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Investigation of the coking behavior of serial petroleum residues derived from deep-vacuum distillation of Venezuela extra-heavy oil in laboratory-scale coking

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ABSTRACT

The coking behavior of serial petroleum residues derived from deep-vacuum distillation of Venezuela extra-heavy oil has been systematically investigated in laboratory-scale coking appliances from the perspectives of distribution and properties of coking products. The usage of residue with deeper distilling cut would favor the decreasing of low-value products, i.e., coke and coking gas. The hydrogen circumstance of coking feedstock indicated by ^{1}H NMR analysis, implies residue with ultra-deep distilling cut as a valid hydrogen evolution potential. By comparison with the de-metallization rate in the hydrodemetallization process (Ni, 61.2%; V, 80.8%) (Zhang et al., 2006), the performance in the study seems more promising. Evidently, the stripping of VGO would notably change the morphological characteristics of resultant coke. However, no secondary assembled or clustered shot coke was observed in the coker, which made the decoking quite easy. A valid linear agreement between the area of green region quantitatively assessing the process flexibility and the metal content has been established. The extrapolation (dot line) of the trend suggests that shot coke formation cannot be avoided in any circumstance of the study if the metal content of coking feedstock is over 1516 $\mu g\,g^{-1}$.

1. Introduction

A utilization preference of unconventional heavy oil (UHO) [1] is to squeeze as many distillates as possible using deep-vacuum distillation technology to increase the distillates yield [2] for more margin, which would generate petroleum residue with rather high content of metals and carbon residue value. Therefore, as suggested by Golden and Barletta, higher capital cost resulted from intensive designs and apparatuses for the petroleum residue would be expected. Meanwhile, when UHO was introduced into refineries that have low-cost units, they were forced to choose an alternative process scheme that is operating at low gas oil cut points [1] because of the inferior processing properties of UHO, e.g. asphaltenes precipitation [3], less thermal stability [4], and faster coking propensity in heater tubes [5]. The solution would be feasible to some extent, but it also means less project revenues for lower product yield per barrel of UHO and more production of residue [1], such as atmospheric residue and/or vacuum residue with low distillation depth, leading to a burden for downstream processes [6].

No matter what process scheme refinery choose, it is believed that delayed coking would be a undoubted solution process for handling residues [7,8]. In general, delayed coking is a process that is of wide practical importance within the refineries worldwide [9] and resistant to high metal and heteroatoms content, and coke formation [10], for so, is recommended to convert "bottom of barrel" materials, i.e. petroleum residue, to more valuable, low molecular weight products with coke production [8]. However, the results adopted from Xue et al. [11] have shown that the chemical and physical properties of petroleum residues with varying distill-cutting temperatures vary remarkably, even though they are derived from the same origin. We and our colleagues have been researching relationships between feed composition and coke formation [12], shot-coke-forming propensity [13], heat of reactions (including heat of pyrolysis and condensation) [14], and controlling of coke morphology [15] for obtaining insight of processing characteristics of petroleum residue derived from an unconventional heavy oil, i.e. Venezuelan extra-heavy oil. The main original interest of these serial works was the optimization and development of coking process, allowing the unconventional heavy oil to be utilized as a processable, even well-handled feedstock in refineries instead of upgraders [6]. Recently, our previous study [11] was implemented from the perspective of distilling scheme of UHO and the characterization of serial petroleum residua which all could be candidates of coking feedstocks dependent on the process technology and material balance in refinery.

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Thus, it is then necessarily important to get insight of the coking behavior diversity of serial petroleum residues, not only for favoring operation optimation to flexibly adjust products distribution and characteristics, but also for providing valuable reference data for design and/or revamps of coker units to be acclimatized to residue from UHO. Then the first goal of the present work addresses the main concerned coking behavior, i.e. the products distribution of serial petroleum residues.

Coking gas is believed to be a good hydrogen source [16] because it is usually composed by low-carbon compounds rich in hydrogen, for instance, methane. The components of coking gas product are primarily concerned for it would remarkably affect the hydrogen generation. Furthermore, petroleum residues derived from UHO are remarkably characterized with high content of metals and heteroatoms, and high carbon residue, which are all destructive to processes with the purpose of lightening the heavy feedstocks, such as Hydrocracking and Residue Fluidized Catalytic Cracking (RFCC) [17]. Especially the metals become a major concern because they are commonly believed to relate to the catalyst deactivation, fouling in the tubes, and corrosion of the turbine equipments [18]. The delayed coking is well-recognized to be tolerant toward feedstocks with high metal content because no catalyst is involved in the whole process [14]. Most importantly, it could complement the converting of heavy fractions to light products synchronously accompanied by demetalization, carbon rejection, and deimpurity of heteroatoms without any more extra capital investments and/or cost. Guo et al. [13] have paid their attention to morphology control of coke (shot coke vs. non-shot coke) generated in the process. It was suggested that petroleum residue (with boiling range of 500 °C+) derived from Venezuelan heavy oil has a rather high propensity of shot-coke formation as it was treated in the simulation coking condition because of high content of asphaltenes contained in the feedstock. Undoubtedly, the shot-coke formation could be inhibited or promoted through the change of coking feedstock and/or the adjustment of coking condition. Our second goal of the work thus lies in obtaining better understanding of coking behavior diversity of various candidates of coking feedstocks, dependent on the process technology and material balance in refinery, from the characteristic perspective of coking products.

2. Materials and methods

2.1. Materials

Six serial petroleum residue samples with varying distil-cut points were prepared via laboratory deep-vacuum distillation technology in molecular distillation KDL-5 (UIC Laboratory, Germany). They are labelled as atmospheric residue (AR, boiling range: above 350 °C), vacuum residue 1 (VR1, boiling range: above 420 °C), vacuum residue 2 (VR2, boiling range: above 500 °C), vacuum residue 3 (VR3, boiling range: above 545 °C), vacuum residue 4 (VR4, boiling range: above 565 °C), respectively. The preparation procedure in detail was reported in literature from Xue et al. and Wang et al. [11,19]. A coking streams acquired from Liaohe Refinery in China was used as the recycled oil in the study. The selected properties of petroleum residues and the coker stream are listed in Table 1.

2.2. Pilot coking plant and sampling

The pilot coking plant used in the study is composed of a 12 cm ID × 100 cm cylindrical coker with a volume of approximately 11.3 L. An electric heating tank was used to load the feedstock with an outlet temperature of 150 ± 3 °C and continuously provided feedstock during the pilot coking test. A battery of pre-heaters were then placed alone with the feed line until the bottom of coker for gradually increasing the temperature of the line. The temperature increase rate of the pre-heaters was around 55 °C m^{-1}, with an outlet temperature of 480 ± 2 °C. The coker inlet temperature generally used in the study was 490 ± 2 °C, which could be ranged from 480 °C to 500 °C if necessary. The coking pressure was 0.15 MPa adopted from the Coking Plant in Liaohe Refinery (Table 2). The coking feed introduction to the coker was designed to be 10–12 h in order to obtain enough coke samples and a rather high repeatability of pilot coking experiments. At the end stage of each experiment, a baking time of ~4 h with no introduced feed in coker and a N_2 gas stripping (200 mL min^{-1}), was taken to ensure carbonization of the nonvolatile and remove the possible volatile left in the coke column. The coking feeds were prepared in advance in a kettle with stirring system, especially when circulation fraction was involved. The preparation was carried out at a temperature of 130 ± 2 °C with a 0.5 h stirring (agitation rate of ~500 rpm) to acquire homogeneous coking feeds. The operation in detail of the pilot coking plant was shown in previous literature [12]. Photos of the pilot coking plant and a representative coke cross section presentation from the coker are shown in Fig. 1.

Coking gas was sampled three times in each run followed the same time pattern and sent to Refinery Gas Analysis. The mean values of main gas composition are presented in Table 3 for discussion. The coking liquid samples were taken out directly from the liquid storage tank in the cold trap after blending. The cokes used for further analysis (e.g. morphological observation) were always sampled from the central region that is 10 cm above the bottom of coke cylinder in order to minimize the disturbance resulted from different sampling locations. The coke samples were then analyzed through SEM when the general optical observation was done. A sequential polarized light observation was implemented by using the coke samples retrieved from SEM analysis trays. The polarized light observation and corresponding morphology analysis in detail is introduced in the next section.

2.3. Polarized-light optical microscopy observation

The coke samples used in the Scanning electron microscopic observation were recycled for the preparation of polarized-light optical microscopy experiments, which were followed a standard procedure suggested by Siskin et al. [21] An observation of optical microscopic samples was performed under the polarized light using SGO-3232 inverted type polarized-light optical microscope of Shanghai Optical Corporation with oil immersion at 500× total magnification in order to reveal optical texture with high contrast. The anisotropic isochromatic units in the optical texture were discriminated and described according to a referenced literature [21]. Based on the description and corresponding definitions, an optical texture index (OTI) for each coke sample was thus calculated using a referenced formula, [22,23] and was then used to quantitatively evaluate the general morphology of coke. Each polarized-light image was marked with a scale of 10 μm for a primary recognition of coke morphology, as recommended by Siskin et al. [21].

3. Results and discussion

3.1. The coking products distribution and gas characterization

3.1.1. Coking products distribution

Notably, the coking products distribution becomes more unfavorable to the payoff of delayed coking process in terms of an increasing tendency of both coke and gas yield as more VGO was abstracted from feed. In the case of VR4, nearly half products belong to the low-value category, in which coking gas accounts for around 10 wt%. It is quite close to the data adopted from Liang et al. [24] A possible explanation for the behavior has been reported by Alvarez et al. [25], Cui [26], and Chen et al. [27] who stated that high-boiling components contained in petroleum, especially in the vacuum bottom of petroleum, would prefer to stay in the liquid status and thus endure more cracking and condensation, statistically resulting in higher yield of gas and coke. It is inspiring to see that the coke yield from the view of overall refining