
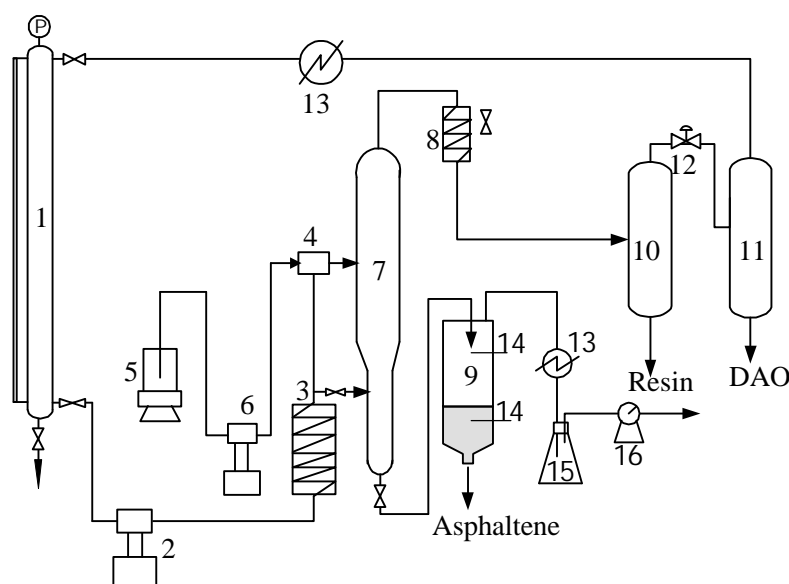
1-Solvent cylinder, 2-solvent pump, 3-preheater, 4-mixer, 5-feed tank, 6- feed pump 7-extractor, 8-heater, 9-spray chamber, 10-resin separator, 11- solvent recovery tower, 12-back pressure regulator, 13- cooler, 14-thermol couple, 15-flask, 16-gas meter

Figure1 Schematic flowsheet of RESS integrated with SEF

Table1 Extraction conditions and products quality

	Pressure MPa	S/F (wt/wt)	Aux. S/Main S.	T_{EXT} ?	T_{SEP} ?	Yield wt%		
						DAO	Resin	Asp.
DgVR -07	4.0	4.0	1.0/3.0	160	165	51.3	26.4	22.3
DgVR-16	5.0	4.5	1.0/3.0	170	175	66.9	17.1	16.0

		Mn	Softening Point ?	Viscosity (70?) mPa.s	CCR wt%	Metals(μ g/g)				
						Ni	V	Na	Ca	Fe
Feed		1159	<35	5650	15.3	81.4	1.3	23.1	37.5	8.9
DgVR –07	DAO	804	/	244.7	6.85	34.2	< 0.1	0.3	0.4	2.8
	Resin	971	/	1006.4	12.34	79.9	0.1	0.7	1.2	9.6

DgVR –16										
	Asp.	$>10^4$	>200	/	43.0	226	2.7	54.9	242	145
	DAO	788	/	245.7	6.92	34.8	0.3	0.3	1.0	2.5
DgVR –16	Resin	989	/	1411.5	13.91	88.4	0.8	1.4	5.4	11.5
		$>10^4$	>200	/	43.4	268	3.7	64.5	222	118

Table 1 lists the products quality under typical conditions. The RESS conditions for asphaltene phase should follow the conditions for extraction and separation. Nozzle size and operating pressure are major variable parameters. Under the conditions as Dg VR-06, a 0.7mm diameter nozzle was used. The temperature at the outlet of nozzle was measured, ranging in 70 to110? , under which pentane is gas and asphaltene is in solid state. Gas pentane is then cooled and measured volume. The solvent is found only 10wt% in the asphaltene phase. Then the nozzle size effects on particle distribution are measured for one

0.7mm and one 1.0 mm diameter. Each were tested under extraction temperature 160? and

pressure 4.0MPa and repeated 7 times. From table 2 it can be seen that wider nozzle diameter tend to produce large particles. While at the small size cumulative yield 10 v% (d(0.1),µ m), the difference in particle diameter between two nozzles are not so big. But as cumulative yield reaches to 50 v% (d(0.5),µ m), the difference become larger. The difference for average diameter is around 50µ m (D[4,3],µ m) and the major difference are due to big particles.

Table 2 nozzle size effects on particle distribution

Nozzle Diameter mm		d(0.1),µ m	(d(0.5),µ m)	d(0.9),µ m	D[4,3],µ m
0.7	Range	38.33-42.67	122.35-178.24	322.26-434.22	154.91-209.18
	Average	41.7	149.1	368.1	179.2
1.0	Range	41.55-73.42	165.36-236.50	382.76-500.85	190.18-261.66
	Average	51.0	208.5	455.5	231.2

Under above conditions particles were found agglomeration as shown in figure 2(a) no matter nozzle size is 0.7mm or 1.0mm. In following experiments 1mm nozzle were used because 0.7mm nozzle was easy to plug. As was found that pressure is one sensitive parameter influencing both DAO quality and yield. Adjusting pressure may affect the RESS results. Figure 2 shows the apparent states of the particles under 4.0, 4.5 and 5.0MPa. The pressure plays a significant role in reducing particles agglomeration. On the left picture it can be seen that a loose ball with diameter of 3cm exists. As pressure increases to 4.5MPa, the situation improved greatly. While pressure rises to 5.0 MPa, the apparent dispersion of particles is quite uniform. The size distribution also becomes narrow as pressure increases and the average size is reduced dramatically as shown in figure 3. Two factors are considered taking function. Higher pressure will extract more oil and make asphaltene 'drier'. On the other hand, higher pressure can give stronger driving force to disperse asphaltene particles. The packing density of particles, another important factor, was found relating to average diameter of particles. The smaller the particles, the less packing density is. The scanning

electron photograph (SEM) under 500 times shown in figure 5 and BET results in table 3 may help illustrating this phenomenon. BET specific surface area and pore size were measured for particles obtained under 5.0MPa, the number are 8.9 m^2/g and 0.02681 cm^3/g and the major pore is within 1-2 nm. But the surface area is the same order of outer surface for this particle distribution. Thus the particles may be viewed as amorphism particles with particles without pores. The true density is 1.000g/cm^3 for this asphaltene. Smaller particles will shear more space, thus resulting less packing density.

（a） 4.0MPa   (b) 4.5MPa   （c） 5.0MPa

Figure 2 Apparent states of fine asphaltene particles   (Full scale= 1cm)
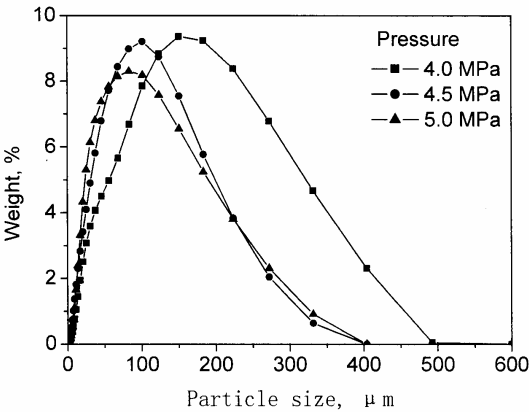

Figure 3 Particle size distribution

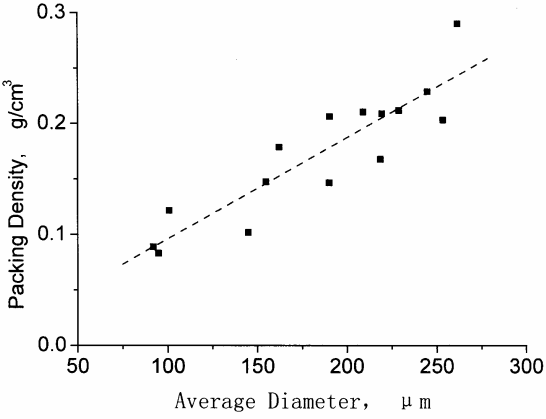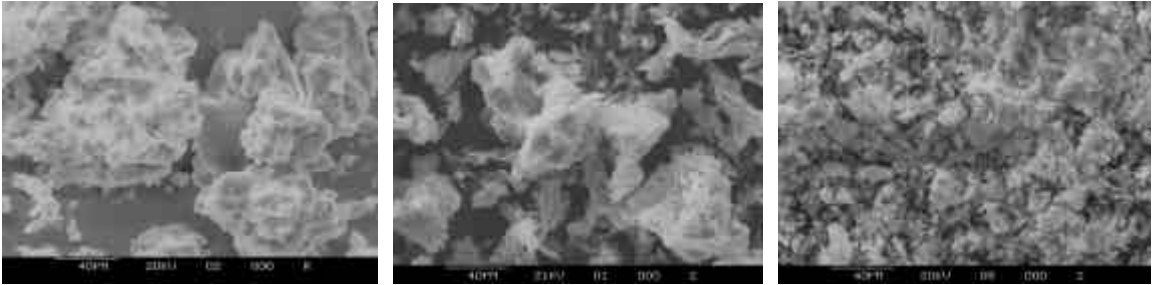Figure 4 Particle packing density as function of average diameter

(a) 4.0MPa   (b) 4.5MPa   (c) 5.0MPa

Figure 5 SEM photograph for asphaltene particles

Table 3   Pore size distribution of asphaltene particles

Pore size, nm	40-30	30-20	20-10	10-5	5-4	4-3	3-2	2-1
Pore volume, $10^{-3}cm^3/g$	4.15	1.06	2.62	3.54	1.49	1.90	2.28	9.75
V%	15.48	3.95	9.77	13.20	5.56	7.09	8.50	36.37

The asphaltene particles was dried under vacuum and high temperature up to 150? and found no mass loss. It means solvent loss with particle discharge may be neglected. This conclusion needs further verification by large scale of experiments. Any way, the developed method can be an efficient one to recover solvent under lower temperature.

3.Conclusion

RESS has been successfully coupled with extraction under subcritical and supercritical extraction process to separate solvent from asphaltene under temperature around 100? ,a much lower number than conventional furnace heating. Higher operating pressure significantly reduces average particle size and improves the agglomeration of particles. The particles are amorphism and without obvious pores. The smaller the particles, the less packing density of particles is.

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