



# Investigation of relations between properties of vacuum residual oils from different origin, and of their deasphalted and asphaltene fractions



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## HIGHLIGHTS

- The VRO  $d_4^{20}$ –Concarbon correlation can be used to verify the correctness of  $d_4^{20}$  measurement.
- VRO dilution with FCC HCO is recommended to measure viscosity and density of high viscous VROs.
- VRO  $d_4^{20}$ , Concarbon, and viscosity correlate with the content of hydrogen, saturate, and asphaltene.
- The converted asphaltenes affect in a lesser extent the VRO viscosity than the virgin asphaltenes.

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## ABSTRACT

36 vacuum residual oils, obtained from all available groups of crude oils in the world along with their deasphalted oils and their asphaltene fractions have been investigated in this work. Correlations were derived which show that the vacuum residual oil bulk properties density, Conradson carbon content, and viscosity correlate with residual oil hydrogen content, H/C atomic ratio, the fraction of aromatic carbon, saturate, and asphaltene content. It was found that the VRO metal (Ni + V) content was almost evenly distributed between the maltene and the asphaltene fractions. The data in this work presented contradictory facts about the molecular weight of the VRO asphaltene fractions. The simulation distillation data (ASTM D-7169) and Goosens' correlation support the statement of Mullins et al. that the asphaltene fractions may have molecular weight of about 750 g/mole. The atmospheric residue physical distillation data (ASTM D-5236) and Riazi's boiling point distribution model, however support the statement that the asphaltenes are concentrated in the higher boiling point, higher molecular weight VRO fractions. The higher the aromaticity of a heavy oil, the higher its viscosity is. Since the asphaltenes are the most aromatic compounds in a heavy oil their influence on the heavy oil viscosity is the biggest among all other heavy oil constituents. The converted vacuum residual oils (from visbreaking and residue ebullated bed H-Oil hydrocracking) demonstrated lower dependence of viscosity on the asphaltene content. This could be a result from decreasing of the dimensions of the macro-structure of the converted asphaltene molecule.

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## 1. Introduction

The importance of bottom of the barrel upgrading technologies becomes very high because of high crude oil prices [1], worsen quality of supplied crude oil and of oil reserves [2], low refining margins [3], and high differential between prices of transportation fuels and heavy fuel oil [4]. The trend of decreased demand of heavy oil products additionally supports the leading role of the bottom of the barrel (BOB) upgrading processes in the refining business [5]. It has been shown that the residual feed quality is

the single variable that has the biggest impact on refinery BOB conversion unit performance [6–10]. Many studies have been devoted to characterization of the most refractory compounds in residual feeds – asphaltenes [11–24]. The next most refractory compounds in residual oils – resins have been investigated in a smaller scale [25–30]. The aromatic and saturate fractions from the residual oils are the least investigated residue compounds [31–34]. Having in mind that the residual feed quality is the most affecting refinery BOB conversion unit performance it is understandable that there is a need to characterize the whole residual feedstock. Bozzano et al. have developed a method for characterization of residual feedstocks based on information of initial boiling point, kinematic

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## Nomenclature

### List of used abbreviations and symbols

VRO	vacuum residual oil	VBR	visbreaker residue
DAO	deasphalted oil	Hydrogen <sub>VRO</sub>	vacuum residual oil hydrogen content, %
BOB	bottom of the barrel	H/C <sub>VRO</sub>	vacuum residual oil H/C atomic ratio
CCR	Conradson carbon residue	CCR <sub>VRO</sub>	vacuum residual oil Conradson carbon content, wt.%
SG	specific gravity	Sat <sub>VRO</sub> (VRO <sub>sat</sub> )	vacuum residual oil saturate content, %
SR/REM	stochastic reconstruction (Generate an equimolar set of N representative molecules)	Asphalt <sub>VRO</sub>	vacuum residual oil asphaltene content, %
MTHS	molecular-type homologous series	Asphalt <sub>ConvertedVRO</sub>	converted vacuum residual oil asphaltene content, %
SOLA	structure-oriented lumping approach	$\eta_{VRO}$	specific viscosity at 120 °C, °E
NMR	nuclear magnetic resonance	$\mu$	dynamic viscosity at 80 °C, cP
SARA	saturates, aromatics, resins, asphaltenes	$f_A$	aromatic carbon fraction
Asphaltene <sub>yield</sub>	yield of asphaltenes, wt.%	MW	molecular weight, g/mole
M <sub>VRO</sub>	weight of vacuum residual oil, g.	TBP	true boiling point
FCC	fluid catalytic cracking	MW <sub>Asphaltene</sub>	average molecular weight of asphaltenes, g/mole
HCO	heavy cycle oil	wt.% <sub>Asphaltene</sub>	asphaltene content in the vacuum residual oil, wt.% of the VRO
$\nu$	kinematic viscosity, mm <sup>2</sup> /s	wt.% <sub>DAO</sub>	maltene fraction (DAO) content in the vacuum residual oil, wt.% of the VRO
S-value	intrinsic stability	MW <sub>DAO</sub>	average molecular weight of the maltene fraction (deasphalted oil), estimated by Goosens' correlation, g/mole
Sa	peptisability or ability of the asphaltenes to remain in colloidal dispersion	MW <sub>VRO</sub>	average molecular weight of the VRO, estimated by Goosens' correlation, g/mole
So	peptising power of oil is the "aromatic" equivalent of the oil	HTVGO	hydrotreated vacuum gas oil
HTSD	high temperature simulation distillation	CII	colloidal index of instability = $\frac{\text{Saturates} + \text{Asphaltenes}}{\text{Aromatics} + \text{Resins}}$
Kw	characterization factor	IN	insolubility number
d <sub>4</sub> <sup>20</sup>	relative density	SBN	solubility blending number

viscosity, specific gravity, sulfur content and Conradson carbon residue (CCR) [7,35–38]. Starting from these easily available in the refinery analysis data the distribution of paraffins, aromatics and naphthenes macro-classes can be evaluated. C.C.R. is a reliable index of the "aromatics" content. C.C.R. in the range 15–25% supposes that the vacuum residue is very rich in aromatic components whilst when it is low (e.g. 1–6), the presence of naphthenes can be higher in quantity. The coupling of Conradson carbon residue data with specific gravity (which is also deeply affected by the presence of aromatics) enables to evaluate the composition of the feedstock in terms of macromolecules. Average molecular weight is strictly connected to the kinematic viscosity [7]. Bozzano, however, in her papers presented only 10 vacuum residual oils having C.C.R. in the range 11.8–24.0% and specific gravity (SG) in the range 0.975–1.065, and two atmospheric residual oils with C.C.R. in the range 9.1–17% and SG in the range 0.98–1.044. Taking this fact into account one cannot categorically argue that the method of Bozzano is sufficiently tested to prove its validity for residual oils whose properties are outside of the range mentioned above. Moreover it is not clear from Bozzano's works how only two parameters (C.C.R. and SG) are adequate to evaluate the composition of the feedstocks in terms of paraffinic, aromatic, and naphthenic macromolecules. Another method for characterization of residual feedstocks is that based on modeling the feedstock composition [39–57]. Composition modeling allows the derivation of the detailed composition of complex mixtures starting from a limited set of mixture bulk properties. The residue feedstock modeling consists of generating a set of molecules whose properties are close to those obtained from the process feedstock analyses. Three alternatives of the method for residue feedstock characterization by composition modeling have been discussed in the open literature: (1) A two-step algorithm (SR/REM): 1.1. Stochastic reconstruction (Generate an equimolar set of N representative molecules; Size of generated mixture: 5000 molecules [54,56]); 1.2. Reconstruction by entropy maximization (Adjust the N representative molecules

mole fractions) [41,42,46–48,54,57]; (2) Using modified molecular-type homologous series (MTHS) representation: 2.1. Bulk properties of the residue and the homologous series of components (Selected core structure) are input data for this algorithm: 2.2. Then objective function is calculated by the use of mixing rules, structure–property relationships and imposed distributions which eventually gives the calculated residue composition [44,49–53]; (3) Structure-oriented lumping approach (SOLA). Its designation is to select a set of initial "seed" residua molecules and allow chemical transformations to generate products that populate the property and composition ranges. The goal of SOLA is the sample molecules to spread evenly across the dimensions of boiling point, density, sulfur content, nitrogen content, aromatic content, and so on. It was found that ~1500 composite molecules are sufficient to cover the compositional diversity found in residua [40].

Unfortunately the residue composition modeling methods have not found wide application in refining practice yet. Some of the methods require analytical information from techniques like <sup>1</sup>H NMR, <sup>13</sup>C NMR, and XRD which are not routinely used in refineries. For that reason characterization methods like physical properties: specific gravity (density), viscosity, boiling point (where applicable); and chemical properties: SARA (saturates, aromatics, resins, asphaltenes), elemental composition, Conradson carbon; and colloidal properties like S-value, P-value, toluene equivalent and others may take place in residue characterization in the refineries. Unfortunately some of these physicochemical properties require relatively long time to measure like SARA for example, which make them inconvenient to apply in refining on a daily base. That is why we decided to investigate the physicochemical properties of 36 vacuum residual oils from different origin and derived thereof deasphalted oils, and asphaltenes with the aim to find relationship between the easy to obtain analytical data and those that require longer time to analyze. The aim of this work is to discuss the obtained results.

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