Fuel Processing Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Stepwise structural characterization of hydrocarbon compounds and polar components during atmospheric residue hydrotreatment

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ARTICLE INFO

Article history:
Received 24 October 2016
Received in revised form 11 December 2016
Accepted 8 January 2017
Available online xxxx

Keywords:
Hydrotreatment
Atmospheric residue
Polar components
Characterization

ABSTRACT

A continuous fixed-bed micro-reactor was adopted to conduct a hydrotreatment experiment on the atmospheric residue obtained from Saudi Arabia. The feedstock and hydrotreated liquid products were subjected to high-temperature gas chromatography to undertake simulated distillation analysis, and to gel permeation chromatography to carry out molecular size investigations. ^{1}H NMR and element analysis were carried out to derive structural parameters. Positive- and negative-ion electrospray ionization Fourier transform-ion cyclotron resonance mass spectrometry was combined with other analytical means to explore the stepwise structural characterization of polar components (especially the nitrogen (N)-containing compounds) when passing through beds filled with different catalysts during the hydrotreatment process. According to the different numbers of nitrogen, oxygen, and sulfur atoms, N-containing compounds could be divided into N_x, N_xO_y, and N_xS_y class species. The results indicated that hydrotreatment process led to more concentrated distribution of hydrocarbon molecules in the products. The heteroatoms, which accounted for the largest proportion in the feedstock and liquid products, were N_1 class species. During the hydrotreatment process, the relative abundance of N_1, N_2, N_1O_1, N_1O_2, and N_1S_1 class species changed significantly with the progress of hydrotreatment process, however the conversion regularity varied among heteroatomic compounds.

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1. Introduction

The requirement for oil refineries to produce clean oil and ensure clean production has become increasingly challenging due to the reasons that the crude oil has become heavier and poorer in quality (contents of sulfur, nitrogen, and metal impurities have increased), whereas the environmental protection laws and regulations have also become stricter [1–3]. Residue hydrotreatment technology has drawn increasing research attention due to its superiority in addressing the aforementioned issues [4–6]. The technology is mainly used to remove sulfur, nitrogen, and metal impurities from the residue, and to reduce the carbon residue to deliver quality feedstock for downstream catalytic cracking [7–9]. Researchers have employed various means to generalize and summarize the residual hydrotreatment process [10,11]. However, ascertaining the regularity of molecular conversion at molecular level is difficult during the residual hydrotreating process due to the complicated composition of residual oil [12]. With its unsurpassed high resolution, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enables the analysis of complex mixtures on a molecular level [13]. The method has been increasingly applied in analyzing the structure of biological macromolecules [14,15], polymers [16], and oil quality [17–25] because of its high resolution, low limit of detection, high sweep speed, and contributions to the development of tandem mass spectrometry (MS/MS) [26–30].

Positive-ion and negative-ion ESI FT-ICR MS can ionize and detect basic and neutral N-containing compounds with high selectivity due to the reason that hydrocarbons cannot be ionized in ESI source [31–38]. Therefore, ESI FT-ICR MS is adopted to analyze the components of polar compounds (especially N-containing compounds) in feedstock and hydrotreating products [32,39–44].

In the present study, atmospheric residue obtained from Saudi Arabia (SZAR) was used as the feedstock. Continuous fixed-bed hydrotreating micro-reactors were filled with hydrodemetallization (HDM), hydrodesulfurization (HDS), and hydrodenitrogenation (HDN) catalysts. Liquid products were obtained from the outlets of different reactors, which were operated under typical conditions. Conventional components were analyzed to gain an understanding of the basic characteristics of the catalytic hydrogenation. The combination of ESI

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http://dx.doi.org/10.1016/j.fuproc.2017.01.007
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Please cite this article as: M. Liu, et al., Stepwise structural characterization of hydrocarbon compounds and polar components during atmospheric residue hydrotreatment, Fuel Processing Technology (2017), http://dx.doi.org/10.1016/j.fuproc.2017.01.007

FT-ICR MS and other analytical means was adopted to explore the physical and chemical properties of the feedstock and liquid products of different catalytic beds. The analysis helped in understanding the stepwise regularity of molecular conversion of hydrocarbon compounds and polar components during the hydrotreatment process.

2. Experimental

2.1. Feedstock

The density, viscosity and carbon residue of SZAR were determined to be 0.968 g/cm^3 (at 20 °C), 48.360 mPa·s (at 100 °C) and 10.989 wt.% (containing 3.44 wt.% sulfur and 0.29 wt.% nitrogen), respectively. The reagents included toluene (AR, 95 wt.%), methanol (AR, 95 wt.%), and heptane (AR, 98.5 wt.%).

2.2. Residue hydrotreatment

The reaction occurred in fixed-bed hydrotreating micro-reactors, the scheme of which has been reported in one of the previous studies [43]. The oil passed through the beds filled with HDM, HDS and HDN catalysts, which have been described elsewhere [44]. The liquid products obtained from the outlets of the three bed layers were denoted as HDM-product, HDS-product, and HDN-product, respectively. The values for reaction pressure, reaction temperature (inside-wall temperature), volume space velocity, volume of added catalyst, oil inflow and hydrogen-to-oil volume ratio were 14.7 MPa, 360 °C, 0.25 h^{-1}, 30 mL, 15 L/h, and 650:1, respectively. Furthermore, to ensure the accuracy of experimental data, each data point was obtained after at least 60 h time-on-stream under the given set of conditions. Fig. 1 showed the simulated distillation data for the feedstock and products obtained from different outlets.

2.3. Gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy

Molecular size distributions of the feedstock and its products were obtained using Waters GPC515-2410 unit coupled with a refractive index detector. The chromatography column was Waters Styragel HT-5 having 1-methyl-2-pyrrolidone (NMP) as the mobile phase. The sample was diluted in tetrahydrofuran (THF) solvent at 1 mg/mL concentration. Considering the low injection concentration, and dilution by mobile phase, the effect of aggregation should be weakened in GPC experiments. The experiments were conducted under a flow rate of 1 mL/min at 30 °C [45]. ^{1}H NMR experiments were conducted at room temperature using a VARIAN UNITY INOVA-500 MHz NMR spectrometer, which was equipped with a 500 mm double resonance broadband probe. The results obtained were listed in Table 1.

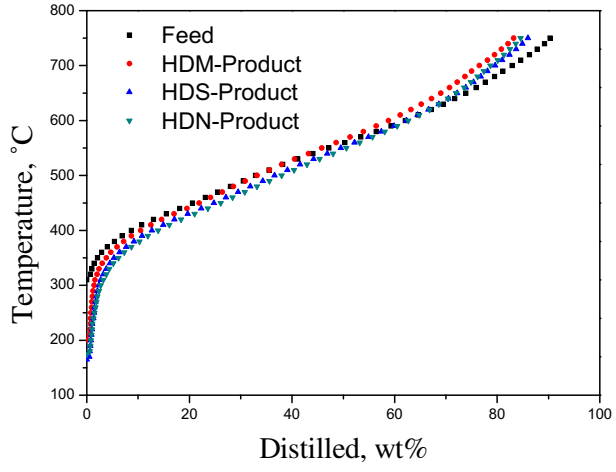

Fig. 1. Nominal boiling point distribution of feedstock and products, using the AC high-temperature SIMDIS analyzer (equipped with Agilent 6890N GC) using the AC HT-750 method.

Table 1
The aromatic carbon rate calculated from ^{1}H NMR.

	H_A	H_α	H_β	H
Feedstock	0.30	0.61	3.39	1
HDM-product	0.25	0.52	3.01	1
HDS-product	0.24	0.48	2.94	1
HDN-product	0.23	0.46	2.96	1

2.4. ESI FT-ICR MS analysis

About 1 mL of toluene was added to 10 mg of samples to prepare 10 mg/mL mother solution. Subsequently, 20 μL of the mother solution was taken and diluted in a toluene/methanol mixture (of 1/3 (v/v), respectively) to prepare 0.2 mg/mL sample. The sample solution was shaken gently to achieve uniform mixing. Around 15 μL of (28 wt.%) ammonia was added to facilitate the process of ionization prior to ESI FT-ICR MS analysis.

2.4.1. Analytical instruments

The FT-ICR MS analysis was performed using a Bruker apex-ultra FT-ICR mass spectrometer, which was equipped with an actively shielded 9.4 T superconducting magnet. An ESI source was used to detect the basic N-containing compounds under positive ion mode, whereas the neutral N-containing compounds were detected under negative ion mode.

2.4.2. FT-ICR MS working conditions

The values for sample injection rate, flow rate of nebulizing gas, flow rate of drying gas and temperature of drying gas were 180 μL/h, 1.2 L/min, 5 L/min, and 200 °C, respectively. The polarization voltage under positive (negative) - ion mode was −4 kV (3.5 kV), while the capillary inlet pressure was −4.5 kV (4 kV). The capillary outlet pressure was 320 V, while the radio frequency was 300 Vp-p. The collision energy was 1.5 V, whereas the source collection time and collection time were 0.01 s and 0.1 s, respectively. The time of flight for ion to be induced to analytical cell was 1.4 ms, whereas the collection quality ranged from 100 Da to 1000 Da. The number of sampling points was 4 M, while the number of scan times was 128.

2.5. Mass calibration and data analysis

Based upon the features of sample composition, the mass spectrum adopted the N_1 homologue which featured high SNR (a higher SNR series was usually used, while the highest was not necessary due to the consideration of quality coverage) for internal calibration. The mass spectra peak featuring an SNR that exceeded 6 was calculated with a data processing software developed within our research group. During calculations, the Kendrick mass defect value was set to 0.0010 for a more accurate CHNOS composition distribution. Furthermore, the details of the data processing have been reported in previous studies [46–48].

3. Results and discussion

3.1. Changes of hydrogenation properties

As shown in Table 2, the density, viscosity, and carbon residue values significantly decreased with the increase in the severity of the process. An increase in the H/C atomic ratio indicated that hydrogenation led to a reduction in the aromatic content. Additionally, the decrease in S/C and N/C atomic ratios showed that the heteroatom content was lower when the extent of hydrotreatment was higher. The simulated

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