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Ultrasonic-Assisted Technique as a Novel Method for Removal of Naphthenic Acid from Model Oil Using Piperidinium-Based Ionic Liquids

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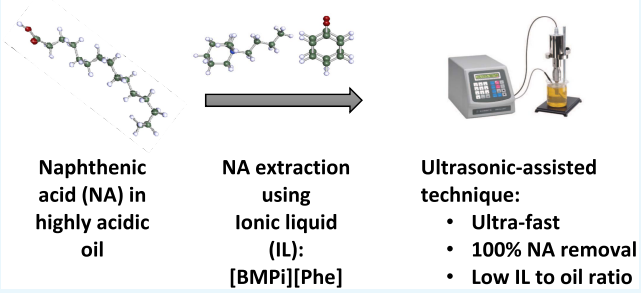
ABSTRACT: In this study, piperidinium-based ionic liquids (IL) containing trifluoromethanesulfonate, phenolate, and dicyanamide anions were synthesized. Using the ILs, extraction of naphthenic acid from highly acidic oil with a total acid number (TAN) of 1.44 was studied. Two agitation techniques have been implemented for the extraction process, which were mechanical stirring and ultrasonic-assisted irradiation. 1-Butyl-1-methylpiperidinium phenolate [BMPi][Phe] showed the best potential in extracting naphthenic acid from oil, with complete removal of naphthenic acid with IL-to-oil ratios of 0.010 and 0.0025 for the mechanical stirring method and the ultrasonic-assisted method, respectively. Ultrasonic-assisted extraction process shows very good potential in enhancing the extraction efficiency of naphthenic acid. Optimization and study on the effects of ultrasonic parameters, namely, IL-to-oil ratio, ultrasonic amplitude, and time, were studied through response surface methodology (RSM). Using [BMPi][Phe], the optimum conditions obtained are IL-to-oil ratio of 0.03, 53.91% of amplitude, and 4.29 min of extraction time. Under these optimum conditions, 100% removal of naphthenic acid was achieved.



1. INTRODUCTION

Exponential advancement in industrialization globally along with the ongoing growth in population leads to an escalation in global energy demand. A significant amount of this demand is being fulfilled using low-acidic crude oil (LAC). This leads to a constant depletion of low-acidic crude oil, which, in turn, requires the use of heavy-acidic crude oil (HAC). Due to its abundance, HAC has a high potential in replacing LAC. HAC has a high total acid number (TAN) of more than 0.5, where the acid is mainly composed of naphthenic acid.[1]

Naphthenic acid is referred to as the mixture of a-cyclic and aromatic carboxylic acids present in crude oil. It is a naturally occurring component of crude oil produced during the reservoir biodegradation.[2] Naphthenic acid has a variety of applications. It is primarily used to produce metal salts, such as copper naphthenate, which is widely utilized in wood preservation. Metal salts derived from naphthenic acids are also used in paint production as paint driers.[3] The corrosive nature of naphthenic acid leads to various subsequent critical problems in the crude oil refinery process, particularly toward the equipment.[4] Naphthenic acid corrosion has been a complex problem since the 1920s. The complexity is due to the large number of parameters that affect its corrosiveness, such as temperature and composition of crude oil, pressure, fluid velocity, and material of construction of the equipment.[5] To decrease the equipment maintenance cost and increase the product quality, removal of naphthenic acid from heavy-acidic crude oil is necessary. The most typical method implemented as a remedy to this problem is via the dilution of HAC using crude oil with a lower TAN to decrease the acidity of HAC to a tolerable value.[6] Other naphthenic acid removal methods include caustic washing, thermal decomposition, and catalytic esterification.[7−9] However, all of these techniques have their weaknesses. For instance, the dilution method requires a large amount of LAC, which is very costly. In thermal decomposition, water vapor and other volatile organic compounds (VOCs) such as carbon dioxide and hydrogen gas are produced due to premature cracking.[8] Meanwhile, caustic washing promotes the occurrence of emulsion, which makes acid recovery more difficult.[7] Catalytic esterification on the

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other hand takes place at a very high temperature of 280 °C, which leads to corrosion problems.[9]

Ionic liquids (ILs) are a new class of solvents that are well known for their characteristics of thermal stability, nonvolatility, and nonflammability. ILs are currently applied in various applications including electrochemistry, catalysis, and extraction.[10−12] The usage of ionic liquids in the petroleum processing industry is continuously increasing due to its environmental sustainability and simplifying process operations. For example, 1-alkyl-3-methylimidazolium ILs with imidazole anion were utilized to extract naphthenic acid. The disadvantages of these techniques are that a large amount of organic solvents are required for the recovery of IL after the extraction process.[13] It has been reported that imidazolium- and pyridinium-based ILs with varying alkyl chain lengths were employed in naphthenic acid removal; however, these ILs are only effective for a model system with TAN less than 0.5, which is very low.[14] An IL produced by mixing 2-methylimidazole and ethanol was utilized in this application. It was reported that the IL was able to reduce TAN of oil from 4.38 to 1.38 at room temperature after 10 min through the mechanical stirring technique. However, an IL-to-oil ratio of 0.4 is required, which is larger than those of other ILs.[13] Phenolate-based ILs with imidazolium cation were implemented in naphthenic acid extraction while also studying the effect of alkyl spacer length on its performance. The study showed that alkyl spacer length significantly affects naphthenic acid extraction performance and the ILs showed remarkable performance.[1] Other examples of ILs that have been utilized in this application are thiocyanate-,[15] sulfate-,[16] amino acid-,[7] and imidazolate-based ILs[17] along with silica-supported solid ionic liquid phases.[18] Although various ILs have been employed in naphthenic acid extraction, the same method of agitation was used, which is mechanical stirring. In this study, an effective new method, namely, ultrasonic-assisted technique is employed. Ultrasonic treatment is very useful in analytical chemistry in the preparation of samples that involves stirring, mixing, and agitation without altering the chemical properties of the samples. Ultrasonic energy has been applied in continuous and batch processes during leaching, along with other chemical processes such as hydrolysis, oxidation−reduction reactions, and enzyme-catalyzed reactions. The use of ultrasonic energy in making a homogeneous mixture within a two-phase liquid system is highly efficient. The operating principle of ultrasonic energy is that it disperses the solvent into microdroplets, allowing mass transfer to occur between two immiscible liquids.[16] Consequently, the efficiency of naphthenic acid removal from crude oil could be enhanced with the application of ultrasonic energy.

This study aims to develop novel ionic liquids to be utilized in the removal of naphthenic acid from crude oil with ultrasonic assistance to further improve the extraction efficiency. Piperidinium-based ILs were synthesized with the anions of trifluoromethanesulfonate, phenolate, and dicyanamide. Piperidinium-based ILs are known to have lower toxicity than the commonly used imidazolium-based ILs. Trifluoromethanesulfonate, phenolate, and dicyanamide anions show good potential in the application of naphthenic acid removal.[1,19,20] These ILs were utilized as a solvent in the deacidification process of naphthenic acid from a model oil. The parameters for extraction were then optimized using the response surface methodology (RSM).

2. RESULTS AND DISCUSSION

2.1. Deacidification of Model Oil Using Mechanical Stirring—Effect of IL-to-Oil Ratio. IL-to-oil ratio is one of the most significant factors in the deacidification process. The effect of IL-to-oil ratio on deacidification efficiency via mechanical stirring was studied. The percent naphthenic acid removal was calculated using different weight ratios of [BMPi][OTF], [BMPi][Phe], and [BMPi][DCN]. The extraction time was 1 h, followed by 15 min of the centrifuge to separate the IL from the oil. The effect of different IL-to-model oil weight ratio on the efficiency of the deacidification process is given in Figure 1.

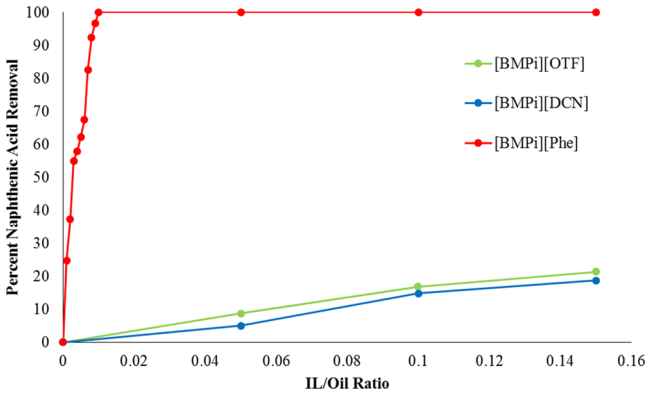

Figure 1. Effect of IL-to-oil ratio on the extraction efficiency of naphthenic acid removal (stirring rate, 500 rpm; reaction time, 1 h).

It can be observed that an increase in the IL-to-oil ratio causes an increase in the percent naphthenic acid removal. The extraction efficiency for the different ILs follows the order of [BMPi][Phe] > [BMPi][OTF] > [BMPi][DCN]. At the highest IL-to-oil ratio, which is 0.150, [BMPi][OTF] and [BMPi][DCN] are only able to achieve extraction efficiencies of 21.35 and 18.72% respectively. As for [BMPi][Phe], a small increase in the IL-to-oil ratio brings a significant increase in extraction efficiency. [BMPi][Phe] can achieve a higher extraction efficiency of 24.72% at an even lower IL-to-oil ratio of 0.001. BMPi][Phe] can achieve 100% naphthenic acid removal from the model oil with an IL-to-oil ratio of only 0.01.

The ability of [BMPi][Phe] to perform well is due to the cyclic structure of the phenolate anion. Naphthenic acid mainly consists of cyclic components,[21] which allows [Phe] and the solute to have a like−like interaction, enabling [Phe] anion to efficiently extract naphthenic acid from the model oil.[1] As for the [OTF] and [DCN] anions, both these anions are noncyclic, which in turn leads to lower performance compared to the [Phe] anion. The [DCN] anion shows a slightly lower efficiency than the [OTF] anion, which could be attributed to the fact that the IL holding an [DCN] anion is more viscous than the IL holding an [OTF] anion.[22,23] The higher viscosity would provide more resistance in the mass transport of naphthenic acid, which leads to a poorer extraction performance. However, a study has shown that diazabicyclo undecane [DBU] as a cation paired with [DCN] shows good performance in naphthenic acid removal. At room temperature, a naphthenic acid removal of 72% was achieved with a TAN of 2.65 using an IL-to-oil ratio of 0.05.[20] This is due to [DBU] having a bicyclic structure as opposed to 1-methylpiperidine only having a monocyclic structure. Naph-

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thenic acid has a nonaromatic cyclic structure; therefore, the bicyclic structure of [DBU] further enhances the interaction between the IL and naphthenic acid due to a stronger like−like interaction.[24]

In this study, a highly acidic model oil with a TAN of 1.5 was used. In comparison to other ionic liquids that have been employed in previous studies on acid removal from model oil, [BMPi][Phe] shows higher performance than 1-ethylpyridinium bromide, 1-butylpyridinium bromide, 1-butyl-3-methylimidazolium bromide, and 1-butyl-3-methylimidazolium phenolate. 1-Ethylpyridinium was only able to achieve an acid removal percentage of 3.47% with an IL-to-model oil ratio of 0.1 and a low TAN of less than 0.5.[14] At the same IL-to-oil ratio but different TAN values, [BMPi][Phe] is also shown to perform better than butyl imidazole-based SIL and diazabicyclo undecane-butyl dicyanamide. A comparison of the extraction efficiencies of various ionic liquids is presented in Table 1.

Table 1. Naphthenic Acid Extraction Efficiencies of Different Ionic Liquids Using the Mechanical Stirring Method

ionic liquid	initial TAN number	IL/oil ratio	extraction efficiency (%)	references
1-ethylpyridinium bromide	0.50	0.10	3.47	14
1-butylpyridinium bromide	0.50	0.10	27.76	14
1-butyl-3-methylimidazolium bromide	0.50	0.10	34.54	14
butyl imidazole-based SIL	2.93	0.05	77.55	18
diazabicyclo undecane-butyl dicyanamide	2.65	0.05	72.00	20
1-butyl-3-methylimidazolium phenolate	1.44	0.05	69.48	1
1-butyl-1-methylpiperidinium phenolate	1.50	0.05	100.00	this work

2.2. Comparison of Ultrasonic-Assisted Technique with the Mechanical Stirring Method. In this study, deacidification of naphthenic acid was done through two different techniques, namely, mechanical stirring and ultrasonic-assisted method. The parameters for these methods are presented in Table 2.

From Figure 2, it can be observed that for the ultrasonic technique, the extraction efficiency tripled for [BMPi][OTF] and quadrupled for [BMPi][DCN] compared to the mechanical stirring technique. [BMPi][Phe] remains at 100% efficiency for both techniques.

Table 2. Parameters for Mechanical Stirring and Ultrasonic-Assisted Technique

parameters	mechanical stirring (MS)	ultrasonic-assisted (US) technique
IL/oil ratio	0.050	
temperature	room temperature	
time	1 h	5 min
stirring rate	500 rpm	
amplitude		50%
pulse		continuous

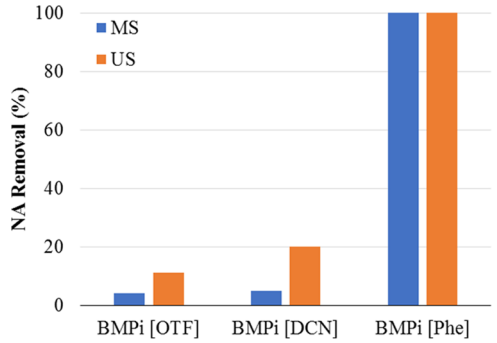

Figure 2. Naphthenic acid extraction efficiency of different ionic liquids for mechanical stirring and ultrasonic-assisted technique.

For mechanical stirring, the total contact area between ionic liquid and model oil is small, which causes the extraction efficiency to be lower than the ultrasonic-assisted technique. This is mainly due to an ionic liquid having a viscous property, which makes it difficult to achieve sufficient contact with the naphthenic acid in oil, thus hindering it from achieving its best potential in naphthenic acid removal. The ultrasonic energy works by dispersing the ionic liquid and oil in the form of small droplets, which increases the total contact area between the ionic liquid and oil, thus allowing mass transfer to be higher and efficient between the two immiscible liquids.[16]

2.3. Confirmation of Extraction through Fourier Transform Infrared (FTIR) Analysis. Figure 3 shows the FTIR spectra of naphthenic acid as well as ILs before and after extraction. Naphthenic acid presents a strong C═O stretching band within the range of 1720−1685 cm^{-1}.[25] This is depicted by the naphthenic acid spectrum where an intense peak exists within that range. All three ILs after naphthenic acid extraction have the C═O peak, indicating that the ILs can extract naphthenic acid from the model oil. The consistencies in all of the other functional groups shown in the spectra for all of the ILs before and after naphthenic acid extraction depict that the ILs stayed intact during the extraction process. Therefore, it can be concluded that the mechanism of extraction was based on physical extraction. It can also be seen that the C═O peak for [BMPi][Phe] is the most significant, which indicates that it holds the highest amount of naphthenic acid compared to [BMPi][OTF] and [BMPi][DCN].

2.4. Effect of Amplitude. In the ultrasonic-assisted technique involving chemical interactions, the amplitude represents the amount of power applied to the chemical system. Theoretically, it can be extended that a larger amplitude will generate a higher amount of energy, thus further increasing its efficiency. High amplitude allows better mixing due to the rapid rate of formation and bursting of bubbles, which promote more efficient mass transfer between IL and model oil. However, the high amplitude may also lead to the formation of cloud bubbles where ultrasonic waves are weakened due to excessive bubbles. These high-turbulence bubbles cause the energy to be absorbed and dispersed, which leads to energy wastage in the system and will not further improve the efficiency of the extraction.[26]

By considering these circumstances, multiple amplitudes within the range of 40−70% were studied for naphthenic acid extraction. Figure 4 shows the effect of amplitude against calorimetric power and removal of naphthenic acid. It can be observed that when the amplitude is increased from 40 to 50%, the calorimetric power increased from 10.59 to 13.84 W,

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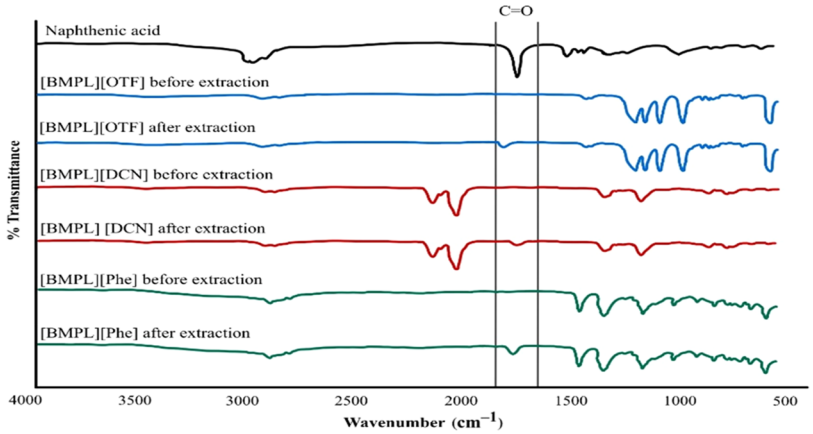

Figure 3. Absorption spectra for C═O functional groups in ionic liquids.

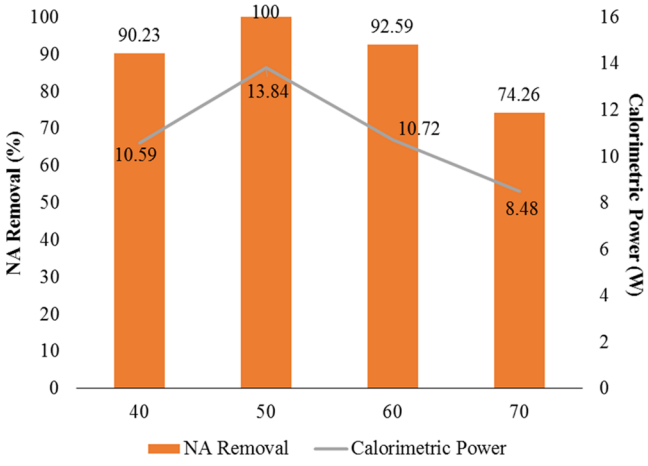

Figure 4. Naphthenic acid extraction at various amplitudes.

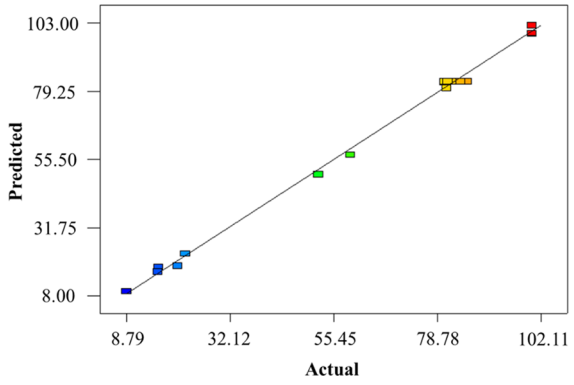

Figure 5. Actual and predicted extraction performance for optimization of naphthenic acid extraction using [BMPi][Phe] with the ultrasonic-assisted technique.

yielding an extraction efficiency of 90.23−100%. This can be attributed to the enhancement of mixing efficiency due to higher power dissipation. However, an increase in the amplitude to 60 and 70% leads to the reduction of calorimetric power to 10.72 and 8.48 W, respectively. Naphthenic acid removal efficiency also decreases to 92.59 and 74.26% for amplitudes of 60 and 70%, respectively. This performance attenuation occurs due to the previously mentioned scattering effect. These trends were also observed in the studies of esterification of fatty acid and preparation of biodiesel.[26,27]

2.5. Experimental Results and Statistical Analysis. *2.5.1. Response Surface Methodology.* The Box−Behnken method is used to study the effect of extraction parameters as well as to obtain the optimum condition for naphthenic acid extraction using [BMPi][Phe] with ultrasonic assistance. [BMPi][Phe] was chosen in this study due to its performance in the preliminary study mentioned in Section 2.2. Parameters studied are IL-to-oil ratio, amplitude, and extraction time with the ranges of 0.001−0.050, 40−60%, and 1−6 min, respectively. Figure 5 shows the relation of predicted and actual extraction values obtained from this study. It can be observed that a good correlation has been achieved for all experimental data. Using the Box−Behnken method, experimental results that have been obtained are used to be fitted with the quadratic regression model. The final model equation is then obtained and is shown below in terms of actual factors

$$Y = -529.369 + 1757.826X_1 + 18.60435X_2 + 27.68971X_3 + 22.79592X_1X_2 + 140.6939X_1X_3 - 0.3801X_2X_3 - 35760.1X_1^2 - 0.1625X_2^2 - 0.4656X_3^2 \quad (1)$$

where Y is the extraction efficiency, X_1 is the IL-to-oil ratio, X_2 is the amplitude, and X_3 is the extraction time.

Table 3 shows the analysis of variance (ANOVA) results, which present a high F-value of 355.88 and a very low p-value of <0.0001. These values signify that the model is very significant and in good agreement with the experimental data.[28] Furthermore, the results obtained show that the F-value for each of the linear terms, interaction, as well as quadratic terms have significant effect on the naphthenic acid extraction efficiency.

All linear factors were observed to have a very significant impact on the model's response. The factor which gives the most significant effect is ionic liquid-to-model oil ratio followed by extraction time and then amplitude. It can also be observed that the interactive factors give a moderate effect on the model's response, while the quadratic factors give much more significant effects except for extraction time. Also, the p-value for the lack of fit obtained is 0.2002, which shows that it is not significant. This indicates that the model is fit and there is an insignificant chance that lack of fit would occur. The values of R^2 and adjusted R^2 obtained are 0.998 and 0.995, respectively, where it can be observed that these values are very close to each other. This signifies that the sample size is

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Table 3. ANOVA for the Quadratic Regression Model for Optimization of Naphthenic Acid Extraction Using Ionic Liquid through Ultrasonic-Assisted Technique

source	sum of square	df	mean square	*F* value	*p*-value prob > *F*	
model	17 976.37	9	1997.37	355.88	<0.0001	significant
A—IL-to-oil ratio	9817.09	1	9817.09	1749.16	<0.0001	
B—amplitude	1717.99	1	1717.99	306.10	<0.0001	
C—time	3384.91	1	3384.91	603.10	<0.0001	
AB	12.91	1	12.91	2.30	0.1679	
AC	30.73	1	30.73	5.48	0.0474	
BC	37.36	1	37.36	6.66	0.0326	
A^2	691.12	1	691.12	123.14	<0.0001	
B^2	396.09	1	396.09	70.57	<0.0001	
C^2	12.70	1	12.70	2.26	0.1709	
residual	44.90	8	5.61			
lack of fit	25.80	3	8.60	2.25	0.2002	not significant
pure error	19.10	5	3.82			
cor total	18 021.27	17				
std. dev.	2.37		R^2	0.998		
mean	63.91		adj. R^2	0.995		
CV (%)	3.71		pred. R^2	0.968		
press	585.31		adeq. R^2	52.422		

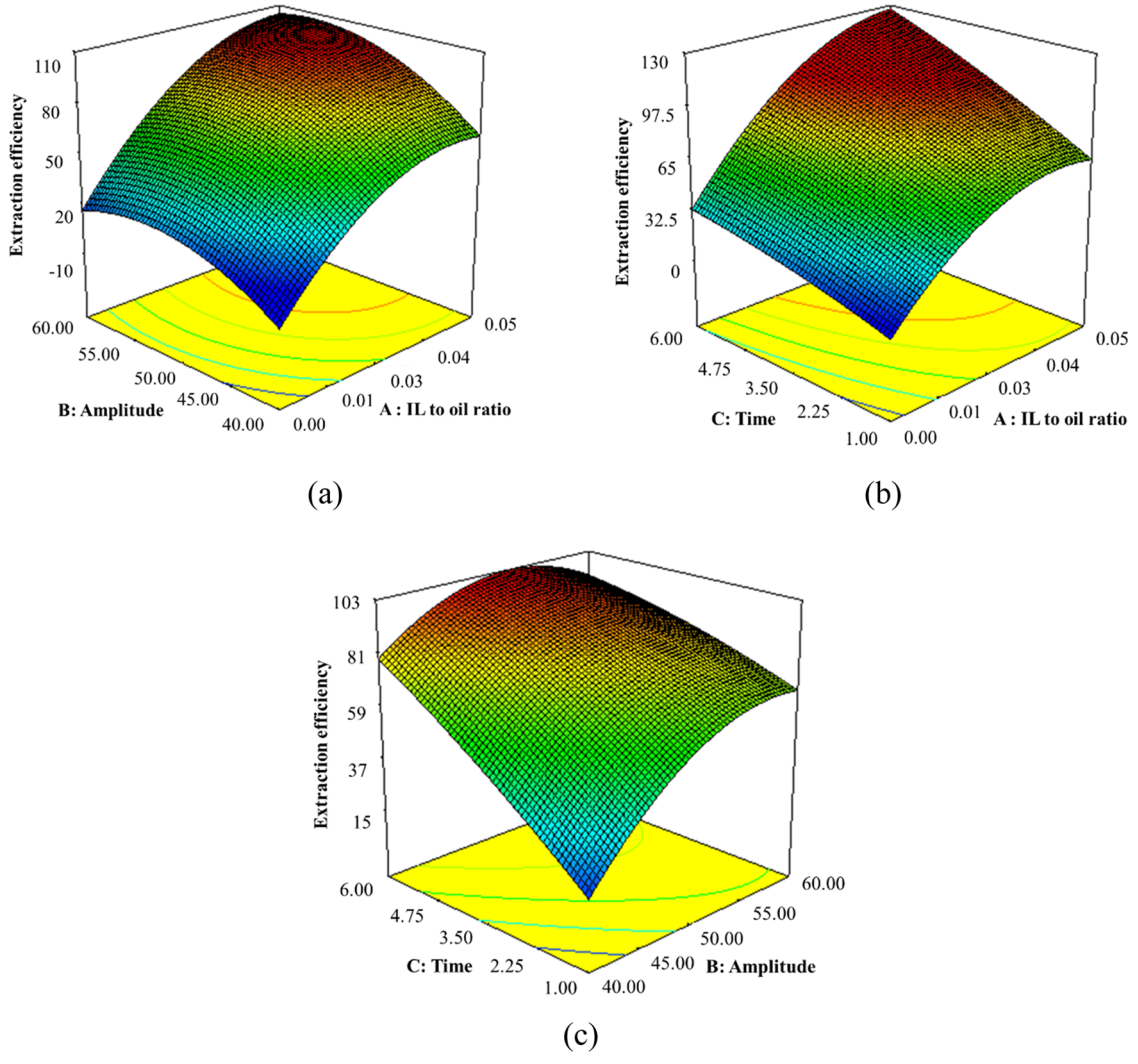

Figure 6. Response surface plot for naphthenic acid extraction (constant parameters for (a) time 3.5 min, (b) amplitude 50%, and (c) IL/oil ratio 0.0255).

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sufficiently large to represent the model where the model can be concluded to be very significant. As for coefficient of variation (CV), a low value of 3.71% has been obtained for this model, where this signifies great dependability in the experiments performed as well as indicating them as very precise.[29] Finally, the adequate precision obtained is 52.422, which signifies that it validates the fitness of the quadratic model, where a value larger than 4 is required to validate the fitness of the model.[30]

2.5.2. Effect of Ionic Liquid-to-Oil Ratio. The effect of IL-to-model oil ratio can be observed in Figure 6a,b, which shows the effect of interacting parameters of IL-to-model oil ratio with amplitude and extraction time, respectively. Based on Figure 6a, at the lowest amplitude of 40% the highest extraction efficiency reached was only 50%. As for amplitudes of 50 and 60%, a 100% extraction efficiency was achieved, even at an IL-to-model oil ratio of 0.05. This means that a higher amplitude is required to assure that a sufficient amount of energy is dissipated to allow more interfacial contact between IL and model oil, thus producing higher extraction efficiency. However, attenuation in the extraction efficiency may occur if the amplitude is too high due to the scattering effect as previously discussed. Further increasing the amplitude of the ultrasonic probe can cause the formation of a bubble cloud, which reduces the efficiency. This is due to the mass transfer resistance that was increased by the contribution of air pockets generated by the bubble cloud. The naphthenic acid must travel through to the air pockets before it can be extracted by the ILs.[26,27]

It can be mentioned that IL-to-model oil ratio has the highest influence on the extraction efficiency. At a low amplitude of 40%, with an increase in IL-to-model oil ratio from 0.001 to 0.05, extraction efficiency drastically increased from 10 to 50%. In comparison, at a low IL-to-model oil ratio of 0.01, an increase in the amplitude from 40% to a maximum of 60% only produces an extraction efficiency of 10−20%. As for the interaction of IL-to-model oil ratio with the extraction time, at the lowest IL-to-model oil ratio of 0.01 and the longest duration of 6 min, the highest extraction efficiency achieved was only 32.5%, and it is doubled to 65% when the IL-to-model oil ratio is increased to 0.05. This further proves that the IL-to-model oil ratio is the most significant factor in affecting the extraction efficiency.[1] The same trend has been observed in the study of the effect of IL-to-model oil in naphthenic acid removal by imidazolium- and hydroxide-based ILs.[13,31]

2.5.3. Effect of Extraction Time. The effect of extraction time on the extraction efficiency of naphthenic acid was studied within the range of 1−6 min. Figure 6b,c shows the effect of extraction time on IL-to-model oil ratio and amplitude, respectively. From Figure 6b, it can be seen that with an IL-to-model oil ratio of 0.05, a minimum time of 3.5 min is required to achieve 100% extraction efficiency. This signifies that extraction efficiency increases with time. Figure 6c shows that even at the lowest amplitude of 40%, extraction efficiency greatly increased from 10 to 81% as the extraction time increases from 1 to 6 min. At the maximum amplitude of 60%, efficiency increases from 60 to 100% from 1 to 6 min. In all instances, an increase in time leads to a higher extraction of naphthenic acid by ionic liquid until naphthenic acid is fully removed. This is due to the sufficient contact time between IL and model oil that allows the naphthenic acid to be removed more efficiently.[1] With a short time of 5 min required to achieve maximum extraction efficiency, the ultrasonic-assisted technique in naphthenic acid removal can be categorized as a rapid extraction technique.[13,16]

2.6. Optimization Process and Data Validation. To obtain the optimized values for the parameters, eq 4 has been used to achieve 100% extraction efficiency. A total of 30 optimized solutions were proposed with the combination of different parameters. Three solutions have been selected for data validation testing where solutions with the lowest IL-to-model oil ratio are selected. Table 4 shows both predicted and experimental extraction efficiencies, where it can be observed that predicted efficiency of 100% is found for all three solutions. The relative errors obtained for the optimized solutions are 0.98, 2.24, and 0.00% where the average relative error is 1.07%, which was very low; thus, the model can be classified as accurate. This also shows that the model has been validated and statistically in good agreement with the experimental data.

Table 4. Experimental and Predicted Data for the Statistical Model Validation

IL/oil ratio	amplitude (%)	time (min)	predicted extraction efficiency (%)	experimental extraction efficiency (%)	relative error (%)
0.03	53.91	4.29	100.00	99.03	0.98
0.03	44.89	5.92	100.00	97.81	2.24
0.03	47.37	5.79	100.00	100.00	0.00

3. CONCLUSIONS

1-Butyl-1-methylpiperidinium trifluoromethanesulfonate, 1-butyl-1-methylpiperidinium phenolate, and 1-butyl-1-methyl-piperidinium dicyanamide were successfully synthesized as proven from the structural characterization of nuclear magnetic resonance (NMR) and FT-IR. [BMPi][Phe] was shown to be highly effective in the removal of naphthenic acid from the highly acidic model oil, where it can completely extract all of the acid at a minimum IL-to-model oil ratio. Ultrasonic assistance shows very high potential in making the extraction of naphthenic acid more efficient, as indicated by the 4 times increase in extraction efficiency and at a much shorter time than the conventional method. Optimum conditions achieved for naphthenic acid extraction using [BMPi][Phe] are 0.03, 53.91, and 4.29 for IL-to-model oil ratio, amplitude, and extraction time, respectively. The results showed that this ionic liquid along with ultrasonic assistance has the potential to extract naphthenic acids from high TAN crude oil at an extremely low IL-to-model oil ratio and in an ultrashort time. This study shows that it is possible to use IL coupled with ultrasonic irradiation to treat crude oil with TAN number as high as 1.5. It proposes further investigation with actual HAC sample, kinetic study, and dynamic process to be investigated for scale-up purposes.

4. METHODOLOGY

4.1. Materials. 1-Methylpiperidine (purity, 99%) is purchased from Acros Organics (Geel, Belgium). Sodium dicyanamide (purity, 96%) and sodium phenoxide trihydrate (purity, 99%) are purchased from Sigma-Aldrich (MO). Bromobutane (purity, 99%), sodium trifluoromethanesulfonate (purity, 98%), dodecane (synthesis grade; purity, ≥99%), and commercial naphthenic acid (technical grade; purity, 90−

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100%) are purchased from Merck (NJ). The chemicals are used as received without any further purification or dilution.

4.2. Synthesis and Characterization of Ionic Liquids.

4.2.1. Synthesis of Ionic Liquids. The synthesis of ILs is a two-step process. The first step is the synthesis of precursor IL, 1-butyl-1-methylpiperidinium bromide ([BMPi][Br]). [BMPi]-[Br] was synthesized by placing an equimolar amount of 1-methylpiperidine and bromobutane into a three-neck round-bottom flask (flask volume). The mixture was left for agitation on a hot plate for 5 days with a stirring rate of 300 rpm at 40 °C in a reflux condenser and a magnetic stirrer. The product was washed using ethyl acetate and diethyl ether. The rotary evaporator was used to remove the solvents from the mixture, which ends up as just the precursor of [BMPi][Br] remained in the flask. The product obtained was a yellowish-white powder.[14]

The second step is the metathesis reaction. Sodium trifluoromethanesulfonate was dissolved in methanol in a round-bottom flask, and an equimolar amount of [BMPi][Br] was added into the mixture. The mixture was stirred overnight at ambient temperature. After the removal of methanol through rotary evaporation, the final product of 1-butyl-1-methylpiperidiniuum trifluoromethanesulfonate ([BMPi]-[OTF]) was obtained, which was then washed using acetone to precipitate the bromide salt. The byproduct was filtered, and finally, acetone was removed through rotary evaporation, giving the final product as a light yellowish liquid. A similar method was used in the synthesis of 1-butyl-1-methylpiperidine phenolate ([BMPi][Phe]) and 1-butyl-1-methylpiperidinium dicyanamide ([BMPi][DCN]), with the only change being replacing sodium trifluoromethanesulfonate with sodium phenoxide trihydrate and sodium dicyanamide, respectively. The final products of [BMPi][Phe] and [BMPi][DCN] were thick brown liquid and light yellowish liquid, respectively.

4.2.2. Characterization of Ionic Liquids. ^{1}H NMR spectra were recorded on a Bruker Advance 500 spectrometer for each of the ILs synthesized, and the deuterated solvent used is deuterated water. (BMPi OTF) ^{1}H NMR δH (ppm): 1.010 (t, 3H), 1.475 (m, 2H), 1.740 (m, 2H), 1.833 (m, 2H), 1.970 (m, 4H), 3.221 (s, 3H) and 3.563 (m, 6H). (BMPi Phe) ^{1}H NMR δH: 0.814 (t, 3H), 1.257 (m, 2H), 1.485 (m, 4H), 1.694 (m, 4H), 2.823 (s, 3H), 3.147 (m, 6H), 6.553 (t, 3H) and 7.059 (t, 2H). (BMPi DCN) ^{1}H NMR δH: 0.848 (t, 3H), 1.299 (m, 2H), 1.535 (m, 4H), 1.748 (m, 4H), 2.890 (s, 3H) and 3.218 (m, 6H).

4.3. Extraction of Naphthenic Acid from Model Oil.

4.3.1. Preparation of Model Oil. Naphthenic acid is mostly present in kerosene and diesel fractions. Dodecane was used as a model oil to represent these oil fractions, which is then mixed with naphthenic acid to be used as the model oil. The initial TAN of the naphthenic acid is 213 mg KOH/g, and the model oil is mixed with a naphthenic acid/dodecane weight ratio of 0.0073, which reduced the TAN of the model oil to 1.5 mg KOH/g. The TAN is measured using a Mettler Toledo T70 autotitrator, which follows the oil industry standard method using ASTM D664.

4.3.2. Extraction Process—Mechanical Stirring Technique. The extraction process of naphthenic acid was executed by mixing 10 g of model oil with different amounts of IL at room temperature with a stirring rate of 500 rpm for 1 h. The mixture was then centrifuged at 4000 rpm for 15 min to achieve a complete separation between the model oil and the IL. The oil was removed from the top of the separating funnel to measure the TAN. Reduction of TAN is calculated to be represented in the form of percent naphthenic acid removal using eq 2

$$\text{percent naphthenic acid removal} = \left(1 - \frac{\text{TAN}_f}{\text{TAN}_i}\right) \times 100\% \tag{2}$$

where TAN_f is the final total acid number and TAN_i is the initial total acid number.

4.3.3. Extraction Process—Ultrasonic-Assisted Technique. The same procedure as mentioned in the mechanical stirring technique was implemented, in addition to the presence of an ultrasonic probe that is used to apply the ultrasonic irradiation to the IL-to-model oil mixture. To maintain the system at a setpoint temperature, the extraction was performed in a glass reactor with a jacket filled with flowing cool water to cool the reactor. The ultrasonic device has a 14 mm horn system with a Sonic Vibracell generator (20 kHz, VCX 750 W, Newton). The time for extraction for the ultrasonic-assisted technique is only 5 min, at 50% amplitude, while maintaining the other parameters similar to the ones used in the mechanical stirring technique. After the extraction process was completed, the mixture was centrifuged at 4000 rpm for 15 min to attain a complete separation between the model oil and IL−naphthenic acid mixture, thus resulting in the formation of two different layers. The top layer was removed for TAN measurement.

4.3.4. Confirmation of Extraction via FTIR Analysis. Fourier transform infrared (FTIR) spectroscopy has been carried out on the used ionic liquids using a Shimadzu IR Affinity-1 FTIR spectrophotometer (Shimadzu, Japan). All sample spectra were subjected to background spectrum, and the spectra were documented within the range of 4000−400 cm^{-1}.

4.4. Effect of Ultrasonic Parameters Study on Extraction Efficiency. The effect of amplitude as an ultrasonic parameter on the extraction efficiency is studied. The ultrasonic energy dispersed into the IL-to-model oil mixture is quantified using calorimetric measurement. This is because most of the ultrasonic energy converts to multiple forms of mechanical energy, which ultimately generates heat.[32] The ultrasonic power, P (W), is calculated using the equation below

$$P = mc_p\frac{dT}{dt} \tag{3}$$

where m is the mass of the irradiated IL-to-model oil mixture (kg), c_p is the heat capacity per unit mass of mixture (J/kg K), and dT/dt is the slope of the temperature rise versus time (K/s).[26]

4.5. Experimental Design. The Box−Behnken method is used in this study as the tool to optimize three independent variables, which are IL-to-oil ratio (X_1), amplitude (X_2), and extraction time (X_3). The ranges for these three variables had been selected based on preexperimentations performed, which are 0.001−0.05, 40−60%, and 1−6 min, respectively. Using Design Expert 8.0, experimental data from the method were analyzed and fitted to a second-order polynomial model. This was done to study all possible interactions between all three factors toward the extraction efficiency. The model follows the response function as shown below

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$$Y = \beta_0 + \sum_{3}^{i=1} \beta_i x_i + \sum_{3}^{i=1} \beta_{ii} x_i^2 + \sum_{2}^{i=1} \sum_{3}^{j=i+1} \beta_{ij} x_i x_j \quad (4)$$

where Y is the removal of naphthenic acid, β_0 is the mean, β_i is the liner term coefficient, β_{ii} is the quadratic term coefficient, β_{ij} is the two-factor interaction coefficient, and x_i and x_j are independent variables. Using ANOVA, the fitness of the model was investigated. Once the model has been obtained, a validation through experimenting is conducted and relative errors are calculated using eq 5. The analysis was done through model significance, coefficient of determination, as well as F-test. Table 5 shows the design of experiment, which has been used in this study.

$$\text{relative error} = \frac{|\text{theoretical value} - \text{experimental value}|}{\text{experimental value}} \quad (5)$$

Table 5. Design of Experiment

factor	name	unit	−1	0	+1
X_1	IL-to-oil ratio		0.001	0.0255	0.050
X_2	amplitude	%	40	50	60
X_3	extraction time	min	1	3.5	6

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Notes

The authors declare no competing financial interest.

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