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Investigation on feasibility to predict the content of saturate plus mono-nuclear aromatic hydrocarbons in vacuum gas oils from bulk properties and empirical correlations

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HIGHLIGHTS

- Quantitative characterization of VGO from bulk properties.
- Gasoline precursor correlation from SG and T_{50}.
- Refractive index correlation from d_{15} and T_{50}.

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ABSTRACT

This work presents a study on feasibility to predict saturates plus mono-nuclear aromatic hydrocarbons content in vacuum gas oils from readily available physical properties and the empirical methods: n-d-M, API, Total, Conoco Phillips (COP), and that of Goosens. As a result of a wide literature search 44 vacuum gas oils (VGO) having saturate plus mono-nuclear aromatic hydrocarbons in the range 13.7–97.0% and specific gravity (SG) in the range 0.8648–1.0903 were selected. Based on the physical properties SG and T_{50} boiling point of the 44 VGOs and the aromatic carbon and hydrogen content predicted by the Conoco-Phillips method a new correlation that predicts VGO saturate plus mono-nuclear aromatic hydrocarbons content with a reasonable accuracy was developed. This correlation based on a wide variation in properties of VGO can be used for a daily optimization of operation of FCC and hydrocracking units.

1. Introduction

The oil refining is currently enforced to manage with increasing crude oil prices [1], worsening quality of supplied crude oil [2], low margins [3], stringent environmental regulations [4] and decreased demand of heavy oil products like fuel oil [5]. Fluid catalytic cracking (FCC), hydrocracking and bottom of the barrel upgrading processes can help refiners to survive in this net of restrictions because of their capability to convert the low value heavy oils in high value transportation fuels. The single variable that has the biggest impact on refinery conversion unit performance is the feed quality. It can be characterized by a few parameters: density, content of impurities like sulfur, nitrogen, oxygen, metals, Conradson carbon, and hydrocarbon group composition. Fisher [6] established that the content of saturate plus mono-nuclear aromatic hydrocarbons in FCC feed correlated with conversion at the point of maximum gasoline yield. He also found that the FCC product yields at the point of maximum gasoline yield correlated with the content of saturate plus mono-nuclear aromatic hydrocarbons in the feed. Based on his findings Fisher [6] qualified the saturate plus mono-nuclear aromatic hydrocarbons containing in a FCC feed as gasoline precursors. Later other researchers, who have accepted Fisher's definition for gasoline precursors [7–10] proved that the gasoline precursor content is among the most important feed parameters that govern conversion level and product yields and quality in the FCC process. Liquid chromatography (LC) along with mass spectrometry (MS) are the analytical techniques which are required to obtain information about vacuum gas oil gasoline precursor content. Unfortunately such analytical techniques are impractical to use in a refinery for daily monitoring of the quality of the FCC unit feedstock. Empirical correlations were developed to relate vacuum gas oil bulk properties with characterizing parameters like content of aromatic, paraffinic and naphthenic carbons and hydrogen [11–15]. These correlations are included in the methods: n-d-M (ASTM D-3238); API [11,12]; Total [13], and that

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Nomenclature

H	hydrogen content, wt.%	SG	specific gravity
C	carbon content, wt.%	API	API gravity
C_A	aromatic carbon content, %	RI	refractive index at 20 °C
C_N	naphthenic carbon content, %	REFI	refractivity intercept
Cp	paraffinic carbon content, %	VGC	viscosity gravity relation
MW	molecular weight	S	sulfur content, wt.%
T_b	normal boiling point or 50% wt. TBP, K	VIS	viscosity at 98.9 °C (210 °F), cSt
T	volumetric average boiling point of ASTM D1160 distillation, °C	SUV	Saybolt universal viscosities at 98.9 °C (210 °F)
		CH	carbon to hydrogen ratio
T_{50}	50% boiling point, °C	I	refractive index parameter
T_{50}^F	50% boiling point, °F	m, v, w, C_R	parameters
d	density at 20 °C, kg/l	K_W	Watson K factor
d_{15}	density at 15 °C, kg/l		

of Goosens [15]. It was shown earlier that these empirically estimated characteristic parameters could be used for prediction of gasoline precursor level in the FCC feedstock [9,10]. In a recent study new correlations for the content of aromatic carbon and hydrogen in heavy oil were proposed based only on heavy oil specific gravity and T_{50} boiling point data [16]. These new correlations called COP (Conoco Philips Prediction method), which require the least information for heavy oil bulk properties, were reported to be superior to the older n-d-M, API and Total correlations [16].

The aim of this work is to evaluate a feasibility of predicting vacuum gas oil (VGO) gasoline precursor content from VGO bulk properties and empirical correlations of the methods n-d-M [13], API Procedure 2B4.1 and 3 [11,12], Total [13], COP [16] and Goosens [15]. For that purpose a wide literature search of data of VGO bulk properties along with LC/MS hydrocarbon group composition data was carried out. As a result 44 VGOs with the searched properties were found. The gasoline precursor content of this data base of VGOs varies between 13.7% and 97.0% (Table 1) and the specific gravity varies between 0.8648 and 1.0903. It is difficult to imagine that a wider range of gasoline precursor level in VGO could be met in refining practice. That is why the 44 VGOs used in this work could be considered as a representative selection of properties of VGO employed in all refineries around the world.

2. Experimental

Determination of hydrocarbon group composition and gasoline precursor content was performed by methods ASTM D-2007 (liquid chromatography) and ASTM D-2786 (mass spectrometry). The empirical methods to characterize the VGOs used in this work are summarized below:

1. Determination of content of paraffinic carbon, naphthenic carbon and aromatic carbon by the n-d-M (ASTM D-3238) [13].

This method requires three physical properties: refractive index, density, and molecular weight and for this reason it is called n-d-M method. The n-d-M method does not directly give composition of vacuum gas oils in terms of paraffins, naphthenes and aromatics. It predicts the distribution of carbon in paraffins (C_P), naphthenes (C_N) and aromatics (C_A) of studied VGOs. The following equations are used for estimation of C_P, C_N, and C_A:

$$C_A = av + 3660/\mathrm{MW} \tag{1}$$

$$C_N = C_R - C_A \tag{2}$$

$$C_P = 100 - C_R \tag{3}$$

Eqs. (1)–(3) include parameters a, v, w and C_R, which are estimated by Eqs. (4)–(7). Eqs. (4)–(7) are summarized below:

$$v = 2.51(\mathrm{RI} - 1.475) - (d - 0.851)$$
$$a = 430 \quad \text{if } v > 0$$
$$a = 670 \quad \text{if } v < 0 \tag{4}$$

$$w = (d - 0.851) - 1.11(\mathrm{RI} - 1.475) \tag{5}$$

if $w > 0$

$$C_R = 820w - 3S + 10{,}000/\mathrm{MW} \tag{6}$$

if $w < 0$

$$C_R = 1440w - 3S + 10{,}600/\mathrm{MW} \tag{7}$$

1. Determination of content of paraffinic (P), naphthenic (N) and aromatic (A) portions by API Procedure 2B4.1 and 3 Refs. [11,12].

API adopted the methods developed by Riazi and Daubert for prediction the content of paraffinic, naphthenic and aromatic portions on the base of data of distillation characteristics, specific gravity, molecular weight (MW) and carbon to hydrogen ratio. The API Procedure for prediction of composition of heavy petroleum fraction with MW > 200 presented with Eqs. (8)–(10) was used in this study:

$$P = 193.82 + 0.74855m - 19.966\mathrm{CH} \tag{8}$$

$$N = -42.260 - 0.777m + 10.7625\mathrm{CH} \tag{9}$$

$$A = 100 - P - N \tag{10}$$

Parameters m and CH of the investigated VGOs were calculated by using the following forms:

$$m = \mathrm{MW}(\mathrm{RI} - 1.4750) \tag{11}$$

$$\mathrm{CH} = \frac{C}{H} \tag{12}$$

Refractive index of studied VGOs was predicted by using of following equations:

$$\mathrm{RI} = \left(\frac{1 + 2I}{1 - I}\right)^{1/2} \tag{13}$$

$$I = 1.8422 \times 10^{-2} \exp(11.6352 \times 10^{-4} T_b + 5.144\mathrm{SG} - 5.92 \times 10^{-4} T_b \mathrm{SG}) T_b^{-0.4077} \mathrm{SG}^{-3.333} \tag{14}$$

API Procedure also includes a correlation for prediction the content of paraffinic, naphthenic and aromatic portions from viscosity, specific gravity and refractive index data. Since it was not possible