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Catalytic decarboxylation of naphthenic acids in crude oils

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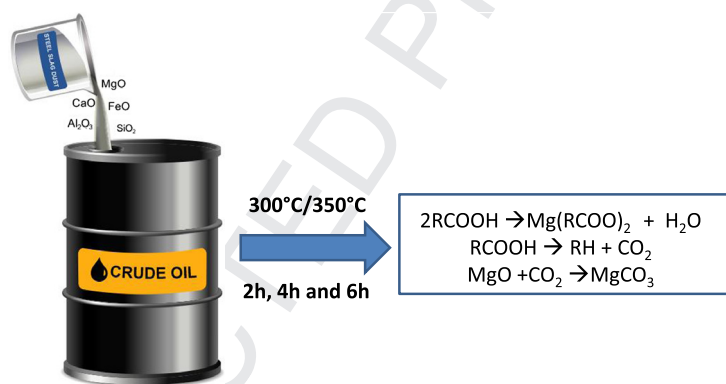
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HIGHLIGHTS

- A steel slag catalyst was evaluated to remove naphthenic acids present in crude oils.
- A high-acidity crude oil (TAN = 4.79 mg KOH g⁻¹ and S = 1.022 wt%) was submitted to thermo-catalytic process.
- The MgO contributed effectively to promote the thermo-catalytic decarboxylation of naphthenic acid species.
- A reduction of TAN of 43.50% (4.79 → 1.89 mg KOH g⁻¹) was observed at 350 °C for 4 h.
- ESI(–)FT-ICR MS data confirmed an increase in the DBE values from 1–5 to 5–18.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 25 February 2015
Received in revised form 23 April 2015
Accepted 5 May 2015
Available online xxxx

Keywords:

Naphthenic corrosion
TAN
ESI(–)FT-ICR MS
Catalytic decarboxylation

ABSTRACT

Naphthenic acids are recognized as the main corrosive species in acidic crude oils, although they represent less than 3 wt%. Alternative methods have been developed in an attempt to remove naphthenic acids from the oil, however, their implementation in petrochemical industry still represents a challenge. Herein, a sub-product of the steel industry, steel slag, is evaluated as an economic alternative catalyst and environmentally feasible to remove naphthenic acids present in crude oils. A high-acidity crude oil (TAN = 4.79 mg KOH g⁻¹ and S = 1.022 wt%) was submitted to thermo-catalytic process at 300 and 350 °C during 2, 4 and 6 h and its degradation products were monitored by negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron mass spectrometry (FT-ICR MS), total acid number (TAN) and total sulfur. The main crystalline phases detected by X-ray diffractometry in the catalyst were calcite (CaCO₃), silica (SiO₂) and magnesia (MgO). Among them, the MgO contributes effectively to promote the thermo-catalytic decarboxylation of naphthenic acid species, with a TAN reduction of 43.50% (4.79 → 1.89 mg KOH g⁻¹) from the original oil to the degraded oil obtained after treatment at 350 °C

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for 4 h. Acid species with lower pK_a values were selectively removed with the ESI(-)FT-ICR MS data confirming an increase in the DBE values from 1–5 to 5–18 for O_2 class. Therefore, the catalyst selectively promoted the removal of naphthenic acids via (i) neutralization reaction; (ii) cracking reaction and (iii) $MgCO_3$ formation from CO_2 molecules produced by a previous thermal decarboxylation reaction.

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1. Introduction

Corrosion problems in operating processes and petroleum refining concerning naphthenic acids (NAs) in crude oils have been reported since the early twentieth century. Since then, the search for solutions to overcome these problems has become a constant challenge for the petrochemical industry [1,2].

Naphthenic acid are carboxylic acids characterized by the presence of a monocarboxylic group attached to an aliphatic group and may be represented by the general formula $R-(CH_2)_n-COOH$, where R is one or more cyclopentane or cyclohexane rings. Naphthenic acids are the main responsible for a great number of operating problems in the petroleum refining processes, such as emulsions stabilizers, naphthenate deposition, gum formation and corrosion problems [3].

Alternative analytical methods have been developed by an attempt to remove naphthenic acids from the oil. In general, these methods can be addressed in two ways. The first involves removal of the carboxyl group by esterification and hydrogenation reactions or thermal decomposition whereas the second involves the separation of the naphthenic acids from the oil by means of liquid–liquid extractions (using an alkaline solution with alcohol and ammonia), adsorption, membrane separation, and electrostatic separation [4].

In 1960, Earl [5] developed an extraction process for naphthenic acids based on solvent extraction and subsequent distillation in the presence of alkaline materials. In the 90s, Gaikar and Maiti [6] developed an extraction method for naphthenic acids through absorption using ion exchange resins. Blum et al. [7] studied the viscosity reduction and the naphthenic acid removal by thermal decomposition processes; however, the naphthenic acid degradation mechanism was not fully explored. In the same year, Smith et al. monitored the effect of thermal treatment on the naphthenic acids from vacuum residues by negative-ion electrospray ionization (ESI) Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) [8]. It was observed that the acidity of the vacuum residue decreased as the heating temperature was increased, as indicated by both reduction in O_2 class intensity and total acid number (TAN). In 2011 Mandal et al. [9] studied the application of supercritical water to reduce TAN, showing an efficiency of approximately 83% at 490 °C.

Most analytical methods developed for extraction or removal of naphthenic acids from crude oil samples requires a large investment due to high energy consumption; thus, the implementation of these methods in the petrochemical industry remains a challenge.

Recently, researches on decomposing naphthenic acid species have focused especially on the development of new catalysts with the aim of maximizing the reaction rate using lower temperatures, thus reducing costs. In 2006, Zhang et al. [10] showed that the catalytic decarboxylation using calcium oxide or magnesium oxide is an effective method to remove naphthenic acids at low temperatures. In 2009 Ding et al. [11] studied the use of alkali metal oxides and zinc oxide as catalysts for the naphthenic acids removal from heavy crude oil feeds. Depending on the catalyst employed, the thermal degradation process can be followed by decarboxylation, neutralization or thermal cracking. In 2014, Wang et al. [12] evaluated the naphthenic acids removal from crude oil applying the Mg–Al hydrotalcite/ $\gamma-Al_2O_3$ as a catalyst. Their results showed a TAN reduction in the crude oils from 2.7 mg KOH g^{-1} to less than 0.5 mg KOH g^{-1} with one-hour treating at 320 °C and 1.013×10^5 Pa.

FT-ICR MS offers the highest available mass resolution, mass resolving power, and mass accuracy, which enables the analysis of complex petroleum mixtures on a molecular level [13]. High-resolution MS data have shown that it is possible to discriminate different compounds [14–16] for taking into account the different ionization efficiencies of the crude oil constituents [17]. Accurate mass measurements [18] allow unambiguous elemental composition ($C_cH_hN_nO_oS_s$) assignment, enabling material classification by heteroatom content and the degree of aromaticity [19–21]. Naphthenic acids can be analyzed by ESI(-) coupled to FT-ICR MS, being detected as deprotonated molecules, $[M-H]^-$ [22,23]. Herein, steel slag was used as catalyst to promote the catalytic decarboxylation of naphthenic acids in a sample of crude oil with TAN = 4.79 mg KOH g^{-1} and total sulfur content of 1.02 wt%. Steel slag [24,25] is commercially known as a sub-product generated in large quantities during the steel industrial production and then it can become an economic and environmentally feasible alternative to remove naphthenic acids from crude oil. Steel slag is composed mainly by metal oxides such as FeO, CaO, MgO, Al_2O_3 and SiO_2 , which have decarboxylation activity documented on

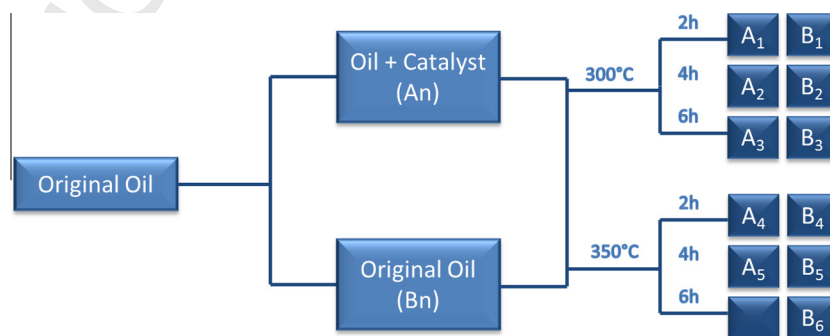


Fig. 1. Scheme of the thermo degradation of the crude oil subjected to treatments at 280, 300 and 350 °C for periods of 2–6 h in the presence (A_n) and absence (B_n) of the steel slag catalyst.

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