



Removal of naphthenic acids from high acid crude via esterification with methanol



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ABSTRACT

Refining of high acid crudes (HACs) is seriously limited by extensive corrosion of refinery equipment due to the presence of intrinsic naphthenic acids (NAs). Herein, in the absence of a catalyst or external hydrogen, effective removal of the NAs contained in HACs was achieved using methanol at moderate temperature and moderate pressure. Several process variables, including the temperature, crude concentration, and reaction time are explored to optimize the removal of NAs from HACs. At 250 °C, 6.4 MPa, and 33.3 wt% crude, a very low total acid number (TAN) of 0.08 mg-KOH/g-oil (96.9% reduction efficiency) with a high oil yield (95 wt%) is achieved. During the reduction of the TAN using methanol, some fraction of the resins and asphaltenes in the crude oil crack to form low-molecular-weight aromatic compounds. Compared to deacidification using methanol, pyrolysis (without methanol) results in a much lower TAN reduction efficiency (38.6%). The major deacidification mechanism using methanol is esterification, while that of pyrolysis (without methanol) is decarboxylation.

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1. Introduction

In recent years, technological advancements and population growth have led to a steep increase in the global energy demand. Current conventional crude oil reserves are not sufficient to sustain the increasing energy demand because of the rapid depletion of oil resources [1]. Unconventional crudes (heavy crudes, high acid crudes, bitumen, oil/tar sand, and shale oil), which account for >70% of the total crude oil reserves, are considered to be the most practical alternatives to conventional crude oils. Despite their abundance, unconventional crude oils possess several operational and environmental drawbacks that make safe and cost-effective utilization of these crudes in existing refineries difficult [2]. For example, unconventional crude oils are highly viscous (up to 10⁶ cP), dense (~1050 kg m⁻³), highly acidic (total acid number (TAN) >0.5 mg KOH/g-oil), and enriched with metallic (e.g., Ni, Ca, Fe, Al, V) and non-metallic (e.g., Si, N, S, clays, minerals) impurities, and they contain high amounts of polar fractions (e.g., asphaltenes and resins) [3].

High acid crudes (HACs), which are much cheaper than conventional crude oil and are consumed in quantities of >9 million barrels/day nowadays [4], contain a substantial amount of naphthenic acids (NAs).

NAs are naturally-existing, complex aliphatic, monocyclic, and polycyclic carboxylic acids. The inherent acidity of HACs engenders severe environmental and economic problems. Direct processing of HACs in existing refineries causes serious adverse effects on various units such as the desalter, distillation unit, pipelines, and catalytic reactors. These effects include erosion, corrosion, and catalyst deactivation, which cause serious operational problems and lead to reduced refinery margins [5]. Moreover, NAs, which are amphiphilic in nature, facilitate the formation of recalcitrant petroleum emulsions during recovery of the crude oil from unconventional oil fields using steam as well as during the desalting operation [6]. For example, the water used for the processing of oil sand is highly toxic because of exposure to the hazardous NAs, and this leads to severe environmental, aquatic, and public health concerns [7,8]. Therefore, from the economic and environmental perspectives, it is highly desirable to develop an effective approach for the removal of NAs from HACs.

There are two main practical approaches for reducing the TAN of HACs. One is the blending of HACs with conventional crude oils with low acidity to diminish the corrosive and toxic impact of NAs. However, the content of HACs in the blended oil is typically very low (around 2–3%) and the NAs are not completely removed from the crude oil mixture. Therefore, some low-boiling-point NAs may be present in the light fraction emitted from the distillation unit, and high-boiling-point NAs may accumulate in the heavy fractions or residues. Caustic washing is another practical treatment method for neutralizing acidic HACs, but the production of a huge amount of wastewater is a major limitation. In

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addition to the above practical methods, various approaches have been proposed to reduce the TAN; for example, treatment using ionic liquids [9], catalytic esterification [10,11], catalytic decarboxylation [12–14], treatment with ammonia solution [15], microwave irradiation [16], physical adsorption [17], and solvent extraction [18]. Nevertheless, these processes have certain drawbacks that should be addressed carefully prior to practical implementation. For example, although the TAN can be reduced by the catalytic, ionic liquid, or ammonia route, the use of expensive chemicals, heterogeneous catalysts, and hydrogen makes these methods economically unfavorable. Catalytic routes have been explored for direct reduction of the TAN of HACs using alkali and alkaline earth metal oxides [12,19] and hydrotalcite [11], but a high-temperature operation ($>300\text{ }^{\circ}\text{C}$) was necessary for effective TAN reduction, and loss of catalyst activity caused by coking was observed. In addition, metallic and non-metallic impurities present in resins and asphaltenes tend to poison catalysts, thereby reducing the TAN reduction activity over time. Solvent extraction and ionic liquids require a large amount of solvent and suffer from solvent recovery problems. Thermal decomposition and hydrogenation are very energy-intensive because of the high-temperature operation ($400\text{--}500\text{ }^{\circ}\text{C}$). Therefore, it is imperative to develop a simple, effective, environmentally-friendly, and economically-viable process for reducing the TAN of HACs for ultimate utilization of low-cost HACs in existing petroleum facilities.

In this study, we develop a new approach for effective deacidification of HACs using methanol in a relatively moderate-temperature and moderate-pressure system without using molecular hydrogen and external catalysts. Methanol under high pressure and high temperature conditions, i.e., supercritical methanol (scMeOH; $T_c = 239\text{ }^{\circ}\text{C}$, $P_c = 8.1\text{ MPa}$), was previously evaluated for reducing the TAN of “neat” NA mixtures [20]. The major mechanism of TAN reduction using scMeOH is esterification of the carboxylic acid group in the NAs to generate the corresponding methyl esters. Although effective TAN reduction was achieved with scMeOH, the high-temperature ($350\text{--}400\text{ }^{\circ}\text{C}$) and high-pressure ($>10\text{ MPa}$) operation would be economically unfavorable on the industrial scale [20]. The low reaction temperature of $300\text{ }^{\circ}\text{C}$ resulted in a low TAN reduction efficiency of $<60\%$ even after 3 h [21]. In contrast, direct reduction of the TAN of “HACs” using methanol under subcritical conditions has not previously been explored in detail. Previously, we showed that scMeOH at $400\text{ }^{\circ}\text{C}$ and 30 MPa could effectively reduce the TAN of HACs, but a considerable loss of crude oil resulted during the TAN reduction by the formation of coke ($15\text{--}20\text{ wt}\%$) [21]; this is undesirable in terms of processing productivity and economics. Therefore, it is highly desirable to develop a technique that could achieve high degree of TAN reduction of HACs, and the same time, suppress coke formation under reduced temperatures and reduced pressures. In this study, we achieved high amount of liquid crude oil recovery ($95\text{--}98\text{ wt}\%$) with negligible coke formation and gasification ($\leq 0.3\text{ wt}\%$) along with high degree of TAN reduction. The other novel aspects of current study is the non-catalytic moderate-temperature and moderate-pressure TAN reduction approach could allow us to use HACs up to 50% with conventional crude oil, which has never been reported in literature. Previously, much higher TAN reduction efficiency has never been achieved at such a moderate temperature and pressure ($\leq 250\text{ }^{\circ}\text{C}$, $\leq 6.5\text{ MPa}$) condition without using catalysts [10,11,19]. Finally, we present quantitative TAN reduction mechanisms in methanol in terms of decarboxylation and esterification with complete decarboxylation calculations based on CO_2 production from reaction mixtures.

Herein, utilization of methanol at relatively moderate temperatures ($\leq 250\text{ }^{\circ}\text{C}$) and moderate pressures ($\leq 6.5\text{ MPa}$) is explored for effective reduction of the TAN of HACs. A TAN below 0.08 mg KOH/g-oil and a TAN reduction efficiency of 96.9% could be achieved under conditions of $250\text{ }^{\circ}\text{C}$, 6.4 MPa , and 90 min reaction time. The degree of TAN reduction observed in this study is quite comparable to those of catalytic TAN reduction, as listed in Table S1. The TAN of the deacidified oil is adequate for current refineries without modification. The effect of the process parameters (temperature, reaction time, and concentration) on reduction

of the TAN is discussed in depth. The liquid and gaseous products are analyzed in detail using gas chromatography-time of flight/mass spectrometry (GC-TOF/MS) and refinery gas analyzer-gas chromatography (RGA-GC) to gain insight into the mechanism of TAN reduction. The content of saturates, aromatics, resins, and asphaltene (SARA) in the raw crude mixture and deacidified oil are analyzed to understand the structural transformation of the heavy fractions of HAC during deacidification. The products from the moderate-temperature methanol reaction are compared with those from pyrolysis and supercritical methanol treatment for comparison of the TAN reduction efficiency and to understand the main deacidification mechanisms.

2. Experimental

2.1. Materials

Unconventional HAC (Laguna, Venezuela) and conventional crude (Kuwait) were provided by SK Innovation (South Korea). HPLC grade dichloromethane (DCM), methanol, and 2-propanol were purchased from Honeywell Burdick & Jackson® (USA). For Karl Fischer titration, 0.1 N KOH in 2-propanol, Hydranal® composite 5.0, and toluene (99.5%) were purchased from Sigma-Aldrich (USA). Distilled and deionized water was prepared by using an AQUAMax™-Basic 360 water purification system (Younglin Instrument Co., Ltd., South Korea). High purity He (99.99%), H_2 (99.99%), and N_2 (99.99%) were obtained from JC Gas Company (South Korea).

2.2. Reaction in methanol

A mixture of HAC from Laguna (TAN = 5.05 mg KOH/g-oil) and conventional crude oil (Kuwait, TAN = 0.09 mg KOH/g-oil) was prepared by mixing equal amounts of the two crudes on a weight basis. The TAN of the oil mixture was 2.57 mg KOH/g-oil . A schematic of the reaction and separation protocols is shown in Fig. S1. The reaction between the crude oil mixture and methanol was conducted in a custom-built SUS 316 batch reactor with an inner volume of 140 mL . The reactor was equipped with a magnetically-driven stirrer and all reactions were carried out at a stirring rate of 700 rpm . The detailed reactor assembly and experimental protocol are explained elsewhere [21]. After completion of the reaction, a wet gas meter (W-NK-2 type, Shinagawa Corporation, Japan) was used to measure the volume of gas produced and the gaseous products were stored in 1 L Tedlar® sampling bag for compositional analysis. After the reaction, the reaction mixture was collected by rinsing with DCM. The solid residue, if formed during the deacidification, was separated from the liquid oil product by filtration of the mixture through a Whatman filter paper. The deacidified crude oil was collected by vacuum evaporation of DCM and methanol at $40\text{ }^{\circ}\text{C}$ and -0.08 MPa for 30 min .

The formulas used to calculate the product yields are as follows:

$$\text{Oil yield (wt\%)} = \frac{\text{Weight of oil}}{\text{Weight of crude oil}} \times 100\% \quad (1)$$

$$\text{Solid residue yield (wt\%)} = \frac{\text{Weight of solid residue}}{\text{Weight of crude oil}} \times 100\% \quad (2)$$

$$\text{Gas yield (wt\%)} = \frac{\text{Weight of gas produced}}{\text{Weight of crude oil}} \times 100\% \quad (3)$$

2.3. Product analysis

The gases collected after the reaction were analyzed using GC to quantify all of the gaseous products, which included H_2 , CO_2 , CO , CH_4 , C_2H_6 , C_2H_4 , and $\text{C}_3\text{--C}_6+$ compounds. A Clarus 580 GC-Model Arnel 1115PPC Refinery Gas Analyzer (RGA) (PerkinElmer, USA) was used

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