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# Softening Point: An Indicator of Asphalt Granulation Behavior in the Selective Asphaltene Extraction (SELEX-Asp) Process

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**ABSTRACT:** Granulation is an effectual method to deal with huge amounts of deoiled asphalt (DOA) produced in the residue selective asphaltene extraction (SELEX-Asp) process, and the softening point of DOA plays an important role in asphalt particle production. In this paper, the variation of the softening point under different operation conditions and its influence on asphalt granulation behavior were studied with various solvents and feedstocks. Moreover, properties and structures of five C7 asphaltenes were analyzed with  $^{13}\text{C}$  nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) measurements to examine the reasons of asphalt softening point differences for various residues under the same operation conditions. Ordered degree index (OI) and softening point index (SI) were proposed to investigate the influence of asphalt ordered aromatic sheets on the softening point. High softening point asphalt could be obtained with lower temperatures and higher pressures of the extractor, a larger mass ratio of solvent to feed, and a heavier solvent. Asphalt tends to form particles with the increase of the softening point, and nice particles would be produced when the softening point is higher than 170 °C. OI of C7 asphaltene is an important factor affecting the asphalt softening point. A close correlation between SI and the softening point was established; that is, feedstocks with a high SI would have the ability to produce high softening point asphalt and possess a good asphalt granulation behavior. The quantity of ordered aromatic sheets in asphalt is the fundamental determinant of the softening point.

## INTRODUCTION

As light crude supplies continue to dwindle, processing of heavy crudes and residuum is becoming more attractive. It is well-known that the amount of heavy crudes, such as oil sands bitumen,<sup>1,2</sup> is huge but in company with high viscosity, density, Conradson carbon residue (CCR), sulfur, nickel, vanadium, and asphaltene.<sup>3,4</sup> Asphaltene has been termed to be “the cholesterol of petroleum”,<sup>5</sup> which can cause problems for producers,<sup>6</sup> leading to catalyst deactivation and fouling and plugging of tubing, pipes, valves, and reactor flow lines.<sup>7</sup>

The supercritical solvent deasphalting process is an effective method to remove most asphaltene and yield high-quality deasphalted oil (DAO) as fluid catalytic cracking and hydrocracking feedstocks because of its low metal (Ni + V) contents.<sup>8–10</sup> A number of studies has been performed to study solvent deasphalting with various solvents and feedstocks.<sup>11–14</sup> Granulation of post-extraction asphalt residue in the selective asphaltene extraction (SELEX-Asp) process is a new development of supercritical solvent deasphalting.<sup>15</sup> The de-oil asphalt (DOA) can be produced in the form of particles<sup>16</sup> and as a feedstock of pitch-water slurry for combustion or gasification. The softening point of asphalt is a very important parameter in asphalt particle production. Unfortunately, there is no distinct explanation about softening point variation with the change of operation conditions and its influence on asphalt granulation behavior. On the other hand, the softening point sometimes varies tremendously (from 120 to 200 °C) for various feedstocks under the same operation conditions in many experiments. This phenomenon is also needed to investigate the convenience of the development of this process.

In view of the importance of the softening point, various residues, solvents, and operation conditions were adopted to

observe the softening point variation and its influence on asphalt granulation behavior. The properties and structures of asphaltene are needed for effective removal of the asphaltene from residue, which is also a contribution to the petroleum chemistry research.<sup>17–19</sup> Lots of studies for asphaltene had been carried out<sup>20–22</sup> and yielded useful information with various methods, such as nuclear magnetic resonance (NMR),<sup>23</sup> X-ray diffraction (XRD),<sup>24–26</sup> small-angle X-ray scattering (SAXS),<sup>27–29</sup> scanning electron microscopy (SEM),<sup>30</sup> transmission electron microscopy (TEM),<sup>31,32</sup> etc. However, the correlation of properties, such as the softening point with structures, has not been well-established. In this paper, the properties and structures of C7 asphaltenes from various feedstocks were studied with  $^{13}\text{C}$  NMR and XRD measurements for the analysis of softening point differences.

## EXPERIMENTAL SECTION

**Raw Material.** Five residues of different origins were selected to make a comparison of properties and structures of asphalt and asphaltenes: Middle East vacuum residue (MEVR), Canada oil sand vacuum-topped bitumen (VTB), China Liaohe vacuum residue (Liaohe VR), Venezuela atmospheric residue (Venezuela AR), and Venezuela vacuum residue (Venezuela VR). Properties of these residues are summarized in Table 1. They are typical heavy oil with high viscosity, density, CCR, sulfur, nickel, vanadium, and asphaltene. The purity of solvents used in this study is equal to 99.5%.

**Residue Supercritical Solvent Deasphalting and DOA Granulation.** The residue supercritical solvent deasphalting and

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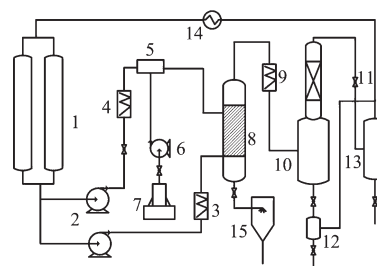
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Table 1. Properties of Residues

properties	MEVR	VTB	Liaohu VR	Venezuela AR	Venezuela VR
density at 20 °C (g/cm <sup>3</sup> )	1.0158	1.0548	1.0271	1.0303	1.0200
CCR (wt %)	23.13	24.94	24.01	18.44	20.06
viscosity at 100 °C (mPa s)	2188	26480	10575	2586	2602
molecular weight		1147	1190	866	
carbon (wt %)	84.85	81.77	87.06	84.00	84.63
hydrogen (wt %)	10.48	9.84	9.88	10.11	10.22
H/C	1.47	1.44	1.36	1.44	1.44
nitrogen (wt %)	0.69	0.78	1.55	1.13	0.76
sulfur (wt %)	4.0	5.8	0.5	4.4	3.6
nickel (wppm)	45	120	175	126	107
vanadium (wppm)	68.5	331	3.6	549	521
saturate (wt %)	25.52	7.80	20.38	20.01	26.97
aromatic (wt %)	46.24	41.52	25.98	40.41	40.49
resin (wt %)	17.21	32.60	38.21	26.76	20.18
C7 asphaltene (wt %)	11.03	18.09	14.60	12.13	12.36

DOA granulation experiments were carried out with a residue SELEX-Asp process (the schematic flowsheet of this process is shown in Figure 1). The main solvent and feedstock were heated and pumped and then mixed with each other, and the mixture then was fed into the extractor, where the extract and bottom phases were separated. The extract was further separated into two fractions in the second-stage separator, producing one light phase of DAO and one heavy phase of DAO. The solvent was recovered in the solvent separator and recycled back to the solvent tank. The bottom phase (DOA) was further extracted in the extractor by auxiliary solvent. The DOA was discharged to a granulation tower from the bottom of the extractor and cooled into solid particles, while the solvent was recovered as gas. The yield of asphalt could be calculated by the weight of feedstock and asphalt particles. In this process, the temperature and pressure of the extractor and mass ratio of solvent (sum of main and auxiliary solvents) to feed are very important factors to affect the separation of extract and bottom phase; therefore, they were defined as operation conditions and discussed in this paper. For the convenience of expression, these three factors can be written in a simplified form, such as 170 °C, 5 MPa, and 4:1, which means the operation conditions are an extractor temperature of 170 °C, an extractor pressure of 5 MPa, and a mass ratio of solvent to feed of 4:1.

**Asphalt and Asphaltene Characterization.** Before the asphalt softening point measurement, 1.64 g of particles was compressed into asphalt cake by a powder compressing machine on the pressure of 10 MPa for 5 min. Then, the softening point was measured with a ball and ring method according to American Society for Testing and Materials (ASTM) E28. The microscopic morphology of asphalt was examined using a scanning electron microscope (FEI Quanta 200F, Hillsboro, OR). Asphalt was sputtering gold/palladium before the microscopic examination. The SEM digital images of asphalt particles were taken at 2000× magnification. The particle size distributions of asphalt were obtained by a laser particle size analyzer. Saturates, aromatics, resins, and C7 asphaltenes (SARA) compositions of feedstocks and asphalts were obtained according to the procedure described by Liang et al.<sup>33</sup> C7 asphaltenes were prepared from residues by mixing 40 mL of *n*-heptane per gram of oil and refluxing for 1 h. The suspension was then left at room temperature overnight. The asphaltenes were then filtered on the filter paper, and then the filter cake was refluxed with filtrate until the effluent was colorless. The asphaltene were dried in a



**Figure 1.** Schematic flowsheet of the SELEX-Asp process: 1, solvent tank; 2, solvent pump; 3, auxiliary solvent preheater; 4, main solvent preheater; 5, mixer; 6, residue pump; 7, residue heating and measuring system; 8, extractor; 9, second-stage heater; 10, second-stage separator; 11, pressure regulator; 12, heavy deasphalted oil evaporator; 13, solvent separator; 14, solvent cooler; and 15, granulation tower.

vacuum at 120 °C for 2 h. Elemental analysis was conducted using a Flash EA 1112 element analyzer. <sup>13</sup>C-NMR was conducted using a Varian Inova 200 MHz NMR apparatus. XRD analysis on asphaltenes was carried out on a Bruck D8 Advance instrument. Cu K $\alpha$  (1.540 56 Å) was selected as the monochromatic energy radiation. The diffraction angles ( $2\theta$ ) was scanned from 5° to 60° at a 1°/min scan rate with a 0.05° step size. The asphaltenes was mortared into fine powders prior to measurements, and all of the measurements were performed at room temperature.

## RESULTS AND DISCUSSION

**Influence of Operation Conditions on the Asphalt Softening Point.** The operation conditions (temperature and pressure of extractor and mass ratio of solvent to feed) can affect the solvent extraction from residue and then have effects on the yield and property of DOA. Figure 2 gives the influence of operation conditions on the yield of asphalt obtained from VTB with *n*-pentane. From this figure, the obvious influence of operation parameters on the yield can be obtained. With low temperatures or high pressures, the solvent has a high density and a much higher solubility, leading to a low asphalt yield. The mass ratio of solvent to feed can alter the quantity of the extraction solvent; the higher this ratio, the more solvent involved in extraction and the lower the asphalt yield obtained. The softening points of these asphalts were given in Figure 3, which shows a close relevance between the asphalt yield and its softening point. In this figure, the softening point decreases from 153.5 to 129.0 °C, accompanied with the increasing asphalt yield from 31.13 to 44.30 wt %. Hence, the high softening point could be achieved by reducing the asphalt yield. When Figures 2 and 3 are combined, the obvious conclusion could be obtained; that is, lower temperatures and higher pressures of the extractor and a larger mass ratio of solvent to feed prefer a high softening point asphalt.

Solvent selection is an important factor in residue supercritical solvent deasphalting and the asphalt granulation experiment, which also belongs to the operation condition parameter. The asphalt obtained from a single residue can present different properties with various solvents. For SARA fractions, saturates and aromatics are named the “soft fraction”, whereas resins and C7 asphaltenes are named the “hard fraction” in a conventional viewpoint. Light solvents could not effectively extract the “soft fraction” of feedstock, which tending to be left in asphalt in a considerable proportion. On the contrary, heavy solvents have the ability to extract the most “soft fraction” in feedstock, which causes a high proportion of “hard fraction” persisting in asphalt. Four solvents were selected to process MEVR under numerous operation

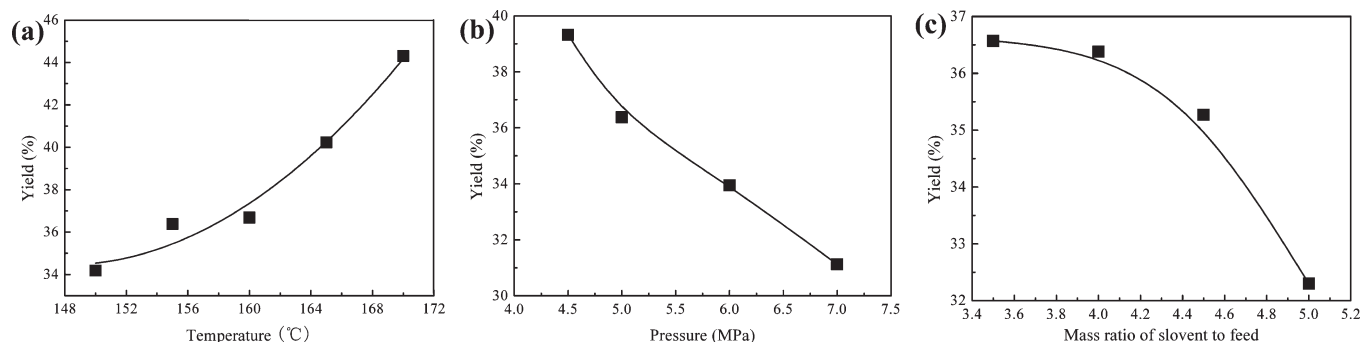


Figure 2. Influence of operation conditions on the asphalt yield: (a) temperature, (b) pressure, and (c) mass ratio of solvent to feed.

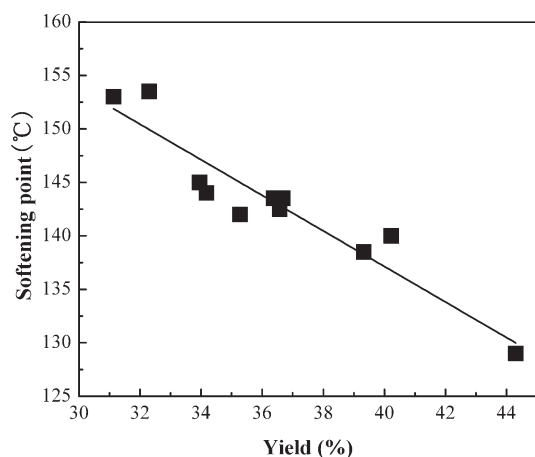


Figure 3. Influence of the asphalt yield on the softening point.

conditions to investigate the effect of solvent selection on the asphalt softening point in Figure 4. The softening point becomes much higher when the heavier solvent is selected with the same asphalt yield. For example, for 30% asphalt yield, the softening point is equal to 147.5 °C using *n*-pentane, while the softening point is equal to 132 °C using *n*-butane. To further study the influence of solvent selection, Table 2 gives the results of experiments with three solvents for Venezuela VR at the same operation conditions, which lists the asphalt yield, SARA composition, CCR, and softening point. When *n*-pentane mixed with *n*-butane, the asphalt yield increased about 10% from 20.6 to 30.7%, whereas the “hard fraction” content, CCR, and softening point decreased to a certain extent. The softening point of asphalt would be lower when adopting light solvent. We can come to a conclusion that the heavy solvent, which could carry out most of the “light fraction”, should be selected for high softening point asphalt production.

**Relationship between the Softening Point and Other Properties of Asphalt.** As an important property of asphalt, the softening point is often closely related to other properties of asphalt. Table 3 gives the softening points and SARA compositions of seven asphalt samples derived from the experiment of VTB and *n*-pentane under different operation conditions. The sum of resins and asphaltenes is also listed in this table. The “soft fraction” content decreases with the increase of the softening point. Correspondingly, the resin and asphaltene contents in high softening point asphalt are much larger than low softening point asphalt. As the “hard fraction”, C7 asphaltenes have the same trend with the softening point, but the resin content is almost unchanged

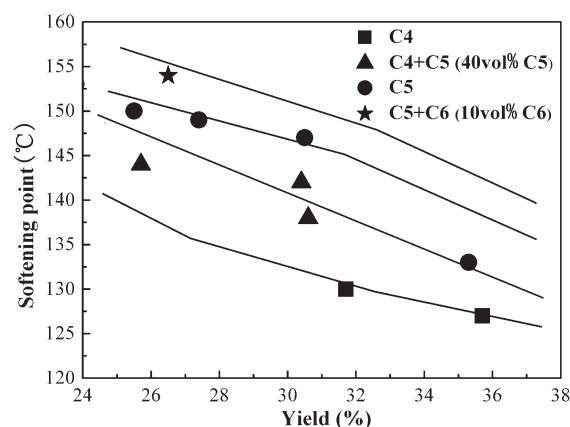


Figure 4. Influence of solvent selection on the asphalt softening point.

with varying the softening point. Therefore, the asphalt with a high C7 asphaltene content will prefer a high softening point.

CCR can indicate the coke forming tendency, which is mainly determined by the precursor of coke [polycyclic aromatic hydrocarbon (PAH)]. PAHs account for a considerable proportion in asphalt; therefore, there must be a correlation between CCR and the softening point. Figure 5 shows the influence of asphalt CCR on the softening point (the data are from the same experiment as Table 3). The softening point becomes much higher when CCR increases in a linear relationship, which proves that a strong correlation exists between the two parameters. The high softening point asphalt has a relatively high C7 asphaltene (shown in Table 3), and the C7 asphaltene composes lots of PAHs; therefore, the CCR of high softening point asphalt must be in a high level. From this aspect, the properties of C7 asphaltene play an important role in asphalt softening point determination.

**Influence of the Softening Point on Asphalt Granulation Behavior.** In the SELEX-Asp process, the softening point of asphalt varies greatly under different operation conditions. To purposefully change the operation conditions with the tendency obtained from Figure 2, we could obtain different yields and softening point asphalts and make an attempt to investigate the different granulation behaviors of these asphalts. Figure 6 gives the patterns of asphalt with different softening points obtained from VTB with the solvent of *n*-pentane. Asphalt tends to form particles with the softening point increasing from 135.1 to 178.0 °C. There is a certain proportion of maltene existing in the 135.1 °C asphalt (soft fraction and resin, the bright section in the picture), which softens the asphalt and reduces the softening



**Table 2. Effect of Solvent Selection on the Asphalt Properties**

solvent	yield (%)	saturates (%)	aromatics (%)	resins (%)	asphaltenes (%)	resins + asphaltenes (%)	CCR (%)	softening point (°C)
C5	20.6	1.70	11.29	33.06	53.95	87.01	49.85	194.2
C5 + C4 (15 vol % C4)	22.7	3.95	10.30	25.87	59.88	85.75	49.46	183.1
C5 + C4 (35 vol % C4)	30.7	2.35	15.13	34.77	47.75	82.52	46.31	174.3

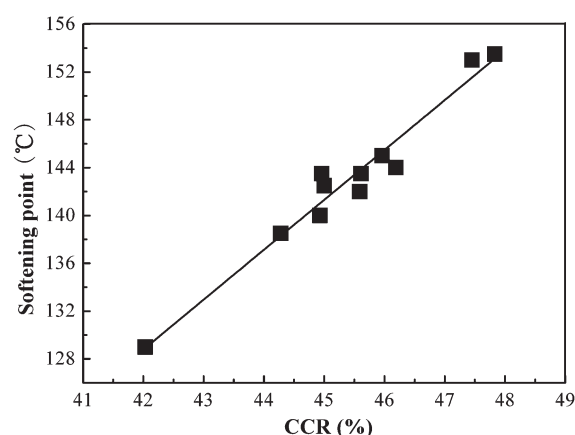
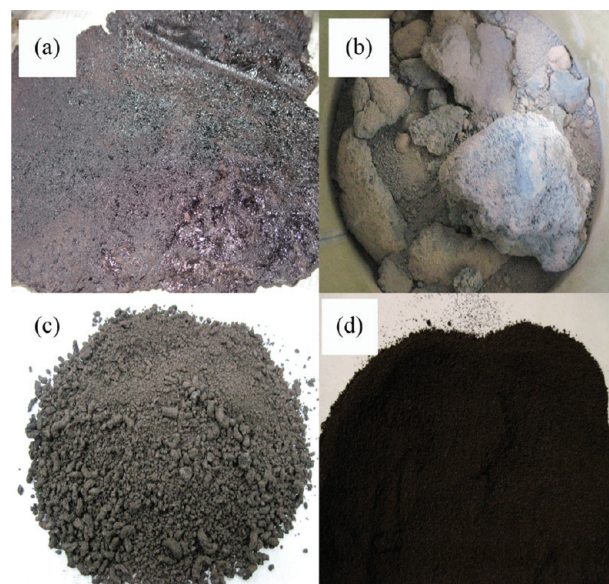
**Table 3. Influence of Asphalt SARA Composition on the Softening Point**

number	softening point (°C)	saturated (%)	aromatics (%)	resins (%)	asphaltenes (%)	resins + asphaltenes (%)
1	129.0	1.56	24.89	31.81	41.74	73.55
2	138.5	5.16	19.45	28.87	46.52	75.39
3	140.0	1.14	21.28	30.95	46.63	77.58
4	143.5	2.91	18.72	28.84	49.53	78.37
5	144.0	6.26	14.55	29.11	50.08	79.19
6	145.0	1.20	18.22	28.92	51.66	80.58
7	153.0	1.82	15.74	29.36	53.08	82.44

point. Therefore, the asphalt formed a bulk and failed to produce particles. When the softening point rises to 162.0 °C, with less maltene, the asphalt became much drier and obtained some particles but there were still some bulks existing in the heap of asphalt. This illustrates that the asphalt with a low softening point could not form nice particles. When the softening point rises to higher than 170 °C, the asphalt can be produced in the form of nice particles, especially with 178.0 °C. From the above analysis, we could obtain a conclusion that the softening point plays an important role in the asphalt granulation. Asphalt would show a good granulation behavior and form nice particles when the softening point is higher than 170 °C.

Microscopic structures of asphalt were studied under the scanning electron microscope at 2000× magnification, which may give an intuitionist understanding about the influence of the softening point. Figure 7 shows the SEM pictures of asphalts with the softening point of 162.0 and 178.0 °C, respectively. The asphalts in Figure 7a join with each other and form a solid bulk with porous surfaces. On the contrary, Figure 7b displays a lot of asphalt sheets stacking together. The apparent conclusion from the comparison of panels a and b of Figure 7 is that the particles from high softening point asphalt have a much dryer and smoother surface, which could be easily separated from each other and form nice particles (a good granulation behavior). The particle size distribution of asphalt is described in Figure 8. The average particle diameters of asphalt with the softening point of 162.0 and 178.0 °C are 297.2 and 199.5 μm, respectively. In comparison to asphalt in Figure 7b, large particles of asphalt in Figure 7a possess a high proportion with respect to small particles. Therefore, the higher softening point asphalt has the smaller particle diameter. The microscopic structures and particle size distribution of asphalt demonstrate that the high softening point asphalt tends to have a good granulation behavior and possess great potential to produce nice particles.

**Difference of the Softening Point from Various Feedstocks.** A much apparent diversity for softening point was presented when the feedstock was changed, just like the data shown in Figure 9. This figure gives the results of two operation conditions with the solvent of *n*-pentane and five feedstocks. The

**Figure 5.** Influence of asphalt CCR on the softening point.**Figure 6.** Patterns of asphalt particles with different softening points: (a) 135.1 °C, (b) 162.0 °C, (c) 170.3 °C, and (d) 178.0 °C.

operation conditions are condition 1 (160 °C, 5 MPa, and 4:1) and condition 2 (170 °C, 5 MPa, and 4:1). The softening points of asphalt vary from lowest to highest in the following order for both conditions: MEVR < VTB < Liaohe VR < Venezuela AR < Venezuela VR. The highest softening point is about 40 °C higher than the lowest for the five residues. A further investigation was conducted for the correlation between the softening point and C7 asphaltene of asphalt for the five feedstocks, and the results were given in Figure 10. Five feedstocks have their own zonal distribution regions of the asphalt softening point and MEVR and Venezuela VR share the same one. With the same C7 asphaltene content of asphalt, such as 50%, Venezuela VR has

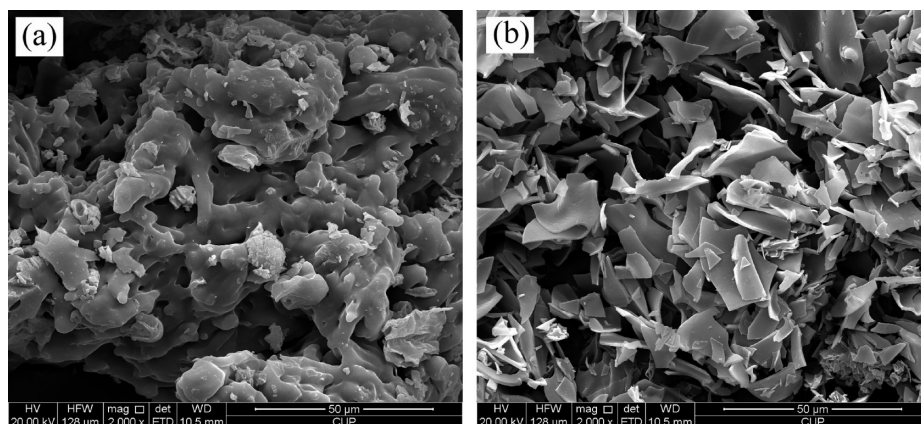


Figure 7. SEM photographs of asphalt at 2000 $\times$  magnification with different softening points: (a) 162.0  $^{\circ}\text{C}$  and (b) 178.0  $^{\circ}\text{C}$ .

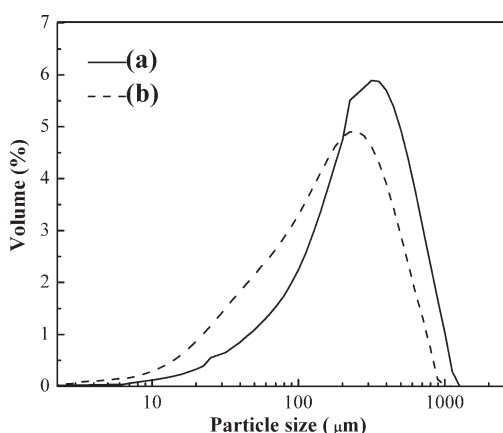


Figure 8. Particle size distribution of asphalt with different softening points: (a) 162.0  $^{\circ}\text{C}$  and (b) 178.0  $^{\circ}\text{C}$ .

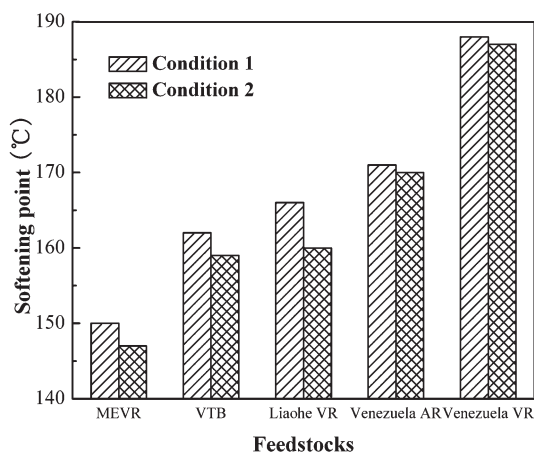


Figure 9. Softening points of asphalt derived from five feedstocks.

the highest softening point and VTB has the lowest, which is exactly the same as the conclusion obtained from Figure 9, except MEVR. Hence, the five feedstocks have distinctly different behaviors in asphalt particle production, and their properties are very important in this process.

**Cause Analysis of Asphalt Softening Point Differences for Various Feedstocks.** A direct comparison of asphalt cannot

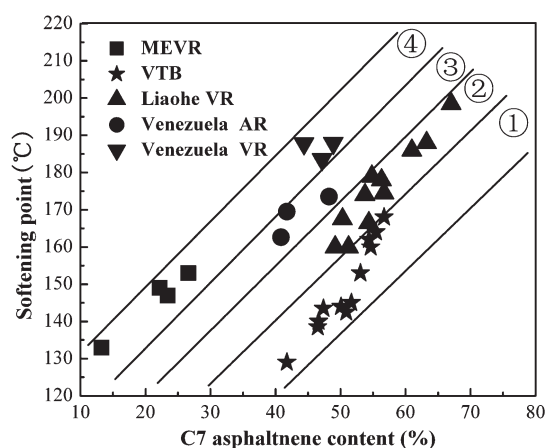


Figure 10. Influence of asphalt C7 asphaltene content on the softening point for five feedstocks.

represent the differences among feedstocks because the asphalt properties could be affected by the variation of operation conditions. A common criterion should be found for the convenience of different feedstocks comparison. A possible resolution of this problem may be the C7 asphaltene of these feedstocks. We may obtain some useful information about the softening point differences with the analysis of C7 asphaltenes.

Aromatic carbons occupied a considerable proportion in the asphaltene molecule and would closely affect the properties of asphaltene and asphalt.  $^{13}\text{C}$  NMR spectra can give the information about carbon classification and distribution in the asphaltene molecule. The  $^{13}\text{C}$  NMR spectra of C7 asphaltenes were shown in Figure 11. The carbon bands of asphaltene load in the 0–170 ppm region,<sup>34</sup> which could be subdivided into two kinds: the aliphatic carbon band (0–70 ppm region) and the aromatic carbon band (100–170 ppm region). Aromaticity  $f_A$  of five C7 asphaltenes were listed in Table 4, which were calculated with the following formula:  $f_A = A_A / (A_A + A_S)$ , where  $A_A$  and  $A_S$  are the areas of aromatic carbon band and aliphatic carbon band, respectively.  $f_A$  of five residues of C7 asphaltenes are very close to each other, approximately 0.50. From the order comparison of  $f_A$  and asphalt softening point, we could not find the distinct relationship between these two parameters. Hence, the aromatic carbon proportion in asphaltene has no apparent influence on the asphalt softening point.

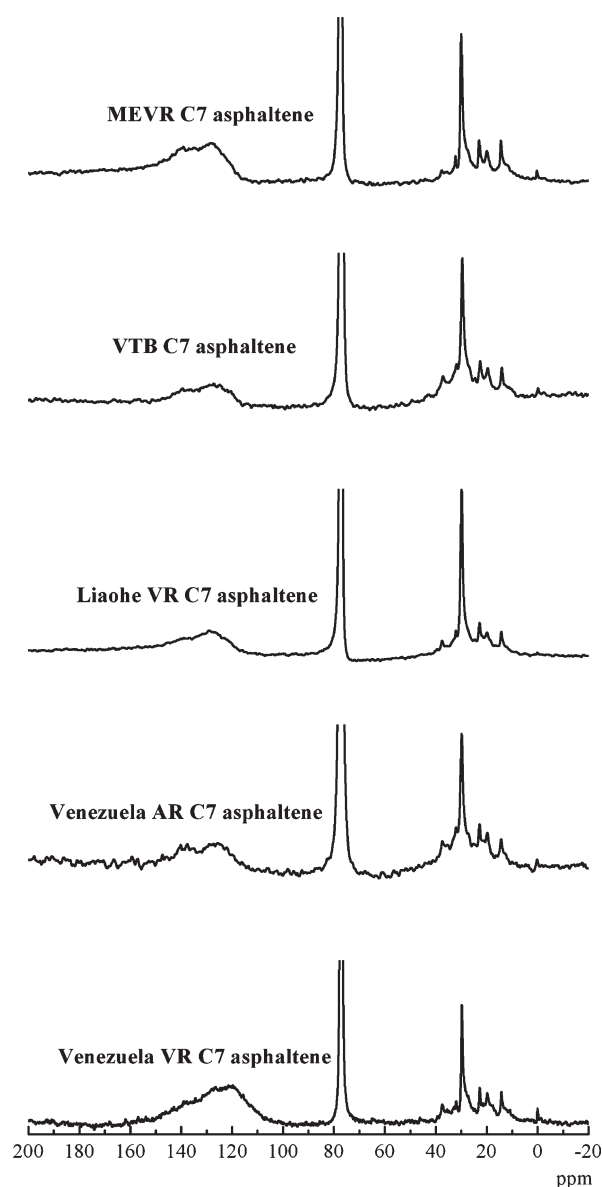


Figure 11. Measured  $^{13}\text{C}$  NMR spectra for five C7 asphaltenes.

The aromatic sheets in asphaltene can form a stacking structure (nanoaggregate), which could be proposed on the basis of the use of the XRD measurement (Figure 12a). Asphaltene nanoaggregates could interact with each other with peripheral alkanes, just like the case shown in Figure 12b. The XRD patterns for the C7 asphaltenes of five feedstocks appear in Figure 13. In general, these five patterns are very similar, and each contains the  $\gamma$  peak, the (002) peak, and the (100) peak at about  $2\theta = 20^\circ$ ,  $25^\circ$ , and  $44^\circ$ , respectively. Aromatic sheet stacking forms layer structures as graphite and makes the contribution to the (002) peak, while other carbons, such as saturated portions of the asphaltene molecule, have their effects on the  $\gamma$  peak. Therefore, many researchers gave another comparative estimate of the aromaticity  $f_A$  based on the peaks areas of  $\gamma$  and 002 bands with the following formula:  $f_A = C_A/C = C_A/(C_A + C_S) = A_{(002)}/(A_{(002)} + A_\gamma)$ , where  $C_S$ ,  $C_A$ , and  $C$  are the number of saturated, aromatic, and total carbon atoms per structural unit. However, this method could not give the correct result about  $f_A$  because the 002 band only represents the stacking aromatic

Table 4. Aromaticity and Ordered Degree Index for Five C7 Asphaltenes

feedstock	MEVR	VTB	Liaohe VR	Venezuela AR	Venezuela VR
$f_A$	0.54	0.48	0.53	0.50	0.53
OI	0.25	0.13	0.15	0.21	0.22

carbons (numbered 1 in Figure 12b) and neglect other aromatic carbons (numbered 2 in Figure 12b) in asphaltene nanoaggregates. Moreover, there are only stacking and ordered aromatic sheets in graphite. The  $\gamma$  peak could not be found in the graphite XRD pattern, which is only composed of (002) and (100) peaks. Hence, the above band area ratio can reflect the ordered degree of aromatic sheets, and this parameter should be renamed the ordered degree index (OI). When the OI approaches 1, asphaltene will have high ordered degree aromatic sheets and form a relative regular layer structure as graphite. OI of five C7 asphaltenes were also given in Table 4. OI has the same order as the asphalt softening point in Figure 9, except MEVR. For example, VTB has only a small OI (0.13) of C7 asphaltene, and its asphalt softening point in Figure 9 is  $160^\circ\text{C}$  on average, whereas Venezuela VR possesses a  $187.5^\circ\text{C}$  asphalt softening point (the OI of C7 asphaltene is 0.22). Asphalt could become more compact and ordered when the asphaltene has more ordered aromatic sheets, which causes more power to be needed to pull the aromatic sheets apart, namely, a high softening temperature (softening point). Then, we could obtain the conclusion that OI is an important factor affecting the asphalt softening point. A phenomenon that should be detected is that MEVR possesses the lowest asphalt softening point but the most ordered aromatic sheets in C7 asphaltene. This exception indicates that OI is not the single parameter in determining the asphalt softening point, and other factors should be studied for the deep understanding of the softening point. However, we are gratified to see that the order of parameter OI could explain the different zonal distribution regions for various residues in Figure 10; the similar OI for C7 asphaltenes of MEVR and Venezuela VR (0.25 versus 0.22) leads to a common region for the two residues.

An apparent influence of C7 asphaltene content on the asphalt softening point could be obtained from Table 2, which reminds us that the C7 asphaltene content should be considered in explaining the exception of MEVR. Therefore, a softening point index (SI) was defined to resolve the problem of the MEVR exception with the formula  $\text{SI} = \text{OI} \times \omega_{\text{C7-asph}}(\text{asphalt})$ , where  $\omega_{\text{C7-asph}}(\text{asphalt})$  (wt %) is the C7 asphaltene content of asphalt. SI could denote the quantity of ordered aromatic sheets in asphalt. Asphalt samples of two operation conditions in Figure 9 were chosen to investigate the relationship between SI and the softening point. C7 asphaltene contents and softening points in comparison are the average values of two operation conditions. The asphalt C7 asphaltene contents in SI calculation are 22.80, 54.52, 51.75, 44.99, and 46.66% for MEVR, VTB, Liaohe VR, Venezuela AR, and Venezuela VR, respectively. Figure 14 shows the relationship between SI and the asphalt softening point for the five residues. SI has a close correlation with the asphalt softening point. Feedstock with a high SI could have the ability to produce high softening point asphalt and possess a good asphalt granulation behavior. The quantity of ordered aromatic sheets in asphalt is the fundamental determinant of the softening point. Therefore, the reason of the softening point differences for various residues could be obtained from the variation of SI. Although this conclusion may not be very perfect, it gives us a



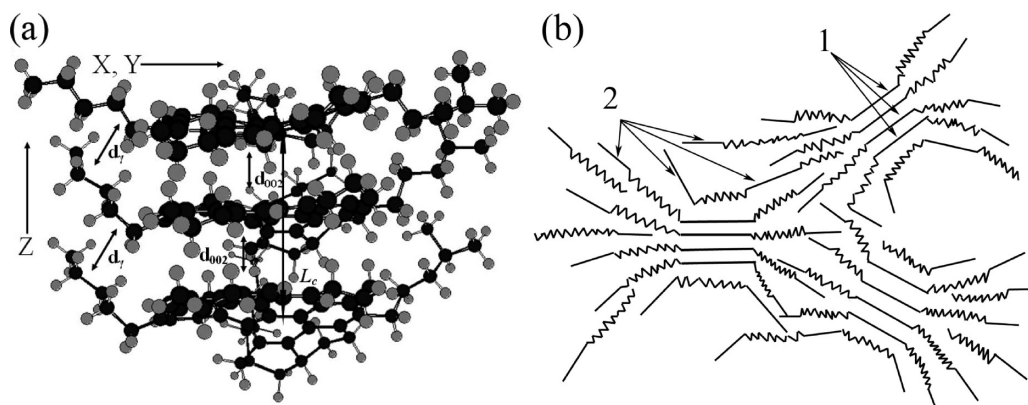


Figure 12. Schematic diagram of asphaltene aggregates: (a) asphaltene nanoaggregate and (b) cross-section of three nanoaggregates.

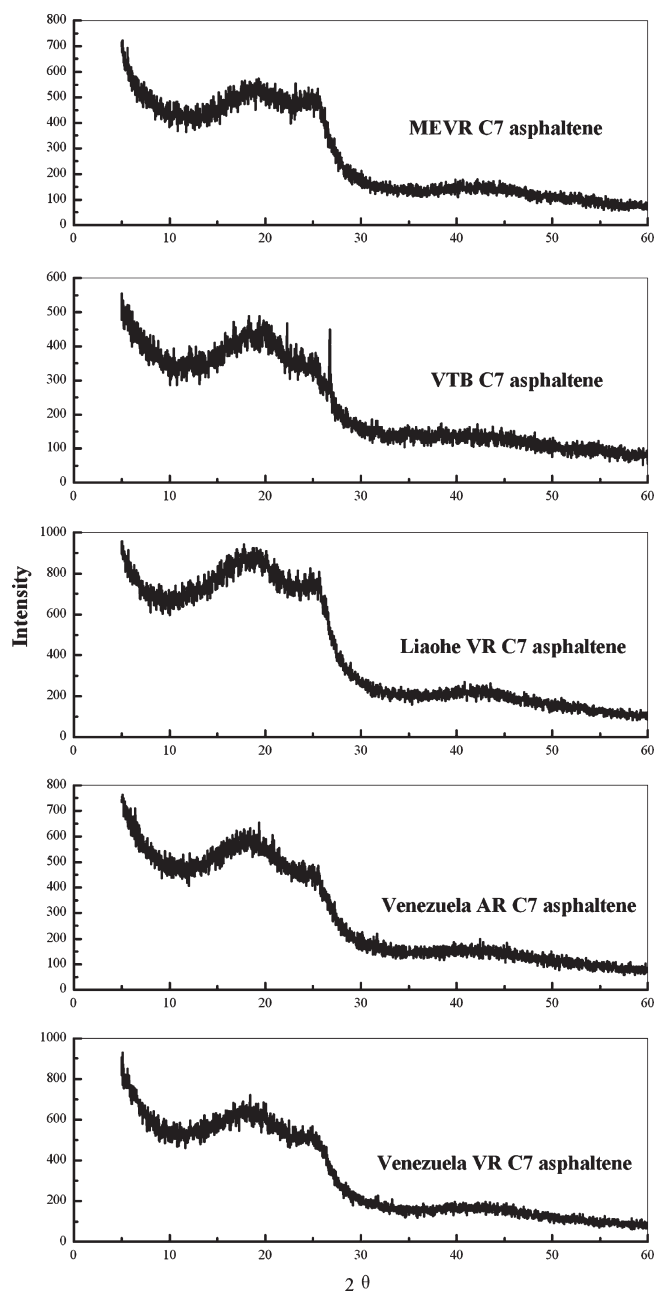


Figure 13. XRD patterns for five C7 asphaltenes.

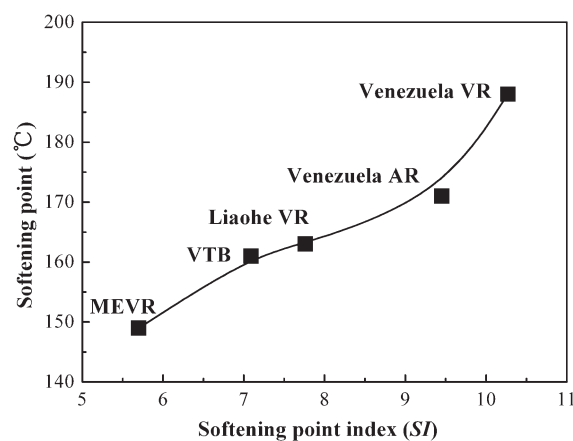


Figure 14. Influence of the softening point index (SI) on the asphalt softening point.

reasonable explanation and indicator about the differences of asphalt softening points and granulation behaviors for various feedstocks. Further research will also be needed to investigate the feasibility and applicability of SI with more residues.

## CONCLUSION

The influence of operation conditions on the asphalt softening point was analyzed in the SELEX-Asp process. Heavy solvent, which could carry out most of the “light fraction”, should be selected for high softening point asphalt production. The variation of operation conditions has an apparent effect on the asphalt yield, which has a close relationship with the softening point. High softening point asphalt could be obtained with lower temperatures and higher pressures of the extractor and a larger mass ratio of solvent to feed.

To purposefully change the operation conditions, we obtained different softening point asphalt and made an investigation about the influence of the softening point on asphalt granulation behaviors. The asphalt with a low softening point forms a bulk, whereas a high softening point asphalt could produce nice particles. Asphalt would show a good granulation behavior and form nice particles when the softening point is higher than 170 °C. The results of SEM and particle size distribution also prove this conclusion.

The softening point has an observable variation under the same operation conditions when the feedstock was changed. Aromaticity of five residues of C7 asphaltenes are very close to each other



(approximately 0.50), which indicates that the aromatic carbon proportion in asphaltene has no apparent influence on the asphalt softening point. The close relationship between the ordered degree of aromatic sheets in C7 asphaltene obtained by the XRD measurement and asphalt softening point could yield a conclusion that C7 asphaltene ordered degree index (OI) is an important factor affecting the asphalt softening point. A further softening point index (SI) denoting the quantity of ordered aromatic sheets in asphalt was proposed with the consideration of asphalt C7 asphaltene content. A good correlation between SI and the softening point shows that the quantity of ordered aromatic sheets in asphalt is the fundamental determinant of the softening point.

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## NOTE ADDED AFTER ASAP PUBLICATION

This paper published May 31, 2011 with an error in the title of Table 4. The correct version published July 21, 2011.