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Abstract:

In our previous experimental study, we have used a desulfurization method, *i.e.,* coupled oxidation-extraction desulfurization. To develop a new insight into industrial-scale desulfurization process by this method, the process simulation study is of great importance. In this work, the industrial-scale of the coupled desulfurization processing of ULSD, wherein $[C_1pyr]H_2PO_4$ is employed in the oxidative desulfurization process and DMF is employed in the extractive desulfurization process, has been examined through the Aspen Plus simulation. Sensitivity of various operating conditions, *i.e.,* IL-to-oil ratio, DMF-to-oil ratio, operating temperature and pressure has been analyzed. Subsequently, the economical comparison of the proposed process and HDS is compared synthetically. It is observed that coupled desulfurization method can effectively remove the S-compounds from the diesel fuel to meet the requirement of stringent legislation of less than 10 ppm. The main objectives of this work are; (i) to propose and design an industrial-scale process of the coupled oxidation-extraction desulfurization of diesel, (ii) to obtain the optimal operating conditions, thus enabling the simulation and optimization of this desulfurization process, and (iii) to verify the experimental results and evaluate the feasibility to scale-up this technology. To the best of our knowledge, it is the first time to design an industrial-scale process for the coupled oxidation-extraction desulfurization of diesel fuel.

Keywords: Coupled oxidation-extraction, Desulfurization, Industrial-scale, Process simulation, Sensitivity analysis

Introduction

Desulfurization of diesel fuel is an essential process in oil refineries to meet the target of ultra-low-sulfur (ULSD) or sulfur-free diesel fuel. [1, 2] The hydrodesulfurization (HDS) is a traditional method which is widely employed in industry. However, there are some disadvantages associated with HDS such as the harsh operation conditions (350~400 °C, 30~100 bar hydrogen pressure), requirement of expensive catalysts, and the ineffectiveness to remove the cyclic

sulfur compounds (S-compounds), [3-5] which bring challenges to the HDS and give rise to the exploration and adoption of some alternative desulfurization methods. Among those, oxidative desulfurization (ODS) using ionic liquids (ILs) [12-14] is more competitive based on the advantageous features of ILs *i.e.,* excellent catalytic and extractive properties, and effectiveness of this method to remove those HDS-immune cyclic S-compounds in diesel fuel under the mild conditions. [15-17]

Although, ODS has good desulfurization performance for some model diesel fuel, [18-20] it experiences difficulty at reducing the sulfur content (S-content) to a desirable level such as less than 10 ppm for the real fuel oils, as reported in the previous literatures[1, 17, 21, 22] enlisted in Table 1. In practice, we have used a desulfurization method, [18-20] *i.e.,* coupled oxidation-extraction desulfurization, which involves the ODS using ILs as both extractants and catalysts with 30 w% of H_2O_2 as oxidant followed by EDS using a solvent. [17, 23-26] This method can effectively desulfurize the diesel fuels and achieve the desirable S-content level (less than 10ppm) according to the stringent legislation. [1, 17, 27] For example, in our previous work, [24] we observed the S-content of real FCC diesel fuel decreased from 224.6 ppm to 37.4 ppm with 83.3% S-removal efficiency after ODS by $[C_1pyr]Cl/ZnCl_2$; then the S-content decreased to 5.3 ppm with 97.6% S-removal efficiency when used furfural as extractive reagent. We also observed the reduction in S-content of FCC diesel fuel from initial of 150 ppm to 8.1 ppm as a result of ODS by $[(CH_2)_4SO_3HMIm][Tos]$ and subsequent EDS by DMF. [23] Moreover, the regeneration and recyclability of ILs and solvents can easily be achieved with a negligible loss in the activity. [23] Therefore, coupled oxidation-extraction desulfurization can be regarded as one of the effective methods of desulfurization, which presents a good industrial prospect.

However, just use the experimental investigations are limited to develop sufficient data which may be helpful for designing an industrial-scale process. Therefore, the process simulation using the Aspen Plus is a promising way to develop a detailed insight into a design and development of a process. [28, 29] Recently, a few studies have been reported which employed the Aspen Plus to simulate the desulfurization process by ILs. [30-33] For example, Nancarrow et al.,[32] used Aspen Plus to perform the process simulation and optimization of an industrial EDS with the $[C_nmim][NTF_2]$

2

series of ILs, and observed that such IL-based extraction as an intermediate treatment can reduce the S-content from

7000ppm to 50 ppm. Song et al., [33] employed Aspen Plus to identify the performance of the top ILs as extractants in

EDS of the model gasoline fuel and observed that proposed technique can be easily extended to screen the favorable

ILs for other practical applications of extraction. However, the studies reported so far were mostly based on some

universal desulfurization methods (such as EDS or ODS) with simple components of model fuel oil. To our knowledge,

the coupled oxidation-extraction desulfurization for the diesel fuel composed of complex components (in order to

unlimited access to real diesel) needs to be studied with the aid of Aspen Plus.

In this work, a coupled oxidation-extraction desulfurization process is designed and simulated as shown in Figure

1, wherein $[C_1pyr]H_2PO_4$ is employed in the ODS process followed by using DMF in the EDS process. The main

objectives of this study are (i) to propose and design an industrial-scale oxidation-extraction desulfurization process,

(ii) to obtain the optimal operating conditions, hence to enable the simulation and optimization of this process, and

(iii) to verify the experimental results and evaluate the feasibility to scale-up this technology.

Methodology

The selection of desulfurization agent and diesel oil

$[C_1pyr]H_2PO_4$, which has smaller mutual solubility with fuel oil and was a good candidate solvent in

desulfurization according to our previous works, [34, 35] is selected in the ODS process. DMF is selected as extractant to

be used in subsequent EDS process, which can serve as perfect extractant in the EDS as reported in our previous works.

[23]

The diesel fuel is composed of 37 components (enlisted in Table 2) based on the straight-run diesel oil supplied

by SINOPEC Beijing Yanshan Petrochemical Co., Ltd. Benzothiophene (BT) and dibenzothiophene (DBT) are

selected as representative S-compounds and the original S-content is 224.12 ppm (mass ratio).

Properties of ILs and NRTL model

3

In this study, simulation is performed with Aspen Plus V8.4. The parameters of ILs (such as critical parameters, saturated vapor pressure parameters, heat capacity, density, and molecular weight) are calculated by the Modified Lydersen-Joback-Reid. [36-41] The group contribution values in the Modified Lydersen-Joback-Reid Method are enlisted in Table S1 and the formulas to calculate the parameters of ILs are given in Table S2. The NRTL model is selected as the thermodynamic model within Aspen Plus. COSMO-RS[33-35] is used to calculate LLE data of the IL-based systems and the multiple interaction parameters of NRTL model are regressed from the LLE data predicted by COSMO-RS.

COSMO-RS calculation

COSMO-RS[42, 43] is based upon the information that is evaluated by quantum chemical methods. The quantum chemical basis of COSMO-RS is COSMO, which was computed by the quantum chemical program packages such as Turbomole, DMOL3 and Gaussian. TZVPD, TZVP, SVP and DNP basis set were used for this quantum calculation. COSMO supposes that molecules are surrounded by a virtual conductor environment and the interactions take place on segments of this perfect/ideal conductor interface taking into account the electrostatic screening and the back-polarization of the solute molecule. The current COSMO database already covers the screening charge density distributions (σ-profiles) of thousands of conventional solvents and most of the reported cations and anions of ILs. The software package COSMOthermX (Version C30_1301) based on COSMO-RS allows for the thermodynamic calculations. In this work, the LLE calculations are performed using the BP_TZVP_C30_1301 parametrization. It should be mentioned that in the COSMO-RS calculation, ILs are treated as electro-neutral mixtures of separated cations and anions. The σ-profiles of the involved cations and anions of ILs, as well as the conventional compounds are directly taken from the standard database of the software. The σ-profiles of new compounds can be conveniently obtained from standard quantum chemical DFT calculations, which used in the geometry optimization.

There are two steps in COSMO-RS calculation: [42, 43] 1) the σ-profiles of components are obtained by quantum chemical calculations; 2) the chemical potential $(\mu_s(\sigma))$ of component is quantified through the statistical thermodynamics treatment of molecular interactions based on the obtained σ-profiles given by eq 1:

4

$$\mu_s(\sigma) = -\frac{RT}{a_{eff}}\ln[\int p_s(\sigma')\exp(\frac{a_{eff}}{RT}(\mu_s(\sigma') - (E_{vdW}(\sigma,\sigma') + E_{HB}(\sigma,\sigma') + E_{MF}(\sigma,\sigma'))/a_{eff}))d\sigma']$$

(1)

In eq 1, a_{eff} is the effective contact area between two surface segments and $P_S(\sigma)$ is the surface screening charge distribution of the whole system.

The LLE data can be determined with $\mu_s(\sigma)$. LLE calculation is explained with a liquid system of phase 1 and phase 2 as an example. The compounds distributed in phase 1 and phase 2 according to the partition equilibrium constants (K_i):

$$K_i = \exp(\frac{u_i^1 - u_i^2}{RT})$$

(2)

where μ_i^1 and μ_i^2 are the chemical potential of compound i in phase 1 and phase 2, respectively.

In order to validate the LLE data calculated by COSMO-RS is reliable for IL-based desulfurization system, we have compared the desulfurization results obtained through Aspen plus simulation (LLE data calculated by COSMO-RS, then regressed the NRTL parameters from the LLE data) with some experimental results. The results (Table S3) indicate that the COSMO-RS can calculate the LLE data of the IL-based system qualitatively and in many cases acceptable quantitatively, which have also been proved by other researches. [44-47]

Process simulation

Parameters of IL: the parameters of $[C_1pyr]H_2PO_4$ which need to be specified in Aspen Plus for the IL-based process are shown in Table S4~Table S6. The multiple interaction parameters of the IL-based systems are listed in Table S7. The flowsheet representing the coupled oxidation-extraction desulfurization process is depicted in Figure 2, where the reactor, extractor, evaporator, mixer, compressor, condenser and filter are modeled by the RYield block, Extract block, Flash block, Mixer block, Comp block, Heater block, and Split block, respectively.

ODS process: as shown in the Figure 2, IL, 30% H_2O_2 and 10,000 kg/hr of diesel fuel are fed in the reactor (B1). After complete reaction, the extracted mixture (S4) is allowed to settle into the decanter (B9), where the two distinct phases *i.e.,* IL phase (S5) and diesel fuel phase (S6) are formed based on their density difference.

5

EDS process: the diesel fuel (S6) is introduced into the extractor (B3) at its bottom, while a certain amount of

DMF (S8) is fed from the top of the extractor (B3). The diesel fuel product (S10) is obtained from the top of the

extractor.

Regeneration process of ILs: regenerations of the used IL (S5) is performed by dilution with water (S7) in the

mixer (B10) because it is hydrophilic while S-compounds are hydrophobic. The mixture (S19) undergoes the filtration

in the filter (B11), whose downstream (S21) enters the flash (B12) where simple distillation occurs. The regenerated

IL (S23) is then recycled through the cooler (B13), to bottom of the reactor column (B1), together with required amount

of fresh IL (S3).

Regeneration process of extractants: the used DMF (S11) is dealt in two evaporators (B4 and B5) for its

regeneration. After, the regenerated DMF is then recycled through the compressor (B6), condenser (B7), and mixer

(B8) into extraction column (B3) from the top, together with required amount of fresh DMF (S9).

Results and Discussion

A sensitivity analysis of operating parameters is performed for optimizing the process conditions of the ODS,

EDS, regeneration process of ILs and extractants, respectively.

IL Feed Rate

The influence of mass-based IL-oil ratio (S/F) on the mass flow of BT and DBT for $[C_1pyr]H_2PO_4$ in the ODS

process (B1) is determined and plotted in Figure 3. As plotted in Figure 3, when the IL-to-oil ratio increases from 0.5

to 1, the mass flow of BT and DBT notably decreases, whereas beyond this value, there is insignificant decrease in the

mass flow of the S-compounds. The influence of the IL-to-oil ratio on the yield of diesel fuel is given in Figure 4,

which shows that the yield of diesel fuel decreases linearly with the increase of the IL-to-oil ratio from 0.5 to 3. For

example, the mass flow of BT and DBT decreases from 9.09 kg/h to 3.72 kg/h and 10.01kg/h to 4.20 kg/h, respectively,

while the efficiency of diesel yield declines from 95.25% to 88.86% when the IL-to-oil ratio increases from 0.5 to 1.

The IL-oil ratio of 1 is selected by comprehensive consideration of the S-content and diesel yield from the industrial

6

application view point. There is mutual solubility between IL and diesel fuel, which can lead to the loss of diesel fuel. [5, 34] The loss can be minimized by selecting more suitable ILs characterized with little or no mutual solubility with diesel fuel, as well as, recycling the diesel during the IL regeneration process.

It should be pointed out that, the RYield block is used for the ODS process and the reaction is not actually simulated because it is difficult to obtain accurate reaction kinetics as the composition of diesel is complex and the products is uncertain.

Organic solvent Feed Rate

As shown in Figure 3, the Non-thiophene S-compounds (dimethyl sulfide and ethanethiol) are completely removed in ODS process (B1), only the remaining BT and DBT are considered for removal in the EDS process (B3).

The influence of the mass-based solvent-to-oil ratio (S/F) on the mass flow of BT and DBT for the selected DMF in EDS process is determined and plotted in Figure 5. It can be seen that, when the solvent-to-feed ratio increases from 0.5 to 1, the mass flow of BT and DBT notably decreases, whereas, after that both decrease slowly and finally become invariant. The influence of the solvent-to-feed ratio on the yield of diesel fuel is shown in Figure 6. As shown, the yield of diesel fuel decreases linearly with the increasing the solvent-to-feed ratio from 0.5 to 3. For example, the mass flow of BT and DBT decreases from 0.02 kg/h to 0 kg/h and 0.11 kg/h to 0.02 kg/h, respectively, while the efficiency of the diesel yield decreases from 100% to 94.45% when the solvent-to-feed ratio increases from 0.5 to 1. Therefore, the solvent-to-feed ratio of 1 can be selected by comprehensive consideration of the of S-content and diesel yield.

IL Regeneration

The requirement of the IL-regeneration process (B12) is to remove the water in the IL-mixture stream (S21) into the S23 stream (Figure 2) since the compounds of sulfone is hardly soluble in water and mostly removed through the filtration (B11) process. The influence of operating temperature and pressure on the removal rate of water is investigated and the results are plotted in Figure 7.

7

The operating pressure and temperature have different effect on removal rate of water from $[C_1pyr]H_2PO_4$ in different manner, *e.g.*, the removal rate of water increases with increasing of the temperature but with decreasing of the pressure. For instance, when the flash (B12) is operated at 0.5 bar, 0.8 bar, and 1 bar, the required temperature for regeneration of $[C_1pyr]H_2PO_4$ are 114 °C, 126 °C, and 138 °C, respectively. To avoid the utilization of vacuum pump as well as to save operating cost, the atmospheric distillation at operating conditions of 1 bar and 138 °C is preferred in the IL regeneration process.

Organic solvents regeneration

The regeneration of DMF, where two flash column (B4 and B5) are employed, needs to remove the impurities of S-compounds in order to ensure the regenerated DMF retains the original extractive performance. The first flash column (B4) is operated under the high pressure and low temperature, whereas, the second flash column (B5) is operated under the low pressure and high temperature.

As shown in Figure 8, there is a general increasing trend of mass flow of the total material, DMF, and the other material with the increasing of temperature. Moreover, when the temperature increases from 120 °C to 180 °C, the mass flow of the total material and DMF increase gradually, after that the mass flow of both increases notably; while the mass flow of the other material increases slowly with the temperature. Since the loss rate of DMF increases greatly above the 180°C, thus, the first flash column is operated under 180 °C in order to minimize the loss of DMF.

The purpose of the second flash column (B5) is to vaporize the DMF for the separation of other impurities. The effect of temperature and pressure on the mass flow and mass fraction of distilled DMF are shown in Figure 9 and Figure 10, respectively. It can be indicated that the mass flow and mass fraction of the distilled DMF increase rapidly from 26.02 kg/h to 12171.02 kg/h and 76.51% to 96.03%, respectively, when the temperature increases from 192 °C to 198 °C. Subsequently, with the further increase in the temperature, the mass flow of DMF remains the same while the mass fraction of DMF decrease and then stay the same. Therefore, the operating temperature of the second flash column (B5) is set at 198 °C. As shown in Figure 10, when the operating pressure increases from 0.6 bar to 0.8 bar at

198 °C, the mass flow of DMF increases rapidly from 0 kg/h to 11988.33 kg/h whereas after that the mass flow remain

the same. The mass fraction of DMF decreases with the pressure. Thus, the operating pressure is set at 0.8 bar.

Simulation results

The results of the coupled oxidation-extraction desulfurization by $[C_1pyr]H_2PO_4$ and DMF for the diesel fuel

under the optimal operating conditions (B1 and B3: 180°C, 1bar, IL-to-oil ratio is 1, DMF-to-oil ratio is 1; B4: 150 °C,

1bar; B5: 198 °C, 0.8bar; B12: 138 °C,1bar) are shown in Table 3. The obtained results clearly reveal that this method

can effectively remove both the non-thiophene S-compounds such as ethanethiol and dimethyl sulfide, as well as the

thiophene-sulfides such as benzothiophene and diphenylthiophene. For instance, the S-removal efficiency of

ethanethiol, dimethyl sulfide, benzothiophene and diphenylthiophene can be obtained of 98.7%, 98.98%, 99.24% and

99.46%, respectively. It is also found that the S-content of the diesel fuel remarkably reduced from 224.12 ppm to 8.32

ppm (total desulfurization efficiency is 96.29%) and meet the requirement of stringent legislation of less than 10ppm.

Aspen Plus has proved to be useful to study the industrial-scale coupled oxidation-extraction desulfurization method. It

is also observed that, this technique as an alternative to HDS, can produce ULSD with the requirement of feasible and

moderate conditions.

Comparison of the proposed process with HDS

Table 4 illustrates the comparative study of the coupled oxidation-extraction desulfurization method and the

traditional HDS from the economic point of view. For both of the processes, mainly, operating cost is a critical

economic consideration. For HDS, the capital investment includes the retrofitting to enable existing equipment for

achieving the ULSD standard, which significantly increases energy requirement as well as the consumption of H_2. [30]

[32] The energy requirement and solvent consumption of ILs-based process are summarized in Table 5. The energy

consumed in the regeneration of ILs and DMF with a capacity of 10000kg/h diesel fuel are about 8985.24 kW and

2138.54 kW, respectively. In case of this method, regeneration of ILs and solvents mainly contributes in the total

operating cost.

9

Compared to HDS, the IL-based desulfurization method can be conducted under milder conditions with simpler equipment. This technology has significant advantages in terms of environmental impact and process safety, and as legislation becomes more stringent in future years, the present method will continue to become more critical in technology selection.

Conclusion

This work is based on simulating a coupled oxidation-extraction desulfurization process which is used to desulfurize the diesel fuel composed of 37 components. This method involves two steps, first ODS by [C$_1$pyr]H$_2$PO$_4$ as an extractant as well as catalyst, second EDS by DMF as extracting agent. The industrial-scale of the coupled desulfurization processing of ULSD has been examined via the Aspen Plus simulation and the optimization of various operating conditions, i.e., IL-to-oil ratio, DMF-to-oil ratio, and operating temperature and pressure. Subsequently, the process is compared economically with the conventional HDS. The main conclusions drawn from this study are: 1) the S-content in the diesel fuel was reduced to only 8.32 ppm from initial of 224.12 ppm with 96.29% S-removal efficiency under the optimized conditions, which indicated that the coupled oxidation-extraction desulfurization method can achieve specifications of ULSD and provide technically feasible and moderate conditions as an alternative to HDS technology; 2) the regeneration of ILs and solvents mainly contributes in the total operating cost in this new technology, and the energy consumption of this process is higher than that in HDS-based process; 3) there is mutual solubility between diesel and extraction solvent and the loss of diesel is mainly because a part of diesel is dissolved into the extraction solvent, which is one of the bottlenecks restricting the industrialization of IL-desulfurization. Therefore, in our next research, we will continue to investigate the IL-desulfurization technology and develop a suitable method to regenerate and recycle the loss diesel. However, expected drop in cost of regeneration of diesel and extraction solvent in future combined with timely constricting environmental legislation and improved performance of process due to continuous research in this field, the proposed technique may become a promising option to replace HDS.

Acknowledgements

10

References

1. Nie, Y.; Dong, Y. X.; Bai, L.; Dong, H. F.; Zhang, X. P. Fast oxidative desulfurization of fuel oil using dialkylpyridinium tetrachloroferrates ionic liquids. *Fuel* **2013**, 103, 997–1002.

2. Wagle, D. V.; Zhao, H.; Deakyne, C. A.; Baker, G. A. Quantum Chemical Evaluation of Deep Eutectic Solvents for the Extractive Desulfurization of Fuel. *ACS Sustainable Chem. Eng.* **2018**, 6, 7525−7531.

3. Ibrahim, J. J.; Gao, S. R.; Abdeltawab, A. A.; Al-Deyab, S. S.; Yu, G. R.; Chen, X. C.; Yong, X. Y. Extractive desulfurization of fuel oils with dicyano(nitroso)methanide-based ionic liquids. *Sep. Sci. Tech.* **2015**, 50, 1166–1174.

4. Abro, R.; Abdeltawab, A. A.; Al-Deyab, S. S.; Yu, G. R.; Qazi, A. B.; Gao, S. R.; Chen, X. C. A review for extractive desulfurization of fuel oils using ionic liquids. *RSC Adv.* **2014**, 4, 35302–35317.

5. Gao, S. R.; Chen, X. C.; Abro, R.; Su, Z.; Abdeltawab, A. A.; Al-Deyab, S. S.; Yu, G. R. Mutual solubility of acidic ionic liquid and model gasoline of n -octane + 1-octene + toluene. *J. Taiwan Inst. Chem. E.* **2016**, 69, 78–84.

6. Zhao, R. J.; Wang, J. L.; Zhang, D. D.; Sun, Y. H.; Han, B. X.; Tang, N.; Zhao, J. H.; Li, K. X. Deep Catalytic Oxidative Desulfurization of Model Fuel Based on Modified Iron Porphyrins in Ionic Liquids: Anionic Ligand Effect. *ACS Sustainable Chem. Eng.* **2017**, 5, 2050−2055.

7. Zhang, G.; Yu, F.; Wang. R. Research advances in oxidative desulfurization technologies for the production of low sulfur fuel oils. *Petroleum & Coal* **2009**, 51, 196–207.

8. Abro, R.; Gao, S. R.; Chen, X. C.; Yu, G. R.; Abdeltawab, A. A.; Al-Deyab, S. S. Oxidative Desulfurization of Gasoline by Ionic Liquids Coupled with Extraction by Organic Solvents. *J. Braz. Chem. Soc.* **2016**, 26, 998–1006.

11

9. Mei, H.; Mei, B. W.; Yen, T. F. A new method for obtaining ultra-low sulfur diesel fuel via ultrasound assisted oxidative desulfurization. *Fuel* **2003**, 82, 405−414.

10. Bhutto, A. W.; Abro, R.; Gao, S. R.; Abbas, T.; SalemS, A. A.; Chen, X. C.; Yu, G. R. Oxidative desulfurization of fuel oils using ionic liquids: A review. *J. Taiwan Inst. Chem. E.* **2016**, 62, 84–97.

11. Zhu, W. S.; Dai, B. L.; Wu, P. W.; Chao, Y. H.; Xiong, J.; Xun, S. H.; Li, H. P.; Li, H. M. Graphene-Analogue Hexagonal BN Supported with Tungsten-based Ionic Liquid for Oxidative Desulfurization of Fuels. *ACS Sustainable Chem. Eng.* **2015**, 3, 186−194.

12. Zhao, H.; Baker, G. A.; Wagle, D. V.; Ravula, S.; Zhang, Q. Tuning Task-Specific Ionic Liquids for the Extractive Desulfurization of Liquid Fuel. *ACS Sustainable Chem. Eng.* **2016**, 4, 4771−4780.

13. Endres, F. Ionic Liquids: Promising Solvents for Electrochemistry. *Z. Phys. Chem.* **2004**, 218, 255–283.

14. Brennecke, J. F.; Maginn, E. J. Ionic Liquids: Innovative Fluids for Chemical Processing. *AIChE J.* **2001**, 47, 2384–2389.

15. Asumana, C.; Yu, G. R.; Li, X.; Zhao, J. J.; Liu, G.; Chen, X. C. Extractive desulfurization of fuel oils with low-viscosity dicyanamide-based ionic liquids. *Green Chem.* **2010**, 12, 2030–2037.

16. Yu, G. R.; Li, X.; Liu, X. X.; Asumana, C.; Chen, X. C. Deep desulfurization of fuel oils using low-viscosity 1-ethyl-3-methylimidazolium dicyanamide ionic liquid. *Ind. Eng. Chem. Res.* **2010**, 50, 2236–2244.

17. Chen, X. C.; Guan, Y. W.; Abdeltawab, A. A.; Al-Deyab, S. S.; Yuan, X. L.; Wang, C. Y.; Yu, G. R. Using functional acidic ionic liquids as both extractant and catalyst in oxidative desulfurization of diesel fuel: an investigation of real feedstock. *Fule* **2015**,146, 6–12.

18. Zhu, W. S.; Li, H. M.; Jiang, X.; Yan, Y. S.; Lu, J. D.; Xia, J. X. Oxidative Desulfurization of Fuels Catalyzed by Peroxotungsten and Peroxomolybdenum Complexes in Ionic Liquids. *Energy & Fuels* **2007**, 21, 2514–2516.

19. Zhang, M.; Zhu, W. S.; Xun, S. H.; Li, H. M.; Gu, Q. Q.; Zhao, Z.; Wang, Q. Deep Oxidative Desulfurization of Dibenzothiophene with POM–Based Hybrid Materials in Ionic Liquids. *Chem. Eng. J.* **2013**, 220, 328–336.

20. Li, F. T.; Kou, C. G.; Sun, Z. M.; Hao, Y. J.; Liu, R. H.; Zhao, D. S. Deep Extractive and Oxidative Desulfurization of Dibenzothiophene with $C_5H_9NO \cdot SnCl_2$ Coordinated Ionic Liquid. *J. Hazard. Mater.* **2012**, 205, 164–170.

21. Chen, X. C.; Song, D. D.; Asumana, C.; Yu, G. R. Deep oxidative desulfurization of diesel fuels by Lewis acidic ionic liquids based on 1- n-butyl-3-methylimidazolium metal chloride. *J. Mol. Catal. A: Chem.* **2012**, 359, 8–13.

12

22. Zhao, D. S.; Sun, Z. M.; Li, F. T.; Shan, H. D. Optimization of oxidative desulfurization of dibenzothiophene using acidic ionic liquid as catalytic solvent. *J. Fuel Chem. Technol.* **2009**, 37, 194–198.

23. Gao, S. R.; Li, J. Y.; Chen, X. C.; Abdeltawab, A. A.; Yakout, S. M.; Yu, G. R. A Combination Desulfurization Method for Diesel Fuel: Oxidation by Ionic Liquid with Extraction by Solvent. *Fuel* **2018**, 2, 123–128.

24. Chen, X. C.; Guo, H. S.; Abdeltawab, A. A.; Guan, Y. W.; Al-Deyab, S. S.; Yu, G. R.; Yu, L. BrÖnsted-Lewis acidic ionic liquids and application in oxidative desulfurization of diesel. *Fuel* **2015**, 29, 2998–3003.

25. Lo, W. H.; Yang, H. Y.; Wei G. T. One-pot desulfurization of light oils by chemical oxidation and solvent extraction with room temperature ionic liquids. *Green Chem.* **2003**, 5, 639–642.

26. Lu, L.; Cheng S. F.; Gao, J. B.; Gao G. H.; He, M. Y. Deep Oxidative Desulfurization of Fuels Catalyzed by Ionic Liquid in the Presence of H_2O_2. Energy & Fuels **2007**, 21, 383-384.

27. Sengupta, A.; Kamble, P. D.; Basu, J. K.; Sengupta, S. Kinetic study and optimization of oxidative desulfurization of benzothiophene using mesoporous titanium silicate-1 catalyst. *Ind. Eng. Chem. Res.* **2011**, 51, 147–157

28. Ma, T.; Wang, J. X.; Du, Z. Z.; Abdeltawab, A. A.; Al-Enizi, A. M.; Chen, X. C.; Yu, G. R. A process simulation study of CO_2 capture by ionic liquids. *International Journal of Greenhouse Gas Control* **2017**, 58, 223–231.

29. Bezzo, F.; Bernardi, R.; Cremonese, G.; Finco, M.; Barolo, M. Using process simulators for steady-state and dynamic plant analysis-An industrial case study. *Chem. Eng. Res. Des.* **2004**, 82, 499–512.

30. Li, Z.; Xu, J.; Li, D.; Li, C. Extraction process of sulfur compounds from fuels with protic ionic liquids. *RSC Adv.* **2015**, 5, 15892–15897.

31. Song, Z.; Zhang, C.; Qi, Z. W.; Zhou, T. Sundmacher K. Computer-aided design of ionic liquids as solvents for extractive desulfurization. *AICHE J.* **2018**, 64: 11.

32. Nancarrow, P.; Mustafa, N.; Shahid, A.; Varughese, V.; Zaffar, U.; Ahmed, R.; Akther, N.; Ahmed, H.; AlZubaidy, I.; Hasan, S.; Elsayed, Y.; Sara, Z. Technical Evaluation of Ionic Liquid-Extractive Processing of Ultra Low Sulfur Diesel Fuel. *Ind. Eng. Chem. Res.* **2015**, 54, 10843−10853.

33. Song, Z.; Zhou, T.; Zhang, C.; Qi, Z. W. Sundmacher K. Systematic Method for Screening Ionic Liquids as Extraction Solvents Exemplified by an Extractive Desulfurization Process. *ACS Sustainable Chem. Eng.* **2017**, 5, 3382−3389.

34. Gao, S. R.; Yu, G. R.; Abro, R.; Abdeltawab, A. A.; Al-Deyab, S. S.; Chen, X. C. Desulfurization of fuel oils: Mutual solubility of ionic liquids and fuel oils. *Fuel* **2016**, 173, 164−171.

35. Gao, S. R.; Chen, X. C.; Abro, R.; Abdeltawab, A. A.; Al-Deyab, S. S.; Yu, G. R. Desulfurization of fuel oil: conductor-like screening model for real solvents study on capacity of ionic liquids for thiophene and dibenzothiophene. *Ind. Eng. Chem. Res.* **2015**, 54, 9421−9430.

36. Valderrama, J. O.; Forero, L. A.; Rojas, R. E. Critical Properties and Normal Boiling Temperature of Ionic Liquids. Update and a New Consistency Test. *Ind. Eng. Chem. Res.* **2012**, 51, 7838−7844.

37. Rebelo, L. P.; Canongia Lopes, J. N.; Esperança, J. M. On the critical temperature, normal boiling point, and vapor pressure of ionic liquids. *J. Phys. Chem. B* **2005**, 109, 6040-6043.

38. Simon, R. H. M. Estimation of critical properties of organic compounds by the method of group contributions. A. L. Lyderren. Engineering Experiment Station Report. *AICHE J.* **1956**, 2, 12S−12S.

39. JOV, And W W S, JAL. Critical Properties, Normal Boiling Temperature, and Acentric Factor of Another 200 Ionic Liquids. *Ind. Eng. Chem. Res.* **2008**, 47, 1318−1330.

40. Valderrama, J. O.; Sang, W. W.; Lazzus, J. A. Critical Properties, Normal Boiling Temperature, and Acentric Factor of Another 200 Ionic Liquids. Ind. Eng. Chem. Res. **2008**, 47, 1318−1330.

41. Joback, K. G.; Reid, R. C. Estimation of pure-component properties from group-contributions. *Chem. Eng. Commun.* **1987**, 57, 233–243.

42. Eckert, F.; Klamt, A. Fast solvent screening via quantum chemistry: COSMORS approach. *AIChE J.* **2002**, 48, 369–385.

43. Eckert, F.; Klamt, A. COSMOtherm, version C3.0; COSMOlogic GmbH & Co. KG: Leverkusen, *Germany* **2013**.

44. Ferreira, A. R.; Freire, M. G.; Ribeiro, J. C.; Lopes, F. M.; Crespo, J. G.; Coutinho, J. A. P. Overview of the liquid-liquid equilibria of ternary systems composed of ionic liquid and aromatic and aliphatic hydrocarbons, and their modeling by COSMO-RS. *Ind. Eng. Chem. Res.* **2012**, 51, 3483−3507.

45. Ferreira, A. R.; Freire, M. G.; Ribeiro, J. C.; Lopes, F. M.; Crespo, J. G.; Coutinho, J. A. P. An overview of the liquid-liquid equilibria of (ionic liquid + hydrocarbon) binary systems and their modeling by the conductor-like screening model for real solvents. *Ind. Eng. Chem. Res.* **2011**, 50, 5279−5294.

46. Anantharaj, R.; Banerjee, T. Aromatic sulfur-nitrogen extraction using ionic liquids: Experiments and predictions using an a priori model. *AIChE J.* **2013**, 59, 4806−4815.

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47. Ferreira, A. R.; Freire, M. G.; Ribeiro, J. C.; Lopes, F. M.; Crespo, J. G.; Coutinho, J. A. P. Overview of the liquid-liquid equilibria of ternary systems composed of ionic liquid and aromatic and aliphatic hydrocarbons, and their modeling by COSMO-RS. *Ind. Eng. Chem. Res.* **2012**, 51, 3483−3507.

15

Fig. 1. Schematic diagram of the coupled oxidation-extraction desulfurization in this manuscript.

Fig. 2. Flow chart of the coupled oxidation-extraction desulfurization

Fig. 3. Influence of the mass ratio [C_1pyr]H_2PO_4/diesel (S/F) on the mass flow of S-compounds

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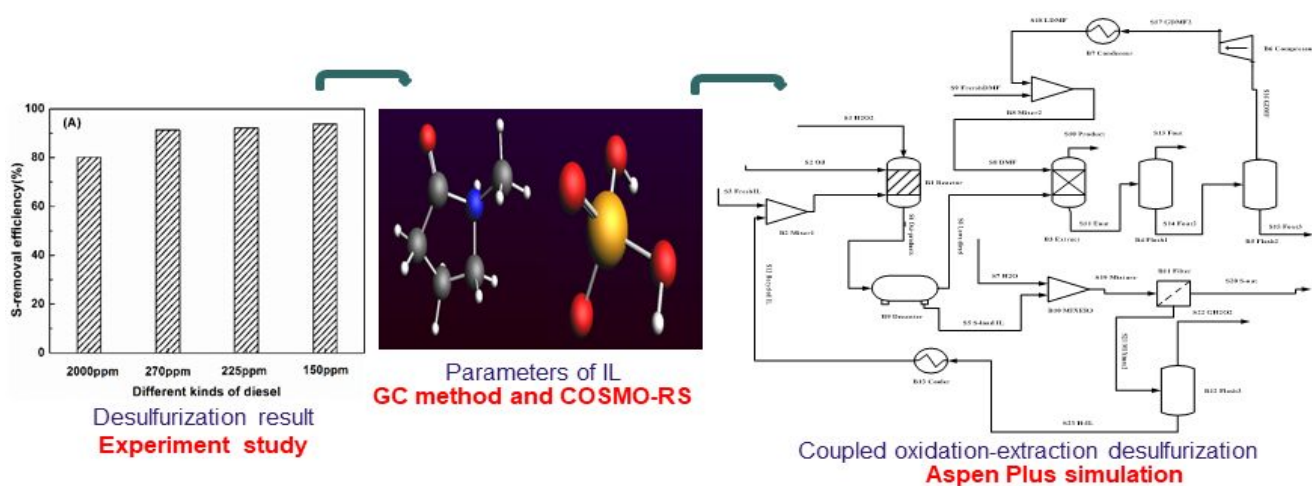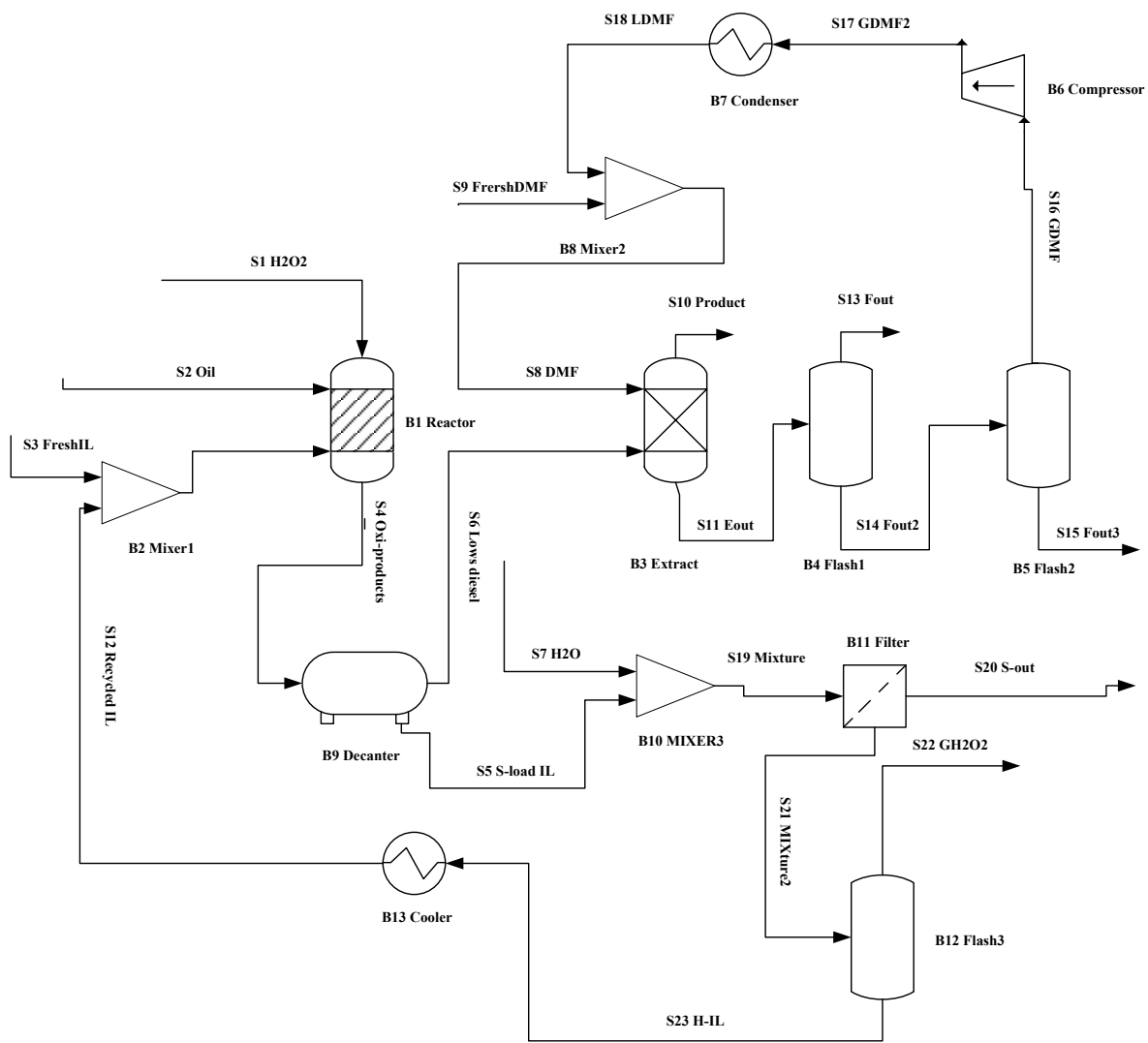50
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Fig. 4. Influence of the mass ratio $[C_1pyr]H_2PO_4$/diesel (S/F) on the yield of diesel

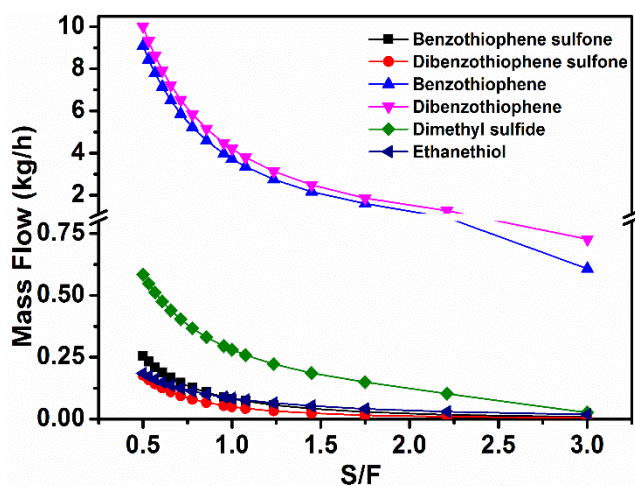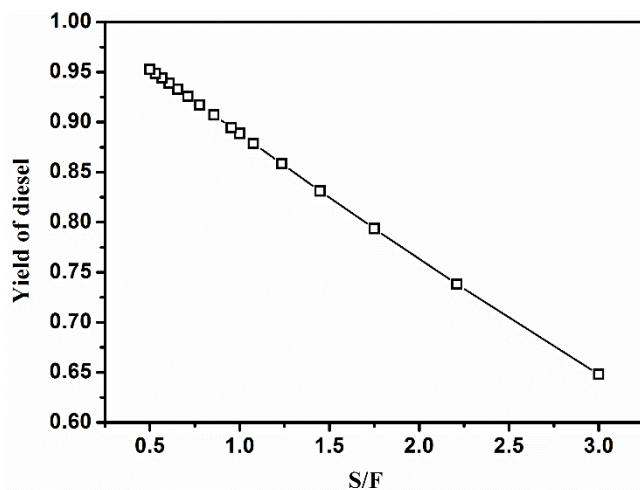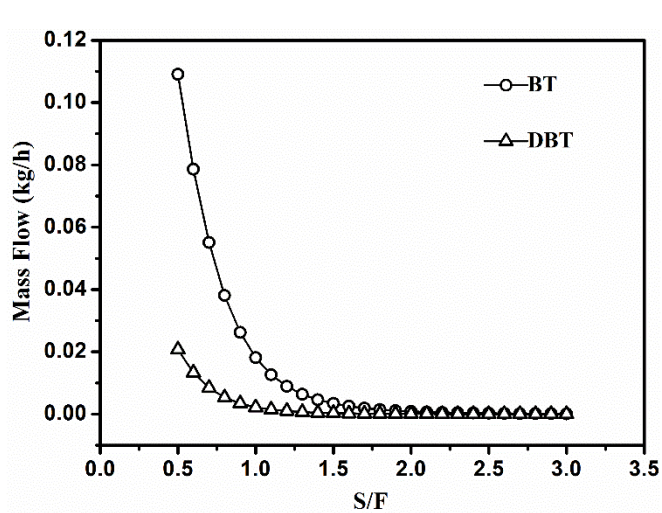**Fig. 5.** Influence of the mass ratio DMF/diesel (S/F) on the mass flow of S-compounds
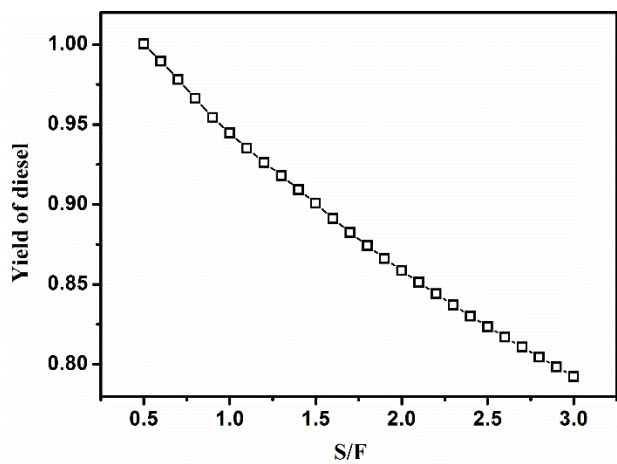
Fig. 6. Influence of the mass ratio DMF/diesel (S/F) on the yield of diesel

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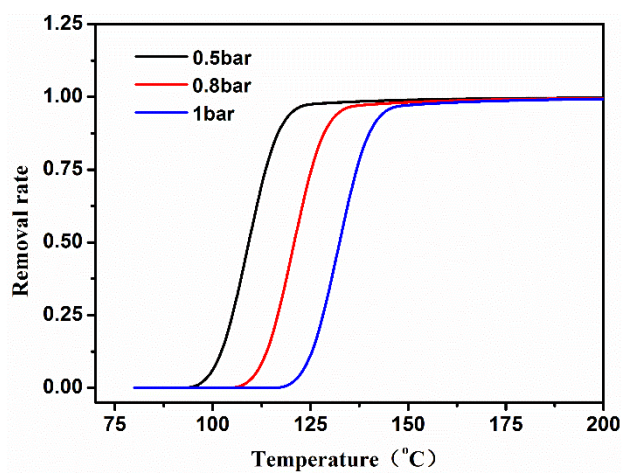
Fig. 7. Influence of temperature and pressure on the removal rate of water

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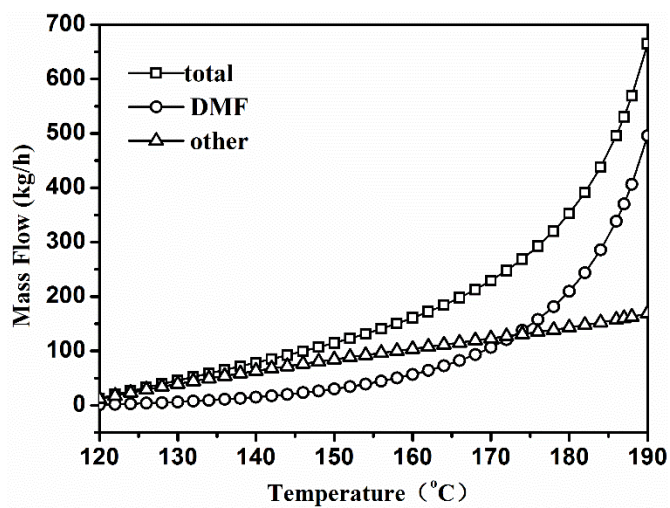
Fig. 8. Effect of temperature on the first flash of DMF

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Fig. 9. Effect of temperature on second flash of DMF

Fig. 10. Effect of pressure on the second flash of DMF

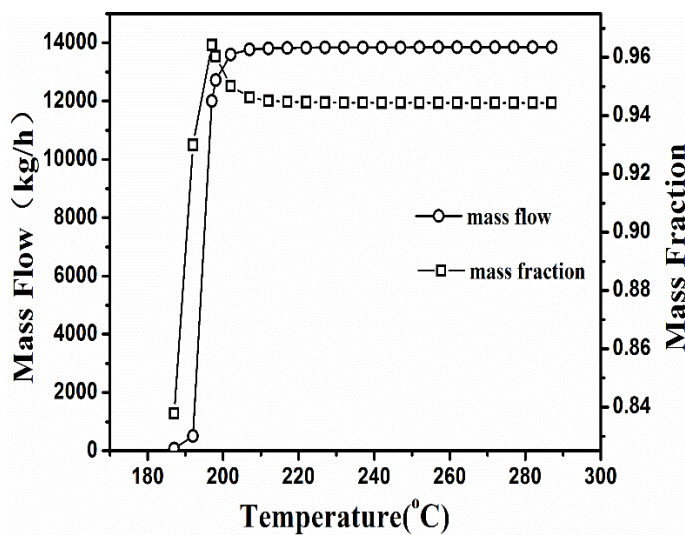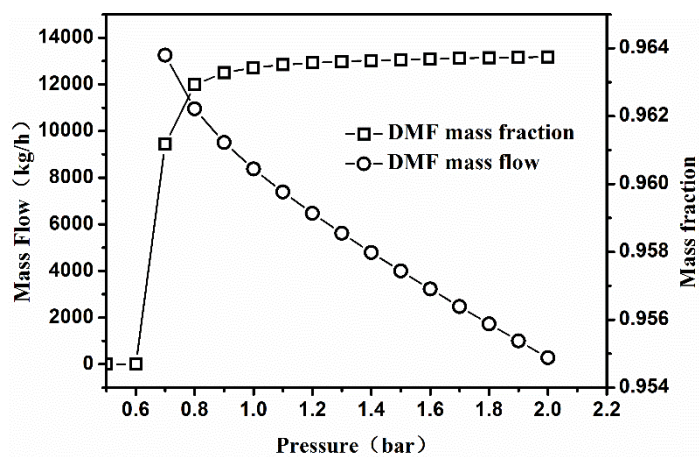**Table 1**. Oxidative desulfurization of real oils by ILs.

ILs	Real oil (initial S-content)	S-removal efficiency	Reaction condition	Ref.
$[C^3{}_8MPy]FeCl_4$	gasoline (468ppm)	44.2%	T, 298K; t, 30min; mass ratio of IL/Oil, 1/3; O/S, 6	[1]
$[C_4mim]Cl/3ZnCl_2$	FCC diesel fuel (460ppm)	63.5%	T, 318.15K; t, 3h; mass ratio of IL/Oil, 1/2; O/S, 60	[21]
$[Hnmp][H_2PO_4]$	diesel fuel (750ppm)	64.3%	T, 333.15K; t, 5h; volume ratio of IL/Oil, 1/1; O/S, 16.	[22]
[(CH2)4SO3HMIm][ZnCl3]	deisel fuel (225ppm)	40.7%	T, 333 K; t, 3 h; mass ratio of IL/Oil, 1/2; O/S, 30	[17]
$[(CH_2)_4SO_3HMIm][Tos]$	deisel fuel (225ppm)	43.7%	T, 348K; t, 3h; mass ratio of IL/Oil, 1/2; O/S, 40	[17]

Table 2. The component of diesel fuel

Component	Mass fraction (%)	Component	Mass fraction(%)
Undecane	0.18	1-Cyclopentyl tridecane	1.74
Dodecane	0.45	1-Cyclopentyl tetradecane	1.05
Tridecane	1.64	Tetradecylcyclohexane	0.56
Tetradecane	5.82	Cetyl-cyclopentane	0.46
Pentadecane	10.87	3-Cyclohexylpropylcyclohexane	1.13
Hexadecane	12.6	4-Cyclohexyl butyl cyclohexane	1.44
Heptadecane	12.65	4,4'-Dimethylamino methazine	1.19
Octadecane	10.89	Undecylbenzene	0.97
Nonadecane	9.62	Lauryl Benzene	0.97
Eicosane	5.84	Tridecylbenzene	0.76
Twenty-one alkanes	2.55	3-Ethyltetramethyl-stilbene	1.35
Docosane	0.2	Heptamethoxime	1.23
Tridecene	0.7	Hexane	1.82
Octyl cyclopentane	0.87	pentane	2.68
1-cyclopentyl nonane	0.97	Hexahydrotoluene	0.256
1-cyclopentyl decane	1.97	Benzothiophene	0.047
Decyl cyclohexane	2.31	Dibenzothiophene	0.053
1-cyclopentyl dodecane	2.16	Ethanethiol	0.003
Dimethyl sulfide	0.001		

Table 3. Results from simulation of desulfurization

Sulfide	Before desulfurization	After desulfurization
Benzothiophene	0.047%	0.000354%
Dibenzothiophene	0.053%	0.000291%
Ethanethiol	0.003%	0.0000383%
Dimethyl sulfide	0.001%	0.0000194%
Benzothiophenone sulfone	0	0.001011%
Dibenzothiophene Sulfone	0	0.00139%
Sulfur content	224.12 ppm	8.32 ppm
Desulfurization rate	96.28%	
Mass yield	87.37%	

28

Table 4. Economical comparison of the proposed process and HDS

criterion	HDS[30]	IL ODS + solvent EDS
Capital investment	Retrofitting of existing unit	Oxidation and extraction units required
Operating cost	High energy and H_2 costs to achieve ULSD	Low energy costs but IL makeup regeneration is significant
Environmental considerations	Energy intensive and high consumption of H_2	Low impact on environment; IL recycled; consumption of H_2O_2 and solvent
Safety considerations	Use of explosive H_2, high temperatures, and pressures	Ambient operating conditions, IL toxicity not fully studied, solvent toxicity
Technological maturity	Existing technology	Requires significant development

29

Table 5. Experimental results of the coupled oxidation-extraction desulfurization (for 10000kg/h diesel fuel)

solvent	temperature (℃)	pressure (bar)	solvent-to-feed ratio (S/F)	yield (%)	energy consumption (kW)
B1	80	1	1	88.86	0
B3	80	1	1	94.45	209.29
B4	150	1	~	96.37	939.15
B5	198	0.8	~	98.41	1199.39
B12	138	1	~	99.76	8985.24

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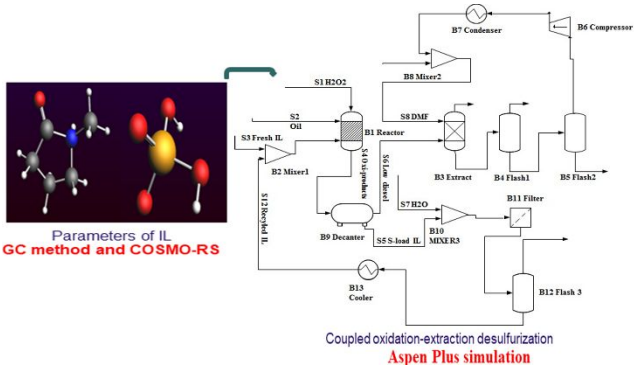
TOC Graphic: Coupled Oxidation-Extraction Desulfurization for Diesel Fuel evaluated by COSMO-RS and Aspen Plus

31