Category D
Topical Literature Review
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Extraction of Naphthenic Acid from Highly Acidic Oil Using Hydroxide-Based Ionic Liquids

ACS Energy Fuels 29 (2015) 106

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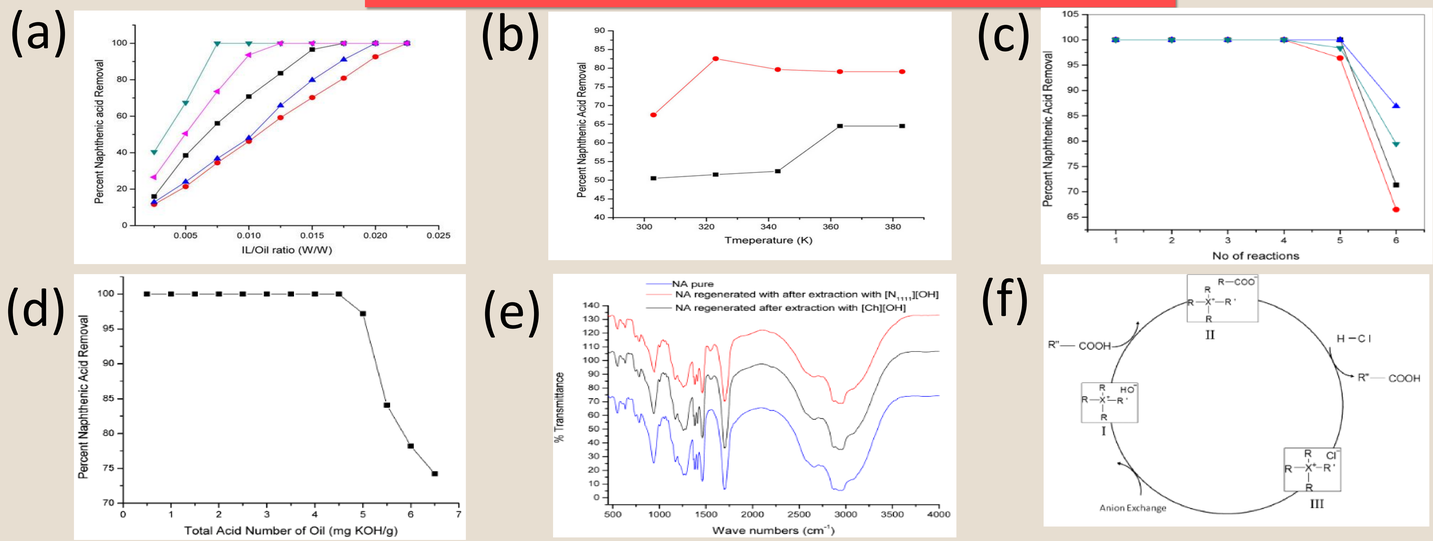
Abstract

The isolation and recovery of naphthenic acid from highly acidic model oil was performed using hydroxide-based ionic liquids. An extremely low ionic liquid/oil ratio was used to completely deacidify the model oil. Tetraalkylammonium and tetraalkylphosphonium hydroxide ionic liquids were employed in this study. Tetraalkylammonium-based ionic liquids are more efficient than tetraalkylphosphonium-based ionic liquids. The recyclability of the ionic liquids for the extraction of naphthenic acid was also studied. The regeneration of the extracted naphthenic acid was achieved.

Experimental

The model acid oil used in this study was prepared by the addition of naphthenic acid to dodecane until the acid number attains a value of 4.74 (±0.01) mg of KOH/g, which is considered as highly acidic crude oil. Dodecane was used in this study because the majority of commercial naphthenic acids are produced from the kerosene and diesel fraction. Kerosene and diesel can be represented by dodecane. The TAN was calculated using a Mettler Toledo autotitrator, following the standard method in the oil industry using ASTM D664. The neutralization of the model oil was carried out by mixing 10 g of dodecane with a set amount of IL in a round-bottom flask with a hot plate, reflux condenser, and magnetic stirrer. The stirring rate was kept at 500 rpm, and the reaction time was1 h. Several temperature settings were used for the reaction to optimize the process temperature. The reaction mixture was then transferred to a separation funnel and kept for 1 h to enable a clear separation between the IL and the model oil. A total of 5 g of oil was withdrawn from the top of the separation funnel, and the TAN was measured.

Results and Discussion



(a)effect of the IL/oil ratio on percent naphthenic acid removal(teal▼,[N1111][OH];magneta ◂,[Ch][OH]; black ■ [N1444][OH]; blue▲,[N4444][OH]; and red●,[P4444][OH]). (b) Effect of the temperature on naphthenic acid removal (black ■, [Ch][OH] with 0.005 IL/oil ratio; red●,[N1111][OH] with 0.005 IL/oil ratio). (c) Recyclability study of ILs (black ■,[N1111][OH] with 0.0075 IL/oil ratio at 303 K; red ●,[N1111][OH] with 0.0075 IL/oil ratio at 323 K; blue▲, [CH][OH] with 0.0125 IL/oil ratio at 303 K; and teal▼, [CH][OH] with 0.0125 IL/oil ratio at 363 K). (d) Effect of the increase in TAN on extraction efficiency of naphthenic acid (black■[N1111][OH] with IL/oil ratio of 0.0075) (e) FTIR spectra of pure and regenerated naphthenic acids after extraction with [N1111][OH] and [Ch][OH].(f) Plausible mechanism for deacidification of naphthenic acid (X, N/P; R, alkyl group; R,CH2−CH2−OH or alkyl group; and R″,aliphatic, aromatic, or cyclic hydrocarbon).

	percent naphthenic acid removal				
IL/oil ratio	$[N_{1111}][OH]$	[Ch][OH]	$[N_{1444}][OH]$	$[P_{4444}][OH]$	$[N_{4444}][OH]$
0.0025	40.41	26.545	16	11.63	12.85
0.0050	67.46	50.52	38.47	21.37	24.022
0.0075	100	73.54	56.06	34.43	36.72
0.0100	100	93.58	70.74	46.27	47.99
0.0125	100	100	83.57	59.21	65.87
0.0150	100	100	96.55	70.18	79.79
0.0175	100	100	100	80.83	91.03
0.0200	100	100	100	92.60	100
0.0225	100	100	100	100	100

The IL/oil ratio is an important parameter in the deacidification process.

Summary

In summery, the hydroxide-anion-based tetraalkylammonium and tetraal-kylphosphonium ILs are very effective in the complete Deacidification of high TAN model oil. Only a very low IL/oil ratio is necessary for the complete extraction of naphthenicacid. When the alkyl spacer length on the cation increases, the extraction performance of the hydroxide-based ILs decreases.The plausible mechanism of extraction is the formation of naphthalenate salt of the tetraalkylammonium or tetraalkyl-phosphonium cation, resulting from the reaction between naphthenic acid and the hydroxide anion of ILs. The extracted naphthenic acid can be regenerated by the addition of anaqueous solution of a mineral acid. The hydroxide IL can be used several times for the extraction process without losing its activity. The results revealed that this method has the potential to extract and regenerate naphthenic acids from high TAN crude oil.