

Effect of Mass Ratio of Solvent to Solute and Pressure in Supercritical Fluid Extraction of Coal Tar

Wen Ji^{1, a}, Hengbo Huang^{2, b}, Yongfei Zhao^{3, c}, Shaohua Zhan^{4, d} and Zhaoxiang Yu^{1, e}

¹Chemical Science and Engineering Institute, Tongji University, 1239# Siping Road, SH, China

²Tongte Chemical and Engineering Company, Room 604, 1818#, Huangxing Road, SH, China

³ Management Committee, Hainan economic development zone, Inner Mongolia, China

⁴Wuhai Blackcat Carbon Black Company, Wuhai, Inner Mongolia, China

^a1334207@tongji.edu.cn, ^bhbb@tongtechem.com, ^cwhszyf2999611@sina.com, ^dzsh660710@126.com,

^ezxyu@tongji.edu.cn

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Abstract. Coal tar sample was extracted by supercritical *n*-pentane. The mass ratios of solvent to solute were researched in different pressures and the extraction yields were explored in 4-12MPa at 215 °C. The results show that, the mass ratio affects extraction yield distinctly and the extraction yield increases gradually with the rise of pressure. The mass ratio was defined as 1:9 and 1:12 when the pressure was below and above 8MPa respectively. A maximum extraction yield was achieved during 10-12MPa as 71.24%. An empirical extraction yield-pressure curve was calculated as $EY=34.857p^{0.3042}$ (%).

Introduction

Coal tar from coke production is as high as 6-8 million tons in China, accounting for 3-4% of coal. Coal tar is a complex mixture composed of thousands of aromatics while only hundreds have been separated[1]. Properties have been widely used in synthesizing plastics, pesticides, medicines, heat-resisting materials, national defense industries, etc., some of which could not be produced or substituted by petroleum processes. Currently, coal tar is mainly for producing light oil, carbolic oil, naphthalene oil, modified coal tar pitch, etc. Moreover, deep processing is implemented for various chemical raw materials like benzene, phenol, naphthol, anthracene, etc. However, plenty of problems like the low processing rate, low processing depth, few product varieties, small production scale and few investing funds are urgently to be solved. In 1980s, the supercritical extraction technology for residuum oil refining was developed by Kerr-McGee company (Residuum Oil Supercritical Extraction, ROSE for short) [2]. In 1990s, this technology was developed in China applying for residuum oil refining [3].

Supercritical fluid extraction and fractionation (SFEF) takes great advantage of its solving ability relating to its density, in other words, conducting by the influence of pressure and temperature, remarkable in quick mass transfer, easy phase separation, low energy consumption, simple device, and flexible adjustment of fractions composition [4]. The solving ability of supercritical fluid is directly proportional to its density and when the pressure reaches to its critical point, small changes

could lead to sharp effects of density [5]. Therefore, for many solids or solutes in fluids, if their miscibilities are limited in certain solvents, the solving abilities of supercritical fluids present obvious correlations with pressure. Besides, different solutes would be affected distinctively [6]. Meanwhile, pressure is restricted by equipment, security and production costs, so the extraction yield should be improved on the bases of production resources and entire operational parameters.

In this experiment, coal tar sample was extracted by supercritical *n*-pentane. Firstly, the mass ratios of solvent to solute were investigated in different pressures to make efficient use of solvent. Secondly, a series of pressures were conducted to research their effects on extraction yield and to achieve a maximum value and variation rules for further accurate fractionation and separation.

Experiments

Raw materials and solvents. Coal tar is obtained from a coking plant in Maanshan Iron and Steel Works. The density is 1.201g/cm³, and Engler viscosity is 12.127. The solvent *n*-pentane is purchased in Luke Chemical Industry and its purity is above 99%. The critical parameters are listed as: $T_c=196.6^\circ\text{C}$, $p_c=3.369\text{MPa}$, $d_c=0.232\text{g/cm}^3$.

SFEF experiment. The SFEF experiment was carried out in a batch extractor and the flowsheet is shown in Fig.1.

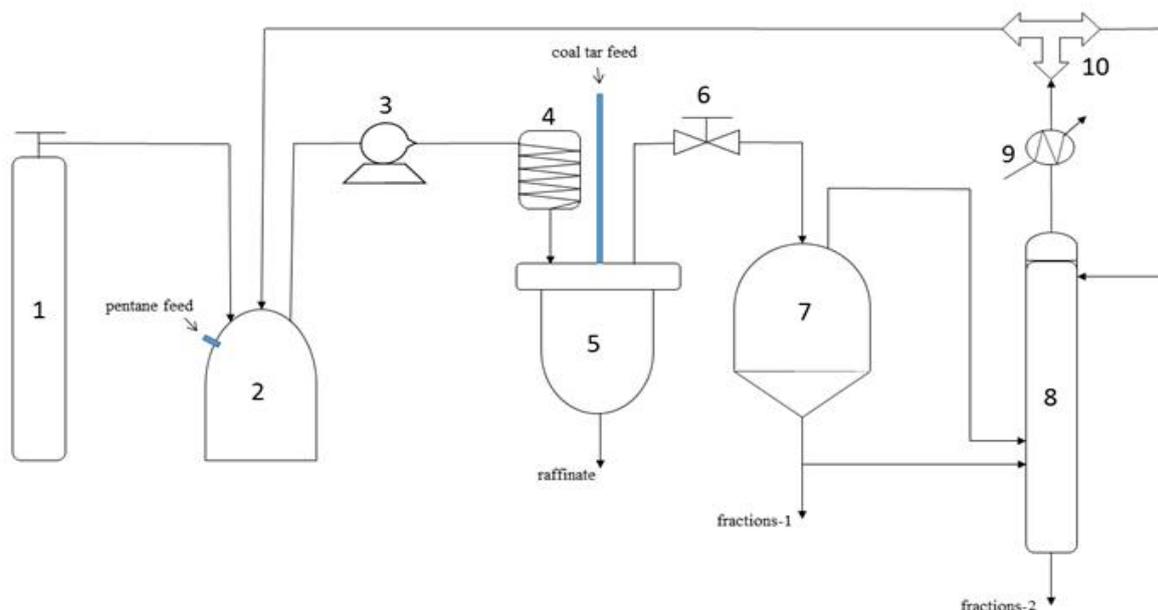


Fig.1 Flowsheet of supercritical fluid extraction and fraction

1-nitrogen cylinder; 2-solvent tank; 3-pump; 4-preheater; 5- high pressure extractor;
6-back-pressure valve; 7-separator; 8- distillation column; 9-condensor; 10-reflux ratio controller.

The core equipments were high pressure extractor and packed distillation column. This system can be divided into 2 parts. The high pressure part was from the pump to the back-pressure valve and the rest of this system was the low pressure part which kept 0.3MPa by nitrogen. Firstly, the preheated coal tar was fed into extractor (215°C), and then *n*-pentane was pumped into the extractor through the preheater (2.7L/h). It was keeping heated by cable to remain the temperature (215±5°C), and the distance between its bottom and the import pipe should be no more than 1cm for complete mixing. The high pressure was controlled by back-pressure valve (4-12MPa). After the pressure and temperature had achieved the aimed conditions, the extraction phase flew into the separator and the

pressure was reduced. In the next step, extraction phase entered into the distillation column, which was packed with θ -ring at the height of 1m. The bottom temperature of distillation column was controlled at 320 °C and the exporting temperature was monitored above 70 °C . The reflux ratio controller (40%-80%) was used for efficient separation of extractant and extraction. When the mass ratio had reached the expected value, the high pressure part stopped while the low pressure part kept running. The left pitch was leaked from the bottom of the extractor, and then the wash oil and fresh *n*-pentane were added into the extractor one after another. After the separation system had accomplished, fractions were collected from the bottom of the distillation column and separator. The extraction yield (EY) could be calculated by equation (1):

$$EY = \frac{m_{ex}}{m_0} \times 100\% \tag{1}$$

Here m_0 is the mass of fed coal tar and m_{ex} is the total mass of collected fractions.

Results and discussion

Mass Ratio of Solvent to Solute. In the supercritical state, the compressibility factor (*Z*) of solvent could be generally defined as Equation (2) [7]:

$$Z = \frac{pV}{RT} \tag{2}$$

Where *p* is pressure, *V* is volume, *R* is the gas constant and *T* is the temperature. Basically, when *p* rises, *Z* of the solvent would increase, so more solvent is required for extraction. To measure the detailed quantity of solvent in different pressures, 4 mass ratios of solvent to solute were projected to calibrate the extraction yields in 4MPa, 8MPa, 12MPa at 215°C. The results are shown in Fig.2.

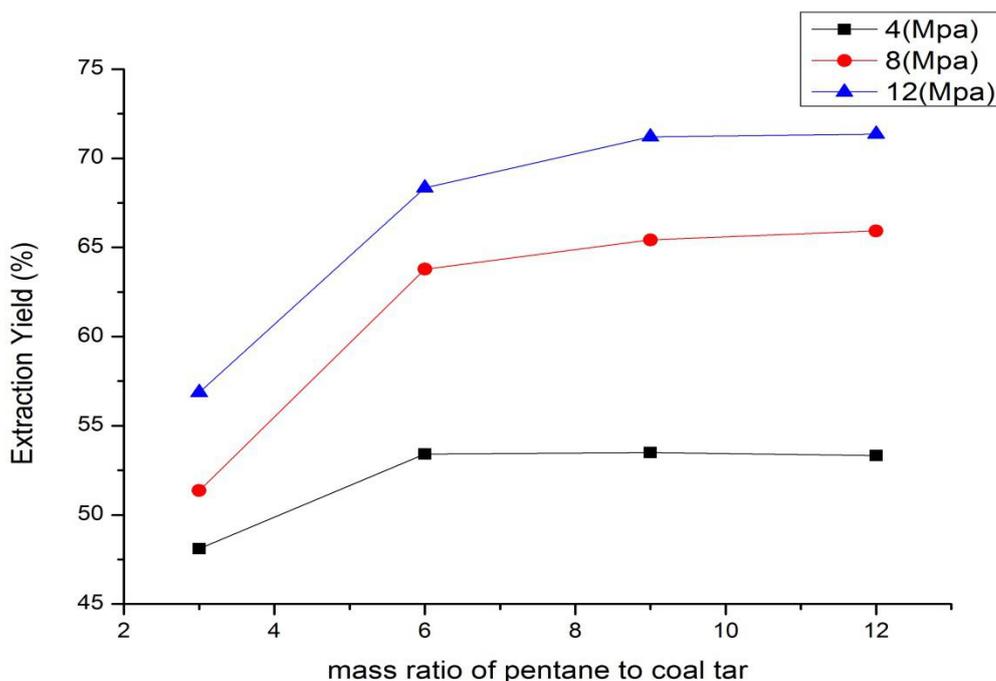


Fig.2 Extraction yields to the mass ratio of solvent to solute

The trend in Fig.2 shows that, in a lower pressure, the extraction yields changed little when mass ratio of solvent to solute was raised. To be specific, in 4MPa, the extraction yields were in the same level when the mass ratios were 1:6, 1:9 and 1:12 (respectively 53.41%, 53.49% and 53.33%). These data indicate that solute could be fully extracted at 1:6 in 4MPa. When the pressure raised to 8MPa, the extraction yield was slightly increased to 51.36% at the mass ratio of 1:3 compared to 4MPa. However, when the mass ratio was 1:6, the extraction yield increased distinctly to 63.78%, and grew to a higher rate in 1:9 (65.42%) and up to 65.93% in 1:12, which illustrates that in this pressure, mass ratio of solvent to solute should be higher than 1:9 for the extraction process. When the pressure was set as 12MPa, the extraction yield continued to increase in lower ratios of 1:3 and 1:6, though gently (respectively 56.87% and 68.34%). When the ratio came to 1:9 and 1:12, the rates changed obviously to 71.20% and 71.36% respectively. Specifically, the rate of former ratio was still in a sharp increasing trend and the later one could be regarded as stable. Therefore, 1:12 should be set for an adequate extraction in this pressure. Accordingly, it was concluded to employ a ratio of 1:9 when the pressure was lower than 8MPa and a ratio of 1:12 when higher.

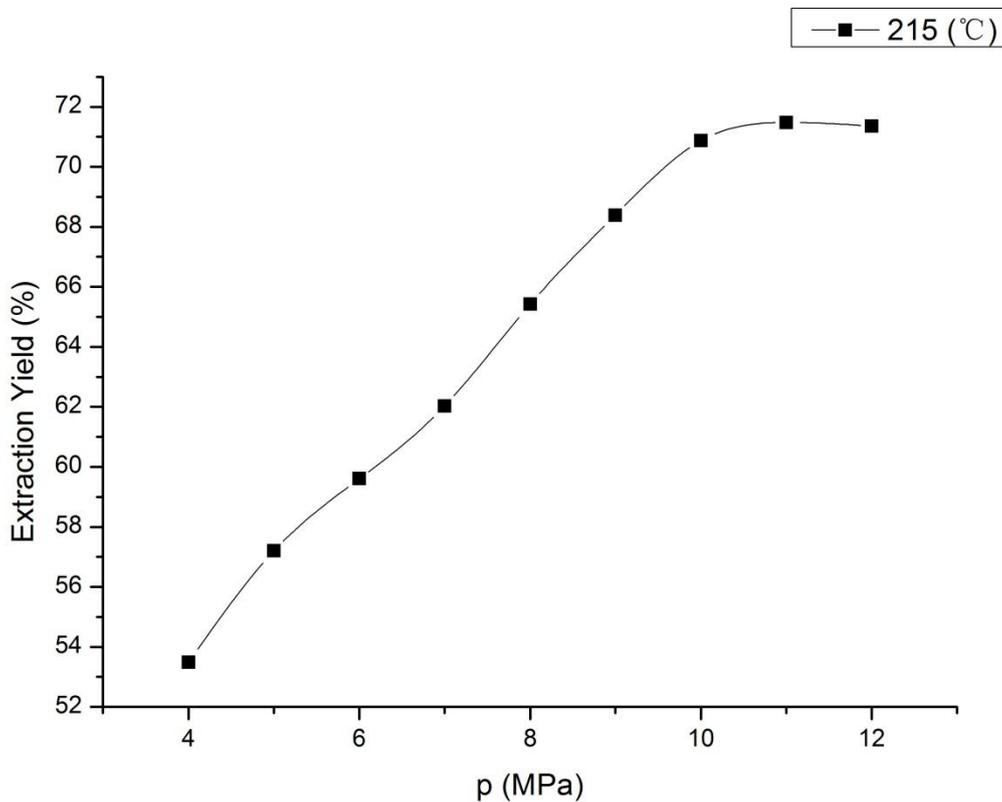


Fig.3 Extraction yields at 215°C

Extraction Results. Extraction experiments were conducted from 4MPa to 12MPa at 215°C and the extraction yields were shown in Fig.3.

Here the extraction yield shows a sharp increasing trend from 4MPa to 10MPa and stabilizes at 11MPa and 12MPa (respectively 71.48% and 71.36%). Considering the solving capability of *n*-pentane [8] and the properties of this coal tar, when more than 70% coal tar had been extracted, it could be concluded that this steady curve stands for the highest extraction yield and the process is well finished in this experiment.

Researches [9] indicate that extraction yield would be affected by temperature, pressure and compressibility factor. Here in our experiment, temperature and compressibility factor had been

regulated and thus pressure was the only variable. Therefore, an empirical equation to calculate extraction yield (EY) can be established inflected for pressure (p) among 4-10MPa:

$$EY=34.857p^{0.3042} (\%). \quad (3)$$

For this equation, standard deviation is 0.9915, which indicates a good fitting and thus Eq.3 could be used for further experiments and monitoring the extracting effects.

Conclusions

In this work, coal tar was extracted and fractionated by supercritical n -pentane. The mass ratio of solvent to solute showed a detectable influence to the extraction process. When the pressure is below 8Mpa, a ratio of 1:9 could satisfy the solvent quantity in extraction process but when the pressure continues to increase, a higher ratio of 1:12 is required. Extraction yield achieves maximum of 71.24% when pressure is above 10MPa. Among 4-10MPa an empirical equation is calculated for further experiment as $EY=34.857p^{0.3042} (\%)$.

References

- [1] Zhengyi Wei, Shengcai Fan: *Development of Coal Tar Processing Technology and Industrialization*, Coal Chemical Industry, No.1 (2007), p. 7-10
- [2] J.A. Gearhart: Solvent deasphalting, U.S. Patent 4, 23, 9616. (1980)
- [3] Renan Wang, Yunxiang Hu, Zhiming Xu, Tong Su: *A New Fractionating Method for Heavy Oil of Petroleum by Supercritical Fluid Extraction and Fractionation*, Acta Petroleisínica (Petroleum Processing Section), Vol. 13(1) (1997), p. 53-59
- [4] Ximing Chen: *Research on Supercritical Fluid Extraction of Coal Tar Processing*, Fuel & Chemical Processes, Vol. 35(4) (2004), p. 46-48
- [5] Ernesto Reverchon: *Supercritical Fluid Extraction and Fractionation of Essential Oils and Related Products*, Journal of Supercritical Fluids, Vol. 10 (1997), p. 1-37
- [6] Zhaolin Gu, Na Chang, Xiongpo Hou, etc.: *Experimental Study on the Coal Tar Hydrocracking Process in Supercritical Solvents*, Fuel, Vol. 91 (2012), p. 33-39
- [7] Sambasiva R. Allada: *Solubility Parameters of Supercritical Fluids*, Ind. Eng. Chem. Process Dess. Dev, Vol. 23 (1984), p. 344-348
- [8] Yihui Ding, Hang Chen, Dongfei Wang, etc.: *Supercritical Fluid Extraction and Fractionation of High-temperature Coal Tar*, J Fuel Chem Technol, Vol. 38(2) (2010), p. 140-143
- [9] Isaac C. Sanchez: *Statistical Thermodynamics of Polymer Solutions*, American Chemical Society, Vol. 11(6) (1978), p. 1145-1156