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Supercritical Propane Fractionation of Wax-Bearing Residue

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ABSTRACT

Supercritical propane fractionation of Sheng-Bei wax-bearing residue was investigated using laboratory-scale apparatus. The residue was fractionated by increasing the pressure stepwise. The properties of the extracted fraction, the wax distribution in the fraction, and the properties of deoiled wax were studied. The experimental results show that this method can fractionate the residue in molecular weight order. It has very high selectivity; the saturates are easier to extract than the aromatics in the process. The application of the process in residue fractionation and upgrading was also discussed.

Key Words: Extraction; Supercritical; Residue

INTRODUCTION

Supercritical fluid extraction is a novel separation technique. Supercritical fluid extraction has several characteristics: fast mass transfer rate, ease of phase separation, low energy consumption of solvent recovery, etc., but the essential characteristic of supercritical fluid extraction is the variable fluid solvent power. Some experimental results show that solvent power of supercritical fluid extraction relies mainly on fluid density, which depends on the extraction temperature and pressure. On the basis of these characteristics, a novel supercritical fluid fractionation process was designed (1, 6) which achieved a higher separation effect. Supercritical CO_2

fractionation was used to fractionate fatty acid esters (2, 3). Supercritical butane was used to separate lubricant oil (4). These experimental results showed that supercritical fluid fractionation is an effective means for the fractionation of complex mixtures. As is well known, petroleum residue is a complex mixture. Fractionation of this residue is very important but also difficult and expensive. For this reason, it is very important to develop an effective residue separation method. For this report, Sheng-Bei wax-bearing residue supercritical propane fractionation was studied with a laboratory-scale supercritical fluid extraction apparatus. The properties of the extracted fractions, the wax distribution in the extracted fractions, and the properties of deoiled wax were studied. Our experimental results show that supercritical propane fractionation offers very high selectivity. The possibility of applying supercritical fluid fractionation to residue fractionation and upgrading are also discussed.

EXPERIMENTAL APPARATUS

Figure 1 is a schematic diagram of the experimental apparatus. The apparatus consists of a solvent pump, solvent heater, residue pump, pressure controller, extractor and solvent separator, etc. The extractor con-

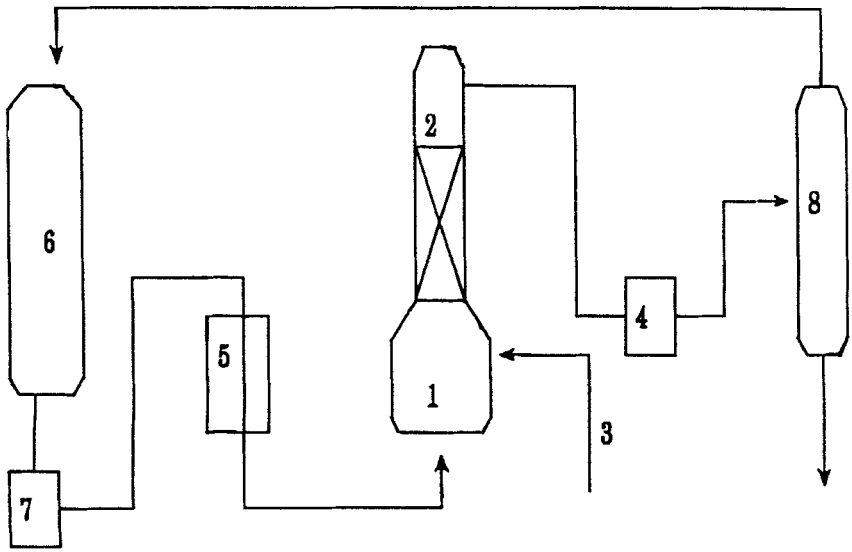

FIG. 1 Schematic diagram of the experimental apparatus: (1) extractor, (2) fractionation column, (3) residue, (4) pressure controller, (5) heater, (6) solvent storage, (7) solvent pump, (8) solvent separator.

sists of two parts: an extraction cell and a fractionation column with stainless steel packings. The height of the extractor is 20 cm and its internal diameter is 4.9 cm, the height of the column is 80 cm and its internal diameter is 3.1 cm. The height of the packing is 60 cm. Four thermocouples are used at different heights to measure the fluid temperature. In a typical experiment the temperature at the top of the column was kept higher than the temperature of the rest of the apparatus. The preheated solvent was fed through the apparatus at 30 mL/min. When the operation conditions of the experiment were established, the residue (180 g) was pumped into the extractor. At a given temperature, the solvent extracted residue in the extraction cell. As the loaded solvent flowed through the column, it was heated, the density of the loaded solvent decreased, and the less volatile components condensed and dropped back into the column. The product remaining in the loaded solvent was isolated in the solvent separator and then collected. The solvent was recycled. In addition, the discontinuous variation of pressure in the extraction vessel led to fractionation. The residue was fractionated by increasing the pressure stepwise. The residual solvent in the collected fractions was removed and then weighed. The qualities of the fractions were characterized. The group composition was determined by chromatographic fractionation. The adsorbent was aluminum oxide. The eluting solvent was heptane and a toluene–heptane mixture. The average molecular weight was determined by the VPO method, and the C/H atom ratio was determined by an elemental analyzer. The other properties were determined by national standard methods.

RESULTS AND DISCUSSION

The properties of the residue are listed in Table 1. The solvent was propane (purity > 95%).

The Properties of Extracted Fractions

The results of supercritical fluid fractionation have shown that the separation effect improves as a temperature gradient forms in the fractionation

TABLE 1
Properties of Residue

d_t^{20}	0.9435	Viscosity (100°C)(Pa·s)	0.076
CCR (m%)	8.43	Ductility (25°C)(cm)	0
Group composition:		Penetration (25°C)(1/10 mm)	38.2
Saturates (m%)	59.09	Softening point (°C)	58.0
Aromatics (m%)	28.78	Ni content (ppm)	12.7
Resin (m%)	20.62		

column. The larger the temperature gradient in the fractionation column, the higher the separation efficiency. But a higher extraction pressure is needed in order to obtain the higher extraction yield. It is very important to select a suitable extraction temperature and pressure. In this experiment the temperature at the top of the column was kept at 384.15 K, and the temperature at the bottom of the column was kept at 373.15 K. The extraction pressure varied from 5.4 to 10.8 MPa.

Figure 2 shows that the yield of extracted fraction is a function of pressure. It is obvious that an extraction yield of over 60 wt% can be obtained with propane as solvent. The extraction yield increases as the pressure increases. Fractions of more than 52% can be extracted under 8.3 MPa. In the pressure range 8.3–10.8 MPa, the yield of fractions only increases 12%. It may therefore be seen that the components in the residue are less soluble in supercritical propane when the extraction yield is over 52%.

Typical properties of the extracted fractions are listed in Table 2, which shows that the average molecular weight of extracted fractions increases as the yield of the fraction increases. This illustrates that the residue can be fractionated in average molecular weight order.

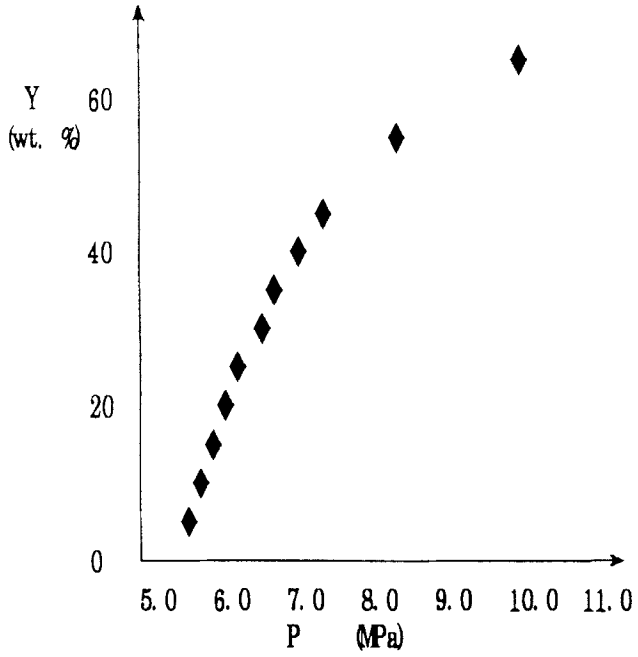

FIG. 2 Relationship between yield of extracted fractions and pressure.

TABLE 2
Properties of Extracted Fractions

No.	Fraction yield (m%)	Total yield (m%)	Saturates (m%)	Aromatics (m%)	CCR (m%)	Mol. wt.	C/H (atom)
1	4.4	4.4	90.8	9.1	0.26	442	0.51
2	4.5	8.9	89.7	10.7	0.34	555	0.52
3	5.8	14.7	89.0	10.9	0.40	563	0.52
4	4.5	19. 2	88.7	11.3	0.48	598	0.52
5	5.7	24.9	87.8	12.2	0.48	624	0.52
6	5.1	30.0	86.2	13.8	0.63	651	0.52
7	5.3	35.3	84.8	15.1	0.83	739	0.52
8	5.7	41.0	82.0	17.1	1.02	748	0.53
9	5.7	46.7	80.7	19.2	1.33	908	0.53
10	5.4	52.1	77.0	20.7	1.77	878	0.53
11	5.7	57.8	74.0	24.0	2.26	998	0.54
12	6.8	64.7	65.6	28.3	2.72	1017	0.54

It should be noted that Conradson Carbon Residue (CCR) of the extracted fractions increases as the yield of the fractions increases. When the yield of the fraction is over 40%, CCR of the fractions changes rapidly with increasing yield of the fractions. This illustrates that the heavier components are extracted as the extracted yields increase.

The results for group composition distribution in extracted fractions show that the saturates content in the fractions decreases and the aromatics content increases as the yield of the fractions increases. When the yield of fractions equals 47%, the saturates content in the fractions is still over 80% (the saturates content in the residue is 50%). This shows that the process has a higher selectivity for saturates. The C/H atom ratio of extracted fractions increases from 0.51 to 0.54 as the extraction yield increases. The results confirm that the saturates are easier to extract than the aromatics in supercritical fluid fractionation. More aromatics can be extracted when the saturates content in the residue is decreasing. There are two possible explanations for this. First, the properties of saturates are similar to the properties of the solvent, which leads to the higher solubility of saturates in propane, Second, the saturates have a higher volatility than the aromatics, and the volatile components are favored for extraction by the supercritical fluid.

Solvent Deoiling of Extracted Fractions

In order to study the wax distribution in extracted fractions and the quality of microcrystalline wax, extracted fraction deoiling was con-

ducted. The deoiling solvent was a toluene–butanone mixture (1:1 by volume), the oil/solvent was 1:10 (by volume), and oil/eluting solvent ratio was 1:7 (by volume). The filtering temperatures were 298 and 278 K. The results for the extracted fractions in Table 2 after solvent deoiling are listed in Table 3.

Table 3 shows that white deoiled wax can be obtained by solvent deoiling of extracted fractions. The deoiled wax consists mainly of saturates. When the yield of the extracted fraction equals 47%, the saturates content in deoiled wax is over 96%. The aromatics content in the deoiled wax is lower (1.66–8.66%). The deoiled wax does not contain nitrogen or sulfur. The H/C atom ratio is 2. The deoiled wax (278 K) content in the extracted fraction approaches 50%.

Application in Residue Fractionation and Upgrading

Residue Fractionation

In order to put the residue to reasonable use, it is essential that its structure and properties be better understood. As is commonly known, residue is an extremely complex material. It is necessary to develop an effective residue separation technique for residue evaluation. The two most widely used techniques are chromatographic fractionation and molecular distillation. The residue can be separated into different groups according to the polarity of components in chromatographic fractionation (e.g., saturates, aromatics, etc.). The method offers a very high separation

TABLE 3
Properties of Deoiled Wax

No.	Content in fraction (m%)	Dropping point (°C)	C/H (atom)	Mol. wt.	Saturates (m%)	Aromatics (m%)
1	36.4					
2	45.4	85.0	0.48	590	98.3	1.66
3	44.1					
4	45.1	—	—	—	—	
5	46.0	89.9	0.49	662	97.8	1.98
6	—	90.7	0.49	704	97.2	2.67
7	39.6	92.1	0.49	705	97.3	2.62
8	46.0	91.8	0.49	1017	96.3	3.10
9	36.0	—	—	—	—	—
10	42.1	94.4	0.50	1019	93.5	6.57
11	44.9	98.7	0.50	1302	91.3	8.66
12	39.2	96.0	0.51	1298	—	—

effect. It has been put to use for residue evaluation, but it is time consuming. Molecular distillation separates residue on the basis of volatility. There are many components in residue which may crack or condense during molecular distillation. There are some limitations in using molecular distillation to evaluate residue, especially vacuum residue. As discussed above, supercritical propane fractionation offers very high selectivity for residue separation. It can fractionate residue into several fractions. Compared with molecular distillation and chromatographic fractionation, the method has the following characteristics: 1) its low separation temperature prevents the residue from cracking and condensing, and 2) it provides more specimens for future study and there are no toxic solvents. Supercritical fluid fractionation is an efficient residue fractionation process with good prospects for application in residue evaluation.

Residue Upgrading

A typical commercial microcrystal wax production process is given in Fig. 3.

In the deasphalting processes, different purposes make different demands. If the process mainly provides cracking units for feedstock (e.g., ROSE, Demex), the aim of the process would be a higher extraction yield. The main solvent used is butane or pentane. If the process is to supply feedstock for lubricant or wax units, higher selectivity must be considered. The solvent mainly used is propane and/or its fraction, but liquid propane deasphalting has some weaknesses such as a low extraction yield. The process used in microcrystal wax processes has caused some difficulties

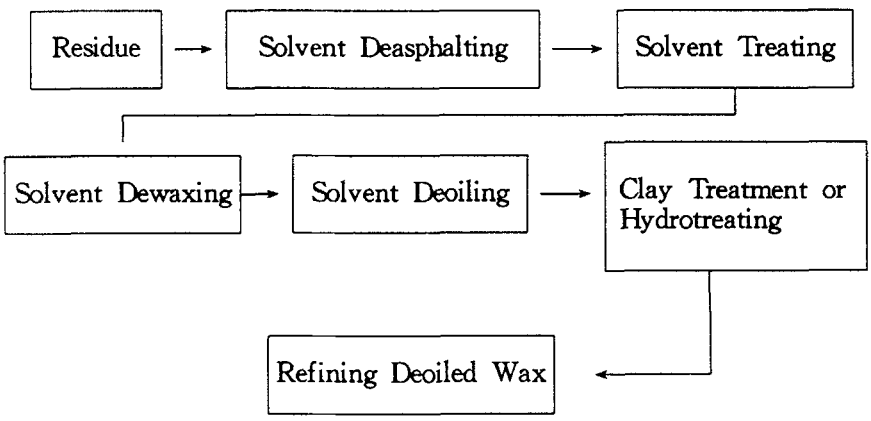

FIG. 3 Typical commercial microcrystal wax production processes.

TABLE 4
Properties of Sheng-Bei Residue Supercritical Propane Fractionation and Liquid Propane Deasphalting

		Supercritical propane fractionation		Liquid propane deasphalting	
		I	I	I	I
Extracted fraction	Yield (wt%)	30.29	46.76	30.1	36.20
	Saturates (wt%)	84.48	86.08	78.17	—
	Aromatics (wt%)	11.26	13.44	15.93	—
	CCR (wt%)	0.35	0.73	0.64	0.87
Deoiled wax	Color	White	White	Brown	—
	Saturates (wt%)	>97	>95	89.80	—

(5); the quality of the extracted fractions is bad, and deoiled wax refining is difficult. Supercritical fluid fractionation is highly selective. Table 4 lists the result of Sheng-Bei residue supercritical propane fractionation compared with liquid propane extraction. Supercritical propane fractionation has some advantages: 1) high extraction yield, 2) a high quality extracted fraction (high saturates content in the fraction and low resin and aromatics contents), and 3) a high wax content in the extracted fraction.

On the basis of our results, a novel microcrystal wax production process is proposed (Fig. 4). This process has the following advantages compared to conventional microcrystal wax production processes:

1. It is a simpler microcrystal wax production process because the supercritical fluid frctionation process offers higher selectivity.
2. There are high quality extracted fractions (higher saturates content

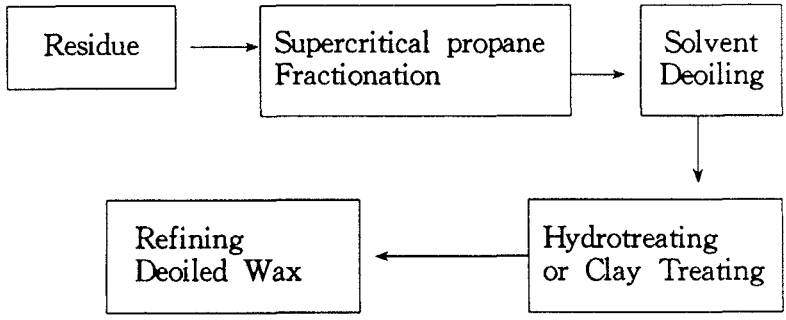

FIG. 4 The novel microcrystal wax production process.

and lower aromatics content in the fractions) and higher extraction yields.
3. Refining of deoiled wax is easier.

Supercritical propane fractionation needs a higher extractive pressure, but we can select the other solvent (e.g., C4) for which the extraction pressure can be decreased. The latest experimental results showed that the separation efficiency of supercritical butane fractionation is similar to that of supercritical propane fractionation, but the extraction pressure is lower.

CONCLUSION

Sheng-Bei residue was fractionated into several fractions by supercritical propane fractionation. The results showed that supercritical propane fractionation is a method with very high selectivity. It fractionates the residue in molecular weight order. The extraction yield and quality are higher than from the liquid propane deasphalting process. High quality deoiled wax can be obtained directly by extracted fractions solvent deoiling.

REFERENCES

1. D. F. Williams, *Chem. Eng. Sci.*, *36*(11), (1981).
2. W. Eisenhach, *Ber. Bunsenges. Phys. Chem.*, *88*, 882 (1984).
3. W. B. Nilsson, *J. Am. Oil Chem. Soc.*, *65*(1), (1988).
4. J. Cheng et al., *Lubricant (China)*, No. 3, (June 5, 1993).
5. H. Zhang, *Pet. Refining Eng. (China)*, p. 4 (1990).
6. K. Zosel, *Angew. Chem., Int. Ed. Engl.*, *17*(10), 702 (1978).

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