



Role of water as the co-solvent in eco-friendly processing oil extraction: Optimization from experimental data and theoretical approaches

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HIGHLIGHTS

- The optimum conditions of PCA removal from furfural-extract oil were investigated.
- A simulation-based procedure was explored to find the optimum co-solvent ratio.
- Solvent selectivity was significantly enhanced by adding appropriate co-solvent.
- COSMO-SAC model and representative molecules were utilized to simulate the LLE.

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ABSTRACT

Furfural solvent extraction is a conventional process that removes toxic polycyclic aromatics (PCAs) from eco-friendly processing oil. To increase the product yield and extraction selectivity, the present study introduces water as the co-solvent and investigates its effect using both experimental and theoretical approaches. The effects of the water content in furfural on the product yield, PCA content, aromatic carbon fraction and hydrocarbon type distribution are systematically investigated and optimized. At the appropriate furfural/water ratio in two-stage extraction, the product yield increases by 9 wt% while maintaining the product quality at an acceptable level. An *a priori* Conductor-like Screening Model for Segment Activity Coefficient (COSMO-SAC) model is used to predict the product composition after extraction. The prediction is consistent with the experimental data. This model can identify the optimal water content using only one experimental result. The result shows that controlling the water content in furfural is critically important during the furfural-extract oil (FEO) furfural extraction process. Both the experimental data and the simulation method in this paper are expected to help control and optimize the extraction process, as well as provide a better understanding of the process.

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1. Introduction

Processing oil is a necessary raw material in the production of rubber; it serves as an additive to improve the quality (e.g., elasticity, flexibility and compatibility) while reducing the cost. Distillate aromatic extract (DAE) was formerly the main process to produce processing oil, but the derived product contains a high percentage of toxic polycyclic aromatics (PCAs), which has led to widespread concerns over potential health issues. On December 9, 2005, the European Parliament and Council Members issued Directive

2005/69/EC, which strictly limited the PCA content in rubber at a low level of less than 3 wt% (Dasgupta et al., 2009). As a result, the development of the high-performance PCA-removing process used to produce eco-friendly processing oil has become increasingly attractive. Currently, treated DAE (TDAE), which is a substitute for DAE, is frequently used. The techniques employed to remove harmful compounds can be divided into two categories: hydrotreating (Gomez et al., 2010) and solvent extraction (Xiong et al., 2011; Shi et al., 2011; Wang et al., 2011; Lu et al., 2011).

Solvent extraction has advantages in its relatively low cost and technological maturity. Selecting an extraction solvent with high selectivity and efficiency is a fundamental problem in process development. In past decades, considerable effort was devoted to identifying proper solvents. A previous study showed that furfural

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is one of the best PCA-removing solvents among tested solvents, such as dimethyl sulfoxide (DMSO), sulfolane, and esters (Xiong et al., 2011). N-methyl pyrrolidone (NMP) has a PCA selectivity that is similar to that of furfural; however, NMP is corrosive, and the corresponding extraction conditions are more severe (Shi et al., 2011). Although furfural is a common solvent in most commercial applications, its PCA extraction performance must be improved. For example, the yield of qualified raffinate product (PCA content <3 wt%) is approximately only 20–30 wt% in the furfural extraction process.

Finding a solvent that offers optimal performance for all aspects of processing oil production is challenging since every solvent has chemical and physical limitations. Mixing solvents with different characteristics may overcome the drawbacks of individual solvents by adjusting the blending ratio, selectivity and efficiency. Therefore, extensive attempts have been made to use mixed solvents. Previous studies have shown that the yield of the raffinate product would be enhanced at a proper mixing solvent ratio (Wang et al., 2011; Lu et al., 2011). The application of co-solvents is currently a common practice in the industrial solvent separation process. In general, the second solvent affects the extraction process as an anti-solvent or an enhanced solvent, which acts against or in parallel with the main solvent, respectively. In the former case, the second solvent decreases the solubility of the main solvent and re-extracts certain ideal components into the raffinate phase. Lukic et al. (2005) and Hoseini et al. (2009) reported that the use of a light hydrocarbon as the second solvent may enhance the yield and aromatic content of the raffinate product in the furfural extraction process. In the latter case, the second solvent increases the polarity and selectivity of the main solvent. Therefore, the second solvent changes the liquid-liquid equilibrium (LLE) distribution and affects the yield and quality of the product. Guan et al. (2014) noted that the selectivity towards aromatics can be improved by adding water to NMP. Chen et al. (2002) reported that using hydrous NMP enhances the product yield in the extraction process.

The proper solvent ratio and corresponding optimal operating conditions are generally identified through repeated experiments. The “trial-and-error” approach is effective but time consuming and costly. Therefore, a theoretical approach to building a thermodynamic predictive model for the solvent extraction process has become increasingly attractive. Traditional thermodynamic models such as the NRTL (Non-Random Two Liquid) and UNIFAC models have been widely used to solve the LLE problem. These models can properly simulate various multi-component systems if the interaction parameters among different components are provided. However, if the interaction parameters are absent, then their application in a complex hydrocarbon system is limited. In the past two decades, the *a priori* method, which requires no experimental evaluation, has been rapidly developed using continuous solvation models based on quantum chemistry. The most successful methods are COSMO-RS (COnductor-like Screen Model for Real Solvent) by Klamt (1995, 2003), Klamt et al. (1998, 2002), Klamt and Eckert (2000) and COSMO-SAC (COnductor-like Screening Model for Segment Activity Coefficient) by Lin and Sandler (2002). Additionally, improved methods were reported by Wang et al. (2006, 2007) and Hsieh et al. (2010, 2010). The significance of the COSMO model is that it uses the sigma profile as the input, which can be calculated using most available quantum mechanical (QM) calculation packages. The COSMO model has been successfully applied to predict the vapor pressures and activity coefficients of pure substances and mixtures (Lin et al., 2011). Reddy et al. calculated the infinite dilution activity coefficient (IDAC) and selectivity values of organic solutes in ionic liquids using the COSMO-RS model (Reddy et al., 2013). Li et al. (2013) and Fang et al. (2016) reported the use of COSMO-SAC to predict the IDACs for a selection of ionic liquid

solvents. However, studies regarding applications of COSMO-SAC to the petroleum fraction are rare because of the complexity of the components.

The present work uses water as the co-solvent with commonly used furfural to enhance the selectivity of PCA removal during processing oil production. Both experimental and theoretical approaches have been used to investigate the effect of the water content. After systematic experimental tests, a high yield of eco-friendly processing oil was obtained at the appropriate furfural/water ratio. The simulation uses the COSMO-SAC method in a simplified compositional representation. The optimal water content in furfural can be predicted without supplemental experimental data. The prediction fits well with experimental data, which indicates its potential application in process optimization.

2. Experimental procedures

2.1. Feedstock and reagents

A commercial vacuum distillate-derived furfural extract oil (FEO) was obtained from a Chinese petrochemical company and used as the feedstock in the extraction experiments. The properties of the feedstock are listed in Table 1. The feedstock contained a considerable amount of aromatics, particularly PCAs, which are not environmentally safe. The density and viscosity were relatively high, and the nitrogen and sulfur contents were notably low, which indicates that the FEO is appropriate for producing eco-friendly processing oil.

The distilled water was self-prepared in the laboratory. Cyclohexane, DMSO and furfural were obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China), and re-distilled before use to avoid oxidation.

2.2. Extraction of FEO

FEO is a complex hydrocarbon mixture that contains a small fraction of paraffins and significant amounts of naphthenes and aromatics. According to the Hildebrand regular solution theory, the aromatics have stronger polarity than paraffins and naphthenes. Therefore, polar solvents such as furfural can be used to extract aromatics from the matrix. The ideal product components are light aromatics such as monocyclics and di-aromatics. The objective of the solvent selectivity and solubility optimization is

Table 1
Properties of the furfural extract oil.

Items	Values	Analytical methods
Dynamic viscosity $\nu_{37.8}$ (mPa·s)	1279.88	Rotary viscometer
Kinematic viscosity ν_{100} (mm ² ·s ⁻¹)	20.70	GB/T 265
Density at 20 °C (kg·m ⁻³)	0.9835	GB/T 1884
Flash point (°C)	230	GB/T 3536
Solidifying point (°C)	30	GB/T 510
Conradson carbon residue (wt%)	3.654	SH/T 0170-92
Ash content (wt%)	0.006	GB/T 508-85
Aniline point (°C)	72	GB/T 262-88
Sulphur content (wt%)	0.387	QZT/JL
Nitrogen content (wt%)	0.563	GB/T 273
RI (refractive index) n_d^{20}	1.5642	Abbe refractometer
VGC (viscosity gravity constant)	0.931	
SARA (wt%)		
Saturate	41.28	SH/T 0509-92
Aromatic	50.24	
Resin	7.49	
n7-asphaltene	1.28	
Carbon composition (wt%)		
C _A	41.97	GB/T 279
C _N	17.29	GB/T 280
C _P	40.74	GB/T 281
Molecular weight	318	GPC
PCA content (wt%)	19.13	IP346

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