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PURIFICATION OF COMMERCIAL AND MODEL DIESEL FUELS BY DEEP EUTECTIC SOLVENTS

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DESs composed of glycerol and chloroacetic acid/$[TEAH]^+[ClCH_2COO]^-$ were prepared and studied as extractants of nitrogen-, sulfuric- and aromatic compounds. Denitrification, desulfurization and dearomatization of model diesel fuels were conducted at room temperature. The LLE times were chosen as 1 and 3 hours. The oxidative desulfurization of diesel fuel was studied at 90°C temperature in 3 hours of mixing times. The results showed that, quinoline was separated completely by Glycerol/6 chloroacetic acid. Aniline and cresol derivatives of model fuels were cleaned with 100% rates by Glycerol/6 chloroacetic acid and Glycerol/6$[TEAH]^+$ $[ClCH_2COO]^-$. Both DESs are selective for the commercial diesel as a desulfurization agent. All extraction processes were controlled by ^1H NMR.

Keywords: *DES, extraction, purification, NMR, diesel*

INTRODUCTION

The combustion of fossil fuels (coal tar, fuel, natural gases) is one of the significant sources of air pollution. The burning of motor fuels with high content of aromatic and heteroaromatic compounds causes SO_x, NO_x and CO_x emissions. Sulfur oxides contribute to acid rains, smog and eutrophication. CO_2, N_2O and NO_2 play a role in the depletion of the ozone layer [1-7]. The production of ultra-low sulfur, nitrogen and aromatic containing fuels are the basic aim of many fuel industries. The content of sulfur and nitrogen compounds has been limited to 10 ppm and 0,1 ppm [8]. Industrially, the purification process of gasoline, diesel fuels called hydrogenation. This technology needs higher temperature, pressure, costly catalysis and hydrogen consumption. On the other side, poly aromatic hydrocarbons are not separated completely from the fuels in hydrotreating. It is so difficult to remove them [9, 10]. Therefore, the study on the removal of organonitrogen, -sulfur and aromatic hydrocarbons from liquid fuels with the alternative methods are the most important issue.

The discovery of deep eutectic solvents promoted to prepared new environmentally purification methods. Liquid-liquid extraction with DESs is the main separation method for the cleaning fuels [11]. Deep eutectic solvents are new type of green extraction solvents which formed one and more hydrogen bond donors and hydrogen bond acceptors. The resulting DESs *(Deep Eutectic Solvents)* showed high thermal and chemical stability. They are cheap and eco-friendly solvents [12-15].

In this study, we reported a new type of deep eutectic solvents for the extraction of nitrogen, sulfuric and aromatic compounds from the model diesel/diesel fuels. Chloroacetic acid and $[TEAH]^+$ $[ClCH_2COO]^-$ are selected as hydrogen bond acceptors and glycerol as hydrogen bond donor of DESs. The molar ratios of HBA/HBD were chosen as 1:6. Quinoline {1,7%}, aniline {1,7%}, indole {1,7%} were as nitrogen, dibenzothiophene {2%} as sulfuric and fluorenone {3,5%}, m-, p- and o-cresols {3,5%} were aromatic compounds of model diesel fuels. The liquid-liquid extraction processes were carried out at room temperature in 1 and 3 hours. The desulfurization of real diesel fuels was conducted at 90° C temperature. All analysis were controlled by ^1H NMR.

EXPERIMENTAL PART

2.1 Chemicals

All chemicals which used in the experiments were obtained from Sigma-Aldrich (Germany). $[TEAH]^+$ $[ClCH_2COO]^-$ was synthesized and confirmed by ^1H NMR analysis.

2.2 The preparation of DESs

The hydrogen bond donor of deep eutectic mixture was selected glycerol. Chloroacetic acid and $[TEAH]^+[ClCH_2COO]^-$ were chosen as hydrogen bond acceptors. All DESs were synthesized at room temperature. HBA (a molar ratio) and HBD (6 molar ratio) was mixing till a homogenous bright yellow liquid appeared.

2.3 The preparation of model fuels

Hexadecane and n-decane was chosen as the components of model diesel fuels. Quinoline, aniline and indole were added 1,7% in the mixture of n-decane and hexadecane. The percentage of aromatic compounds was 3,5 % in the model fuel. Dibenzothiophene was selected as sulfuric compound with 2%. The volume ratios of n-decane/hexadecane was 1:1.

2.4 The liquid-liquid extraction

LLE processes were conducted at room temperature in 1 and 3 hours of mixing time. The volume ratios of DESs/model fuels were as 1:1. The desulfurization of commercial diesel fuel was studied at 90° C temperature. The processes were continued in 3 hours of mixing.

2.5 NMR analysis

The LLE processes were controlled using of NMR spectrometer (UltraShield Magnet) AVANCE 300 MHz (300 MHz for the ^1H).

RESULTS AND DISCUSSION

3.1 Characterization of DESs

The physical properties of DESs were shown in the Table 1. As we know, deep eutectic solvents also called “designer solvents”. Their physical and chemical properties can be tailorized by the changing of HBA and HBD [16, 17].

Table 1.

The physical properties of DESs

The physical properties	**Types of DESs**	
	DES1	DES2
Density at 20° C, g/cm^3	2,01114	1,93941
Viscosity at 20° C, mm^2/s	67,877	98,475
Viscosity at 40° C, mm^2/s	19,473	31,551

3.2 Liquid-liquid extraction process

Two types of DESs were selected and investigated as extractive solvents of model diesel/diesel fuels. The components of DES1 consist of chloroacetic acid (1) and glycerol (6) molar ratio. $[TEAH]^+$ $[ClCH_2COO]^-$ (1) and glycerol (6) are formed DES2. Liquid-liquid extraction of heteroaromatic and aromatic compounds of model fuels studied at room temperature. The mixing times were 1 and 3 hours.

As can be seen from the Table 2, quinoline and aniline were extracted completely by DES1 in 1 hour. The high separation efficiency of indole was observed in 1 hour with 28%. o- and m-cresols were purified with 92% and 100%. DBT and fluorenone showed the lowest extraction results in both mixing times.

Table 2.

The extraction of heteroaromatic/aromatic compounds by DES1 at room temperature

DES1[$ClCH_2COOH$/6Glycerol]			
The number of aromatic/heteroaromatic compounds	*LLE conditions*		Separation efficiencies, %
	DES: Fuel (Volume ratios)	Time (hour)	
Quinoline {1,7%}	1:1	1	100
Aniline {1,7%}	1:1	1	100
Indole {1,7%}	1:1	1	28
Indole {1,7%}	1:1	3	22
Fluorenone {3,5%}	1:1	1	4
Fluorenone {3,5%}	1:1	3	6
Dibenzothiophene {2%}	1:1	1	2
Dibenzothiophene {2%}	1:1	3	4
o-cresol {3,5%}	1:1	1	92
p-cresol {3,5%}	1:1	1	20
p-cresol {3,5%}	1:1	3	35
m-cresol {3,5%}	1:1	1	82
m-cresol {3,5%}	1:1	3	100

From the Table 3, among the nitrogen compounds, the highest purification rates of quinoline, aniline and indole were achieved in 1 hour at room temperature. The LLE with DES2 for the cresol derivatives was 95% and 100%. The same separation results of fluorenone and DBT were obtained by $[TEAH]^+[ClCH_2COO]^-$/6Glycerol as DES1.

Table 3.

The extraction of heteroaromatic/aromatic compounds by DES2 at room temperature

DES2[[$TEAH^+$] [$ClCH_2COOH^-$]/6Glycerol]			
The number of aromatic/heteroaromatic compounds	*LLE conditions*		Separation efficiencies, %
	DES: Fuel (Volume ratios)	Time (hour)	
Quinoline {1,7%}	1:1	1	73
Quinoline {1,7%}	1:1	3	57
Aniline {1,7%}	1:1	1	100
Indole {1,7%}	1:1	1	51
Indole {1,7%}	1:1	3	27
Fluorenone {3,5%}	1:1	1	3
Fluorenone {3,5%}	1:1	3	3
Dibenzothiophene {2%}	1:1	1	4
Dibenzothiophene {2%}	1:1	3	7
o-cresol {3,5%}	1:1	1	95
p-cresol {3,5%}	1:1	1	100
m-cresol {3,5%}	1:1	1	100

The deep oxidative desulfurization of commercial diesel was carried out in 3 hours of mixing time with 30% H_2O_2. The sulfur content in diesel fuels was detected according to ASTM D1266 standard.

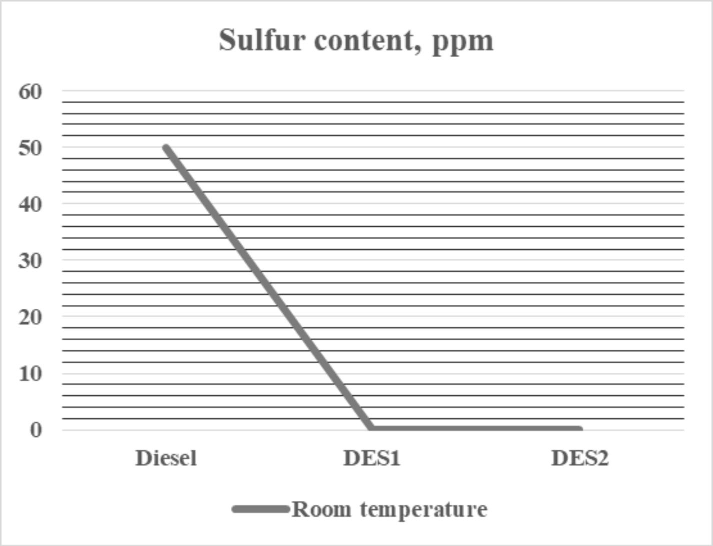

Fig. 1. The sulfur content in diesel fuels after LLE at 90° C temperature by DESs

As seen from the Figure 1, 2 sulfuric components from the commercial diesel fuel were cleaned by both DESs.

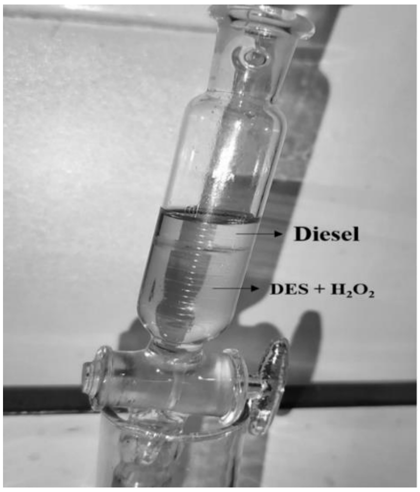

Fig. 2. ODS of the commercial diesel by DES2

CONCLUSION

Glycerol-based DESs were prepared and investigated as a greener extractive agent for the purification of model diesel/diesel fuels. This review summarizes the application of DESs for the separation of quinoline {1,7%}, aniline {1,7%}, indole {1,7%}, dibenzothiophene {2%}, fluorenone {3,5%}, and m-, p- and o-cresols {3,5%} from the model fuels. On the other side, oxidative desulfurization (ODS) of commercial diesel fuels was also studied by eutectic solvents and detected according to ASTM standard.

LLE of model fuels was carried out at room temperature. The mixing times of extraction processes were chosen as 1 and 3 hours. DES1, which is consist of $ClCH_2COOH$/6Glycerol separated quinoline, aniline, and o-cresol from the model fuel in 1 hour of mixing time. M-cresol was purified completely in 3 hours with same DES.

The highest extraction efficiencies of aniline and cresol derivatives were also observed with DES2 at 1 hour. The higher purification of quinoline and indole was exhibited in 1 hour with 73% and 51% rates.

ODS of commercial diesel was studied at 90° C temperature in 3 hours with both DESs. H_2O_2 was an oxidative agent with 30%. ^1H NMR analysis and the results of laboratory experiments according to ASTM standards showed that the sulfur content (ppm) of diesels decreased up to zero by the purification with DES1 and DES2.

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DƏRİN EVTEKTİK HƏLLEDİCİLƏR İLƏ DİZEL VƏ MODEL DİZEL YANACAQLARININ TƏMİZLƏNMƏSİ

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Qliserin və monoxlorsirkə turşusu/trietilammonium monoxlorasetatdan ibarət DEH-lər hazırlanmış və azotlu, kükürdlü və aromatik birləşmələrin ekstragenti kimi öyrənilmişdir. Model dizel yanacaqlarının azotsuzlaşdırılma, kükürdsüzləşdirilmə və aromatiksizləşdirilməsi otaq temperaturunda aparılmışdır. Maye-maye ekstraksiya müddətləri 1 və 3 saat kimi seçilmişdir. Dizel yanacağının oksidləşdirici kükürdsüzləşdirilməsi isə 3 saat qarışdırılma müddətində 90°C temperaturda öyrənilmişdir. Nəticələr göstərir ki, qliserin/6monoxlorsirkə turşusu ilə xinolin tamamilə ayrılmışdır. Qliserin/6monoxlorsirkə və qliserin/6 trietilammonium monoxlorasetat ilə isə anilin və krezol törəmələri 100% göstərici ilə təmizlənmişdir. Hər iki DEH dizel yanacağının kükürdsüzləşdirici agenti kimi selektivdir. Bütün ekstraksiya prosesləri ^{1}H NMR ilə izlənilmişdir.

Açar sözlər: *DEH, ekstraksiya, təmizlənmə, NMR, dizel.*

ОЧИСТКА КОММЕРЧЕСКОГО И МОДЕЛЬНОГО ДИЗЕЛЬНОГО ТОПЛИВА С ИСПОЛЬЗОВАНИЕМ ГЛУБОКОЭВТЕКТИЧЕСКИХ РАСТВОРИТЕЛЕЙ

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Глубокоэвтектические растворители (ГЭР), состоящие из глицерина и хлороцетовой кислоты/[TEAH]+[ClCH2COO]−, были синтезированы и исследованы в качестве экстрагентов для удаления азотсодержащих, серосодержащих и ароматических соединений. Процессы денитрификации, десульфуризации и деароматизации модельных дизельных топлив проводились при комнатной температуре. Время проведения жидкостно-жидкостной экстракции составляло 1 и 3 часа. Окислительная десульфуризация дизельного топлива исследовалась при температуре 90 °C в течение 3 часов перемешивания. Результаты показали, что хинолин был полностью удалѐн с помощью ГЭР на основе глицерина и 6 моль хлороцетовой кислоты. Анилиновые и крезольные производные модельного топлива были удалены с эффективностью 100 % с помощью как глицерин/6 хлороцетовая кислота, так и глицерин/6[TEAH]+[ClCH2COO]−. Оба ГЭР проявили селективность в отношении коммерческого дизеля как десульфуризирующие агенты. Все процессы экстракции контролировались с использованием ЯМР ^{1}H.

Ключевые слова: *ГЭР, экстракция, очистка, ЯМР, дизельное топливо.*