Cocarbonization Properties of Heat-treated FCC Decant Oils with Low Sulfur Vacuum Residue Leading to Production of Needle Coke

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(Received October 27, 1989)

Cocarbonization properties of a particular FCC decant oil (FCC-DO) of paraffinic nature with low sulfur vacuum residue (LSVR) were studied in an attempt to find guiding principles of its thermal modification for production of better quality needle coke, using a tube bomb, as these oils do not always make excellent coke of homogeneous quality because of difference existing in the oils properties. FCC-DO was heat-treated under some conditions of temperature and residence time before cocarbonization with LSVR, to eliminate the unfavorable bottom mosaic coke. The heat-treatment of FCC-DO removed paraffins and alkyl groups of longer chains on aromatic ring, which increased the aromaticity. Highly aromatized FCC-DOs increased solvency, at early stage cocarbonization, dissolving viscous mesophase derived from the most reactive portion in LSVR which is believed to cause bottom mosaic structure. The coefficient of thermal expansion (CTE) of the coke was maintained at optimum range for graphite electrodes by selecting adequate carbonization conditions for the particular feed.

1. Introduction

Cocarbonization of a low sulfur petroleum vacuum residues (LSVR) with fluid catalytic cracking decant oils (FCC-DO) has been recognized to be an effective procedure for the production of premium needle coke¹⁾. However DOs do not always give excellent coke for graphite electrodes, forming mosaic coke in the bottom of the tube bomb and deteriorating homogeneity and quality of the coke as reported in previous papers^{2),3)}.

The present authors have been looking for plausible solutions to the problem in a series of studies^{2)~6)}.

In the present study, heat-treatment of a particular FCC-DO of higher paraffin content (denoted G in a series of papers) which was reported to produce such a coke in its cocarbonization with LSVR^{3),4)} was investigated to improve its properties as a cocarbonizing complement in terms of coefficient of thermal expansion (CTE) of the whole coke-lump and the amount of the bottom mosaic coke.

Heat-treatment under adequate conditions is expected to aromatize slightly paraffinic FCC-DO through pyrolytic reactions without producing unfavorable carbonaceous substances. Dealkyla-

tion from aromatic rings and paraffin cracking can improve capability of the cocarbonizing complement to dissolve the carbonized products from the most reactive species in LSVR, which tend to precipitate in paraffinic carbonizing matrix at the initial stage carbonization, forming bottom mosaic coke³⁾.

2. Experimental

Some analytical data of a FCC-DO(G) and LSVR are described in the preceding paper⁶⁾.

About 20 g of the FCC-DO in an aluminium foil tube was heat-treated in a stainless steel tube bomb that was inserted and kept in a sand bath at prescribed conditions of temperature and time. The heating rate was about 250°C/min. The pressure was adjusted by the initial nitrogen pressure and adequate purging through a control valve during the heat-treatment. The heat-treated product was quenched in cold water and its whole quantity was recovered in the foil.

The heat-treated FCC-DO and LSVR were blended at 80°C, while stirring. Cocarbonization of the blends was performed at 480 and 490°C in the manner same as that of the heat-treatment. The coke-lump was examined in terms of anisotropic texture and CTE (at temperatures ranging from room temperature to 500°C) of the middle portion

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after calcination at 1,000°C.

The heattreated FCC-DO was extracted with pentane (Pe), hexane (H), and benzene (B) to characterize its fractions on analytical basis. ^1H -NMR of benzene soluble fractions in both original and heattreated DOs after dewaxing were measured with 400 MHz FT-NMR (Varian). Pentane soluble fraction was also analyzed with TLC-FID (thinlayer chromatography-flame ionization detector).

3. Results

3.1 Coke Produced by Cocarbonization of LSVR with Original and Heattreated FCC-DOs

Montage microphotographs of lump coke produced at 480°C by cocarbonization of LSVR with an original and heattreated DOs are shown in Fig. 1. The original FCC-DO with LSVR produced an area of mosaic texture at the bottom of the lump, although the middle and upper parts showed excellent flow texture of uni-axial arrangement as shown in Fig. 1(a) and (b). DO heated at 410°C for 1 h produced a lump coke of essentially the same appearance as that of the original DO except for reduced height of bottom mosaic as shown in Fig. 1(c) and (d). A longer heattreatment by 5 h at the same temperature certainly provided better properties to cocarbonized DO. There were no bottom mosaic texture produced, any more, in the resultant lump coke, having excellent flow texture at its middle and upper parts, as shown in Fig. 1(e) and (f).

At higher temperature of 430°C, it was possible to modify DOs more rapidly to eliminate the mosaic coke in the course of its cocarbonization. One hour appeared sufficient at 430°C, although the microphotographs of the coke obtained from that heattreated for 3 h are illustrated in Fig. 1(g) and (h). The flow, or domain flow, textures prevailed in the coke, although the alignment thereof was not always parallel to the axis. Some of the textures were laying perpendicular to the axis.

A further higher temperature of 450°C gave similar results with shorter time of heattreatment.

3.2 CTE and Coke Yield

The values of CTE and yields of the cocarbonized cokes at 480°C are summarized in Table I. The top and bottom portions of the lumps were cut off before measurement. The cocarbonization of LSVR with original FCC-DO provided and excellent CTE value of $0.2 \times 10^{-6}/^\circ\text{C}$, although mosaic texture 1.1 mm high formed at the bottom of the lump.

The heattreatment at 410°C for 5 h essentially maintained the level of CTE as low as $0.3 \times 10^{-6}/^\circ\text{C}$.

(a), (b): Original FCC-DO. (c), (d): 410°C-1 h heattreated FCC-DO. (e), (f): 410°C-5 h heattreated FCC-DO. (g), (h): 430°C-1 h heattreated FCC-DO.

Fig. 1 Montage Microphotograph of Lump Coke

Thus, the heattreatment of DO served to realize both excellent CTE and elimination of mosaic coke at the bottom. DOs heattreated at higher temperatures of 430 and 450°C gave lump coke having unfavorable CTE of $1.1-1.4 \times 10^{-6}/^\circ\text{C}$. The values were comparable to those of commercial needle coke⁷⁾, but certainly higher than those of the

Table 1 Properties of Lump Needle Coke

	CTE [$\times 10^{-6}/^{\circ}\text{C}$]	Thickness of bottom mosaic [mm]	Coke yield [%]
Unheattreated			
FCC-DO	0.2	1.1	29
410°C- 1.0 h	1.0	0.4	38
410 - 5.0	0.3	none	43
410 -10.0	0.2	none	47
430 - 1.0	1.2	none	35
430 - 3.0	1.1	none	43
430 - 5.0	—	none	47
450 - 1.0	0.4	none	36
450 - 3.0	1.5	none	44

Carbonization conditions: 480°C, 8 kg/cm² A

Table 2 Solubility of Heattreated FCC-DO

Heattreatment		Yield on feed [%]	Fraction yield [%]				
Temp. [°C]	Time [h]		PeS	PeI-HS	HI-BS	BI-QS	QI
Original DO	—	—	99	1	0	0	0
410	1.0	86	97	1	1	1	0
↓	5.0	83	76	7	16	1	0
↓	10.0	68	71	3	24	2	0
430	1.0	82	86	4	8	2	0
↓	3.0	77	69	7	22	2	0
↓	5.0	69	33	12	48	7	0
450	1.0	70	68	9	19	4	0
↓	3.0	55	20	15	41	24	0

better coke obtained in the present study. Using DO heattreated at 430°C for 3 h, higher cocarbonization temperature of 490°C improved the CTE of the cocarbonized coke to 0.3×10⁻⁶/°C. The heattreatment increased the coke yield (carbonized feed basis) of the cocarbonization from 30% to 35—47%. Significant increase of coke yield may be worthy of note. The longer treatment tended to give higher yield, regardless of heattreatment temperature.

3.3 Characterization of DOs

The yield and solubilities of heattreated DOs are summarized in Table 2. The original DO was essentially soluble in pentane. The heattreatment cracked and evaporated a considerable amount of reacted fraction, depending on the treatment temperature and time. At 410°C, 14% of DO was removed in 1 h, small amounts of PeI-HS, HI-BS and BI-PS (of 1%) being produced. Longer treatment times of 5 and 10 h decreased the yields to 83 and 68%, respectively, producing significant amounts of PeI-HS and HI-BS. The content of BI-PS stayed low. Higher temperatures decreased the yields and produced pentane insoluble fractions more rapidly. It should be noted that no QI was formed, even at 450°C for 3 h, although the content of PeS dropped to a very low.

Some instrumental analytical data of DOs heattreated at 410°C for 5 h, which appeared to be the best complement, are summarized in Tables 3

Table 3 TLC Analyses of PeS in FCC-DO

	Satu.	Arom.	Resin	Asph.
Original DO	17(17)	81	2	0
410°C-5.0 h	11(7)	86(54)	1(1)	2(1)

() : Based on products heattreatment 83% × 76 = 63

Table 4 Hydrogen Distribution of BS in DOs

	Hydrogen distribution [%]				
	H _{aro.}	H _α	H _β	H _γ	H _δ [8.2—10 ppm]
Original ¹⁾	21	21	39	19	3
Heattreated ²⁾	52	27	18	3	13

- 1) dewaxed original FCC-DO
- 2) dewaxed benzene soluble fraction of FCC-DO heattreated at 410°C for 5.0 h

and 4, including those of the original DO for comparison.

By heattreatment, the saturate fraction was removed by 8%, increasing the aromatic fraction by 7%, as shown in Table 4. ¹H-NMR spectra of the dewaxed BS fraction in original and heattreated DOs are illustrated in Fig. 2. It is certainly definite that the alkyl side chain was removed by the treatment as suggested by a marked decrease of H_β and H_γ to increase aromaticity. The alkyl groups of longer chains may be preferentially removed by heattreat, as indicated in Table 4. It is of significance to note that H_α increased significantly. Difficulty of demethylation or preferential fission

A: BS fraction of original FCC-DO (Wax free)
 B: BS fraction of heat-treated FCC-DO at 410°C-5 h
 (Wax free)

Fig. 2 ^1H -NMR Spectra

of benzyl position are suggested. The heat treatment intensified the peak at 8.2–10 ppm. The larger aromatic ring may be concentrated or produced during the heat treatment.

4. Discussion

The heat treatment at 410–450°C, in the present study, was found to be highly effective to modify DO so as to become compatible with LSVR in their cocarbonization, reducing and eliminating the formation of the bottom mosaic coke texture in the resultant lump coke obtained at 480–490°C. The DO treated at optimum conditions, of 410°C for 5 h, produced a lump free from mosaic textures, with CTE of as low as $0.3 \times 10^{-6}/^\circ\text{C}$. Thus, such heat treatment of FCC-DO could be applied to a commercial coking process where coke of excellent homogeneity and low CTE are expected all through in the coking drum. Treatment at higher temperatures (430–450°C) was also effective to remove mosaic textures by cocarbonization at 480°C. The CTE values of the lumps, however, were somewhat greater at this temperature, which is suitable for combination of original DO and LSVR. It appears that slightly higher temperature of the carbonization is required

for the optimization.

The heat treatment removed, as indicated by NMR and TLC, preferentially, paraffins and alkyl groups of longer chain. Such an aromatization increased capability of FCC-DO in the early stage of the carbonization to dissolve the mesophase derived from the reactive portion of the asphaltene, which is believed to cause bottom mosaic texture³.

By heat treating, coke yield of FCC-DO increased by eliminating the non-coking portion, hence fixed mixing ratio of LSVR/FCC-DO at unity is favorable for the heat-treated DO. Less amount of long paraffins produced from FCC-DO at the early stage of carbonization was also favorable to keep the dissolving ability of the matrix high, which resulted from the origin of such products in DO being removed by the heat treatment.

It is of significance to comment that heat treatment of DO at 410°C for 5 h is a requisite to produce lump coke of low CTE at 480°C. Alkyl side-chains of limited amount that still remain might keep its reactivity to provide the temperature and sources for the gas evolution at the solidification stage. High value of H_a may assure the production of methane at the solidification stage. The gas evolution is believed to be essential for uni-axial alignment along the tube axis at solidification⁹. Severe heat treatment may enhance further the aromatization of DO. While it is favorable to eliminate the mosaic texture, excess aromatization may stabilize DO to such an extent as to remove sources of gas evolution in the carbonization. Hence a slightly higher temperature of carbonization to accelerate pyrolytic reactions is the optimum for such feedstocks. Such an explanation is very reasonable on the basis of the mechanisms proposed by the present authors⁹. By selecting the optimum conditions, both elimination of mosaic texture and assurance of low CTE of the lump coke produced in the cocarbonization of LSVR are realized with the use of preheat-treated DO as complement.

References

- 1) Stocke, C. A., Guercio, V. J., *Erdel & Kohle Erdgas Petrochemie*, **38**, 31 (1985).
- 2) Mochida, I., Korai, Y., Fujitsu, H., Oyama, T., Nesumi, Y., *Carbon*, **25**, 259 (1987).
- 3) Nesumi, Y., Todo, Y., Oyama, T., Mochida, I., Korai, Y., *Carbon*, **27**, 359 (1988).
- 4) Mochida, I., Korai, Y., *Sekiyu Gakkaishi*, **33**, (5), 318 (1990).
- 5) Nesumi, Y., Azuma, A., *Ind. Eng. Chem.*, **29**, 1793 (1990).
- 6) Mochida, I., Korai, Y., Abe, S., Todo, Y., Oyama, T., *Sekiyu Gakkaishi*, **33**, (6), 367 (1990).
- 7) Mochida, I., Ogawa, M., Takeshita, K., *Bull. Chem. Soc., Japan*, **49**, 514 (1976).
- 8) Mochida, I., Oyama, T., Korai, Y., *Carbon*, **26**, 49 (1988).
- 9) Mochida, I., Oyama, T., Fei, Y. Q., *Fuel*, **67**, 1171 (1988).

要 旨

ニードルコークス製造における熱処理 FCC デカント油と
低硫黄減圧残さ油の共炭化性

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FCC デカント油 (FCC-DO) と低硫黄減圧残さ油 (LSVR) から共炭化によってニードルコークスを製造する場合, FCC デカント油の性状によっては均質なコークスが得られないことがある。本研究ではこのように, 均質なコークスの得られないパラフィン系の FCC デカント油を, あらかじめ熱処理することによって, コークス品質の改善, とくにボトムモザイクコークスの消去を試みた。ここでは本 DO に 410°C-5 ~ 10 h, 430°C-1 h, 450°C-1 h の熱処理を施すことによって LSVR との共炭化によって生じるニードルコークス塊からボトムモザイクコークスを消去し, かつ熱膨張係数 (CTE) を $0.3 \sim 1.1 \times 10^{-6}/^{\circ}\text{C}$ とすることができた (Fig. 1, Table 1)。

FCC デカント油は熱処理によって芳香族環の長アルキル側鎖が切断し, 芳香族性が向上することが NMR, TLC によって確認できた (Tables 2, 3, 4)。熱処理によって生成した高芳香族性 FCC デカント油は, 共炭化初期段階において低硫黄残さ油中の反応性の高い成分から生成する粘性の高いメソフェーズを溶解する能力が高いため, ボトムモザイク消去に有効であると理解できる。ニードルコークス生成機構を考慮し, 熱処理した DO と LSVR の組み合わせ, 共炭化条件を選ぶことによって, 高温熱処理によって芳香族性を高めた DO からコークスの熱膨張係数 (CTE) を $0.3 \times 10^{-6}/^{\circ}\text{C}$ にすることができた。

Keywords

Cocarbonization, Coking, FCC decant oil, Needle coke, Bottom mosaic coke