CHARACTERIZATION OF ASPHALTENES FROM MARLIM VACUUM RESIDUE USING HEPTANE TOLUENE MIXTURE

B.Avid, S. Sato, T. Takanohashi, I.Saito

Institute of Energy Utilization, National Institute of Advanced Industrial Science, 16-1 Onogawa, Tsukuba 305-8569, Japan

Introduction

Thermal cracking processes are commonly used today to convert petroleum vacuum residue (VR) into distillable liquid products. Petroleum asphaltenes (AS), the heaviest, most aromatic component of crude oil, tend to precipitate to cause coking during thermal and catalytic processing of petroleum residues. Except of the temperatures and residence times of the cracking, a number of factors are important during coking such as, the asphaltene concentrations in the feed, molecular weight, structure, aromaticity, metal and heteroatom content of the asphaltenes and nature of solvent [1-4]. The objective of this process is to maximize the yield of cracked products, on the other hand, to avoid the formation of coke deposits. These goals are only achievable through a better understanding of mechanism of the process and asphaltene structure. It is well recognized that asphaltenes from different crude oil sources can have vastly different properties. For example, two types of asphaltenes exist in the Athabasca bitumen- one type tending to lower molecular weight and having a few condensed aromatic rings per unit and the other type having a higher molecular weight and considerably more (up to c.30) condensed aromatic rings per unit [5]. Rahimi pointed out that only a portion of the asphaltenes converted to coke while the remaining portion converted to maltenes and gases [1]. Most of these studies have been concerned with simplified systems, in which asphaltenes had been extracted from their natural medium by precipitation in an excess of n-heptane (or n-pentane) and then redissolved in different solvents or re-mixing with VR to characterize the asphaltenes structure, molecular size, coke formation, aggregation and so on. Despite of these efforts, there are currently not clear picture of the asphaltene structure, conversion and mechanism of thermolysis.

The objective of this work was to separate the Marlim VR by using n-heptane-toluene mixtures and examine the behavior of the separated fractions in the coking test. The elemental analysis, NMR and GPC were applied to characterize the separated asphaltenes.

Table 1. Properties of Marlim Vacuum Residue

Elelental analysis	
C, wt %	87.2
H, wt %	10.6
N, wt %	0.69
S, wt %	0.98
O, wt %, by diff.	0.53
H/C ratio	1.45
V, ppm	73
Ni, ppm	59
fa	0.29
Molecular weight	935
Asphaltene, wt %	13.3

Experimental

The VR from Marlim crude oil (Brazil) has been used in this experiment (Table 1). The asphaltenes were precipitated from VR using n-heptane-toluene mixture (heptol), and soluble part, i.e. maltene (MA) was recovered from heptol. The content of toluene in the mixture was ranged from 0 % to 60% (by volume) and separated products were named as AS0%-AS60% and MA0%-MA60%, respectively. All samples were analysed by NMR, GPC and elemental analyses.

NMR analysis was carried out by a JEOL Lambda 500 spectrometer by applying inverse gated decoupling and DEPT pulse sequence of 45° and 135°. The distribution of aliphatic CH_3, CH_2 and CH and quaternary aromatic carbon were determined by ^{13}C-NMR and DEPT techniques [6-8].

Average molecular weight was measured by GPC system (JASCO) using KF403HQ Shodex column (exclusive limit 70,000) and Evaporative Laser Scattering Detector (ELSD) with chloroform as an eluent and polyethylene as calibration standard for molecular weight. Experiments for coke formation were carried out batchwise in an 18 ml quartz tube. The tube was loaded with 3 g of reactant and placed in a 50 ml metal reactor and pressurized with nitrogen at 1 MPa. The reactor was heated in an agitated oven at 430 °C for 1 hour and cooled to room temperature. Then reactor was vented and gas was analysed by GC, liquid product was washed by toluene and kept overnight.

The toluene insoluble product (coke) was separated by centrifuge and cake was washed again by toluene. Toluene was removed from the filtrate by rotary evaporation followed by vacuum drying at 60 °C overnight to give the coke yield.

Results and discussion

The Marlim VR was separated into the asphaltene (AS) and maltene (MA) fractions by heptol. In the case of 60% heptol, the VR was completely dissolved (no precipitation), meanwhile yield of AS 40 % was negligible, and therefore the separated products from 0 to 30 % heptol were used in further investigations. The Marlim VR and different maltene fractions (MA0%-MA30%) were examined by coking test and results of these shown in Fig.1.

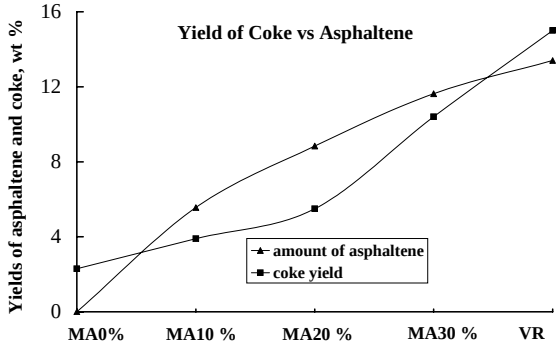

Fig.1. The correlation between coke and asphaltenes

The purpose of the experiment was just to examine the conversion of different asphaltene fractions into coke under normal processing condition. Coke is defined is insoluble in an aromatic solvent such as benzene or toluene. As mentioned before, the high content of asphaltene in vacuum residues tends to give high yield of coke. As

shown in Fig. 1, the yield of the coke was increased by 2.2 wt% with increasing of asphaltene by 9.3 wt% in the MA0% to MA 20%. The influence of asphaltene for the coke formation was negligible. But from the MA20% to MA30 %, yield of the coke was increased obviously, i.e. coke yield was raised from 5.5 to 10.5 wt%, even the content of asphaltene increased just by 3.1 wt% in this range. In this case, the increment of coke was two times higher than asphaltene increment. As can be seen from the results obtained in this work, the asphaltene exerts differently for the coke formation due to asphaltene properties. i.e. asphaltenes in the MA0%-MA30% fractions were not same, or according to Rahimi [1], the portions of asphaltenes, which are converted into the coke or maltene were significantly different in the fractions. By the other hand, portion of asphaltenes converts into maltene or gas was higher in the AS of the MA10% and MA20 % than in the MA 30%, or portion of asphaltene converts into coke was higher in the MA30%. In order to clarify the properties of different asphaltene fractions, Marlim VR asphaltene was separated into AS 0-10%, AS10-20%, AS 20-30% and AS 30 % and these fractions were analysed by elemental analysis, NMR (Fig.2) and GPC (Table 2).

The elemental analyses of the separated AS were similar, except hydrogen content. The hydrogen content of fractions is decreasing from AS0-10 % to AS30 %, and as well AS0-10% and AS10-20 % have a higher H/C ratio than AS20-30% and AS30 %. Average molecular weights (Mn) of the AS are in the range of 690 to 810 daltons. Also there is a little increase of Mn from AS0-10 % to AS20-30%. But the difference is not so high. The ^{1}H NMR analysis shows a similar distribution of the different asphaltene fractions. The aromatic proton content (Ha) is around 11%. The aromaticity (*fa)* is increasing from fraction AS0-10% to AS30 %, i.e. AS20-30% and AS30 % have a higher *fa* (0.53) than first 2 fractions and total AS (0.48). The AS20-30 % and AS30% had the highest percentage of quaternary aromatic carbon (*QAC)*, which are equal to around 40 wt% and AS 0-10% and AS10- 20% had a lower *QAC* (35-37 wt%). The distribution of non aromatic carbons shows that fraction of CH is decreasing from AS0-10% to AS30 %, the distribution of CH_2 was opposite, i.e. increasing in this range. It is likely that the AS, which have a higher aromaticity and quaternary aromatic carbon, produces more coke than AS with lower *fa* and *QAC*. Therefore, AS 0-10% and AS10-20 % were named as GOOD AS and AS20-30% and AS30 % are BAD AS.

Conclusions

The Marlim VR was separated into asphaltene (AS) and maltene (MA) fractions using n-heptane-toluene mixtures and separated MA fractions examined for coking test and results show that the AS is consisted of BAD AS and GOOD AS. So the asphaltene were fractioned into AS 0-10%, AS10-20%, AS 20-30% and AS 30 %. The AS 20-30% and AS30% have a higher aromaticity and quaternary carbons and produce more coke than the AS 0-10% and AS10-20%.

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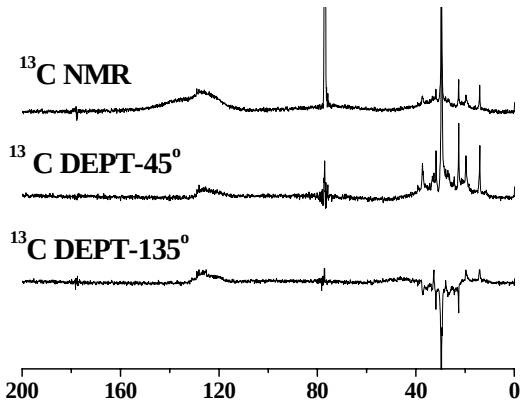

Fig.2. Typical NMR spectra of the asphaltene fractions

Table 2. Properties of the Marlim VR Asphaltenes

Sample name	Total AS	AS0-10%	AS10-20%	AS 20-30%	AS 30%
Recovery, wt%	14.2	4.1	4.7	3.6	1.8
Elemental analysis, wt%					
C	86.2	85.9	86.5	87.3	85.8
H	8.01	8.40	8.27	8.11	8.01
N	1.28	1.25	1.29	1.32	1.19
S	1.27	1.27	1.21	1.21	1.24
O	3.24	3.22	2.73	2.06	3.76
H/C	1.11	1.17	1.14	1.11	1.11
Mn (GPC)	691	743	748	806	758
NMR analysis, %					
^{1}H-NMR					
Ha	10.5	11.1	11.4	12.4	11.1
Hα	16.7	15.7	16.7	16.5	16.3
Hβ	51.6	56.8	56.2	53.0	52.7
Hγ	21.2	16.3	15.6	18.1	19.9
^{13}C-NMR					
fa	0.48	0.49	0.50	0.53	0.53
QAC	34.9	36.2	37.4	39.1	40.5
Distribution of non-aromatic carbons					
CH	20.53	15.90	15.89	13.57	10.09
CH2	61.24	64.39	64.85	67.43	70.56
CH3	18.23	19.71	19.26	19.00	19.35

QAC- Quaternary aromatic carbon