Journal of Industrial and Engineering Chemistry 48 (2017) 133–141

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Meliorate optical textures and mesophase contents by promising approach of deasphalting of petroleum residues

Subhash Kumar[a,b,*], Manoj Srivastava[a,b]

[a] Academy of Scientific and Innovative Research (AcSIR) at CSIR-Indian Institute of Petroleum, Dehradun 248005, India
[b] Heavy Oil Processing Area, CSIR-Indian Institute of Petroleum, Dehradun 248005, India

ARTICLE INFO

Article history:
Received 24 October 2016
Received in revised form 17 December 2016
Accepted 26 December 2016
Available online 3 January 2017

Keywords:
Vacuum residue
Deasphalted oil
Asphaltenes
Mesophase

ABSTRACT

The aim of this work is to study melioration in mesophase formation behaviour by deasphalting of petroleum residues. Pitches prepared from VRs have undesirable high values of physico-chemical properties as compared to their corresponding DAOs pitches. This is due to presence of high molecular weight asphaltenes molecules in VRs. The optical microscopic images of VR-390-1 and VR-390-2 pitches showed that they have small sized, distorted and agglomerated types of mesophase having mesophase contents (MC) 25 vol% and 22 vol% respectively but deasphalting of these VRs improve the growth and optical texture of mesophase in DAO-390-1 (29 vol%) and DAO-390-2 (35 vol%).

Introduction

Petroleum is one of the world's most important sources of energy since mid-1950s and also used as raw materials for the synthesis of many chemical products such as solvents, fertilizers, pesticides, and plastics. In recent decades, the demand for petroleum-derived fuels for internal combustion engines, jet engines and fuels for heating purposes has increased growth in the operating capacities of petroleum refineries. Therefore, the world's supply of light crude oil is declining and refiners are forced to depend increasingly on nonconventional feed stocks such as heavy oils and bitumen to fulfil the increasing demand for fuels. Not all of the crude oils can be commercially exploited and residues from various distillation and cracking procedures remain within the refinery. The disposal of these low economic valued petroleum residues is becoming a very big problem for the petroleum industry. Furthermore, direct burning of these petroleum residues will undoubtedly pollute the air and also contributes to serious environmental problems such as CO_2 emissions and global warming due to their high sulphur content. Therefore, from both economic and environmental viewpoints, there are significant developments for the commercial use of these petroleum residues, mainly in the production of higher value and clean carbon products [1,2].

Number of carbon products being used in different industries is high, especially those derived from fossil fuels worldwide. Petroleum pitch and coal tar are used for the preparation of carbon products because of their low price and wide range of specifications. Moreover, in industries quality of the products and reduction of costs is continuously requiring improvement. Petroleum residue is routinely investigated as low value carbon product feed stock. Petroleum residues generally include blends of decant oil (DO), vacuum residue (VR), and pyrolyzed fuel oil (PFO), which have different chemical composition, viscosity, and impurities according to the different refining operation conditions. Furthermore, these low valued residues have undefined chemical components comprising varying polycyclic aromatic hydrocarbons which have high carbon contents. Therefore, they attract many carbon engineers and scientists towards the preparation of different carbon materials because of their unique structural properties and extremely rich aromatic contents [3,4].

Generally pitch can be prepared from various organic sources of heavy oils such as fluid catalytic cracking decant oil, vacuum residue, coal tar etc. at temperatures greater than 300 °C under a nitrogen flow for several hours [5–7]. Different heavy oils have different physico-chemical properties, so different modified methods such as direct thermal polymerization [8,9], catalytic polymerization [10,11] hydrogenation treatment, [12,13] and co-carbonization [14] were used to prepare the mesophase pitches which meliorate the quality of the mesophase based advanced

* Corresponding author at: Academy of Scientific and Innovative Research (AcSIR) at CSIR-Indian Institute of Petroleum, Dehradun 248005, India. Fax: +91 135 2660202.
E-mail addresses: dangwalx75@gmail.com, subhashiip@gmail.com (S. Kumar).

http://dx.doi.org/10.1016/j.jiec.2016.12.031
1226-086X/

carbon products. Among these methods, direct thermal polymerization is the most employed one, performed by maintaining the feedstock isothermally for a certain time.

Mesophase pitch, which is composed of planar disc-like aromatic compounds of high molecular weight, is regarded as an excellent precursor for making a wide variety of industrial and advanced engineering carbon products of different structure and properties such as carbon fibres [15], needle coke [16], C–C composites [17], Li-ion battery anodes [18], mesocarbon microbeads (MCMB) [19], carbon foam [20] and many more. Therefore, the demand for mesophase pitch based advanced carbon products are constantly increasing. At present, only two excellent precursors for preparing mesophase pitch are universally known i.e. A240 pitch and naphthalene pitch which are generally prepared from fluid catalytic cracking decant oil and catalytic polymerization of pure naphthalene respectively [21]. The above mentioned two pitches are costly as compared to the pitches prepared from vacuum residues. Wider application of mesophase pitch based carbon products requires lowering the cost of precursors and the use of simpler synthesis processes to prepare the mesophase pitch.

Generally, vacuum residue has high viscosity and contains high asphaltenes proportions. These high asphaltenes content rapidly deactivate the sites of catalysts and act as poison for fluid catalytic cracking and hydrocracking. Therefore, vacuum residue is used as a feed stock for non catalytic processes such as 'delayed coking' and 'visbreaking' for production of valuable transportation fuels and petroleum coke as a by-product. The cokes (shot coke or sponge coke) produced in delayed coking process are of poor quality due to the presence of higher asphaltenes contents, carbon residues, heteroatom contents, and metal contents (Ni and V) present in the feed stocks. Nowadays, demand of needle coke is growing rapidly because of its low coefficient of thermal expansion (CTE), low porosity, and low levels of impurities, such as sulphur, ash, or metals and is used for making graphite electrodes required for steel production. The demand of graphite electrodes is increasing continuously every year, there is need to produce needle coke in large quantities. Earlier work showed that such vacuum residua are not suitable feed stocks for production of needle coke. Eser and Jenkins reported that asphaltenes molecules present in petroleum feed stocks play an important role in controlling the optical texture of petroleum cokes, more important in comparison with maltenes (saturate, aromatic and resins) [22]. Another important requirement for needle coke formation regards to the fact that feed stock should pass through mesophase formation an intermediate phase that is characterized as a discotic nematic liquid crystal [23–25]. It is well known that for pitch preparation various types of mechanisms are involved such as condensation, polymerization, volatilization, aromatization and cracking reactions [21,26,27], however in the case of pitch preparation from naphthalene and anthracene by using Bronsted acid type catalysts, aromatization and condensation mechanisms are involved [10].

The formation of mesophase in the petroleum feed stocks or mesophase pitch depends mainly on the feed stock's composition and process conditions i.e. thermal treatment temperature, heating rate, residence time, gas flow rate and stirring rate [23]. In the literature, several researchers observed mesophase formation in vacuum residues but in a very small quantity [28].

Our previous reported article [29] describes the effect of externally added asphaltenes on optical textures of semi-coke and pitches prepared from vacuum residues (i.e. Haldia Refinery, Reliance Jamnagar Refinery respectively) and clarified oil (CLO) & aromatic extract (AE) respectively. This study revealed that asphaltenes either present in the petroleum feed stock or externally added over the feed stock play a negative role on the mesophase development as well on the semi-coke texture. However, in the present paper, we have taken other two different vacuum residues (i.e. Numaligarh Refinery Limited, Hindustan Petroleum Corporation Limited respectively) whose physico-chemical properties are totally different from that of vacuum residues reported in our previous article [29] to study the effect of deasphalting on mesophase development. The main objective of this study is to produce good quality feed stocks for mesophase pitch formation from low value petroleum refinery streams. This can be achieved by removing asphaltene molecules from the feed by deasphalting process so that these feed stocks then can be used for the preparation of mesophase pitch. Therefore, there is a need to explore the possibility of producing mesophase pitch from vacuum residues and study the effect of deasphalting on mesophase formation. Currently, there is no indigenous production of petroleum derived mesophase pitch and needle coke in India. This material is essentially needed for making graphite electrodes and carbon anodes for steel and aluminium industries in the country. The current studies will help petroleum refiners to identify/screen available refinery feed stocks suitable for production of mesophase pitch/premium quality needle coke.

In this paper, we prepared petroleum pitches by thermal treatment of two vacuum residues and their deasphalted oils (DAOs). These pitches were characterized by determining their physico-chemical properties and by analytical techniques such as Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), scanning electron microscopy (SEM), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and optical microscopic imaging to study the melioration in mesophase formation behaviour by deasphalting of vacuum residues. This study also confirmed that presence of asphaltenes suppress the mesophase formation in the vacuum residues.

Experimental section

Materials

In this study, we have taken vacuum residues namely VR-1 and VR-2 (i.e. Numaligarh Refinery Limited, Hindustan Petroleum Corporation Limited respectively) obtained from two different petroleum refineries and their deasphalted oils (DAOs) namely DAO-1 and DAO-2 respectively for preparing petroleum mesophase pitches. Physico-chemical properties of vacuum residues and their deasphalted oil (DAOs) are given in Table 1. For deeper understanding about nature of feed stocks, vacuum residues were subjected to SARA (saturates, aromatics, resins and asphaltenes) analysis by using standard procedure [30] based on adsorption chromatography and their distribution into saturates, aromatics, resins and asphaltenes are given in Table 1. Metals such as nickel

Table 1
Physico-chemical properties of vacuum residues and deasphalted oils.

Characteristics	Test method	VR-1	VR-2	DAO-1	DAO-2
Density d_4^{15} g/mL	IP 190	1.0234	1.0580	1.0143	1.0338
Sp. Gravity 60/60 °F		1.0240	1.0587	1.0149	1.0344
°API Gravity		6.7	2.2	7.9	5.3
Viscosity 100 °C (cSt)	ASTM D 445	1875.8	5485.9	1068.10	1983.95
MCR[a] wt%	ASTM D 4530	17.7	24.9	14.3	21.1
Pour Point (°C)	ASTM D 97	+75	+51	+69	+42
Ni (ppm)		7.00	40.00	5.80	26.20
V (ppm)		1.00	153.80	<1.00	104.00
SARA analysis (wt%)					
Saturates		35.27	24.13		
Aromatics		40.23	50.91		
Resins		11.80	11.90		
Asphaltenes		12.70	13.06		

[a] Micro carbon residue.