



Influence of presence/addition of asphaltenes on semi-coke textures and mesophase development in petroleum feed stocks



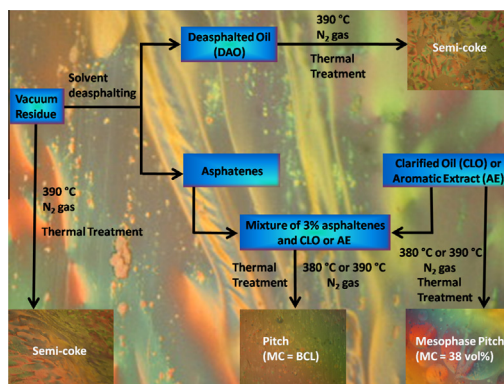
Subhash Kumar, Manoj Srivastava*

Academy of Scientific and Innovative Research (AcSIR) at CSIR – Indian Institute of Petroleum, Dehradun 248005, India
Heavy Oil Processing Area, CSIR – Indian Institute of Petroleum, Dehradun 248005, India

HIGHLIGHTS

- Vacuum residues give mosaic type textures of semi-coke.
- Deasphalted oils give improved texture of mesophase.
- Asphaltenes have a negative impact on mesophase development and semi-coke texture.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 August 2015
Received in revised form 21 November 2015
Accepted 5 January 2016
Available online 21 January 2016

Keywords:

Vacuum residue
Deasphalted oil
Asphaltene
Mesophase
Semi-coke

ABSTRACT

In this paper, effect of asphaltenes on optical textures of semi-coke and pitches prepared from vacuum residues (VRs) and their deasphalted oils (DAOs) during heat treatment at a temperature 390 °C was investigated. Optical microscopic image analysis shows that VR-1 which contains 10.44 wt% asphaltene produces semi-coke VR-390-1 having 29 vol% mesophase content and flow type coalescence. On the other hand, VR-2 which contains 24.57 wt% asphaltene produces semi-coke VR-390-2 having 27 vol% mesophase content and mosaic type texture. Further, it was observed that deasphalting of these vacuum residues improve the optical textures as well as enhance the mesophase content in DAO-390-1 (48 vol%) and DAO-390-2 (36 vol%) semi-coke. Furthermore, we have also concluded that asphaltene molecules affect the growth of mesophase development in an adverse manner. In this study, we have prepared pitches from clarified oil (CLO) and aromatic extract (AE) having very low asphaltene content at temperatures 380 and 390 °C respectively without and with the addition of 3% asphaltene. Optical microscopic images of these pitches show that mesophase contents were decreases with the addition of asphaltene externally. In addition, semi-coke and pitches were also characterized by using elemental analysis, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and thermogravimetric analyses (TGA). The study revealed that asphaltene either present in the feed stock or externally added in the feed stock play a negative role on mesophase development as well as on coke texture.

Crown Copyright © 2016 Published by Elsevier Ltd. All rights reserved.

* Corresponding author at: Heavy Oil Processing Area, CSIR – Indian Institute of Petroleum, Dehradun 248005, India. Tel.: +91 135 2525772; fax: +91 135 2660202.
E-mail address: manoj@iip.res.in (M. Srivastava).

1. Introduction

Petroleum coke is a by-product of petroleum refining process i.e. coking. It is a concentrated carbon solid residue that is leaving behind after the coking process whose main purpose is to convert bulk of the crude oil into more valuable gases and liquid products such as gasoline and diesel [1]. Besides having very high carbon content over 90%, petroleum coke is used as a precursor for many carbon materials. There are three types of coking processes: delayed, fluid and flexi coking, but among them delayed coking is most widely used coking process. In delayed coking process [2], vacuum residue is used as main feed stock. Besides vacuum residue, petroleum coke can also be prepared from other petroleum streams and coal tar derivatives which include fluid catalytic cracking (FCC)-decant oil, coal tar pitch and their blends. Nowadays, due to increasing industrial demand of both feed stocks and petroleum cokes, more effort has been carried out to minimize the production cost. To accomplish this, thermal cracking process is employed which convert the low value by-product from petroleum and coal into more preferential microstructural orientation. Various factors are responsible for deciding structure and quality of petroleum coke but it mainly rely on the type of hydrocarbons present in the coker feed.

Based on physical and chemical properties of petroleum cokes, they are classified as shot, sponge or needle coke. The presence of asphaltenes in the feed stock is also a deciding factor for formations of these three types of cokes. Generally, feed stocks having asphaltenes contents in the range of 13–29 wt% produces shot coke [3] and it has predominantly mosaic type optical texture [4]. The production of this type of petroleum coke is less undesirable because of its relatively low electrical conductivity and it usually contains large amounts of sulfur and metals. Shot coke because of its very low price used in power plants and other industries as fuel. Whereas, sponge coke is produced from feed stocks those have asphaltene content in the range of 6–12 wt% [3]. Sponge coke has flow domain texture [4]. This type of coke is required for carbon anode manufacture used in aluminum industry. It was observed that vacuum residues containing substantial amount of asphaltenes in delayed coking process are converted into isotropic phase and then finally converted into shot or sponge coke without passing through intermediate mesophase stage. The third type of coke is a premium quality needle coke the demand of which is increasing day by day because of their excellent properties i.e. good thermal and electrical conductivity, stiffness, low coefficient of thermal expansion (CTE), etc. This type of coke is produced from aromatic rich feed stocks having very low asphaltenes content (i.e. up to 1 wt%) [5], low sulfur, low mineral matter and low quinoline insoluble (QI) material. Premium quality needle coke is used to make ultra high power (UHP) graphite electrodes for steel industry.

The pathway of needle coke formation is conversion of aromatic rich feed stocks having very low or no asphaltenes content into isotropic phase, mesophase, semi-coke and finally into needle coke during thermal soaking. The chemical reactions involved during needle coke formation are dealkylation of alkyl aromatics, dehydrogenation of naphthenes, polymerization and condensation of aromatics. All these reactions proceed via free radical mechanism. The differences in the structure and properties of these three types of cokes is due to difference in chemical composition and reactivity of hydrocarbons present in the feed stocks, although these cokes be produced in the same delayed coker drum.

To a considerable level, the nature and properties of three types of petroleum cokes are decided by their crystalline structure which is mainly rely on the nature of the intermediate phase i.e. carbonaceous mesophase formed during thermal treatment of the feed stocks [6]. Carbonaceous mesophase is produced either by thermal [7,8] or catalytic polymerization [9–12] processes from aromatic rich feed stocks. During thermal soaking of petroleum feed stocks, dealkylation of alkyl aromatics, aromatization of naphthenoaromatics, ring opening, polymerization and condensation reactions take place via free radical mechanism [13]. Once condensation of aromatic hydrocarbons in feed stock has achieved at a certain level, the highly condensed species form spherical units of anisotropic phase. On the basis of optical microscopic studies development of different optical textures, formation of anisotropic structures of cokes passes through the following four stages: (1) Formation of spheres of mesophase, (2) Growth in size of mesophase spheres, (3) Coalescence of the mesophase spheres, (4) Formation and development of bulk mesophase. During these reactions complex polycyclic aromatic hydrocarbons (PAHs) are formed having molecular weight in the range of 200–1600 amu [12]. More work has been done, in the past, to examine the effect of chemical composition of feed stocks on semi-coke texture and their characterization during the thermal treatment processes [4,14–16].

In the present work, we have studied the effect of presence of asphaltenes on semi-coke textures produced from vacuum residue and its deasphalted oil (DAO) by thermal treatment at 390 °C under inert atmosphere. To the best of my knowledge, in previous reported literature there is no report on direct addition of asphaltene molecules into petroleum feed stocks to examine the effect of asphaltenes on the growth of mesophase formation. Therefore, we have studied that if asphaltenes is added into petroleum feed stocks, how the externally added asphaltenes modify/alter the mesophase development behavior in petroleum residues. For a better understanding of the structural features of semi-cokes produced during thermal treatment for different durations were investigated by elemental analysis, solubility test (TI, QI), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), optical microscopy (OM) and thermogravimetric analysis (TGA).

Table 1
Selected physico-chemical properties of vacuum residues and their deasphalted oils.

Characteristics	Test methods	VR-1	VR-2	DAO-1	DAO-2
Density d_4^{15} gm/mL	IP 190	1.0376	1.0554	1.0202	1.0258
Sp. Gravity 60/60 °F		1.0382	1.0561	1.0208	1.0264
°API gravity		4.8	2.48	7.1	6.4
Viscosity 100 °C (cSt)	ASTM D 445	2113.8	25795.68	1074.43	2095.00
MCR ^a (wt%)	ASTM D 4530	24.24	26.62	20.33	19.69
Pour point (°C)	ASTM D 97	+42	+72	+36	+45
C (wt%)		85.41	86.30	84.43	84.23
H (wt%)		9.51	8.18	11.75	11.84
N (wt%)		0.35	0.50	0.11	0.37
S (wt%)		4.73	5.02	3.71	4.16
Ni (ppm)		31.10	51.70	25.10	24.60
V (ppm)		71.90	198.00	50.40	109.40

^a Micro carbon residue.

Download English Version:

<https://daneshyari.com/en/article/205227>

Download Persian Version:

<https://daneshyari.com/article/205227>

[Daneshyari.com](https://daneshyari.com)