Total Acid Number Reduction of Naphthenic Acid Using Subcritical Methanol: A Kinetic Study

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ABSTRACT: *The aim of this study is to explore the capability of subcritical methanol to reduce the acidity of naphthenic acids and to determine reaction kinetics for large-scale reactor design. The experiments were carried out in a 25 mL autoclave reactor (China) at temperatures of 70-120ºC, Methanol Partial Pressures (MPPs) of 0.1-1.5 MPa, and reaction times of 0-60 min. The total acid number content of the samples was analyzed using ASTM D 974 techniques. Experimental results reveal that total acid number reduction of naphthenic acids increased with increasing reaction temperature, MPP, and reaction time. Approximately 74.20% total acid number was reduced at a temperature of 120ºC, a MPP of 1 MPa, and a reaction time of 60 min. Experimental data revealed that total acid number removal reaction kinetics followed second-order kinetics with an activation energy of 11.27 kcal/mol. Therefore, subcritical methanol is able to reduce the total acid number of naphthenic acids without the addition of any catalyst.*

KEYWORDS: *Naphthenic acid; Subcritical methanol; Total acid number; Petroleum oil; Reaction kinetics.*

INTRODUCTION

Naphthenic Acids (NAs) present in heavy oil are the fundamental contributor to heavy oil acidity [1, 2]. NAs are intricate mixtures of alkyl-substituted acyclic and cycloaliphatic carboxylic acids found in petroleum deposits such as oil sands bitumen, and crude oils [3, 5]. Corrosive NAs cause many problems in the oil and gas industry such as equipment failure, elevated maintenance cost, more frequent turnaround, product quality reduction, and disposal [6]. Research results have revealed that corrosion happens at Total Acid Number (TAN) level of 1.5 mg KOH/g and above [7]. Additionally, NAs create an emulsion in refinement process that is difficult to separate during separation steps. As a consequence, crude oils with high TAN content are often marketed at lower market prices [8]. The determining an appropriate method to remove or reduce acidic substances from petroleum oils is a major issue facing the oil and gas industry [9].

Many TAN reduction techniques have been proposed by previous researchers to reduce acidity in crude oil. Ding et al. [10] have classified TAN reduction techniques into two methods: (1) destructive methods, such as thermal cracking and hydrogenation process; and

(2) non-destructive methods, such as adsorption and solvent extraction. The solvent extraction processes produce stable emulsion and excessive industrial waste water making the process non-selective [11, 12]. On the other hand, the adsorption process is said to be less effective in treating highly viscous crude oil. The thermal deacidification process requires a high temperature (400°C), implying a high cost. *Rudolf* [13] also found that this process consumed more time and decomposition of NA for some cases was incomplete. The chemical decomposition processes reduce acidity by converting acids to salt, and salts removing processes are also cost sensitive. The hydrogenation process requires a very large amount of hydrogen gas on-site for continuous treatment [14], making the process inefficient.

To alleviate the above-noted deficiencies, the researches have recently concentrated on reducing the acidity of NAs using green processes such as ionic liquids (ILs)- and SuperCritical Fluid (SCF)-based technologies. IL-based technology can reduce the acidity of crude oil implies a high cost. Methanol below its critical point (T_c= 239.45°C and P_c = 8.10 MPa) and above its bubble point (T_{bp} = 64.6°C and P_{bp} = 0.1 MPa) is considered subcritical methanol (SubC-MeOH). *Mandal et al.* discovered that SuperCritical Water (SCW) [6] and supercritical methanol (SC-MeOH) [15] have the potential to reduce the acidity of NAs. The requirements of high temperature and pressure render both of the above methods costly. In fact, TAN value of NAs needs to reduce at a temperature lower than distillation temperature of the crude oil and low pressure for reducing corrosion in production, storage, and transportation of heavy oil. SubC-MeOH appears to be an optimal option for acidity reduction at low cost.

The aim of this technical paper is to explore the capability of SubC-MeOH to reduce acidity of NAs at parameters which can be achieved at reasonable cost: temperatures of 70-120°C, methanol partial pressures (MPPs) of 0.1-1.5 MPa, and reaction temperatures of 0-60 min. In addition, TAN removal kinetics was also explored.

EXPERIMENTAL SECTION
Equipment and materials used
All experiments were performed in a 25-mL autoclave reactor (Shanghai Yanzheng Experiment Instrument Co., Ltd.,

China) for the maximum temperature of 230°C and pressure of 3 MPa (gauge). NAs (grade: technical, density: 0.92 g/mL at 20°C) were purchased from Sigma-Aldrich and used without further treatment. Other reagents - toluene, 2-propanol, potassium hydroxide, and phenolphthalein - were obtained from EMD Millipore Corporation and used without further treatment.

Experimental Procedure
Approximately 0.05 g of NAs and 0.03 - 0.5 g (0.04 - 0.63 mL) of methanol were charged into the autoclave reactor. Methanol amount was calculated using Peng-Robinson equation of state in Patrick Barrie's program for solving the cubic equation of state by fixing temperature and pressure. The reactor was then loaded into a furnace that was preheated to the planned temperature. After loading the reactor into the furnace, the temperature decreased slightly for a short period and subsequently started to increase again to achieve the set temperature. This study defines zero reaction time as the time when the temperature of the furnace started to increase again after the reactor was loaded. After a specific reaction time, the reactor was removed from the furnace and placed in a water bath to allow sufficient time for cool to room temperature. Finally, the products were collected in sample bottles by washing the reactor interior at least three times with solvent.

Analytical Procedure
ASTM D 974 method was used to evaluate TAN values. In this process, a mixture of toluene and 2-propanol in 1:1 ratio was used as the solvent, and phenolphthalein was used as an indicator. The titrant used was recently-prepared standard potassium hydroxide of approximately 0.05 mol/L. The following terms are used in this study.

TAN was calculated using the following equation:

$$TAN\left(\frac{mgKOH}{gNA}\right) = \left[\frac{V_{KOH} \times N_{KOH} \times 56.10}{W_{NA,0}}\right] \tag{1}$$

Where V_{KOH} is the volume of KOH in mL, N_{KOH} is the concentration of KOH in mmol/mL, and $W_{NA,0}$ is the amount of NA in g.

TAN reduction was calculated using the equation shown below:

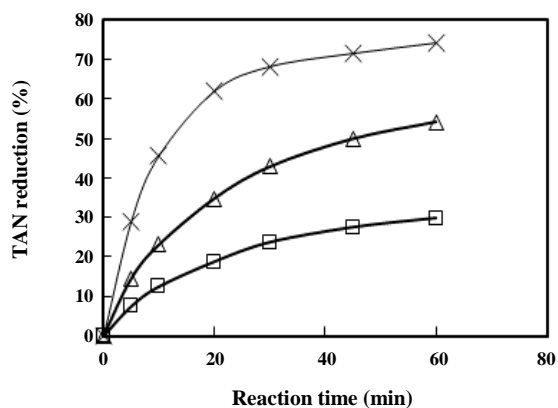*Fig. 1: Variation of TAN reduction at a function of temperature and reaction time (Symbol: □, 70ºC; △, 90ºC; ×, 120ºC temperatures).*

$$\text{TAN reduction}(\%) \frac{\text{TAN}_0 - \text{TAN}_t}{\text{TAN}_0} \times 100 \qquad (2)$$

Where TAN_0 is the initial TAN in loaded NA and TAN_t is the TAN at reaction time, t.

All experiments were conducted three times. The error margin of the achieved data was less than 5% resulting in a confidence level of 95%.

RESULTS AND DISCUSSION
TAN reduction

Mandal et al. [6] discovered the capability of SC-MeOH to reduce approximately 100% TAN of NAs at a temperature of 350ºC and a MPP of 10 MPa; these conditions, though, are too extreme (higher than crude oil distillation conditions) for heavy oil pre-treatment to reduce corrosion. Quiroga-Becerra et al. [12] discovered that approximately 95% TAN was reduced from NAs obtained from Colombian heavy crude oil at the temperature of 250ºC, the reaction time of 600 min, and a methanol to acid ratio of 20:1. Thus, SubC-MeOH has clearly demonstrated its ability to reduce the acidity of NAs. In our study, to observe the capability of SubC-MeOH for TAN reduction of NAs, approximately eighteen experiments were performed at temperatures of 70-120ºC, a MPP of 1 MPa, and reaction times of 0-60 min. NAs used in this study had an initial TAN value of 241.35 mg KOH/ g NA. Fig. 1 shows that TAN removal of NAs increased with increasing reaction temperature and time. Approximately 74.20% TAN was removed at a temperature of 120ºC, a MPP of 1 MPa, a reaction time
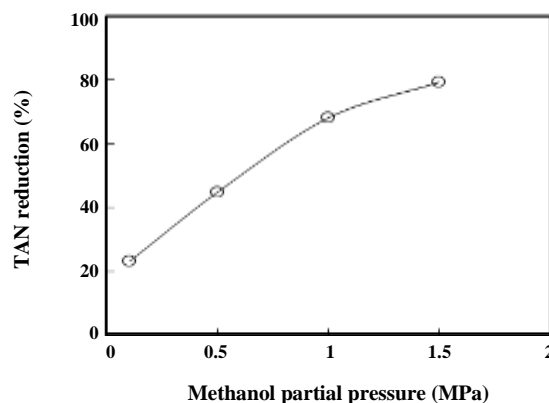

Fig. 2: Variation of TAN reduction at a function of methanol partial pressure at a temperature of 120ºC, and a reaction time of 30 min.

of 60 min. SubC-MeOH has proven to be an effective solvent able to dissolve many organic feedstocks such as petroleum oil. One reason for this is that NA and methanol mix properly with increasing temperature, increasing their respective collisions events and thus increasing the reaction rate.

Methanol partial pressure effect

To investigate MPP effects on TAN removal of NAs, four experiments were carried out at a temperature of 120ºC, MPPs of 0.1 – 1.5 MPa, and a reaction time of 30 min. The obtained results are depicted in Fig. 2. It is seen that TAN removal increased linearly from a MPP of 0.1 MPa to that of 1 MPa; beyond this, TAN removal increased at a decreasing rate up to the MPP of 1.5 MPa. These results show that SubC-MeOH actively reduced the acidity of NAs with approximately 79.36% TAN removed at a temperature of 120ºC, a MPP of 1.5 MPa and a reaction time of 30 min.

TAN reduction kinetics

Reaction kinetics is highly important for chemical reactor design. *Mandal et al.* [15] have shown that reaction of NA and SC-MeOH follow first order kinetics. In addition, the reaction between some organic acids and fatty alcohol have also shown first-order kinetics with respect to acid [16]. On the other hand, *Wang et al.* [17] have shown that reaction kinetics of esterification reaction between NA and methanol with and without SnO catalyst follows the second order. Likewise, esterification reaction between oleic acid and methanol under pressure
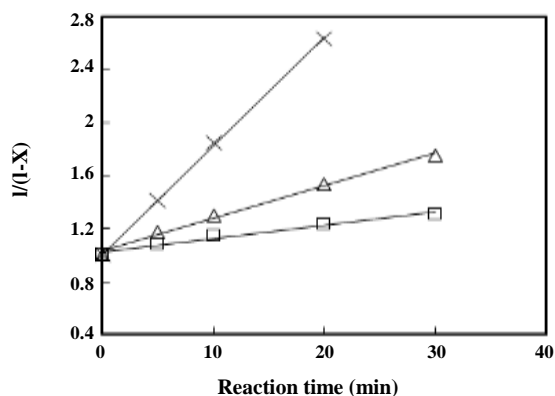
Fig. 3: TAN reduction kinetics plot (Symbols: □, 70ºC; △, 90ºC; ×, 120ºC temperatures).

Fig. 4: Arrhenius plot.

also shows second-order kinetics [18]. Similarly, kinetics of the esterification process of NAs in Colombian heavy crude oil using methanol with no catalyst addition follows second order kinetics [12]. To discern the reaction order between NAs and SubC-MeOH, a plot of (1/1-X), where X denotes the fraction of TAN reduction and 1-X indicates the fraction of TAN of the reaction products, versus reaction time (t, min) is plotted [Fig. 3]. At zero reaction time, the TAN reduction value was close to zero, and TAN value was the initial TAN value. At this condition, the value of (1/1-X) was 1 fraction^{-1}. Each set of data gives a straight line obtained with the least square method, that passes almost exactly through the initial TAN value; this indicates second-order kinetics with respect to TAN removal as it follows the second-order kinetic equation, $(1/1-X=1/(1-X)_0 +kt)$, where k is rate constant in concentration^{-1}time^{-1}. Reaction kinetics analyses of this study were tested and evaluated to a maximum of 62% TAN removal as kinetics data were more compatible with second-order kinetics at this extent [19]. From the slope of the straight lines of Fig. 3, the respective rate constant was determined, and an Arrhenius-type temperature dependency acidity removal rate constant plot was then plotted (Fig. 4). By exploring this plot, activation energy and pre-exponential factor of the said reaction were discovered with respective values of 11.27 kcal/mol and 2491.54 fraction^{-1} s^{-1}. Thus the Arrhenius equation can be rewritten as:

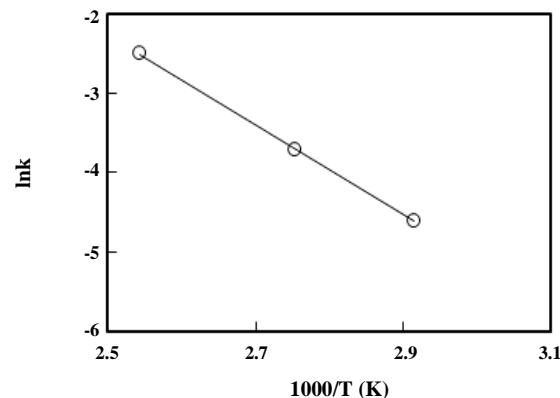$$k_{ubC-MeOH} = 2491.54e^{\frac{-11.27}{RT}} \qquad (3)$$

The activation energy for the reaction between SC-MeOH and NAs is 5.78 kcal/mol [15]. *Wang et al.* in 2006 [17] obtained activation energy of 36.74 kcal/mol and 24.89 kcal/mol for esterification reaction between methanol and NA with 1wt.% SnO catalyst and without catalyst respectively. In addition, the activation energy for the esterification reaction of NAs in Colombian heavy crude oil and methanol at temperatures of 150-250ºC is 17.27 kcal/mol [12]. Thus, SubC-MeOH was found to require higher energy than SC-MeOH but lower energy than the alternative methods presented by *Wang et al.* and *Quiroga-Becerra et al.* The methanol in this reaction behaved not only as reaction medium but also as the reactant.

CONCLUSIONS

The ability of SubC-MeOH on TAN to reduce NA was explored in this study. TAN reduction was affected by the reaction temperature, MPP, and treatment time, and increased with increasing reaction temperature, MPP, and residence time. SubC-MeOH reduced approximately 74.20% TAN of NAs at a temperature of 120ºC, a MPP of 1 MPa, and reaction time of 60 min. The kinetics of TAN reduction of NAs using SubC-MeOH without the addition of catalyst at specified reaction conditions was adjusted to a second-order rate law with respect to the TAN reduction of NAs. The calculated activation energy of the reaction is 11.27 kcal/mol.

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