

Treatment of Petrochemical Pyrolysis Gasoline (PG) Using Novel Eco-friendly Choline Chloride-based Deep Eutectic Solvents (DESS)

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Abstract

To compare the performance of conventional solvent (N-formylmorpholine or NFM) with deep eutectic solvents (DESS) for benzene extraction, some (choline chloride : ethanolamines) based DESS were selected as extraction solvents. Liquid – Liquid extraction measurements were conducted on a petrochemical cut (pyrolysis gasoline) as feedstock. The influence of the solvent to feed ratio, temperature and extraction time on the (pyrolysis gasoline + NFM or DES) mixtures were investigated. Moreover, the selectivity (S) and solute distribution coefficient (β) were determined for the studied conventional solvent and DESS. Results show that the benzene extraction performance using one of the deep eutectic solvents (choline chloride: monoethanolamine with (1:5) mole ratio) is better than that of the conventional extraction solvent (NFM) at the studied conditions. In addition, lower contamination of extracted benzene (with NFM and other extractors) and immiscibility of DES in the hydrocarbon phase (NFM is partially miscible in the hydrocarbon phase) are among other advantages of this replacement.

Keywords: Deep Eutectic Solvents (DES), Environment, N-Formylmorpholine (NFM), Liquid -Liquid Equilibria (LLE), Green Extraction.

Introduction

Recovery of aromatic hydrocarbons from aromatic and non-aromatic hydrocarbons (HCs) mixtures can be achieved via liquid-liquid extraction (LLE). Generally, the mixture of aromatic-aliphatic hydrocarbons presents an azeotropic behavior near their boiling point, which could be resolved by the addition of the third component (for example, N-formylmorpholine (NFM) or sulfolane (SULF)). These additional third components verify the mixtures relative volatility. Basically, aromatic/non-aromatic separation continues with recovering the used solvents (NFM or SULF) [1-5].

However, there are some problems which are associated with the use of NFM as an extractive solvent for extraction. First, that NFM compounds are listed as toxic and environmental pollutant solvent [6].

Also, at the liquid-liquid equilibria of the pyrolysis gasoline and NFM, some impurities of solvent (NFM) will enter to the product (aromatics), which requires further purification process. Considering the limitations mentioned above in SULF and NFM applications, finding an effective and more environmentally friendly solvent for aromatic/non-aromatic extraction, which works at ambient conditions, is one of the global research priorities [6].

In general, some key criteria of a proper solvent for extraction are as follows: selectivity [7], capacity in solvation of solutes [7], high boiling point and low volatility [8], the extraction performance [9], reasonable cost [10], low toxicity [11], stability [12], non-corrosive effects [13,14], and low viscosity [15,16].

During the last decade, ionic liquids (ILs) have been studied for aromatics – aliphatics mixtures separations [17-22]. These studies were continued with deep eutectic solvents (DESS) as novel introduced green extraction agents [23-25]. Due to the easy way to prepare and their biodegradability, DES applications in LLE extraction have grown rapidly during these years. Their low costs and availabilities have led to more studies of these neoteric compounds as extraction agents [3,26-27].

In this research, pyrolysis gasoline of Tabriz Petrochemical Company (TPC) was selected as model fuel. N-formylmorpholine and deep eutectic solvents including: DES (choline chloride : monoethanolamine (1:5)), DES (choline chloride : diethanolamine (1:5)) and DES (choline chloride : triethanolamine (1:5)) were used as extraction solvents. The selection of DESS was based on the results of previous studies for benzene extraction [28]. The influence of solvent to feed ratio, temperature and extraction time on the experimental liquid-liquid

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equilibrium for selected mixtures, including pyrolysis gasoline plus NFM or DES, was investigated. In this study, the temperature varied from 303.15 to 323.15 K at atmospheric pressure, and extraction time have been equal to 4, 8 and 12 h at ambient temperature and atmospheric pressure. The performance of NFM and the selected DESs for liquid-liquid extraction is discussed herein.

Materials and Methods

Materials

Choline chloride was used as quaternary ammonium salt, and the hydrogen bond acceptor (HBA). Ethanol was used for the re-crystallization of choline chloride.

Table 1 Pyrolysis gasoline of Tabriz petrochemical company (TPC) components and those values.

	pyrolysis gasoline components	mass fraction
1	Cyclopentene	2.01
2	Cyclohexane	2.36
3	n-hexane	4.13
4	Iso-hexane	9.10
5	Benzene	74.51
6	Methylcyclohexane	2.32
7	Toluene	5.21
8	Isopropyl benzene	0.36

N-formyl morpholine (NFM) and ethanolamines were also used as solvent and hydrogen bond donors respectively. Moreover, pyrolysis gasoline of TPC was applied as a hydrocarbon media for the study of benzene extraction. The components of pyrolysis gasoline and their mass ratios are listed in Table 1. A report of the used chemicals, their specifications, sources and purities are listed in Table 2. Apparatus and Procedure

The analytical balance (AND, GR202, Japan) with a precision of $\pm 10^{-8}$ kg was used in the preparation of mixtures in molar bases. The studied mixtures were prepared in well-sealed glass vials to avoid contamination or mixture evaporation. Measurements were done immediately after mixtures preparation.

The experimental LLE data were determined at $T = 303.15$ to 323.15 K and ambient pressure. In this study, the LLE data were determined via the equilibrium cell method. For this determination, quantitative amounts of pyrolysis gasoline and extraction solvents were poured into the sealed 15 cc GC vials. The stirrer was used to do the mixing of the prepared systems at 500 rpm for 4 hours. Next, the mixed systems were left into a thermostatic bath to settle all overnight. After reaching the equilibrium and phase separation, the hydrocarbon and solvent phases were sampled by a needle – syringe. The samples were analyzed with the help of gas chromatography (GC).

Table 2 Chemicals used in this work.

Material	Provenance	Structure	Purity (mass percent)	Purification method	Water content (mass fraction)
Choline chloride	Merck		$99 \leq$	Recrystallization	$\leq 0.5 \%$
N-Formylmorpholine	BASF		$99.8 \leq$	NA	NA
Mono-Ethanolamine	Shazand Petrochem.		$99 \leq$	NA	$\leq 0.2 \%$
Di-Ethanolamine	Shazand Petrochem.		$98.5 \leq$	NA	$\leq 0.15 \%$
Tri-Ethanolamine	Shazand Petrochem.		$99 \leq$	NA	$\leq 0.2 \%$
Benzene	Merck		≥ 99.5	NA	NA
Pyrolysis gasoline	Tabriz petrochemical company	C_5-C_9	$99 \leq$	NA	NA
Ethyl alcohol	Merck		≥ 99.9	NA	$\leq 0.1 \%$

The experimental LLE data were determined with the GC (Varian-3800), connected to the CP - Wax 52 CB (30 m x 0.25 mm x 1.25 μm) column and FID type detector.

The analysis conditions were as following: start from $T = 323.15$ K (1 minute), increasing the temperature 1 (K/min) up to $T = 343.15$ K, 20 (K/min) up to $T = 393.15$ K, and then 40 (K/min) up to $T = 523.15$ K, at last, remaining at a temperature of $T = 523.15$ K (20 minutes).

The helium gas was the carrier, and injector/detector temperatures were held at $T = 473.15$ and $T = 523.15$ K (respectively).

The preferred Injection split ratio was (30/70). The hydrocarbon phase samples were injected without any dilution.

The studied extraction agents have low vapor pressure, and then samples of our solvent phase were injected into gas chromatography after ten times dilution with ethanol. The sample injection amounts were 1 and 5 μl for the hydrocarbon and diluted solvent phases.

Finally, the average values of three measurements were reported as our result. It is good to mention that the relative

standard deviation in this test is less than 1 (mole fraction).

Preparation of DESs

In the beginning, adequate amounts of ammonium salt (re-crystallized choline chloride) and hydrogen bond donors (HBDs) were mixed in a reaction flask (three-neck flask-250 ml) at about $T = 373.15$ K until a transparent liquid was obtained [29].

Results and Discussion

Liquid-liquid Equilibria (LLE)

A basic method to understand the liquid-liquid extraction process is the study of liquid-liquid equilibrium. In this study, it is treated with DES as single species by us. This assumption is considered to be correct until the DESs constituent's ratio remains unchanged. On the other hand, if DES losses to the hydrocarbon phase, this assumption would not be used [30]. Regarding the LLE results from gas chromatography, there are no components of DES in the hydrocarbon phase rather than pyrolysis gasoline components (Tables 3 and 4).

Table 3 Experimental liquid-liquid equilibria data, in mass fraction, for the studied systems including the different mass ratio of {pyrolysis gasoline / N-formylmorpholine (NFM) or DESs (choline chloride: monoethanolamine 1:5) or (choline chloride: diethanolamine 1:5) or (choline chloride: triethanolamine 1:5)} at atmospheric pressure and $T = (303.15$ to $323.15)$ K. The extraction time was set to 4 h. Solutes including distribution coefficient (β) values for each feed to solvent ratio. ^a

Component	Hydrocarbon rich phase (mass ratio) Feed to the solvent ratio (mass fraction)			Solvent rich phase (mass ratio) Feed to the solvent ratio (mass fraction)			β		
	1:1	1:2	1:3	1:1	1:2	1:3	(β (1:1)	(β (1:2)	(β (1:3)
NFM, $T = 303.15$ K									
Cyclo-pentene	0.02105	0.02094	0.02084	0.00013	0.00016	0.00018	0.00618	0.00764	0.00864
Cyclo-hexane	0.02282	0.02264	0.02246	0.00014	0.00017	0.00020	0.00613	0.00751	0.00890
n-hexane	0.03940	0.04019	0.04101	0.00020	0.00023	0.00025	0.00508	0.00572	0.00610
Iso-hexane	0.08900	0.09080	0.09264	0.00033	0.00039	0.00036	0.00371	0.00430	0.00389
Benzene	0.75430	0.75062	0.74696	0.10955	0.18405	0.31294	0.14523	0.24520	0.41895
Methyl cyclo-hexane	0.01967	0.02009	0.02052	0.00013	0.00015	0.00017	0.00661	0.00747	0.00828
Toluene	0.05020	0.04980	0.04940	0.00010	0.00011	0.00012	0.00199	0.00221	0.00243
Isopropyl benzene	0.00360	0.00368	0.00376	0.00002	0.00002	0.00002	0.00556	0.00543	0.00532
NFM, $T = 313.15$ K									
Cyclo-pentene	0.02109	0.02098	0.02088	0.00014	0.00018	0.00020	0.00678	0.00839	0.00948
Cyclo-hexane	0.02289	0.02271	0.02253	0.00015	0.00019	0.00022	0.00673	0.00824	0.00977
n-hexane	0.03956	0.04035	0.04117	0.00022	0.00025	0.00028	0.00556	0.00627	0.00668
Iso-hexane	0.08971	0.09153	0.09338	0.00036	0.00043	0.00040	0.00405	0.00469	0.00424
Benzene	0.75468	0.75100	0.74733	0.10736	0.18037	0.30668	0.14226	0.24017	0.41037
Methyl cyclo-hexane	0.01983	0.02025	0.02068	0.00014	0.00017	0.00019	0.00721	0.00815	0.00904
Toluene	0.05060	0.05020	0.04980	0.00010	0.00011	0.00012	0.00194	0.00215	0.00236
Isopropyl benzene	0.00363	0.00371	0.00379	0.00002	0.00002	0.00002	0.00540	0.00528	0.00517
NFM, $T = 323.15$ K									
Cyclo-pentene	0.02194	0.02182	0.02172	0.00016	0.00019	0.00022	0.00717	0.00887	0.01003
Cyclo-hexane	0.02380	0.02362	0.02343	0.00017	0.00021	0.00024	0.00712	0.00871	0.01033
n-hexane	0.04114	0.04196	0.04282	0.00024	0.00028	0.00030	0.00588	0.00663	0.00706
Iso-hexane	0.09330	0.09519	0.09712	0.00040	0.00047	0.00044	0.00428	0.00496	0.00449

Benzene	0.75694	0.75325	0.74958	0.10521	0.17676	0.30055	0.13900	0.23467	0.40096
Methyl cyclo-hex-ane	0.01991	0.02033	0.02077	0.00016	0.00018	0.00021	0.00790	0.00893	0.00991
Toluene	0.05075	0.05035	0.04994	0.00010	0.00011	0.00012	0.00189	0.00210	0.00231
Isopropyl benzene	0.00363	0.00371	0.00379	0.00002	0.00002	0.00002	0.00529	0.00517	0.00506
DES (choline chloride : monoethanolamine 1:5), $T = 303.15$ K									
Cyclo-pentene	0.02158	0.02146	0.02136	0.00013	0.00015	0.00017	0.00581	0.00719	0.00813
Cyclo-hexane	0.02339	0.02321	0.02302	0.00014	0.00016	0.00019	0.00578	0.00707	0.00838
n-hexane	0.04039	0.04119	0.04204	0.00019	0.00022	0.00024	0.00478	0.00539	0.00574
Iso-hexane	0.09123	0.09307	0.09496	0.00032	0.00038	0.00035	0.00349	0.00404	0.00366
Benzene	0.73544	0.73185	0.72829	0.11503	0.19325	0.32859	0.15641	0.26406	0.45118
Methyl cyclo-hex-ane	0.02016	0.02059	0.02103	0.00013	0.00014	0.00016	0.00622	0.00703	0.00780
Toluene	0.04895	0.04856	0.04817	0.00011	0.00012	0.00013	0.00215	0.00238	0.00262
Isopropyl benzene	0.00351	0.00359	0.00367	0.00002	0.00002	0.00002	0.00598	0.00585	0.00573
DES (choline chloride : monoethanolamine 1:5), $T = 313.15$ K									
Cyclo-pentene	0.02175	0.02164	0.02153	0.00014	0.00017	0.00019	0.00634	0.00785	0.00887
Cyclo-hexane	0.02358	0.02339	0.02321	0.00015	0.00018	0.00021	0.00630	0.00771	0.00915
n-hexane	0.04071	0.04152	0.04237	0.00021	0.00024	0.00027	0.00522	0.00588	0.00626
Iso-hexane	0.09195	0.09381	0.09572	0.00035	0.00041	0.00038	0.00381	0.00441	0.00399
Benzene	0.74133	0.73771	0.73411	0.11273	0.18939	0.32202	0.15206	0.25672	0.43865
Methyl cyclo-hex-ane	0.02032	0.02076	0.02120	0.00014	0.00016	0.00018	0.00679	0.00767	0.00851
Toluene	0.04934	0.04894	0.04855	0.00010	0.00011	0.00012	0.00209	0.00231	0.00254
Isopropyl benzene	0.00354	0.00362	0.00370	0.00002	0.00002	0.00002	0.00582	0.00569	0.00557
DES (choline chloride : monoethanolamine 1:5), $T = 323.15$ K									
Cyclo-pentene	0.02192	0.02181	0.02170	0.00015	0.00019	0.00021	0.00692	0.00857	0.00968
Cyclo-hexane	0.02377	0.02358	0.02339	0.00016	0.00020	0.00023	0.00688	0.00842	0.00998
n-hexane	0.04103	0.04186	0.04271	0.00023	0.00027	0.00029	0.00569	0.00642	0.00683
Iso-hexane	0.09269	0.09457	0.09648	0.00039	0.00046	0.00042	0.00416	0.00482	0.00436
Benzene	0.74726	0.74361	0.73999	0.11047	0.18560	0.31557	0.14784	0.24959	0.42646
Methyl cyclo-hex-ane	0.02049	0.02092	0.02137	0.00015	0.00018	0.00020	0.00741	0.00837	0.00929
Toluene	0.04973	0.04933	0.04894	0.00010	0.00011	0.00012	0.00203	0.00225	0.00247
Isopropyl benzene	0.00357	0.00365	0.00372	0.00002	0.00002	0.00002	0.00566	0.00553	0.00541
DES (choline chloride diethanolamine 1:5), $T = 303.15$ K									
Cyclo-pentene	0.02082	0.02071	0.02061	0.00013	0.00016	0.00018	0.00642	0.00794	0.00897
Cyclo-hexane	0.02257	0.02239	0.02222	0.00014	0.00017	0.00021	0.00637	0.00780	0.00925
n-hexane	0.03897	0.03975	0.04056	0.00021	0.00024	0.00026	0.00527	0.00595	0.00633
Iso-hexane	0.08803	0.08981	0.09163	0.00034	0.00040	0.00037	0.00385	0.00446	0.00404
Benzene	0.75383	0.75015	0.74649	0.10629	0.17857	0.30361	0.14099	0.23804	0.40672
Methyl cyclo-hex-ane	0.01946	0.01987	0.02030	0.00013	0.00015	0.00017	0.00687	0.00776	0.00861
Toluene	0.05262	0.05220	0.05178	0.00010	0.00011	0.00012	0.00192	0.00213	0.00235
Isopropyl benzene	0.00377	0.00386	0.00394	0.00002	0.00002	0.00002	0.00537	0.00525	0.00514
DES (choline chloride diethanolamine 1:5), $T = 313.15$ K									
Cyclo-pentene	0.02099	0.02088	0.02078	0.00015	0.00018	0.00020	0.00700	0.00866	0.00979
Cyclo-hexane	0.02275	0.02257	0.02239	0.00016	0.00019	0.00023	0.00696	0.00851	0.01010
n-hexane	0.03928	0.04007	0.04089	0.00023	0.00026	0.00028	0.00576	0.00649	0.00691
Iso-hexane	0.08874	0.09053	0.09237	0.00037	0.00044	0.00041	0.00420	0.00487	0.00441
Benzene	0.75534	0.75165	0.74799	0.10097	0.16964	0.28843	0.13368	0.22569	0.38561

Methyl cyclo-hex-ane	0.01961	0.02003	0.02046	0.00015	0.00017	0.00019	0.00749	0.00847	0.00939
Toluene	0.05304	0.05261	0.05219	0.00010	0.00011	0.00012	0.00187	0.00207	0.00228
Isopropyl benzene	0.00380	0.00389	0.00397	0.00002	0.00002	0.00002	0.00522	0.00510	0.00499
DES (choline chloride diethanolamine 1:5), $T = 323.15$ K									
Cyclo-pentene	0.02116	0.02104	0.02094	0.00016	0.00020	0.00022	0.00764	0.00945	0.01069
Cyclo-hexane	0.02293	0.02275	0.02257	0.00017	0.00021	0.00025	0.00759	0.00929	0.01102
n-hexane	0.03960	0.04039	0.04122	0.00025	0.00029	0.00031	0.00628	0.00708	0.00754
Iso-hexane	0.08945	0.09126	0.09310	0.00041	0.00048	0.00045	0.00459	0.00531	0.00481
Benzene	0.76138	0.75766	0.75397	0.09693	0.16285	0.27690	0.12731	0.21494	0.36725
Methyl cyclo-hex-ane	0.01977	0.02019	0.02062	0.00016	0.00019	0.00021	0.00818	0.00924	0.01025
Toluene	0.05346	0.05304	0.05261	0.00010	0.00011	0.00012	0.00182	0.00202	0.00222
Isopropyl benzene	0.00383	0.00392	0.00400	0.00002	0.00002	0.00002	0.00507	0.00496	0.00486
DES (choline chloride triethanolamine 1:5), $T = 303.15$ K									
Cyclo-pentene	0.02009	0.01999	0.01989	0.00014	0.00017	0.00019	0.00682	0.00843	0.00953
Cyclo-hexane	0.02178	0.02161	0.02144	0.00015	0.00018	0.00021	0.00677	0.00829	0.00983
n-hexane	0.03761	0.03836	0.03914	0.00021	0.00024	0.00026	0.00560	0.00632	0.00673
Iso-hexane	0.08495	0.08667	0.08843	0.00035	0.00041	0.00038	0.00409	0.00474	0.00429
Benzene	0.75586	0.75218	0.74851	0.09757	0.16392	0.27872	0.12908	0.21793	0.37236
Methyl cyclo-hex-ane	0.01878	0.01918	0.01959	0.00014	0.00016	0.00018	0.00729	0.00824	0.00914
Toluene	0.05404	0.05361	0.05318	0.00010	0.00011	0.00012	0.00181	0.00201	0.00221
Isopropyl benzene	0.00388	0.00396	0.00405	0.00002	0.00002	0.00002	0.00506	0.00495	0.00484
DES (choline chloride triethanolamine 1:5), $T = 313.15$ K									
Cyclo-pentene	0.02025	0.02015	0.02005	0.00015	0.00019	0.00021	0.00744	0.00920	0.01040
Cyclo-hexane	0.02196	0.02178	0.02161	0.00016	0.00020	0.00023	0.00739	0.00904	0.01072
n-hexane	0.03791	0.03867	0.03946	0.00023	0.00027	0.00029	0.00611	0.00689	0.00734
Iso-hexane	0.08563	0.08736	0.08913	0.00038	0.00045	0.00042	0.00447	0.00517	0.00468
Benzene	0.76191	0.75819	0.75450	0.09269	0.15573	0.26478	0.12166	0.20539	0.35094
Methyl cyclo-hex-ane	0.01893	0.01933	0.01974	0.00015	0.00017	0.00020	0.00796	0.00899	0.00998
Toluene	0.05447	0.05403	0.05360	0.00010	0.00011	0.00012	0.00176	0.00195	0.00215
Isopropyl benzene	0.00391	0.00399	0.00408	0.00002	0.00002	0.00002	0.00492	0.00481	0.00471
DES (choline chloride triethanolamine 1:5), $T = 323.15$ K									
Cyclo-pentene	0.02042	0.02031	0.02021	0.00017	0.00020	0.00023	0.00812	0.01004	0.01135
Cyclo-hexane	0.02213	0.02196	0.02178	0.00018	0.00022	0.00025	0.00806	0.00987	0.01170
n-hexane	0.03821	0.03898	0.03977	0.00025	0.00029	0.00032	0.00667	0.00752	0.00801
Iso-hexane	0.08632	0.08806	0.08985	0.00042	0.00050	0.00046	0.00487	0.00565	0.00511
Benzene	0.76343	0.75971	0.75601	0.08806	0.14794	0.25154	0.11534	0.19473	0.33273
Methyl cyclo-hex-ane	0.01908	0.01948	0.01990	0.00017	0.00019	0.00022	0.00869	0.00981	0.01089
Toluene	0.05490	0.05447	0.05403	0.00009	0.00010	0.00011	0.00171	0.00190	0.00209
Isopropyl benzene	0.00394	0.00402	0.00411	0.00002	0.00002	0.00002	0.00478	0.00468	0.00458

^a Standard uncertainties u are $u(T) = 0.1$ K, $u(p) = 0.02$ bar, $u(w) = 0.015$.

Table 4 Experimental liquid-liquid equilibria data, in mass fraction, for the studied systems including the different mass ratio of {pyrolysis gasoline / N-formylmorpholine (NFM) or deep eutectic solvent DES (choline chloride: monoethanolamine 1:5)} at atmospheric pressure and $t = 4, 8$ and 12 h. The temperature was set to 303.15 K. solutes, including distribution coefficient (β) values for each feed to solvent ratio. ^a

Component	Hydrocarbon-rich phase (mass ratio) Feed to the solvent ratio (mass fraction)			Solvent rich phase (mass ratio) Feed to the solvent ratio (mass fraction)			β		
	1:1	1:2	1:3	1:1	1:2	1:3	β (1:1)	β (1:2)	β (1:3)
NFM, $t = 4$ h									
Cyclo-pentene	0.02105	0.02094	0.02084	0.00013	0.00016	0.00018	0.00618	0.00764	0.00864
Cyclo-hexane	0.02282	0.02264	0.02246	0.00014	0.00017	0.00020	0.00613	0.00751	0.00890
n-hexane	0.03940	0.04019	0.04101	0.00020	0.00023	0.00025	0.00508	0.00572	0.00610
Iso-hexane	0.08900	0.09080	0.09264	0.00033	0.00039	0.00036	0.00371	0.00430	0.00389
Benzene	0.75430	0.75062	0.74696	0.10955	0.18405	0.31294	0.14523	0.24520	0.41895
Methyl cyclo-hexane	0.01967	0.02009	0.02052	0.00013	0.00015	0.00017	0.00661	0.00747	0.00828
Toluene	0.05020	0.04980	0.04940	0.00010	0.00011	0.00012	0.00199	0.00221	0.00243
Isopropyl benzene	0.00360	0.00368	0.00376	0.00002	0.00002	0.00002	0.00556	0.00543	0.00532
NFM, $t = 8$ h									
Cyclo-pentene	0.02122	0.02111	0.02101	0.00014	0.00018	0.00020	0.00660	0.00853	0.00952
Cyclo-hexane	0.02300	0.02282	0.02264	0.00015	0.00019	0.00022	0.00652	0.00833	0.00972
n-hexane	0.03972	0.04051	0.04134	0.00022	0.00025	0.00028	0.00554	0.00617	0.00677
Iso-hexane	0.08971	0.09153	0.09338	0.00036	0.00043	0.00040	0.00401	0.00470	0.00428
Benzene	0.76033	0.75662	0.75294	0.10736	0.18037	0.30668	0.14120	0.23839	0.40731
Methyl cyclo-hexane	0.01983	0.02025	0.02068	0.00014	0.00017	0.00019	0.00706	0.00839	0.00919
Toluene	0.05060	0.05020	0.04980	0.00010	0.00011	0.00012	0.00198	0.00219	0.00241
Isopropyl benzene	0.00363	0.00371	0.00379	0.00002	0.00002	0.00002	0.00551	0.00539	0.00528
NFM, $t = 12$ h									
Cyclo-pentene	0.02139	0.02128	0.02117	0.00016	0.00019	0.00022	0.00748	0.00893	0.01039
Cyclo-hexane	0.02319	0.02300	0.02282	0.00017	0.00021	0.00024	0.00733	0.00913	0.01052
n-hexane	0.04003	0.04084	0.04167	0.00024	0.00028	0.00030	0.00600	0.00686	0.00720
Iso-hexane	0.09043	0.09226	0.09413	0.00040	0.00047	0.00044	0.00442	0.00509	0.00467
Benzene	0.76642	0.76268	0.75896	0.10521	0.17676	0.30055	0.13728	0.23176	0.39600
Methyl cyclo-hexane	0.01999	0.02041	0.02085	0.00016	0.00018	0.00021	0.00801	0.00882	0.01007
Toluene	0.05101	0.05060	0.05019	0.00010	0.00011	0.00012	0.00196	0.00217	0.00239
Isopropyl benzene	0.00366	0.00374	0.00382	0.00002	0.00002	0.00002	0.00547	0.00535	0.00524
DES (choline chloride : monoethanolamine 1:5), $t = 4$ h									
Cyclo-pentene	0.02158	0.02146	0.02136	0.00013	0.00015	0.00017	0.00602	0.00699	0.00796
Cyclo-hexane	0.02339	0.02321	0.02302	0.00014	0.00016	0.00019	0.00599	0.00689	0.00825
n-hexane	0.04039	0.04119	0.04204	0.00019	0.00022	0.00024	0.00470	0.00534	0.00571
Iso-hexane	0.09123	0.09307	0.09496	0.00032	0.00038	0.00035	0.00351	0.00408	0.00369
Benzene	0.73544	0.73185	0.72829	0.11503	0.19325	0.32859	0.15641	0.26406	0.45118
Methyl cyclo-hexane	0.02016	0.02059	0.02103	0.00013	0.00014	0.00016	0.00645	0.00680	0.00761
Toluene	0.04895	0.04856	0.04817	0.00011	0.00012	0.00013	0.00225	0.00247	0.00270
Isopropyl benzene	0.00351	0.00359	0.00367	0.00002	0.00002	0.00002	0.00570	0.00557	0.00545
DES (choline chloride : monoethanolamine 1:5), $t = 8$ h									
Cyclo-pentene	0.02175	0.02163	0.02153	0.00014	0.00017	0.00019	0.00644	0.00786	0.00882
Cyclo-hexane	0.02358	0.02340	0.02320	0.00015	0.00018	0.00021	0.00636	0.00769	0.00905
n-hexane	0.04071	0.04152	0.04238	0.00021	0.00024	0.00027	0.00516	0.00578	0.00637
Iso-hexane	0.09196	0.09381	0.09572	0.00035	0.00041	0.00038	0.00381	0.00437	0.00397
Benzene	0.74132	0.73770	0.73412	0.11273	0.18939	0.32202	0.15207	0.25673	0.43865
Methyl cyclo-hexane	0.02032	0.02075	0.02120	0.00014	0.00016	0.00018	0.00689	0.00771	0.00849
Toluene	0.04934	0.04895	0.04856	0.00010	0.00011	0.00012	0.00203	0.00225	0.00247

Isopropyl benzene	0.00354	0.00362	0.00370	0.00002	0.00002	0.00002	0.00565	0.00553	0.00541
DES (choline chloride : monoethanolamine 1:5), t = 12 h									
Cyclo-pentene	0.02193	0.02180	0.02170	0.00015	0.00019	0.00021	0.00684	0.00871	0.00968
Cyclo-hexane	0.02377	0.02358	0.02339	0.00016	0.00020	0.00023	0.00673	0.00848	0.00983
n-hexane	0.04104	0.04185	0.04272	0.00023	0.00027	0.00029	0.00560	0.00645	0.00679
Iso-hexane	0.09270	0.09457	0.09649	0.00039	0.00046	0.00042	0.00421	0.00486	0.00435
Benzene	0.74725	0.74361	0.73999	0.11047	0.18560	0.31557	0.14783	0.24959	0.42645
Methyl cyclo-hexane	0.02048	0.02092	0.02137	0.00015	0.00018	0.00020	0.00732	0.00860	0.00936
Toluene	0.04974	0.04934	0.04894	0.00010	0.00011	0.00012	0.00201	0.00223	0.00245
Isopropyl benzene	0.00357	0.00365	0.00373	0.00002	0.00002	0.00002	0.00561	0.00548	0.00536

^a Standard uncertainties u are u(T) = 0.1 K, u(p) = 0.02 bar, u(w) = 0.015.

With that said, the assumption of treatment with DES as pseudo-pure species is justified.

The experimentally measured composition for the hydrocarbon and solvent phases (pyrolysis gasoline / NFM or DESs) at T = (303.15- 323.15) K and atmospheric pressure is reported in Table 3.

Also, a comparative graph of distribution ratios among our studied solvents is depicted in Figure 1.

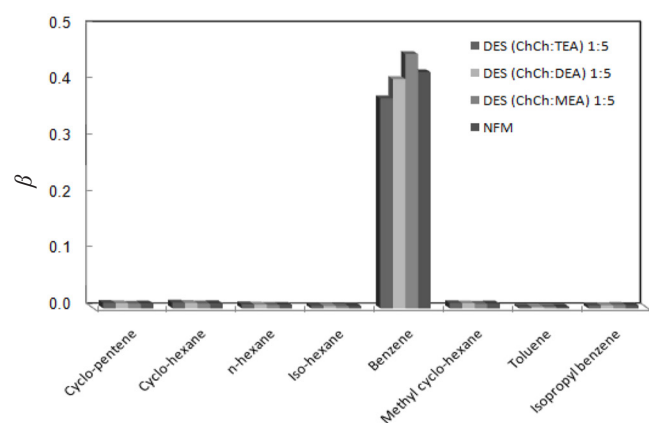


Fig. 1 Distribution ratios of the studied solvents including N-formylmorpholine (NFM), deep eutectic solvent (choline chloride : monoethanolamine 1:5) or DES (ChCl: MEA) 1:5, deep eutectic solvent (choline chloride : diethanolamine 1:5) or DES (ChCl: DEA) 1:5 and deep eutectic solvent (choline chloride : triethanolamine 1:5) or DES (ChCl: TEA) 1:5, at T = 303.15 K and a feed to the solvent ratio of 1:3.

The extraction efficiency can be determined by two factors:

the distribution coefficient (β) and the selectivity (S). The distribution coefficient (β) depends on the slope of tie lines.

When the distribution coefficient is increasing, the number of extraction stages decreases. On the other side, the selectivity (S) parameter indicates the extraction agent's ability in the solvation of a target solute without solving other contaminations from the initial mixture. These parameters are calculated via the following equations:

$$\beta_i = \frac{x_i^{II}}{x_i^I} \tag{1}$$

$$\beta_{Aromatics} = \frac{x_{benzene}^{II} + x_{toluene}^{II} + x_{Isopropyl\ benzene}^{II}}{x_{benzene}^I + x_{toluene}^I + x_{Isopropyl\ benzene}^I} \tag{2}$$

$$\beta_{non-Aromatics} = \frac{x_{Cyclu-Pen\ tane}^{II} + x_{Cyclu-hexane}^{II} + x_{n-hexane}^{II} + x_{Iso-hexane}^{II} + x_{Methycycb-hexane}^{II}}{x_{Cyclu-Pen\ tane}^I + x_{Cyclu-hexane}^I + x_{n-hexane}^I + x_{Iso-hexane}^I + x_{Methycycb-hexane}^I} \tag{3}$$

$$\beta_{Aromatics / nonAromatics} = \frac{\beta_{Aromatics}}{\beta_{nonAromatics}} \tag{4}$$

where xi relates to the mass fractions of component (i), and the superscripts II and I relate to the solvent phase and the hydrocarbons phase, respectively.

The β values obtained for the various solvent to feed ratios at T = (303.15 to 323.15) K are reported in Tables 4.

Table 5 shows parameters calculated for the various solvent to feed ratios at T = 303.15 K and t = 4, 8 and 12 h.

Table 5 The obtained distribution coefficient (β) and selectivity (S) values of experimental liquid-liquid equilibria data for the N-formylmorpholine and deep eutectic solvent (choline chloride: monoethanolamine 1:5) including systems at t = 4 h.

Temperature (K)	β						$S_{Aromatics/non-Aromatics}$		
	$\beta_{Aromatics}$			$\beta_{non-Aromatics}$			S (1:1)	S (1:2)	S (1:3)
	β (1:1)	β (1:2)	β (1:3)	β' (1:1)	β' (1:2)	β' (1:3)			
Solvent = N-formylmorpholine									
303.15	0.13571	0.22905	0.39129	0.00485	0.00565	0.00587	28.00949	40.53372	66.61060
313.15	0.13287	0.22425	0.38308	0.00530	0.00618	0.00642	25.07674	36.29037	59.63858
323.15	0.12982	0.21911	0.37430	0.00562	0.00656	0.00682	23.08311	33.40441	54.89452
Solvent = DES (choline chloride : monoethanolamine 1:5)									
303.15	0.14615	0.24667	0.42139	0.00456	0.00532	0.00553	32.03956	46.36579	76.19467
313.15	0.14209	0.23982	0.40969	0.00498	0.00581	0.00604	28.54433	41.30770	67.88252
323.15	0.13815	0.23316	0.39831	0.00543	0.00634	0.00659	25.43041	36.80141	60.47715

As seen in these tables and Figures 2 to 4, the best resulting DES (choline chloride: monoethanolamine 1:5) offers a better distribution ratio for benzene than NFM in similar conditions.

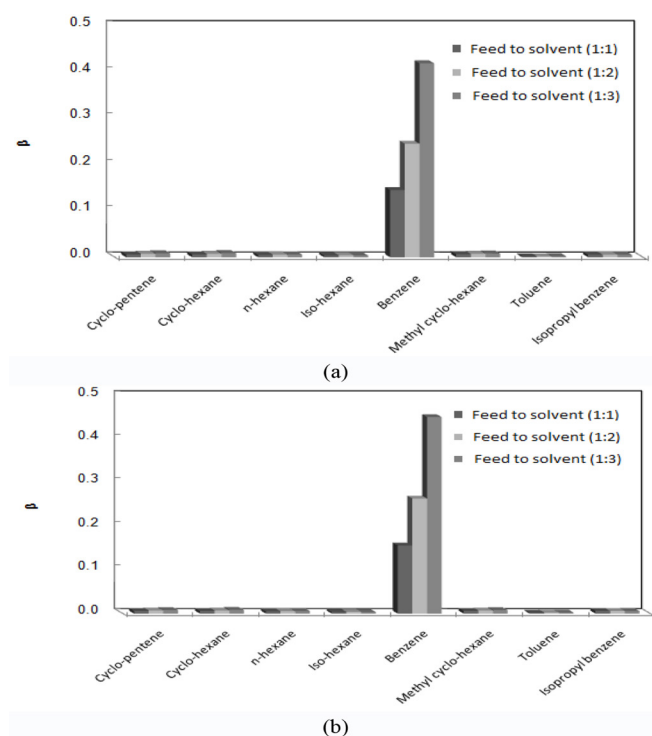


Fig. 2 Influence of feed to the solvent ratio on benzene extraction: (a) with N-formylmorpholine, (b) with deep eutectic solvent (choline chloride: monoethanolamine 1:5) at $T = 303.15$ K.

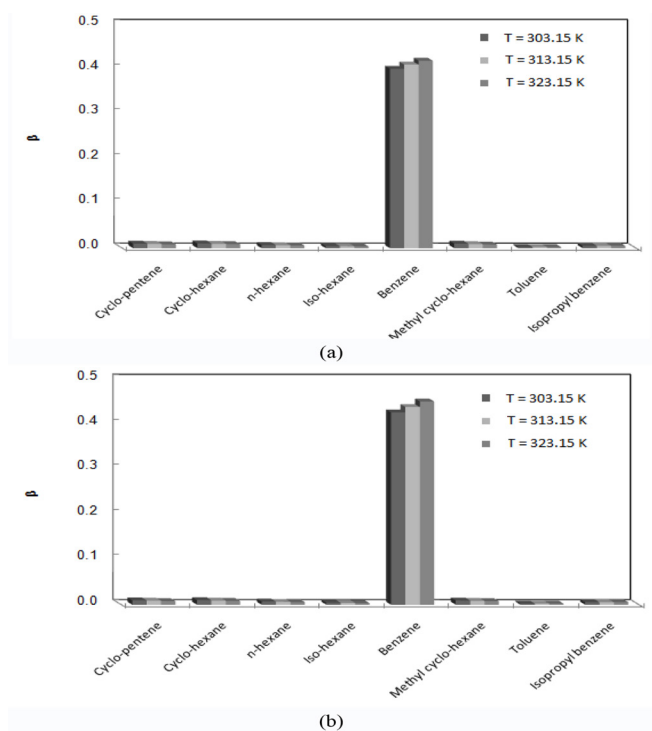


Fig. 3 Influence of temperature on benzene extraction: (a) with N-formylmorpholine, (b) with deep eutectic solvent (choline chloride: monoethanolamine 1:5) at a feed to the solvent ratio of 1:3.

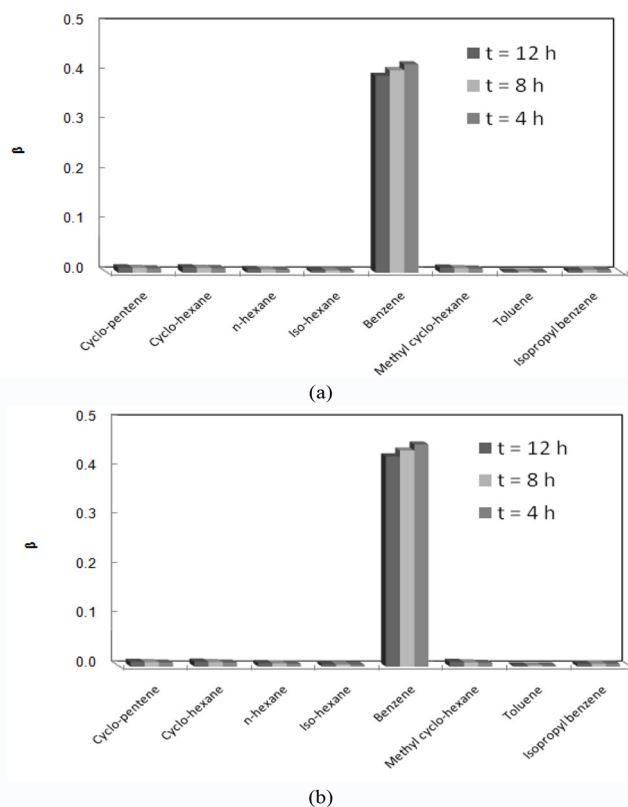


Fig. 4 Influence of extraction time: (a) with N-formylmorpholine, (b) with deep eutectic solvent (choline chloride: monoethanolamine 1:5) at a feed to the solvent ratio of 1:3.

The $S_{Aromatics/non-Aromatics}$ values were calculated via Equation 4, and they were listed in Table 5.

The obtained S values are higher than 1 for the studied systems, which shows the applicability of extraction agents used for aromatic (benzene) extraction from non-aromatics. Also, the solute distribution ratios (β) are lower than 1 in the studied systems, which indicates that a high solvent amount is required for the separation. However, it is not going to pose a significant challenge because extractors can be reused after recovery.

The greater β is a major advantage of DESs during this extraction. Two other important aspects of our chosen solvent for benzene extraction are lower contamination of extracted benzene than the other 7 components and immiscibility of DESs in the hydrocarbon phase (NFM is partially miscible in the hydrocarbon phase) [31].

According to Figure 1, the best resulting DES (choline chloride: monoethanolamine 1:5) has shown better solubility for benzene than NFM compared to other studied DESs (Table 3) in DES (choline chloride: monoethanolamine 1:5) > NFM > DES (choline chloride: diethanolamine 1:5) > DES (choline chloride: triethanolamine 1:5) order.

Also, benzene solubility in the studied solvents was more than other existing aromatics, including isopropyl benzene and toluene. It could be explained by existing additional hydrocarbon branches on their rings, possibly leading to the space barrier and lower solubility.

The non-random liquid equation (NRTL) [32] was utilized to

correlate measured experimental LLE results.

Furthermore, activity coefficients of liquid mixtures could be predicted with NRTL. Moreover, the maximum capacity and selectivity of DESs can be evaluated by activity coefficient at infinite dilution (γ^∞) [33 - 34], referred to as the solute-solvent interaction at an infinite dilution range of concentration. For determining the required solvent for extraction of the target component, the capacity of a solvent for solute (C^∞) can be used (Table 6) which was calculated using the following equation,

$$C^\infty = \frac{1}{\gamma^\infty} \quad (5)$$

The binary parameters of NRTL (Δu_{ji}) were obtained through the regression of LLE data with Aspen Plus V8.2 (T-x-x sets). Then, the activity coefficient was determined by the following equation:

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^m \tau_{rj} G_{rj} x_r}{\sum_{l=1}^m G_{li} x_l} \right) \quad (6)$$

$$\alpha = \alpha_{\bar{j}} = \alpha_j \quad (7)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (8)$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT} \quad (9)$$

where g indicates the energy parameter of interaction between species, x shows the components' mole fraction, and R is the non-randomness parameter. Also, in this study, α is assumed to be 0.3 [35].

Calculation of the root mean square deviation (σx) is done by the following equation:

$$\sigma x = 100 \cdot \sqrt{\frac{\sum_{i=1}^{m-1} \sum_{j=1}^{n-1} (x_j^{I, \text{exp}} - x_j^{I, \text{cal}})^2 + (x_j^{I, \text{exp}} - x_j^{I, \text{cal}})^2}{2m}} \quad (10)$$

where, n is the number of components, and m is the number of tie lines.

This is a way to compare the experimental and calculated mole fraction of the components for each tie-line.

The binary interaction parameters, the root mean square

deviation (σx), the calculated γ^∞ , C^∞ and the root mean square deviation of activity coefficient at infinite dilution are reported in Table 6.

The γ^∞ values of aromatic components in the DES solvent are lower than those in NFM. It is referred to as better aromatic – solvent molecules interaction with our studied DES (choline chloride: monoethanolamine 1:5). The values of calculated capacity (C^∞) are important because they impact the production cost.

Regarding Table 6, the selectivity of our studied DES (choline chloride: monoethanolamine 1:5) towards various components of pyrolysis gasoline at (1:3) ratio of solvent to feed is as benzene > cyclo-pentene > toluene and methylcyclohexane > cyclo-hexane > n-hexane > isopropyl benzene.

As it can be found in this order, the DES (choline chloride: monoethanolamine 1:5) has shown the highest capacity toward benzene among other pyrolysis gasoline components and upper capacity for aromatic components than aliphatic. There is a similar trend for NFM extraction process, in which DES (choline chloride: monoethanolamine 1:5) shows a better capacity for benzene extraction than NFM.

Influence of Feed to The Solvent Ratio on Benzene Extraction

Figure 2 indicates that the solvent to feed ratio influences the benzene extraction performances of our selected extraction solvents (NFM and DES (choline chloride: monoethanolamine 1:5)).

In the petrochemical company where our studies have been carried out, the ratio of NFM to pyrolysis gasoline is around 2:1 (mass ratio). Therefore, in this study, mass ratios of (1:1), (2:1) and (3:1) for investigation of solvent (NFM or DES (choline chloride: monoethanolamine 1:5)) to feed ratio influence on benzene extraction were selected by us.

The results showed that the extraction rate of benzene increases with the increase in the solvent to pyrolysis gasoline ratio as (3:1) > (2:1) > (1:1). Comprehensively, the studied DES showed a little better extraction distribution ratios than those related to NFM, and (3:1) was the best solvent (NFM or DES (choline chloride: monoethanolamine 1:5)) / pyrolysis gasoline ratio, at which the benzene extraction distribution ratio could reach to $\beta = 42.62\%$ with DES (choline chloride: monoethanolamine 1:5) at $T = 303.15$ K and $t = 4$ h. Also, it is noticeable that all of the studied pyrolysis gasoline components followed the same pattern.

Table 6 The obtained activity coefficient (γ^∞), selectivity (S^∞) and capacity (C^∞) of the N-formylmorpholine (NFM) and deep eutectic solvent (DES) (choline chloride: monoethanolamine 1:5) at infinite dilution at $T = 303.15$ K.

	pyrolysis gasoline components	γ^∞		C^∞		$\sigma(\gamma^\infty)$	
		NFM	DES	NFM	DES	NFM	DES
1	Cyclopentene	0.547	0.545	1.828	1.834	0.005	0.004
2	Cyclohexane	0.565	0.554	1.771	1.806	0.003	0.004
3	n-hexane	0.828	0.818	1.208	1.223	0.006	0.005
4	Iso-hexane	0.551	0.561	1.782	1.814	0.007	0.007
5	Benzene	0.546	0.540	1.831	1.852	0.002	0.009
6	Methyl cyclo-hexane	0.546	0.551	1.831	1.815	0.010	0.006
7	Toluene	0.571	0.551	1.751	1.815	0.004	0.005
8	Isopropyl benzene	0.848	0.825	1.179	1.212	0.006	0.004

Influence of Temperature on Aromatic Extraction

Temperature is an important parameter in the aromatic extraction process by extraction. Also, heating is a major capital cost for the chemical engineering process. The impact of temperature on the aromatic extraction has been studied and illustrated in Figure 3.

The results revealed that (i) for NFM, compared to the studied DES (choline chloride: monoethanolamine 1:5), the temperature had a lower influence on the benzene extraction rate. Both for NFM and DES (choline chloride: monoethanolamine 1:5), when the temperature decreased, benzene extraction rates remarkably reduced due to the lower solubility of benzene in the solvents at higher temperatures. Therefore, the best extraction temperature for the studied DES (choline chloride: monoethanolamine 1:5) was 303.15 K.

Influence of Extraction time

In this study, the influence of extraction time on the aromatic extraction performance was also investigated, and the results are shown in Figure 4.

The figure manifests that the impact of extraction time varies a lot for different extractants, but extraction time has little influence on the yield of sweet model gasoline in all cases. The results have manifested that N-formylmorpholine has extremely strong extraction ability, which only needs 8 min to reach extraction equilibrium [23]. However, its benzene extraction efficiency decreases with the increase in extraction time as $12\text{ h} < 8\text{ h} < 4\text{ h}$. Also, on the basis of LLE data, similar to NFM, our studied DES (choline chloride: monoethanolamine 1:5) requires a short time to reach the phase equilibrium, but in the same manner, the benzene extraction rate of DES (choline chloride: monoethanolamine 1:5) decreased with the extension of extraction time.

Conclusions

In the work, the conventional organic solvents (NFM) applicability with that of some novel green solvent (mono-, di-, tri- ethanolamine-based DESs) for benzene extraction from pyrolysis gasoline was compared. The LLE data of the {pyrolysis gasoline (1) + solvents (2)} were determined: (I) in the various solvent to feed ratios (1:1), (1:2) and (1:3), (II) at $T = (303.15\text{ and }323.15)\text{ K}$ and ambient pressure, and (III) by extending of extraction time at $t = 4, 8$ and 12 h .

The selectivity values (S) and solute distribution coefficient (β) were determined, and the obtained results were compared for conventional solvent and the selected DESs.

It was found that the β values of monoethanolamine based DES were more than that of NFM and other studied DESs. Thus indicating that the performance of DES (choline chloride: monoethanolamine 1:5) was better than the conventionally used solvent (NFM) in the studied temperature and atmospheric pressure. Also, DES (choline chloride: monoethanolamine 1:5) showed a higher capacity toward benzene extraction among the other pyrolysis gasoline components.

Also, it was seen that the extraction rate of benzene increased by the increasing solvent to pyrolysis gasoline ratio as $(3:1) > (2:1) > (1:1)$; in addition, both for NFM and DES (choline chloride: monoethanolamine 1:5), by increasing

temperature, benzene extraction rates remarkably decreased. Finally, benzene extraction efficiency for the studied solvents decreased with the increase in extraction time, similar to the previous cases.

This study indicated that selected DES (choline chloride: monoethanolamine 1:5) was a proper solvent to use as an effective extractor for the benzene extraction process from pyrolysis gasoline, among other studied solvents and NFM.

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Nomenclatures

DES: Deep Eutectic Solvents

LLE: Liquid-liquid extraction

ILs: ionic liquids NFM: N-formylmorpholine

PG: Pyrolysis gasoline

S: Selectivity

β : Solute distribution coefficient

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