

Coupling of subcritical methanol with acidic ionic liquids for the acidity reduction of naphthenic acids

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The presence of naphthenic acids (NAs) in crude oil is the major cause of corrosion in the refineries and its processing equipment. The goal of this study is to reduce the total acid number (TAN) of NAs by treating them with subcritical methanol in the presence of acidic ionic liquid (AIL) catalysts. Experiments were carried out in an autoclave batch reactor and the effect of different reaction parameters was investigated. It was observed that TAN reduction was positively dependent on the temperature and concentration of the AIL whereas excess of methanol has a negative effect. Approximately 90% TAN reduction was achieved under the optimized reaction conditions using [BMIM]HSO₄ as catalyst. It was also perceived from the experimental results that the AILs with longer alkyl chain exhibited higher catalytic activity. The activity and stability of AIL showed that they can be promising catalyst to esterify NAs under subcritical methanol.

Keywords: Naphthenic Acids; Subcritical Methanol; Acidic Ionic Liquids; Total Acid Number; Esterification.

INTRODUCTION

Naphthenic acids (NAs) are originally identified as carboxylic acids with single or multiple saturated rings, in the phrase broadly used to include all acidic compounds in crude oils that may even contain an aromatic functionality. The general formula of NAs is C_nH_{2n+z}O₂, where “n” is the number of carbon atoms and “z” is referred to hydrogen deficiency, which is due to the formation of rings¹⁻³. Total acid number (TAN) is the most common measures of corrosive potential of the crude oil, which is the amount of KOH required to neutralize one gram of crude oil¹. Although, the presence of NAs is established in all types of crudes. But the crude oil is only considered as acidic if it has a TAN value greater or equal to 0.5 mg KOH/g. Thus, these acidic crudes have an adverse impact on refinery reliability and operations with corrosion, desalter problems, fouling, catalyst poisoning, product degradation, and environmental discharges⁴. Global production of acidic crudes has increased to 10% of the total crude oil production, and this continues to increase due to depleting light crude reserves⁵. However, with the associated financial opportunities, these crudes develop technical challenges for the oil industry.

Removal of NAs from crude oil and crude fractions have been extensively studied by several researchers. There are different methods available in the open literature which are usually classified into subcategories as destructive and non-destructive. In the non-destructive method, NAs are extracted without destroying the carboxylic group of the acid. In this methods, caustic treatment can effectively remove the NAs but with the formations of a large quantity of waste water and emulsion which in return is problematic^{6, 7}. Other methods include adsorption, membrane separation and solvent extraction by ionic liquids and basic solution⁸⁻¹⁰. These methods got varying success for low TAN crudes but are not very effective for high TAN crudes. Moreover, these methods also possess the problem of solvent loss, as the separation methods are not very effective⁷. Destructive methods are relatively more effective for high

TAN crude oil. These methods include hydrogenation, catalytic decomposition, and esterification. Hydrogenation is generally used for industrial distillates but requires a large quantity of hydrogen and large investment in the equipment⁸. Thus, this process is not applied for heavy crude oil upgradation. Thermal and catalytic decarboxylation of NAs requires high temperature, therefore, research is mainly focused on the development of new catalysts with the objective to maximize the reaction rate and minimize the reaction severity³.

Among all the techniques available in open literature, esterification of NAs has effectively reduced the TAN of highly acidic crudes^{7, 11, 12}. Esterification process is a most fundamental reaction in synthetic chemistry and has wide applications in the industrial synthesis of different products. Esterification of NAs is a slow reaction, various acid and base catalysts have been applied previously with a motive to reduce the reaction time and severe reaction conditions^{7, 13-15}. Esterification reaction is usually catalyzed by homogenous catalyst such as sulfuric acid which has shown high catalytic activity, but these acids are itself very corrosive and can cause serious environmental issues^{16, 17}. On the other hand, heterogeneous catalysts are easily recoverable but have the problem of operation loss, difficult synthesis, mass transfer limitations and deactivation due to the heavy crude oil^{7, 18}. In this course, non-catalytic supercritical methanol has been effective in converting NAs to its corresponding esters in shorter reaction time^{19, 20}. Mandal et al. (2013) investigated non catalytic supercritical methanol to reduce the acidity of NAs and approximately 100% TAN reduction was achieved at the reaction time of just 60 min. However, the reaction conditions were very high i.e. temperature of 350°C and pressure of 10 MPa¹⁹. Later on, Kashif et al. (2016) utilized supercritical methanol technique on NAs mixture and high acidic crude and reported that approximately 94% TAN reduction was achieved for high acidic crude with the reaction time of just 60 min²⁰. Although, high TAN reduction with high reaction rate was achieved, but still the severity of

reaction parameters like critical temperature and critical pressure of methanol are not easy to achieve and effect the feasibility of the process.

As an alternative, subcritical methanol with much milder condition could be employed. Methanol becomes supercritical at the temperature and pressure of 239.5°C and 8.1035 MPa respectively. Subcritical methanol conditions are the conditions below the critical point and above the boiling point of methanol. Where small change in the temperature and pressure will effect large changes in density, ultimately effecting its solubility. This technique has shown advantages in terms of reducing the reaction time and severity of the process but the catalyst is indispensable^{21, 22}. The criteria set for any catalyst to be selected for any process is the product purity, catalyst recovery and reusability. Continuous effort are being made to replace the acidic liquid catalyst with non-corrosive, non-toxic, environment-friendly and easy to handle catalysts²³.

Recently, Ionic liquids (ILs) have been considered as a greener replacement for the potentially harmful organic and inorganic solvents and acceptable catalyst for different reactions^{23–25}. ILs generally possesses properties like wide liquid range, high thermal and catalytic stability, non-volatility, easy recovery and reusability^{25–27}. Acidic ionic liquids (AILs), a class of ILs that are acidic and viewed as a substitute for the acid catalyzed reactions. Previously, they have been employed as catalysts for biodiesel production in esterification and trans-esterification reactions. Most of the AILs are hydrolysis stable and easily separated from the product mixture as it is normally associated with the solid catalysts and also provides high selectivity and yield which is usually associated with the liquid catalysts. Their ease of separation from the reaction mixture helps in promoting the reaction to the product side²⁴.

Therefore, to overcome the difficulties associated with supercritical methanol and traditional catalysts, a new methodology is proposed using subcritical methanol and AILs to reduce the TAN of NAs. The AILs with halogen containing anions (i.e. BF_4^- , PF_6^- , CF_3OO^- , CF_3SO_3^-) limits their greenness due to their biodegradability issue. So, we have selected hydrogen sulfate HSO_4^- as an anion with imidazolium as cation, which is halogen free and are considered environment benign and recyclable catalysts for a number of reactions^{23, 24, 28}.

The objective of this paper is to explore the capability of a mixture of subcritical methanol and AILs i.e. butyl-methylimidazolium hydrogen sulfate ([BMIM]HSO₄), ethyl-methylimidazolium hydrogen sulfate ([EMIM]HSO₄), butylimidazolium hydrogen sulfate ([BIM]HSO₄) and methylimidazolium hydrogen sulfate ([MIM]HSO₄) for the acidity reduction of NAs under mild reaction conditions. Influence of different reaction parameters was investigated to develop a comprehensive understanding of TAN reduction under a wide range of reaction conditions. The stability of AIL and the product of reaction mixture were analyzed by FT-IR spectroscopy.

EXPERIMENTAL

Feedstock and chemical reagents

Pure NAs, which was a complex mixture of different cyclic and alicyclic carboxylic acids was purchased from Sigma-Aldrich and used without further treatment. The TAN value of the feedstock was measured according to the ASTM D974 method and it was 250 mg KOH/g with the density of 0.92 g/mL at 20°C. This NA mixture was yellowish in color and has a pungent smell. Other chemicals were purchased from EMD Millipore Corporation i.e. potassium hydroxide (KOH) ($\geq 85\%$), methanol ($\geq 99.8\%$), ethanol ($\geq 99.5\%$), 2-propanol ($\geq 99.8\%$), toluene ($\geq 99.9\%$) and Phenolphthalein (Indicator grade). AILs [BMIM]HSO₄, [EMIM]HSO₄, [BIM]HSO₄ and [MIM]HSO₄ were synthesized, their characterization and thermo physical properties are given in another research paper²⁹.

Equipment used

The experiments were carried out in an autoclave batch reactor made by Shanghai Yanzheng Experiment Instrument Co., Ltd., China. The reactor is made of stainless steel and equipped with Teflon chamber of polytetrafluoroethylene (PTFE). The volume of the Teflon chamber is 20 mL. This reactor can sustain a maximum temperature of 230°C and pressure of 3 MPa.

Experimental procedure

The potential experiments were performed according to the methodology developed by Mandal et al.¹⁹. For the experiments, the reactor was loaded with 0.50–3 g of naphthenic acid, 0.10–0.80 g of AIL and precise amount of methanol calculated by Peng-Robinson equation of state. The methanol volume is important in defining the methanol partial pressure inside the reactor^{19, 20}. This also eliminates the need of external gas to maintain the desired pressure inside the reactor. The reactor was heated inside an electric oven for the set temperature and reaction time. Prior loading the reactor to the oven, the oven was heated to the desired temperature. When the reactor was loaded into the oven there was a decrease in the oven temperature and it takes 3–4 minutes to regain the set temperature, this study defines the zero time as the time consumed to stabilize the temperature after the reactor loading. After the defined reaction time, the reactor was taken out of the oven and submitted to quenching using cold water to immediately stop the reaction. After the reactor is cooled to the room temperature reaction mixture was collected in a flask.

Extraction of the ionic liquid

Upon completion of the reaction, there was no complete separation of the product from the reaction mixture as it was reported by other researchers^{27, 30}. To completely separate the product from the reaction mixture, 3 mL of diethyl ether and 3 mL of distilled deionized water was added. Resulting in the spontaneous separation of the layers. The heavy phase consists of the AIL, water and methanol were separated by decantation and washed 3 times with diethyl ether to remove any dissolved organics. Then the excess of water and methanol was removed by distillation from the AIL before it was used in the next

reaction. The separated light phase consisting of NA esters, unreacted NAs and diethyl ether was used to check the TAN reduction and FTIR analysis.

TAN analysis

Total acid number of the NAs and the reaction product was calculated by ASTM D974 method. This method has proved to be effective for TAN calculations with high repeatability and reproducibility than other methods^{19,31}. Exactly 0.1 M solution of KOH was prepared in the solution of toluene and propanol at a ratio of (1:1). Phenolphthalein was used as an indicator instead of p-naphtholbenzein. Then the prepared KOH solution was added to the reaction mixture until the stable pink color was achieved. TAN was calculated in milligrams of KOH required per gram of oil (mg KOH/g). The equation used to determine TAN is given below:

$$TAN\ of\ Sample = \frac{C_{KOH} \times V_{KOH} \times CF}{M_s}$$

Here, C_{KOH} is the concentration of the standard KOH solution, V_{KOH} is the amount of titrant solution consumed in mL, CF is the convergent factor which is 56.10 and M_s is the mass of the sample in grams.

Percentage of the TAN reduction was calculated using the following equation:

$$TAN\ of\ Reduction\ (\%) = \frac{TAN\ of\ the\ base\ stock - TAN\ of\ the\ Reduction}{TAN\ of\ the\ base\ stock}$$

FT-IR analysis of product and AILs

The FT-IR analysis was performed using Perkin Elmer Frontier spectroscopy to compare pure NAs and the product mixture. The spectra were recorded by using PerkinElmer spectrum software (version 10.4.4) with a wavelength resolution of 4 cm^{-1} and 16 scans per single spectrum. The working temperature was 25°C . FT-IR analysis of the NAs and the product was to verify that the TAN reduction of the NAs after the treatment was due to the formation of esters.

Stability of the ionic liquid

Before using the AILs under the subcritical methanol conditions, the stability of AILs under the optimized experimental conditions was checked. The sample of these AILs was exposed to the subcritical methanol (i.e. at 150°C and 2 MPa) for 180 min and then analyze through FTIR. The obtained spectra were then compared with the spectra of ILs not exposed to the subcritical methanol.

RESULTS AND DISCUSSION

Before performing the potential experiments, few solubility experiments were performed which showed that these AILs were soluble in water and polar solvents like methanol, ethanol, acetone etc. and they were partially immiscible with non-polar solvents like alkane, alkenes, and aromatics. It was also observed that the NAs and AILs were soluble with methanol at room temperature and form a single phase, so the reaction system was considered as a homogenous system.

Effect of ILs cation size on the TAN reduction

The effect four AIL catalysts with varying alkyl chain length on the imidazolium moiety was monitored for the

acidity reduction of NAs. The results were compared with the industrial catalyst H_2SO_4 . The experiments were performed at the temperature of 130°C , methanol partial pressure of 2 MPa, reaction time of 180 min, NAs to IL ratio of 1:0.20 (wt./wt.) and NAs to methanol ratio of 1:14 (wt./wt.). The results are given in Table 1.

Table 1. TAN reduction with different AILs and H_2SO_4 at reaction temperature of 130°C , NAs to MeOH ratio of 1:14 (wt./wt.), NAs to Catalyst ratio of 1:0.20 (wt./wt.) and reaction time of 180 min

Ionic Liquid	TAN reduction [%]
H_2SO_4	92.1
[BMIM]HSO ₄	85.5
[EMIM]HSO ₄	76.3
[BIM]HSO ₄	69.5
[MIM]HSO ₄	65.1

As shown in the Table 1, all the four AILs have shown high catalytic ability to reduce the TAN under subcritical methanol conditions. But comparatively H_2SO_4 has shown high TAN reduction as compared with the AILs. However, H_2SO_4 possess some drawbacks like it has corrosive nature, separation problem and considered environment polluting. While on the other hand ILs have the features that negate these problems^{24, 30}.

AILs with HSO₄ as anion has shown good usability in a number of reactions as a catalyst and as a solvent^{24, 28, 32}. For example, first reported IL with HSO₄ anion was used in Friedel-crafts alkylation, after that they have been used in several other organic reactions like esterification, carbonylation, and polymerization with excellent yield and selectivity. These ILs are deemed suitable for industrialization because of their lower price, easy recovery and reusability. The physiochemical properties of ILs can be tuned by changing the alkyl chain on the cation like their thermal stability, density and viscosity²⁹.

All the four AILs showed a varying trend in the TAN reduction as the highest TAN reduction achieved was in this order [BMIM]HSO₄ > [EMIM]HSO₄ > [BIM]HSO₄ > [MIM]HSO₄. Approximately 85% TAN reduction was achieved with [BMIM]HSO₄ on the experimental conditions listed above. High conversion with AILs can be attributed to two factors. Firstly, the acidity of ionic liquids, it is found that the acidity of ILs will increase with the increase in alkyl length at cation which is directly related to the TAN reduction. Similar statements were also recorded by other researchers^{24, 30}. Secondly, the use of AILs with subcritical methanol which will help in decreasing the viscosities of AILs which in return will increase the mixing and effective collision between the reactant molecules. As [BMIM]HSO₄ has shown the higher catalytic ability as compared to other AIL with the highest TAN reduction, therefore it was considered for the further studies.

Stability of [BMIM]HSO₄

Prior doing the optimization study with [BMIM]HSO₄, its stability was checked under the subcritical methanol conditions of 150°C and methanol partial pressure of 2 MPa. FTIR analysis was performed for this purpose and is shown in Figure 1. The FTIR spectra suggested that [BMIM]HSO₄ is completely stable with subcritical

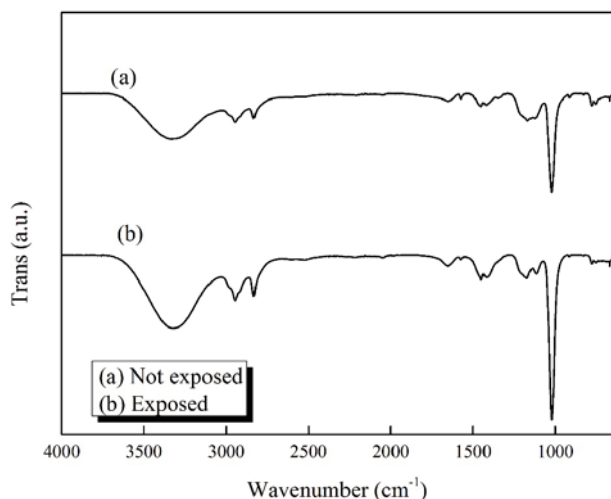


Figure 1. [BMIM]HSO₄ spectra before and after exposure to subcritical methanol

methanol as the peaks of IL before and after exposure to subcritical methanol were the same. This verifies that the [BMIM]HSO₄ structure was completely intact and it can be a potential substitute for harmful organic and inorganic solvents and catalysts under subcritical methanol conditions.

The FTIR spectra of the [BMIM]HSO₄ verifies the structure and the stability of this AIL after exposure to subcritical methanol. The peaks at a wavenumber of 2946 cm⁻¹ and 2846 cm⁻¹ are the aliphatic symmetric and asymmetric (C-H) vibrations, and in-plane vibrations for methyl group at 1190 cm⁻¹ and 1115 cm⁻¹. Peaks at wavenumbers of 1661 cm⁻¹ and 1460 cm⁻¹ are the peaks of (C=C) and (C=N) stretching. The peak at a wavenumber of 780 cm⁻¹ is due to (C-N) stretching vibrations. The peaks at 3100–3500 cm⁻¹ range represent the stretching due to -OH group of methanol. The peak stretching at 1030.2 cm⁻¹ is due to HSO₄ of AIL^{23,33}. Based on these results it is confirmed that [BMIM]HSO₄ is preserved chemically and structurally with subcritical methanol. The finding of Caldas et al. (2016)²³ also proved the stability of [HMIM]HSO₄ with supercritical ethanol at the conditions of 255°C temperature and ethanol partial pressure of 9.6 MPa, our results for [BMIM]HSO₄ coincides with the Caldes et al. results.

Optimization study of different parameters

The activity of [BMIM]HSO₄ for the esterification reaction of NAs with subcritical methanol was investigated. The effect of different reaction conditions i.e. IL dosage, NA to methanol ratio, reaction temperature and time on the TAN reduction of NAs was studied to maximize the acidity reduction.

Effect of NAs to IL ratio

The amount of IL used for any reaction is very important. For this study [BMIM]HSO₄ amount was varied according to the naphthenic acid amount by making the other variables constant i.e. temperature 130°C, methanol partial pressure of 2 MPa and the reaction time of 180 min. From the Figure 2a, it can be seen that the amount of IL has a direct effect on the TAN reduction. The ratio of NAs to IL (wt./wt.) was varied from 1:0.05 to 1:0.30 at 130°C. When the ratio was 1:0.05 the conversion was 42% and when the ratio was increased to

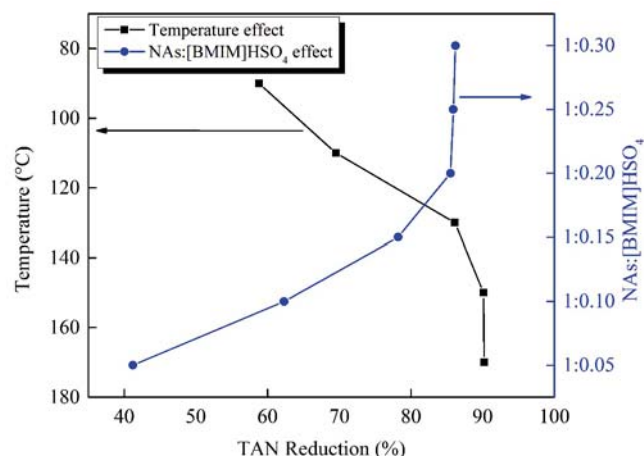


Figure 2. (a) Effect of NAs to IL ratios using [BMIM]HSO₄, temperature 130°C, pressure 2 MPa, reaction time 180 min, NAs to methanol ratio of 1:14 (wt./wt.). (b) Effect of different temperatures using [BMIM]HSO₄, pressure 2 MPa, reaction time 180 min, NAs to methanol ratio of 1:7 (wt./wt.) and NAs to AIL ratio of 1:0.20 (wt./wt.)

1:0.20 the conversion increased to 85%. However, with further increase in the IL amount does not exert significant effect on the TAN reduction. This demonstrates that with a lower amount of IL there were less active sites to catalyze the reaction and the optimum value for TAN reduction achieved at 1:0.20. Thus, considering the conversion and cost of the IL, the optimum ratio of NA to IL was 1:0.20.

Effect of NAs to methanol ratio

The amount of methanol for the reaction is also a very important parameter to consider for the conversion of NAs. The NAs to methanol ratio (wt./wt.) was varied from 1:1 to 1:28 at fixed parameter i.e. reaction temperature of 130°C, methanol partial pressure of 2 MPa, NAs to [BMIM]HSO₄ ratio of 1: 0.2 (wt./wt.) and reaction time of 180 min.

Theoretically, one mole of NAs is required to react with one mole of methanol to produce one mole of corresponding ester and one mole of water³⁴. However according to Le Châtelier's principle excess of one of the reactants will shift the equilibrium to the product side for reversible reactions like esterification. Figure 3 shows that when the ratio of NAs to Methanol was 1:1, the conversion was very low which increases gradually with the increase in methanol amount. At 1:7 maximum conversion was achieved which was 86%. It can be perceived from the results that with 1:1 the TAN reduction was low due to the reversible reaction, and secondly with the gradual conversion of methanol the partial pressure of methanol will decrease as methanol amount defines the inside reactor pressure. Which will ultimately effect the movement and mixing of the reactants. The low conversion with a high ratio of NAs to methanol like above 1:14 is because more amount of methanol will dilute the reaction mixture which will decrease the contact efficiency of methanol and NAs with the IL molecules.

So, considering the environmental point of view a minimum quantity of methanol should be utilized to achieve the maximum conversion. However, an excess of methanol is always used to shift the reaction to the product

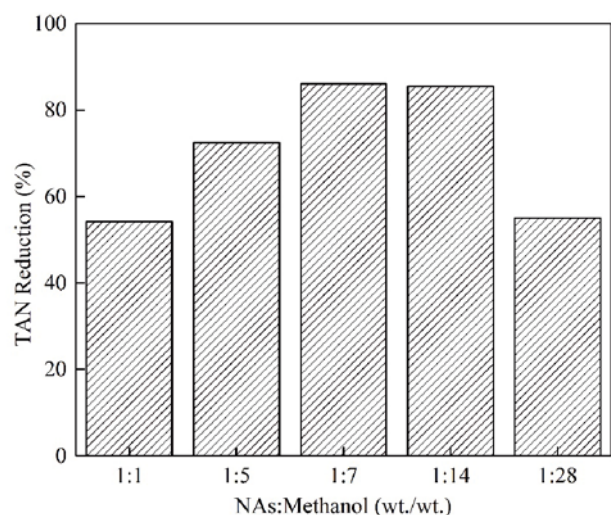


Figure 3. Effect of different NAs to Methanol ratios (wt./t.) in the presence of [BMIM]HSO₄, temperature 130°C, pressure 2 MPa, reaction time 180 min, NAs to [BMIM]HSO₄ ratio of 1:0.20 (wt./wt.)

side and also it absorbs the water produced during the reaction to avoid hydrolysis³⁴. Likewise, similar results were reported by other researchers^{13, 18}. These results imply that the optimum ratio of methanol to NAs is 1:7.

Influence of reaction temperature

Temperature has a vital role in the TAN reduction of naphthenic acids. In general increasing the temperature will increase the rate and yield of the reaction. As these experiments were performed at subcritical methanol condition which will increase the movement of reactant molecules inside the reactor, allowing the probability of effective collision among the molecules²³. To understand the effect of temperature, the temperature was varied from 90–170°C while keeping the other parameters constant such as methanol partial pressure 2 MPa, the reaction time of 180 min, IL to NAs ratio of 1:0.20 and NAs to methanol ratio of 1:7.

As the esterification is an endothermic reaction, increasing the temperature will have a direct effect on the TAN of NAs. It can be seen from the Figure 2b that the percentage of TAN reduction increases with the increase in temperature, the maximum conversion of 90% was achieved at 150°C, further increase in the temperature produces no significant effect on the TAN reduction. This demonstrates that increasing the temperature will also increase the catalytic ability of IL. It was reported by previous researchers that drying of crude oil significantly increases the esterification reaction to the product side however AILs possess the advantage by dissolving the water and forming a separate layer from the product. This eventually promotes the esterification reaction in the forward direction without utilizing the drying process⁷.

Influence of reaction time

Reaction time effect was investigated at a temperature of 150°C, methanol partial pressure of 2 MPa, NAs to IL ratio of 1:0.20 and NAs to Methanol ratio of 1:7. Figure 4 shows that the TAN reduction follows increasing trend with the increase in the reaction time up to the reaction time of 180 min. Initially, more active

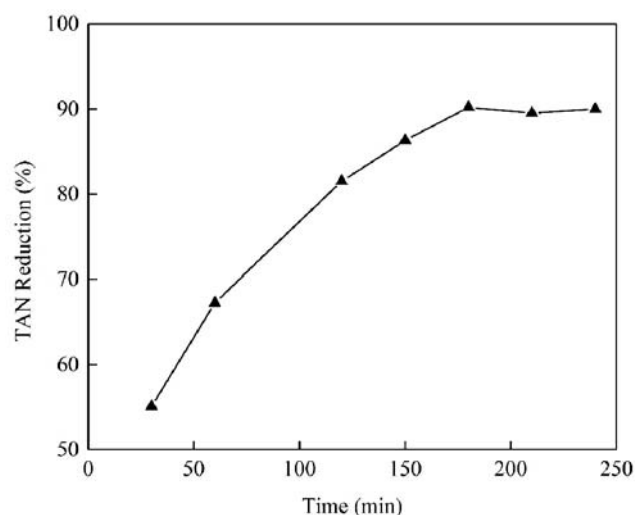


Figure 4. Effect of reaction time using [BMIM]HSO₄, temperature 150°C, pressure 2 MPa, NAs to methanol ratio of 1:7 (wt./wt.)

reactants were present so the reaction rate was very fast as 55% conversion was achieved in 30 min of reaction time. After that reaction gradually proceeds towards the equilibrium, and equilibrium was attained at the reaction time of 180 min. Approximately, 90% TAN was reduced at a reaction time of 180 min and with further increase in the reaction time does not effect the overall TAN reduction. This indicates that the reaction is a reversible reaction and it approaches equilibrium at 180 min of reaction time.

The other reason for incomplete conversion can be the resistant of some of the NAs present in the feedstock. It was reported by Kashif et al. (2016) that there were some branched carbon atoms present near the carboxylic acid group which limits the access of methanol molecules by increasing the steric hindrance for commercial NAs. As for some of the recalcitrant NA species, a very high reaction temperature and pressure was required with non-catalytic supercritical methanol i.e. 400°C and 10 MPa²⁰. So with the current reaction parameters, the reaction time of 180 min is considered as the optimum reaction time for 90% conversion of NAs to the product side.

Product analysis by FTIR

The FTIR spectra of the pure NAs is given in Figure 5. A broad peak at 1701.7 cm⁻¹ was observed which represents the carboxylic acid group (-COOH). Usually, for carboxylic acid, the peak stretch appeared at 1708.7 cm⁻¹ but here the peak is at 1701.7 cm⁻¹ because NAs exists as dimer due to the hydrogen bonding between the neighboring (-COOH) group present.

Figure 5 also shows the spectra of the product obtained at 150°C, 2 MPa and 180 min of reaction time in the presence of [BMIM]HSO₄. It can be observed that the carboxylic group (-COOH) peak has been reduced and a new peak appears at 1735.11 cm⁻¹, which is the characteristic peak of ester (R-COO-R'), a six atom ring. At 1410 cm⁻¹ the peak of (-OH) for carboxylic acid also disappeared in the product spectra. Which shows that (-OH) of the carboxylic acid has been replaced by the alkyl substitute from methanol. This indicates that the main reaction here was esterification reaction as NAs were converted into corresponding esters. The peak vibration at

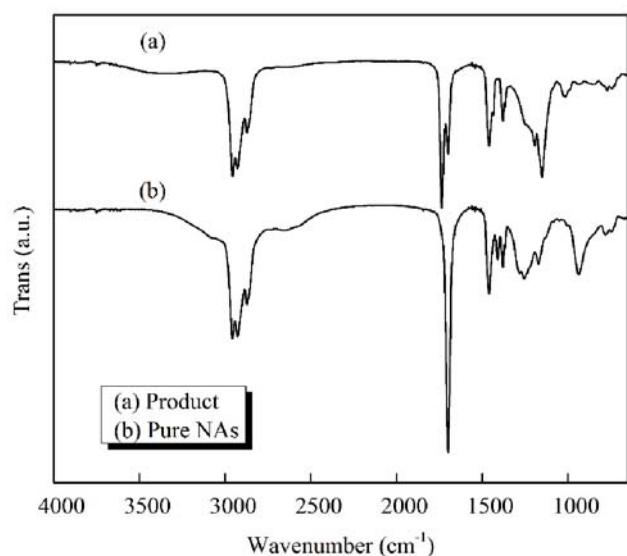


Figure 5. FT-IR spectra of the pure NAs and the reaction product

1461 cm^{-1} for aromatic (C=C) stretching has disappeared in the product mixture which indicates the breaking of aromatic compounds to new aliphatic products. The new peak appeared at 1196 cm^{-1} and 1151 cm^{-1} , which are the characteristic peaks of tertiary alcohols (C-H) and esters (C-H) that were not present in the base stock. This indicates that besides esterification reaction there were some side reaction resulting in different alcohols and hydrocarbons formation. The general esterification reaction of NAs is given in Figure 6. The same kind of results were reported by different researches applying supercritical methanol technique^{19, 20}.

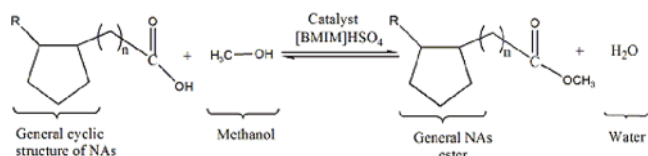


Figure 6. Proposed esterification reaction of NAs in the presence of subcritical methanol and [BMIM]HSO₄ catalyst. Where “R” is the alkyl chain and “n” is the number of carbons

Recyclability of AIL

The recyclability of a catalyst is an important factor that defines the industrial viability by reducing the cost of the process. The recyclability of [BMIM]HSO₄ was examined for the esterification of NAs on the optimized reaction condition, the results are shown in the Figure 7. It was observed that the TAN reduction of NAs slightly decrease from 90% to 85% when it is used for four times. These results shows the high catalytic activity and stability under subcritical methanol conditions. The structure of the [BMIM]HSO₄ was examined after recycling and the FTIR results agrees well with the structure of [BMIM]HSO₄ before the reaction. Although some loss in the weight of the IL did happen in the extraction process which was fulfilled by adding fresh IL.

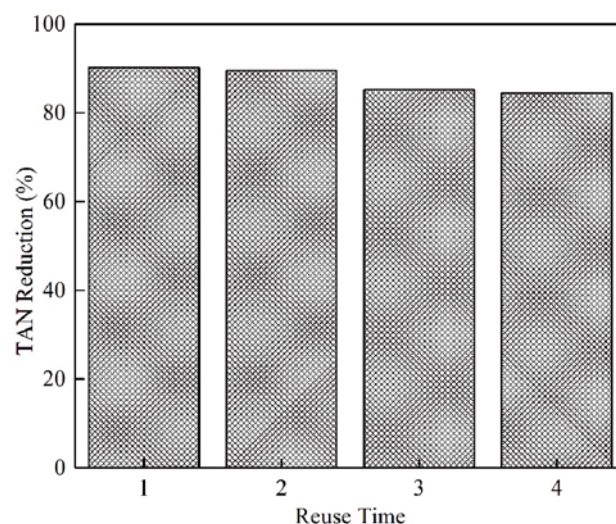


Figure 7. Recyclability of [BMIM]HSO₄

CONCLUSION

Four hydrogensulfate (HSO₄) based acidic ionic liquids were tested with subcritical methanol for the acidity reduction of NAs. The results conclude that the activity of AILs increases with the increase of side chain at the cation part i.e. imidazole. AIL [BMIM]HSO₄ has given the highest TAN reduction comparing to the other AILs used. These findings agree with the previous work of researchers where the increment in the alkyl chain has produced better results with similar kind of reactions. Approximately 90% TAN reduction was achieved by using [BMIM]HSO₄ at a temperature of 150°C, methanol partial pressure of 2 MPa and reaction time 180 min. Optimization of AIL to NAs and methanol to NAs ratio are necessary to achieve the high TAN reduction. It is also concluded that increasing the reaction temperature and time will increase the TAN reduction. The stability test of [BMIM]HSO₄ revealed that it is stable with subcritical methanol operating conditions and its property of phase separation helped in shifting more reaction to the product side resulting in more TAN reduction. The [BMIM]HSO₄ retain 95% efficiency after recycling it for four times. The product analysis showed ester as the abundant product with indications of side products as well. The key merit of this study is the TAN reduction at very low temperature and pressure condition then required for supercritical methanol. Furthermore, this process can be applied to reduce the acidity of heavy oil in an environmentally friendly way.

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LITERATURE CITED

- Clemente, J.S. & Fedorak, P.M. (2005). A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids. *Chemosphere* 60(5), 585–600. DOI: 10.1016/j.chemosphere.2005.02.065.
- Headley, J.V., Peru, K.M. & Barrow, M.P. (2016). Advances in mass spectrometric characterization of naphthenic acids

fraction compounds in oil sands environmental samples and crude oil—a review. *Mass Spectr. Rev.* 35(2), 311–328. DOI: 10.1002/mas.21472.

3. Mandal, P.C. & Nagarajan, T. (2016) Kinetics and reaction pathways of total acid number reduction of cyclopentane carboxylic acid using subcritical methanol. *Pol. J. Chem. Technol.* 18(3) 44–49. DOI: 10.1515/pjct-2016-0047.

4. Shi, L.J., Shen, B.X. & Wang, G.Q. (2008). Removal of naphthenic acids from Beijiang crude oil by forming ionic liquids. *Energy Fuels* 22(6), 4177–4181. DOI: 10.1021/ef800497p.

5. Lirong, D. (2005). Formation mechanism and model of oil and gas accumulations in the Melut Basin, Sudan. *Bulletin of Mineralogy Petrol. Geochem.* 24(1), 50–57.

6. Shukri, N.M., Bakar, W.A.W.A., Jaafar, J. & Majid, Z.A. (2015). Removal of naphthenic acids from high acidity Korean crude oil utilizing catalytic deacidification method. *J. Ind. Eng. Chem.* 28, 110–116. DOI: 10.1016/j.jiec.2015.02.005.

7. Wang, Y.Z., Li, J.Y., Sun, X.Y., Duan, H.L., Song, C.M., Zhang, M.M. & Liu, Y.P. (2014). Removal of naphthenic acids from crude oils by fixed-bed catalytic esterification. *Fuel* 116, 723–728. DOI: 10.1016/j.fuel.2013.08.047.

8. Nasir Shah, S., Mutalib, M.I.A., Pilus, R.B.M. & Lethesh, K.C. (2014). Extraction of Naphthenic Acid from Highly Acidic Oil Using Hydroxide-Based Ionic Liquids. *Energy Fuels* 29(1), 106–111. DOI: 10.1021/ef502169q.

9. Shah, S.N., Chellappan, L.K., Gonfa, G., Mutalib, M.I.A., Pilus, R.B.M. & Bustam, M.A. (2016). Extraction of naphthenic acid from highly acidic oil using phenolate based ionic liquids. *Chem. Eng. J.* 284, 487–493. DOI: 10.1016/j.cej.2015.09.017.

10. Shohaimi, N.A.M., Bakar, W.A.W.A. & Jaafar, J. (2014). Catalytic neutralization of acidic crude oil utilizing ammonia in ethylene glycol basic solution. *J. Ind. Eng. Chem.* 20(4), 2086–2094. DOI: 10.1016/j.jiec.2013.09.037.

11. Wang, Y.Z., Sun, X.Y., Liu, Y.P. & Liu, C.G. (2007). Removal of naphthenic acids from a diesel fuel by esterification. *Energy Fuels* 21(2), 941–943. DOI: 10.1021/ef060501r.

12. Zifeng, L., Songbai, T. & Zijun, W. (2009). Study on esterification for reducing total acid number of high acid crude oil by Mg/Al oxides [J]. *Pet. Process. Petrochem.* 8, 024.

13. Wang, Y.Z., Duan, H.L., Song, C.M., Han, X.T. & Ma, X.R. (2014). Removal of naphthenic acids from crude oils by catalytic decomposition using Mg–Al hydrotalcite/ γ - Al_2O_3 as a catalyst. *Fuel* 134, 499–504. DOI: 10.1016/j.fuel.2014.06.026.

14. Wang, H., Duan, W., Lei, Y., Wu, Y., Guo, K. & Wang, X. (2015). An intracrystalline catalytic esterification reaction between ethylene glycol intercalated layered double hydroxide and cyclohexanecarboxylic acid. *Catal. Commun.* 62, 44–47. DOI: 10.1016/j.catcom.2015.01.004.

15. Lee, Y.H., Park, J.Y., Park, S.Y., Kim, C.H., Nam, J., Kim, Y.J. & Bae, J.W. (2016). Removal of benzoic acid in heavy oils by esterification using modified Ferrierite: Roles of Brønsted and Lewis acid sites. *Energy Fuels*, 30(7), 5391–5397. DOI: 10.1021/acs.energyfuels.6b00448.

16. Dastjerdi, Z. (2010). The Esterification of Naphthenic Acids for Methyl Ester Production. *Environ. Prog. Sustain. Energ.* 32(2), 406–410. DOI: 10.1002/ep.11606.

17. Quiroga-Becerra, H., Mejía-Miranda, C., Laverde-Cataño, D., Hernández-López, M. & Gómez-Sánchez, M. (2012). A kinetic study of esterification of naphthenic acids from a Colombian heavy crude oil. *CT&F-Ciencia, Tecnología y Futuro* 4(5), 21–31. Retrieved on December 30, 2016, from http://www.scielo.org.co/scielo.php?pid=S0122-53832012000100002&script=sci_arttext

18. Li, X., Zhu, J., Liu, Q. & Wu, B. (2013). The removal of naphthenic acids from dewaxed VGO via esterification catalyzed by Mg–Al hydrotalcite. *Fuel Process. Technol.* 111, 68–77. DOI: 10.1016/j.fuproc.2013.01.016.

19. Mandal, P.C., Sasaki, M. & Goto, M. (2013). Non-catalytic reduction of total acid number (TAN) of naphthenic acids

(NAs) using supercritical methanol. *Fuel Process. Technol.* 106, 641–644. DOI: 10.1016/j.fuproc.2012.09.058.

20. Khan, M.K., Insyani, R., Lee, J., Yi, M., Lee, J.W. & Kim, J. (2016). A non-catalytic, supercritical methanol route for effective deacidification of naphthenic acids. *Fuel* 182, 650–659. DOI: 10.1016/j.fuel.2016.06.023.

21. Sitthithanaboon, W., Reddy, H.K., Muppaneni, T., Ponnusamy, S., Punsuvon, V., Holguim, F., Dungan, B. & Deng, S. (2015). Single-step conversion of wet Nannochloropsis gaditana to biodiesel under subcritical methanol conditions. *Fuel* 147, 253–259. DOI: 10.1016/j.fuel.2015.01.051.

22. Wan, L., Liu, H. & Skala, D. (2014). Biodiesel production from soybean oil in subcritical methanol using MnCO_3/ZnO as catalyst. *Appl. Catal. B.* 152, 352–359. DOI: 10.1016/j.apcatb.2014.01.033.

23. Caldas, B.S., Nunes, C.S., Souza, P.R., Rosa, F.A., Visentainer, J.V., Oscar de Olivera, S. & Muniz, E.C. (2016). Supercritical ethanolysis for biodiesel production from edible oil waste using ionic liquid $[\text{HMIM}][\text{HSO}_4]$ as catalyst. *Appl. Catal. B.* 181, 289–297. DOI: 10.1016/j.apcatb.2015.07.047.

24. Ullah, Z., Bustam, M.A. & Man, Z. (2015). Biodiesel production from waste cooking oil by acidic ionic liquid as a catalyst. *Renew. Energ.* 77, 521–526. DOI: 10.1016/j.renene.2014.12.040.

25. Andreani, L. & Rocha, J. (2012). Use of ionic liquids in biodiesel production: a review. *Braz. J. Chem. Eng.* 29(1), 1–13. DOI: 10.1590/S0104-66322012000100001.

26. Seddon, K.R. (1997). Ionic liquids for clean technology. *J. Chem. Tech. Biotech.* 68(4), 351–356. DOI: 10.1002/(SICI)1097-4660(199704)68:4<351::AID-JCTB613>3.0.CO;2-4

27. Olkiewicz, M., Plechkova, N.V., Earle, M.J., Fabregat, A., Stüber, F., Fortuny, A., Font, J. & Bengoa, C. (2016). Biodiesel production from sewage sludge lipids catalysed by Brønsted acidic ionic liquids. *Appl. Catal. B* 181, 738–746. DOI: 10.1016/j.apcatb.2015.08.039.

28. Kumar, M., Sharma, K. & Arya, A.K. (2012). Use of SO_3H -functionalized halogenfree ionic liquid ($[\text{MIM}(\text{CH}_2)_4\text{SO}_3\text{H}][\text{HSO}_4]$) as efficient promoter for the synthesis of structurally diverse spiroheterocycles. *Tetra. Lett.* 53(34), 4604–4608. DOI: 10.1016/j.tetlet.2012.06.085.

29. Ullah, Z., Bustam, M.A., Muhammad, N., Man, Z. & Khan, A.S. (2015). Synthesis and thermophysical properties of hydrogensulfate based acidic ionic liquids. *J. Sol. Chem.* 44(3-4), 875–889. DOI: 10.1007/s10953-015-0329-x.

30. Aghabarari, B., Ghiaci, M., Amini, S.G., Rahimi, E. & Martinez-Huerta, M. (2014). Esterification of fatty acids by new ionic liquids as acid catalysts. *J. Taiwan Inst. Chem. Eng.* 45(2), 431–435. DOI: 10.1016/j.jtice.2013.08.003.

31. Mahajan, S. & Konar, S.K. (2006). Determining the acid number of biodiesel. *J. Am. Oil Chem. Soc.* 83(6), 567–570. DOI: 10.1016/j.fuel.2016.06.023.

32. Li, Y., Hu, S., Cheng, J. & Lou, W. (2014). Acidic ionic liquid-catalyzed esterification of oleic acid for biodiesel synthesis. *Chin. J. Catal.* 35(3), 396–406. DOI: 10.1016/S1872-2067(14)60005-X.

33. Dharaskar, S.A., Wasewar, K.L., Varma, M.N., Shende, D.Z. & Yoo, C. (2016). Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel. *Arab. J. Chem.* 9(4), 578–587. DOI: 10.1016/j.arabjc.2013.09.034.

34. Chuah, L.F., Bokhari, A., Yusup, S., Klemeš, J.J., Abdullah, B. & Akbar, M.M. (2015). Optimisation and kinetic studies of acid esterification of high free fatty acid rubber seed oil. *Arab. J. Sci. Eng.* 1–12. DOI: 10.1007/s13369-015-2014-1.