

Solvent recovery in solvent deasphalting process for economical vacuum residue upgrading

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Abstract—The solvent deasphalting (SDA) process is a heavy oil upgrading process and used to separate asphaltene, the heaviest and most polar fraction of vacuum residue (VR) of heavy oil, by using density differences, to obtain deasphalted oil (DAO). The SDA process consists of two main stages: asphaltene separation and solvent recovery. Solvent recovery is a key procedure for determining the operating cost of the SDA process, because it uses a considerable amount of costly solvent, the recovery of which consumes huge amounts of energy. In this study, the SDA process was numerically simulated by using three different solvents, propane, *n*-butane, and isobutane, to examine their effect on the DAO extraction and the effect of the operating temperature and pressure on solvent recovery. The process was designed to contain one extractor, two flash drums, and two steam strippers. The VR was characterized by identifying 15 pseudo-components based on the boiling point distribution, obtained by performing a SIMDIS analysis, and the API gravity of the components. When *n*-butane was used, the yield of DAO was higher than in the other cases, whereas isobutane showed a similar extraction performance as propane. Solvent recovery was found to increase with temperature and decrease with pressure for all the solvents that were tested and the best results were obtained for propane.

Keywords: Solvent Deasphalting, Vacuum Residue, Solvent Recovery, Numerical Simulation, Propane, Butane

INTRODUCTION

The distillation of crude oil at atmospheric pressure produces high-value petroleum products, such as LPG, gasoline, naphtha, jet fuel, kerosene, and diesel. The residue resulting from this atmospheric distillation process can be separated into vacuum gas oil and lubricating oil through a vacuum distillation process, leaving behind the vacuum residue (VR). The current demand for high-value petroleum products is increasing steadily, yet the supply is unable to meet the demand. This shortfall could be addressed by upgrading low-value VR to produce high-value petroleum products. The technologies for VR upgrading can also be applied to upgrade unconventional oils, such as oil sands bitumen and extra heavy oil, due to similarities such as a high viscosity, large molecular weight, and high asphaltene content [1,2]. Processes for upgrading heavy oil are mainly based on two methods: carbon rejection and hydrogen addition. The carbon rejection method uses processes such as thermo cracking, catalytic cracking, and solvent extraction, whereas hydrogen addition uses both catalytic and non-catalytic hydrogenation.

The solvent deasphalting (SDA) process is a carbon rejection method that involves the separation of asphaltene from the VR by utilizing the difference in density rather than the difference in boiling point, ultimately leading to the production of deasphalted oil (DAO) [3]. The asphaltene separated from this process is used as

asphalt for road or roofing surfaces and also for heat and hydrogen production by gasification. The DAO can be further upgraded by using it as a feedstock for fluid catalytic cracking (FCC) or hydrocracking units [4,5]. The SDA process has a relatively low operating cost due to its simplicity and moderate operating conditions and is useful for recovering large quantities of high-value oil that can be further upgraded. The most popular commercial SDA processes are Kerr-McGee's residue oil supercritical extraction (ROSE) and UOP's DEMEX [6,7]. The SDA process generally involves the use of alkane solvents with carbon numbers ranging from 3 to 6. Increasing the carbon number of the solvent increases the yield of DAO but reduces its quality, because solvents with a higher carbon number are able to dissolve heavier oil components, which would lead to an increase in the amount of DAO that could be produced. Therefore, it is possible to control the quality and yield of oil products by selecting an appropriate solvent. Commercial SDA processes mainly use propane and butane as solvents. An SDA processing plant consists of a unit for removing the asphaltene component, which is achieved by using solvent extraction, and solvent recovery units for the recovery of this solvent [8,9]. However, the disadvantage of the SDA process is that the amount of solvent used in the extraction stage of the process is four to ten times the amount of VR. Apart from this, the energy consumed by the solvent recovery stage of the SDA process forms a large proportion of the total energy demand [10-12], the reduction of which would therefore require the development of an efficient and economical solvent recovery step. However, most previous studies of the SDA process focused on the extraction step [13-16], whereas studies on the solvent recovery step are rare [17].

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This study involved a numerical simulation of the SDA process using the alkane solvents, propane and butane. The performance of the solvent extraction step, that is, the separation of asphaltene from VR, was evaluated for the different solvents. In addition, the solvent recovery stage was analyzed under various temperature and pressure conditions for each solvent.

NUMERICAL SIMULATION

1. Thermodynamic Model

In this study, the predictive Soave-Redlich-Kwong (PSRK) equation of state, an extension of the SRK equation of state, was used as the estimation method to simulate the SDA process. The PSRK model can be used to predict the vapor-liquid equilibrium (VLE) for a wide range of temperatures and pressures and may easily be extended to supercritical systems. The PSRK model is also capable of providing acceptable results for systems consisting of mixed non-polar and polar components, such as the SDA process, which involves a mixture of a non-polar alkane solvent and oil, and polar asphaltene [18-20].

2. VR and Solvents

For modeling purposes, the physical properties of the VR were based on those of the VR produced from a commercial vacuum distillation process in a plant operated by SK Innovation (Ulsan, Korea). The API (American Petroleum Institute) gravity of the VR

was measured at 60 °F by using a density meter (Anton Paar, DMA 4500). The boiling point distribution of the VR was obtained by conducting a gas chromatography analysis (HP/AC SIMDIS Alliance Product G1540A) with the simulated distillation (SIMDIS) technique (ASTM D1655 method). Propane (C3), *n*-butane (C4), and isobutane (C4) were used as solvents, of which the character-

Table 1. Characteristics of solvents

	Propane (C3)	<i>n</i> -Butane (C4)	Isobutane (C4)
Molecular weight (g/mol)	44.10	58.12	58.12
Liquid density (g/cm ³)	0.582	0.601	0.594
T _b (°C)	-42.1	-0.5	-12.0
T _c (°C)	96.9	153.2	134.7
P _c (MPa)	4.3	3.8	3.6

Table 2. Six different solvent cases

Solvent (vol%)	Case					
	A	B	C	D	E	F
Propane	100	-	-	50	50	-
<i>n</i> -Butane	-	100	-	50	-	50
Isobutane	-	-	100	-	50	50

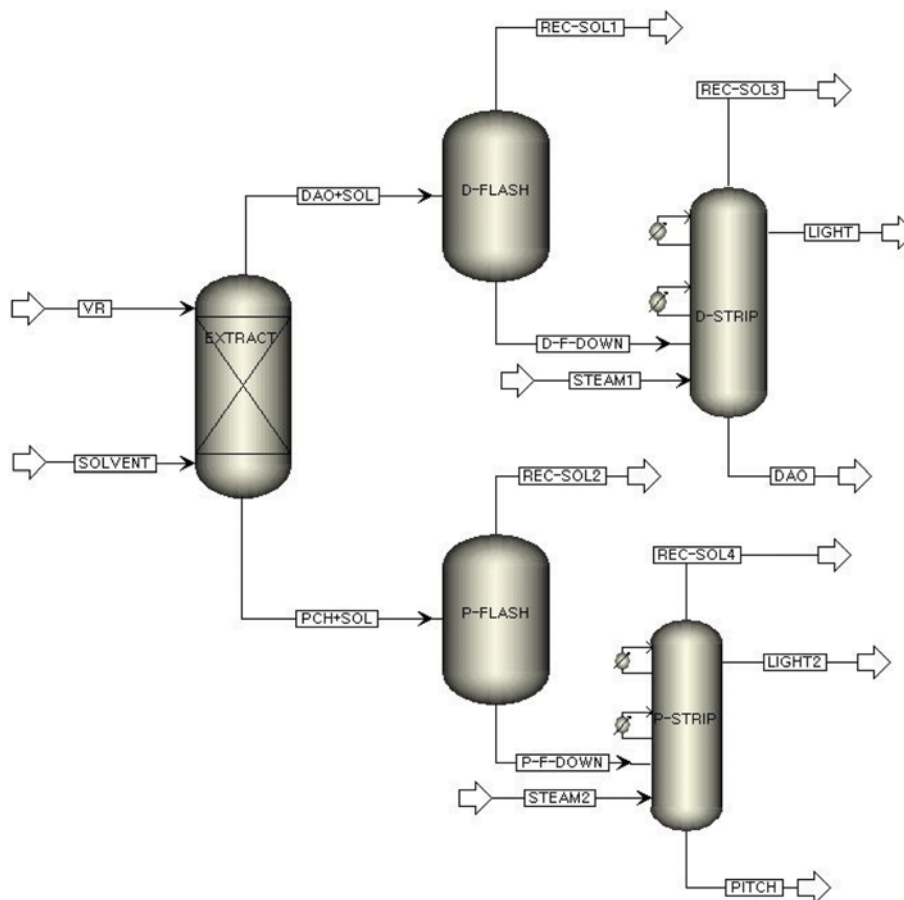


Fig. 1. Schematic diagram of the SDA process used for the numerical simulation.

istics are listed in Table 1 [21]. Testing involved six different solvent cases, of which the compositions are listed in Table 2. Solvent cases A, B, and C involved pure propane, *n*-butane, and isobutane, respectively. Case D is a mixture of propane and *n*-butane, case E is a mixture of propane and isobutane, and case F is a mixture of *n*-butane and isobutane. In cases in which a mixture of two solvents were used the ratio was fixed at 1 : 1 by volume.

3. Asphaltene Separation Process

Fig. 1 shows the configuration diagram of the SDA process that was used for the numerical simulation. The process includes an extractor, two flash drums, and two steam strippers. The extractor was designed to consist of 10 stages. Solvent extraction occurred in the extractor with the VR and the solvent as feedstock, whereas the used solvent in the extract and raffinate streams originating from the extractor was recovered in the flash drums and steam strippers. The volumetric ratio of the VR and alkane solvent streams was kept at 1 : 5.6 [22]. Our simulation was designed to allow the VR stream to flow to the first stage and the solvent stream to flow to the 10th stage of the extractor to enable the two streams to flow counter-currently to each other to allow for effective mixing in the extractor. The operating temperature and pressure settings of the extractor were adjusted for each solvent case and the conditions are listed in Table 3 [22].

4. Solvent Recovery Process

The extract and raffinate streams, effluents from the extractor, were allowed to flow into each flash drum on the upstream and downstream sides, respectively. In the flash drum, partial evaporation occurs when the feed undergoes a reduction in pressure, after which most of the solvent is in the vapor phase due to its low boiling point. This was followed by a separation step in which the vapor and liquid phases were separated, allowing the solvent from the extract and raffinate streams to be recovered.

The solvent recovery effectiveness of both of the two flash drums was calculated by varying the temperature and pressure for each flash drum, and by maintaining constant extraction conditions. The results obtained from this numerical simulation were subsequently used to calculate the recovered solvent quantities (weight basis) from the flash drums (S_1 , S_2) and steam strippers (S_3 , S_4), and the yield of solvent recovered from each unit. The solvent recovery from each unit was calculated as follows:

$$SR_i (\text{wt}\%) = \frac{S_i}{S_0} \times 100, \quad i=1, 2, 3, 4 \quad (1)$$

Table 3. Operating conditions of solvent extraction for six different solvent cases

Operating condition	Solvent case ^a						
	A	B	C	D	E	F	
Temperature (°C)	1 st Stage	62.0	112.6	92.1	87.1	77.1	102.6
	10 th Stage	60.8	110.2	91.0	85.4	76.0	101.1
Pressure (MPa)	4.8	3.9	3.9	4.0	4.0	3.9	

^aA, B, and C are cases of pure propane, *n*-butane and isobutane, respectively. D, E, and F are cases of equal volume mixture of propane and *n*-butane, propane and isobutane, and *n*-butane and isobutane, respectively

where, S_0 is the solvent weight in the extractor input stream, SR_1 and SR_2 are the weights of solvents recovered from the flash drum for the extract and raffinate, respectively, and SR_3 and SR_4 are the weights of the solvents recovered from the steam stripper for the extract and raffinate, respectively. The total solvent recovery (SR_{total}) was calculated using the following equation:

$$SR_{total} (\text{wt}\%) = \frac{S_1 + S_2 + S_3 + S_4}{S_0} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

1. Determination of Pseudo-components for VR

Because the VR is a highly complex mixture, it was considered as a mixture of pseudo-components (P-Cs) for the purposes of the numerical simulation. The P-Cs were categorized according to their boiling point distribution and API gravity values. The measured specific gravity and API gravity of the VR were 1.04 and 5.08, respectively. Fig. 2 shows the true boiling point distribution of the VR

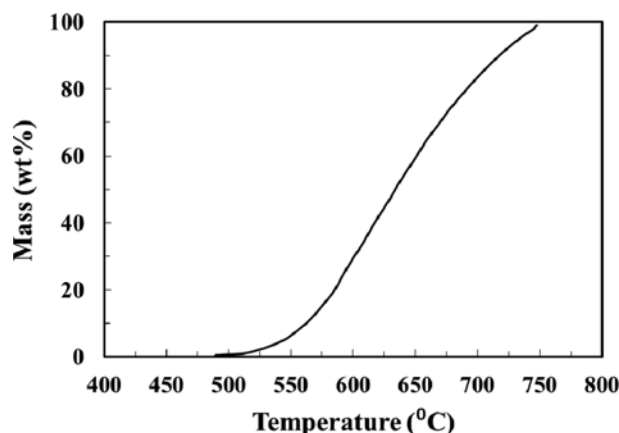


Fig. 2. Boiling point distribution of VR obtained by performing a SIMDIS analysis.

Table 4. Pseudo-components for VR and the properties of each component

P-C	NBP (°C)	Composition (wt%)	SG	MW (g/mol)
1	370	0.008	0.920	297.4
2	378	0.084	0.924	305.6
3	392	0.086	0.930	320.1
4	406	0.094	0.936	335.3
5	420	0.100	0.943	350.7
6	441	0.235	0.952	375.1
7	469	0.300	0.965	408.6
8	500	0.989	0.978	447.7
9	528	3.039	0.989	482.9
10	554	7.266	1.000	517.9
11	581	14.265	1.011	554.1
12	607	16.900	1.021	590.2
13	635	16.453	1.032	627.9
14	674	26.468	1.046	682.5
15	726	13.713	1.065	753.4

Table 5. Solvent extraction results for the six different solvent cases

		Solvent case ^a					
		A	B	C	D	E	F
Yield of oil components (wt%)	Extract	19.43	60.60	29.04	28.88	19.77	43.11
	Raffinate	80.57	39.40	70.96	71.12	80.23	56.89
Solvent split (wt%)	Extract	93.48	96.62	93.66	93.42	93.22	94.78
	Raffinate	6.52	3.38	6.34	6.58	6.78	5.22
Asphaltene split (wt%)	Extract	0.85	13.72	2.71	2.47	1.08	6.31
	Raffinate	99.15	86.28	97.29	97.53	98.92	93.69

^aA, B, and C are cases of pure propane, *n*-butane and isobutane, respectively. D, E, and F are cases of equal volume mixture of propane and *n*-butane, propane and isobutane, and *n*-butane and isobutane, respectively

that was obtained by performing a SIMDIS analysis. Based on this boiling point distribution, 15 P-Cs were identified. The analysis additionally provided the normal boiling point (NBP), volume percent, weight percent, specific gravity (SG), and molecular weight (MW) of each P-C and the results are listed in Table 4.

In general, asphaltene has a boiling point of about 730 °C, an MW of about 750, and its content in extra heavy oil such as bitumen is 15-16 wt% [23-26]. In comparison, P-C 15, from the VR analysis, has an NBP of 726 °C and MW of about 753, and forms 13.7 wt% of the VR (Table 4). Therefore, for the purposes of this study, P-C 15 was regarded as asphaltene due to the similarity of its physical and chemical properties to those of the actual component.

2. Solvent Extraction

The solvent extraction was simulated by using the six different solvent cases described in Table 2. The operating temperature and pressure for solvent cases A and B were obtained by referring to a previous study and conditions used in commercial processes [22], whereas for the other cases, the values that were used for the temperature and pressure depended on the physical properties of the particular solvent. Table 5 lists the yield calculated for the oil components in the extract and raffinate streams, after separation from the solvent extractor, for each solvent case. The raffinate stream contains the residue that remained after the light oil components were separated by solvent extraction. In addition, the results in Table 5 are also divided according to the weight percentage of solvent in the respective extract and raffinate streams for each of the solvent and asphaltene components.

In the case of solvent B (pure *n*-butane), the yield of oil components in the extract is larger than in the other solvent cases, whereas the yield of oil components from the extract stream has the lowest value in case A, in which pure propane was used as the solvent. In solvent case C (pure isobutane), the yield of oil components in the extract was found to be between those of solvent cases A and B, and the results were rather closer to those of case A. In all of the solvent cases, the amount of solvent entering the extract stream exceeded 93 wt%. Moreover, over 93 wt% of the asphaltene component was determined to enter the raffinate stream, except in the case of solvent B. This indicates that most of the asphaltene is separated from the VR in the solvent extraction step and retained in the raffinate. The heavier the solvent, that is, the greater its density, the larger the percentage of asphaltene component separated into the extract stream. These results correspond to experimental data

reported in previous studies [7,27], namely, when a heavier solvent was used, the yield of DAO increased, but the product quality was reduced because the fraction of asphaltene component in the extract stream increased.

A comparison of solvent cases B and C revealed a considerable difference in their extraction performance, even though both of these solvents (*n*-butane and isobutane) have the same carbon number. This result was ascribed to the difference in molecular structure of these solvents. The structure of *n*-butane consists of a straight chain; thus, it has a higher density compared to isobutane, which has a branched structure [28]. For this reason, the solubility of higher oil components is higher in solvent case B (*n*-butane) than in case C, which results in a higher percentage of asphaltene in the extract stream of case B.

3. Solvent Recovery

Fig. 3 shows the solvent fraction recovered from the flash drum and steam stripper for the six different solvent cases. The operating conditions for the solvent recovery simulation were fixed at 200 °C and 2 MPa. In all six cases, over 92 wt% of solvent was recovered

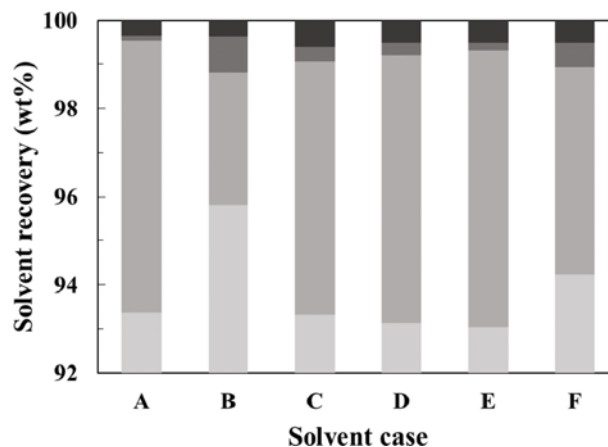


Fig. 3. Fraction of solvent recovery for six different solvent cases operated at 200 °C and 2 MPa. ■: from extract flash drum (SR1), ■: from raffinate flash drum (SR2), ■: from extract steam stripper (SR3), ■: from raffinate steam stripper (SR4). A, B, and C are cases of pure propane, *n*-butane, and isobutane, respectively. D, E, and F are cases of equal volume mixture of propane and *n*-butane, propane and isobutane, and *n*-butane and isobutane, respectively.

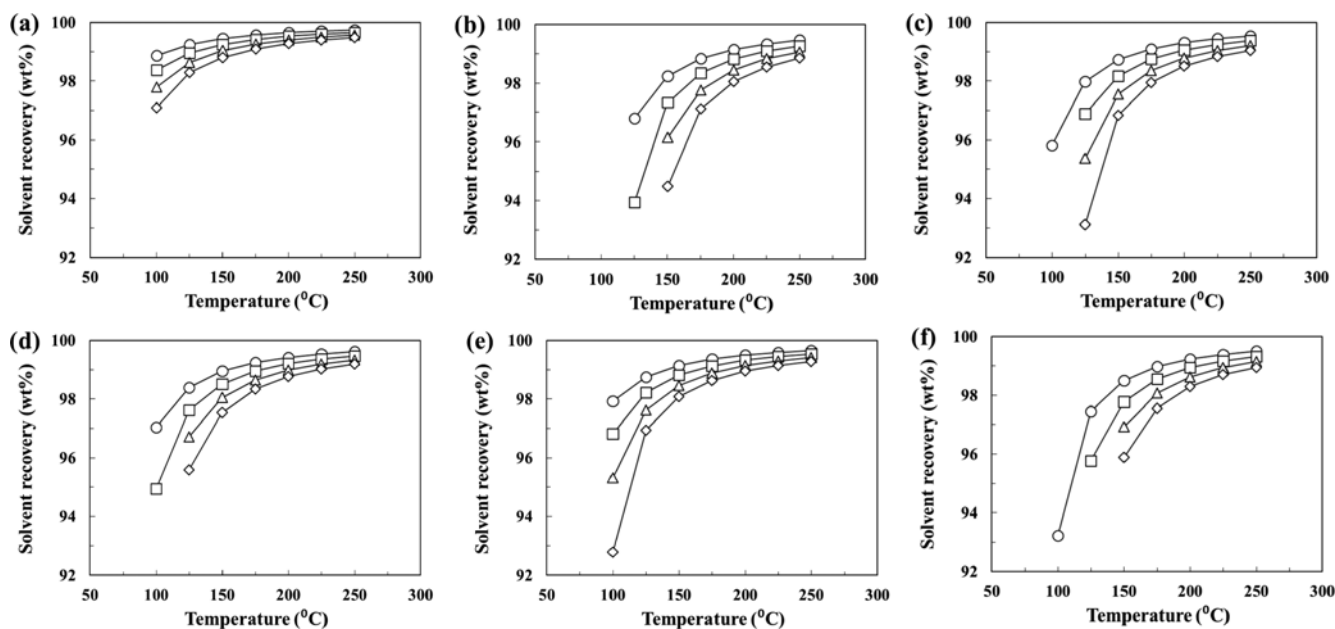


Fig. 4. Solvent recovery from two flash drums under various temperatures and pressures for (a) solvent A (pure propane), (b) solvent B (pure *n*-butane), (c) solvent C (pure isobutane), (d) solvent D (mixture of propane and *n*-butane), (e) solvent E (mixture of propane and isobutane), and (f) solvent F (mixture of *n*-butane and isobutane). ○: 1.5 MPa, □: 2.0 MPa, △: 2.5 MPa, ◇: 3.0 MPa.

from the flash drum connected to the extract stream, whereas 3–6 wt% of solvent was recovered from the flash drum connected to the raffinate stream. This indicates that it would theoretically be possible to recover over 98 wt% of the solvent by using flash drums. Therefore, the use of flash drums to maximize solvent recovery is very important for the development of an energy efficient SDA process.

Fig. 4 shows the results of detailed studies of solvent recovery from two flash drums operating at various temperatures and pressures in the ranges 100–250 °C and 1.5–3 MPa, respectively. Under the operating conditions that were used in the test, the solvent recovery ability of all solvent cases exceeded 90 wt%. At constant pressure, solvent recovery was found to increase as the temperature of the flash drum was increased, and the tendency was more pronounced in the high-pressure region. Furthermore, the effect of pressure on solvent recovery was also found to be more prominent in the lower temperature region. At the same temperatures and pressures, solvent case A was capable of the highest solvent recovery, whereas solvent case B had the lowest solvent recovery among the six solvent cases. This could be explained by the lower boiling point of propane (solvent case A), which would evaporate more readily in the flash drum, compared to *n*-butane (solvent case B).

CONCLUSIONS

The SDA process was numerically simulated using different alkane solvents. The simulation results of the solvent extraction step showed that over 90 wt% of the solvent flows into the extract stream with the DAO, whereas the heavy components and the remainder of the solvent enter the raffinate stream, which was found to contain most of the asphaltene. When butane was used as the solvent, the

yield of the DAO was enhanced compared to when propane was used, because oil solubility increases for solvents with a larger number of carbon atoms. However, although *n*-butane and isobutane have the same number of carbons, the fraction of heavy oil components entering the extract stream is larger when the former is used as the solvent, because of its higher density.

The simulation results of the solvent recovery step revealed that the use of flash drums would enable the recovery of over 98 wt% of the solvent. Therefore, ensuring efficient solvent recovery at this stage of the SDA process would be very important for improving the cost-efficiency of the process. A more detailed study of the efficiency of the flash drums was performed by evaluating the solvent recovery, which was done by changing the operating temperature and pressure in the ranges 100–250 °C and 1.5–3 MPa, respectively, for each solvent case. The highest solvent recovery was achieved with propane as the solvent, whereas the lowest solvent recovery was obtained for the *n*-butane solvent case. The solvent recovery performance was mainly found to depend on the volatility of the solvent. The solvent mixtures did not appear to have a mixing effect and their solvent recovery performance was between two pure-solvent cases. This research can be a guideline for the decision of proper solvent and the development of economical SDA process.

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