



Full Length Article

A non-catalytic, supercritical methanol route for effective deacidification of naphthenic acids



Muhammad Kashif Khan ^a, Rizki Insyani ^b, Jinkee Lee ^a, Minhoe Yi ^{c,d}, Jae Woo Lee ^d, Jaehoon Kim ^{a,b,*}

^a School of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^b SKKU Advanced Institute of Nano Technology (SAINT), 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea

^c SK Innovation, 325, Exporo, Yuseong-gu, Daejeon 305-712, Republic of Korea

^d Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

HIGHLIGHTS

- Naphthenic acids (NAs) and HAC's were deacidified using sc-methanol.
- TAN reduction of NA and HAC was achieved up to 96.9 and 94.0% at 400 °C.
- Esterification was major reaction pathway for deacidification.
- Recalcitrant NAs were branched hydrocarbons located near carboxylic acid group.

ARTICLE INFO

Article history:

Received 9 February 2016

Received in revised form 2 June 2016

Accepted 4 June 2016

Available online 11 June 2016

Keywords:

Naphthenic acids

Total acid number

High acid crudes

Supercritical methanol

Esterification

ABSTRACT

High acid crudes contain large amounts of naphthenic acids (NAs), which lead to severe corrosion in oil refinery equipment and serious environmental problems. The goal of this study is to develop a non-catalytic supercritical methanol (scMeOH) route for effective deacidification of NA mixtures and high acid crudes (Laguna and Bachaquero-13). Various reaction parameters, including temperature, pressure, reaction time, and NA-to-methanol ratio, are explored to find effective reaction conditions for reducing the total acid number (TAN) of the mixtures. Almost complete TAN reduction of naphthenic acid (96.9%) is achieved at 400 °C, 10 MPa, and 3 h. The reaction in scMeOH at 400 °C, 30 MPa and 1 h is effective in the TAN reaction of high acid crudes (93.6–94.0%). The chemical composition of the liquid products obtained under the different reaction conditions, analyzed using gas chromatography-mass spectroscopy, show that esters are the most abundant species, indicating that esterification with scMeOH is the major reaction pathway. The most recalcitrant NA species, which remained after the reaction, are found to be 2-ethyl-2,3,3-trimethyl-butanoic acid and 2,3-dimethyl-2-(1-methylethyl)-butanoic acid. This is attributed to the branched hydrocarbons located near the carboxylic acid groups, which hinder the access of methanol molecules.

Crown Copyright © 2016 Published by Elsevier Ltd. All rights reserved.

1. Introduction

The depletion of conventional oil reserves has increased the importance and marketability of unconventional oils, such as high acid crudes (HACs) and heavy crudes. These unconventional crude oils typically exhibit high densities, viscosities, total acid numbers (TANs), and carbon to hydrogen ratios. The processing of HACs in existing refinery infrastructure causes serious corrosion problems

in various refinery facilities, including furnaces, atmospheric/vacuum distillation towers, and pipelines [1,2]. The acidity of HACs is caused by naturally occurring polar monobasic carboxylic acids, known as naphthenic acids (NAs) [3]. NAs are groups of indigenous interfacially active molecules, consisting mainly of alkyl-substituted cycloaliphatic carboxylic acids together with acyclic aliphatic acids and trace amounts of olefinic, aromatic, hydroxyl, and dibasic acids [4]. NAs cause the formation of highly stable oil-water emulsions and increase the toxicity of underground and fresh water bodies [5]. Furthermore, NAs lead to foaming in desalters and other refinery units, as well as carrying alkali metal cations (e.g., Ca⁺, Na⁺) through the refinery process, which can

* Corresponding author at: School of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, Gyeong Gi-Do 16419, Republic of Korea.

E-mail address: jaehoonkim@skku.edu (J. Kim).

cause severe deactivation of the catalysts that are used in the downstream sector of petroleum refineries [6]. For these reasons, the removal of intrinsic NAs from HACs is of paramount importance.

One of the most widely used industrial processing methods for treatment of HACs consists of blending them with conventional, low TAN crude oils to mitigate the corrosion of refinery equipment; however the volume of HACs that can be processed using the blending method is extremely limited. Another industrial method is neutralization of NAs with caustic washing, but the formation of highly stable emulsions that are very difficult to breakdown in the subsequent processing as well as the generation of huge amounts of waste water are the major drawbacks. Therefore, various alternative chemical methods (e.g., esterification [7,8], catalytic decarboxylation [9], use of ionic liquids [6], catalytic decomposition [10], and advanced oxidation [11]) and physical methods (e.g., solvent extraction [12], ammonia treatment [13], adsorption [14,15], and membrane separation [16]) have been explored for the removal or separation of NAs. Although many chemical conversion methods have demonstrated effective reduction of NAs to acceptable levels, they typically involve the use of heterogeneous catalysts, molecular hydrogen and expensive chemicals. Additionally, the frequent regeneration of catalysts deactivated due to the presence of various impurities, and the high cost of this process needs to be addressed. Physical separation methods can be cost-effective alternatives to chemical methods, but the efficiency of NA removal is relatively low, and both large amounts of absorbents and separation of NAs using organic solvents after adsorption are required. Therefore, there is still significant effort being made to develop simpler, cheaper, and more effective NA removal techniques to maximize the utilization of HACs in existing refineries.

Over the last few decades, supercritical methanol (scMeOH, critical temperature $T_c = 239.6$ °C, critical pressure $P_c = 8.1$ MPa) has been widely investigated as an effective reactant in the transesterification of natural triglycerides for the production of fatty acid methyl esters (FAMES) to be used as biodiesel [17]. In addition, the esterification of free fatty acids such as oleic acid in scMeOH has been investigated in order to understand their kinetic and thermal decomposition behaviors [18]. From the previous (trans)esterification studies in scMeOH, it is logical to think that non-catalytic esterification of NAs in scMeOH could be a promising route to the deacidification of NAs [19]. In this study, the influence of process parameters on NA conversion was investigated under a wide range of reaction conditions to provide a comprehensive understanding of scMeOH-based NA conversion behaviors. The process parameters examined in this study included temperature (300–400 °C), pressure (10–30 MPa), reaction time (1–3 h), and NA-to-methanol ratio (1:5–1:20). The liquid products were characterized in detail using gas chromatography-time-of-flight/mass spectroscopy (GC-TOF/MS) to understand their chemical composition and determine the NA species that were most resistant to the reaction.

2. Experimental

2.1. Materials

A commercially available NA mixture, consisting of a viscous liquid mixture of various carboxylic acids with a boiling point range of 106.4–333.6 °C at 0.1 MPa, was purchased from Sigma-Aldrich (MO, USA, product number: 70,340; lot number: BCBP2363) and used without further treatment. Two types of HACs (Laguna and Bachquero-13) were obtained from Venezuela. Methanol (HPLC grade), 2-propanol (HPLC grade), and dichloro-

methane (HPLC grade) were purchased from Honeywell Burdick & Jackson® (PA, USA). 0.1 N KOH in 2-propanol, Hydranal® composite 5.0 for the Karl Fischer titration, toluene (99.5%), and deionized water were purchased from Sigma-Aldrich. High purity H₂ (99.99%), He (99.99%), and N₂ (99.99%), which were used for gas chromatography (GC) and purging the reactor system, were purchased from JC Gas Company (South Korea).

2.2. Reaction in scMeOH

A series of NA mixture conversions in scMeOH were performed in a custom-built batch reactor made from SUS 316 stainless steel with an inner volume of 140 mL. The reactor was equipped with a magnetically driven stirrer and all reactions were carried out at stirring rate of 500 rpm (maximum 1500 rpm). Two heating systems, one consisting of cartridge heaters inserted inside the reactor wall and the other of an electric furnace (used to heat the reactor externally), were used to quickly reach the experimental temperature. In a typical experiment, the desired amounts of the NA mixture and methanol were loaded in the reactor. The partial pressure of methanol was controlled by calculating the amount of methanol required to reach the desired experimental pressure using the Peng-Robinson-Gasem equation of state (PRG-EOS) under the specific temperature and constant reactor volume conditions to be used. This precise volume of methanol was then loaded into the reactor. The reactor was sealed and purged with N₂ gas three times to replace the air with the inert medium, and then pressurized with N₂ at 1.0 MPa prior to heating. The reactor temperature was then increased to the experimental temperature of between 300 and 400 °C using the two heating systems at an average heating rate of 15 °C min⁻¹. After maintaining the temperature and pressure for the specified reaction time (0–3 h), the heating was stopped and the reactor was quickly cooled to 100 °C by quenching in water, and then to room temperature using an electric fan. The time required for temperature ramping (about 25 min) and cooling (8–10 min for water quenching and about 50 min for air cooling) was not included in the reaction time (see Fig. S1 for representative temperature and pressure profiles during the reaction). After reaching ambient temperature, the volume of gas produced during the reaction was measured using a wet gas meter (W-NK-2 type, Shinagawa Corporation, Japan) and collected in 1 L Tedlar® gas sampling bag for analysis. The liquid products in the reactor were collected and analyzed using TAN measurement and GC-TOF/MS. To determine the effect of pressure on TAN reduction, experiments were conducted at different pressures (10 and 30 MPa), which were reached by controlling the amount of methanol in the reaction mixture while keeping mass ratio of the NA mixture to methanol constant. In case of treating the HACs in scMeOH, the liquid and solid products were collected by rinsing with dichloromethane. After filtering with Whatman filter paper to separate solid residue, the deacidified crude oil was collected by removing dichloromethane at 40 °C at 0.06 MPa vacuum pressure for 30 min. TAN values of the HACs and the deacidified crude oil were to find out the efficiency of TAN reduction.

2.3. Product analysis

The gases collected after reaction were analyzed by GC to catalogue all the gaseous products, which included H₂, CO₂, CO, CH₄, C₂H₆, C₂H₄, and C₃–C₅ compounds. The GC used was a PerkinElmer Clarus 580 GC-Model Arnel 1115PPC Refinery Gas Analyzer (RGA) (PerkinElmer, CT, USA) with two different detectors: a thermal conductivity detector (TCD) and a flame ionization detector (FID), the latter of which was specifically used to measure hydrocarbon gas samples. The GC was equipped with nine different columns, including seven packed columns and two capillary columns. A

Download English Version:

<https://daneshyari.com/en/article/6633524>

Download Persian Version:

<https://daneshyari.com/article/6633524>

[Daneshyari.com](https://daneshyari.com)