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Short communication

Reduction of total acid number (TAN) of naphthenic acid (NA) using supercritical water for reducing corrosion problems of oil refineries

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ABSTRACT

Naphthenic acid (NA) are present in crude oil and lead to corrosion problems within the oil refineries. The objective of this study is to reduce total acid number (TAN) from NA in an environmentally benign way, suppressing the solid deposition using supercritical water (SCW). The reaction was carried out in an 8.8 mL batch reactor fabricated from Hastelloy C-276 with respective design temperature and pressure of 500 °C and 50 MPa. The ability of SCW to reduce TAN was explored at temperatures from 400 to 490 °C and water partial pressures (WPPs) from 0 to 45 MPa. Experimental results revealed that TAN removal was 83% at a temperature of 490 °C, WPP of 45 MPa and reaction time of 90 min. The TAN removal followed first order kinetics, with Arrhenius parameters of activation energy 66 ± 4 kJ/mol and a pre-exponential factor $(1.4 \pm 0.2) \times 10^5\ s^{-1}$. Solid deposition was drastically reduced at WPP of 45 MPa. These results suggest that SCW is capable of reduction of TAN from NA with no use of catalyst or additives.

1. Introduction

Acidity is one of the most challenging properties of crude oils. Naphthenic acid (NA), also known as petroleum acids, are an important group of trace organic pollutants predominantly comprising saturated aliphatic and alicyclic carboxylic acids [1]. The presence of these acids in crude oil in greater or lesser amounts lead to multiple problems: they are corrosive [2], tend to cause equipment failures, lead to high maintenance costs and more frequent turnarounds than would otherwise be necessary, reduce product quality, and cause environment disposal problems [3,4]. A significant amount of literature exists that deal with NA removal by conversion or absorption. These traditional methods have particular drawbacks making the process non-profitable that are given elsewhere [3,5].

Water's critical point is a temperature of 374 °C and a pressure of 22.1 MPa. Above these conditions, it becomes supercritical, where phase boundaries between liquid and gas disappear. Supercritical water (SCW) has various uncommon properties which differentiate it from subcritical water; SCW has very high solubility toward organic compounds and infinite miscibility with gases. SCW also acts as a hydrogen donor [6], and water molecules often take part as collision partners [7]. SCW has shown itself capable of removing nickel from nickel tetraphenylporphine, a model compound of heavy oil [8]. This study reports on the reduction of TAN from NAs through the reacting NA with SCW at temperature ranges of 400–490 °C and at water partial pressure (WPP) of 30–45 MPa in the absence of catalysts and additives.

2. Experimental section

Experiments were performed using an 8.8 mL batch reactor fabricated from Hastelloy C-276. The reactor was designed and tested by AKICO (Tokyo, Japan) for a maximum temperature of 500 °C and maximum pressure of 50 MPa. NA, having a boiling point of 160–198 °C (6 mm Hg), a density of 0.94–0.98 g/mL (20 °C), was obtained from Wako Pure Chemical Industries Ltd., and used without further treatment. NA is basically a blend of carboxylic acids. MALDI TOF/MS analyses revealed that molecular weight of NA vary from 50 to well over 600. The following chemicals were also used, all also supplied by Wako: 2-propanol (anhydrous, 99.50%), toluene (99.50%), phenolphthalein (indicator grade), and potassium hydroxide (KOH). Approximately 0.60 g of NA and 0–3.02 mL of distilled water were loaded to the batch-type reactor for SCW reactions. Detail experimental procedure is given elsewhere [8].

2.1. Analysis

Mahajan et al. [9] showed that ASTM D 974 is a good method for evaluating the acid number of petroleum oils. This method was undertaken in this study, but phenolphthalein was used as indicator

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instead of p-naphtholbenzein. The solvent was prepared by mixing toluene with 2-propanol in 1:1 ratios. About 0.05 mol/L standard potassium hydroxide solution was prepared before analyzing the samples every day. Definitions of the terms used in this study are given below.

Acidity of NA is measured through titration with potassium hydroxide to estimate TAN as milligram of KOH required titrating 1 g of NA. The TAN was calculated as follows:

$$TAN\left(\frac{\text{mg KOH}}{\text{g NA}}\right) = \left[\frac{V_{KOH} \times N_{KOH} \times CF}{W_{NA,o}}\right] \quad (1)$$

where V_{KOH} = volume of KOH in mL, N_{KOH} = concentration of KOH in mmol/mL, $W_{NA,o}$ = weight of loaded NA in g and CF = conversion factor = 56.10 mg/mmol.

The TAN reduction, X, defined as follows, was used to evaluate the extent of reduction of acidity of NA.

$$TAN\ reduction\ (\%) = \frac{TAN_o - TAN_t}{TAN_o} \times 100 \quad (2)$$

where TAN_0 = initial TAN in loaded NA and TAN_t = TAN at reaction time t.

The portion of reaction mixture that does not dissolve in solvent, mixture of toluene and 2-propanol in equal ratios, is called solid. The yield of solid is defined as:

$$Yield\ of\ solid\ (\%) = \frac{W_s}{W_{o,NA}} \times 100 \quad (3)$$

where W_s = weight of solid in gram and $W_{o,NA}$ = weight of NA in gram loaded.

Molecular-weight distribution of the samples were done by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI TOF/MS), made by Bruker Daltonics, using autoflex version 3.3.1. In addition, low-molecular-weight components in the reaction liquid mixture were identified by Gas Chromatography–Mass Spectrometry (GC/MS) (Hewlett Packard, HP 6890 Series).

All experiments were conducted three times. The error margin of the acquired data is less than 3%, with more than 95% confidence.

3. Results and discussion

3.1. TAN reduction and solid deposition

The initial TAN of NA was 241 ± 2 (mg of KOH/g of NA). Fig. 1 shows the effect of reaction temperatures, reaction times and WPPs on the TAN removal rate. TAN removal is very temperature sensitive and increases with reaction time. Experimental results revealed that only 6.50% TAN was removed at a temperature of 400 °C, WPP of 45 MPa, and reaction time of 90 min, but this value increased to 83% at a temperature of 490 °C. The solid samples were not analyzed due to insufficient amount of solid. But MALDI TOF/MS analysis of liquid samples revealed that there was a tendency to produce high-molecular-weight compounds. So, this solid was nothing but lean hydrogen content high-molecular-weight hydrocarbons that is not dissolve in organic solvent. No solid deposition was observed at temperatures of 400–450 °C; solid formation indicates loss of valuable compounds and thus potential revenue. Conversely, solid deposition was detected at a temperature of 490 °C, but depended on WPP and reaction time (Fig. 2). Though TAN removal was high in treatment without water, a significant amount of solid was deposited: 4.25% solid was deposited after a reaction time of 90 min when water was not loaded. However, this value fell to 2.46% and 0.20% at WPPs of 30 MPa and 45 MPa, respectively, indicating that solid deposition is drastically reduced at a WPP of 45 MPa. In addition, a high WPP improves TAN reduction slightly compare to a low WPP. Gaseous products that are not quantified in this study were detected in the presence of water and at a temperature of 490 °C. The gases produced are primarily water vapor, CO_2 and CO by virtue of the decomposition of the NAs [3,5]. Zhang et al. [10] showed that the gaseous products obtained from the decomposition of formic acid in SCW were composed of H_2 and CO_2 as major components, and CO as a minor one. These results indicate that a high temperature is suitable for reducing TAN of NA and that a WPP of 45 MPa is optimal for reduction of solid deposition, making the process profitable.

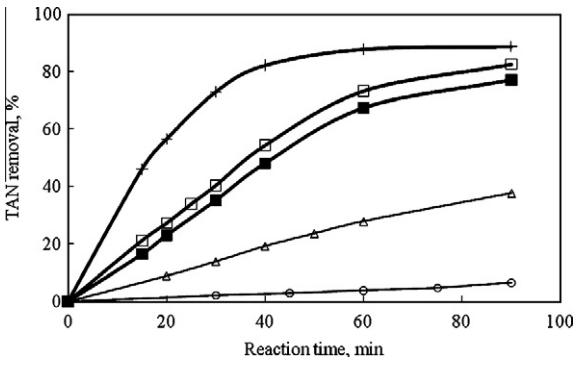

Fig. 1. Variation of TAN as a function of reaction times, temperatures and WPPs (symbols: ○, 400 °C, 45 MPa; △, 450 °C, 45 MPa; □, 490 °C, 45 MPa; ■, 490 °C, 30 MPa; +, 490 °C, no water).

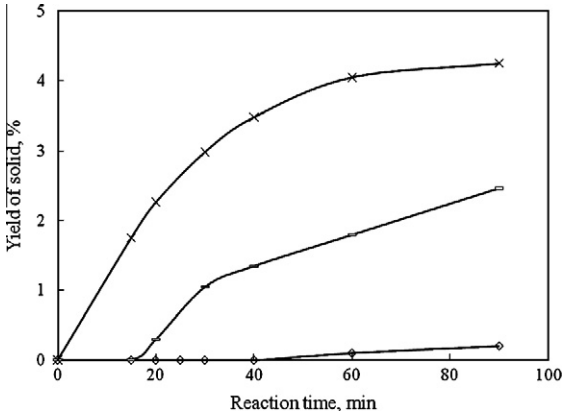

Fig. 2. Solid deposition as a function of reaction times and WPPs at a temperature of 490 °C (symbols: ×, treatment without water; –, WPP of 30 MPa; ◇, WPP of 45 MPa).

3.2. Kinetics and TAN reduction mechanism

The global reaction order for TAN removal was determined by conducting a series of experiments at temperatures of 400, 450 and 490 °C under a constant WPP of 45 MPa; plots of $-\ln(1-X)$ versus reaction time, t, were then constructed as shown in Fig. 3a. The straight lines which were obtained with the least squares method passed almost exactly through the origin, indicating first order kinetics. Fig. 3b shows the Arrhenius type dependency of the NA removal rates on temperature. The activation energy and pre-exponential factor calculated on the basis of the Arrhenius equation were 66 ± 4 kJ/mol and $(1.4 \pm 0.2) \times 10^5\ s^{-1}$ respectively.

Though GC/MS analysis does not cover all components present in the samples, it can detect many hydrocarbons that were not present in NA. MALDI TOF/MS analysis was an evidence to form high-molecular-weight hydrocarbons. These hydrocarbons are formed through decarboxylation of NA followed by long-chain