

Characterization of Volatile Matter in Raw Petroleum Coke and Possibilities of In Situ Utilization for Better Yield and Properties of Calcined Product

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Introduction

Co-relations of certain physical properties of calcined petroleum coke (cpc), with temperature of calcination and residence time at maximum temperature has been well established(1-4). Changes in physical properties of raw petroleum coke (rpc) during heat treatment at different temperature and effect of rate of heating upto calcination temperature has already been reported by us (5). In the present paper, we report, nature and amount of volatile matter (v.m) present in rpc from identical crude produced by different refineries, and its effect on properties of cpc. Possibilities of in-situ utilisation of volatile substances during calcination, has been investigated for the first time in a specially built vertical reactor and results will be discussed.

Experimental

Samples of rpc produced in delayed coker of two refineries based on identical crude with two extreme level of volatile percentage were selected. These are marked G-1 and G-2 with 8.3 and 9.8% v.m. and D-1 and D-2 with 11 and 13.3% v.m. respectively. Quality of cpc produced under identical conditions are given in the table. Gravimetric heat loss curves were obtained from 200-1000°C with 1 g sample of grain size 4.699 mm to 0.208 mm. Identical samples were heated in s.s. reactor with gas collection assembly and tar condenser for chromatographic gas analysis. Heating rate and max. temperature were 10°C/m and 1000°C respectively.

Possibilities of in-situ utilisation of v.m during calcination was studied in specially designed vertical s.s. reactor consisting of three chambers maintainable at 400, 800 and 1200°C by external heating (Fig.1). A central shaft with interlocking valves, separated the chambers and a downward movement of the shaft, with a head pulley, changed the material inside from one chamber to another in the series. Arrangement of inter-connecting side tubes and a pressure gradient device allowed the v.m. to circulate in the chambers. A continuous batch of 200 g cpc obtained after every 1.5 hr and tested. A similar portion of sample was flash calcined as before (5) for comparison.

Cracking of hydrocarbons was studied in a nitrogen purged atmosphere, where v.m. of rpc was passed through a column of cpc maintained at 1000°C in s.s. reactor and continuously monitored in gas chromatograph. Aminco porosimeter (15000 psi) was used when required.

Table 1. Properties of CPC Produced

Properties	G-1	G-2	D-1	D-2	FC	RC
RPC (v.m)	8.3	9.8	11.0	13.3	-	-
RD. (g/cc)	2.07	2.065	2.067	2.06	2.04	2.02
P.D. "	1.45	1.40	1.28	1.24	1.28	1.47
B.D. "	.72	.69	.64	.62	.64	.73
A.D. (Hg 1.78) "	1.60	1.55	1.45	1.43	1.45	1.55
A.D. (Hg 14.7) "	1.71	1.68	1.58	1.56	1.55	1.68
Porosity % <100 μ	9.4	9.7	11.7	13.3	11.7	6.4
100 μ <18 μ	6.4	7.7	8.2	8.3	6.4	7.7
>18 μ	17.3	18.6	23.5	24.3	24.0	16.8

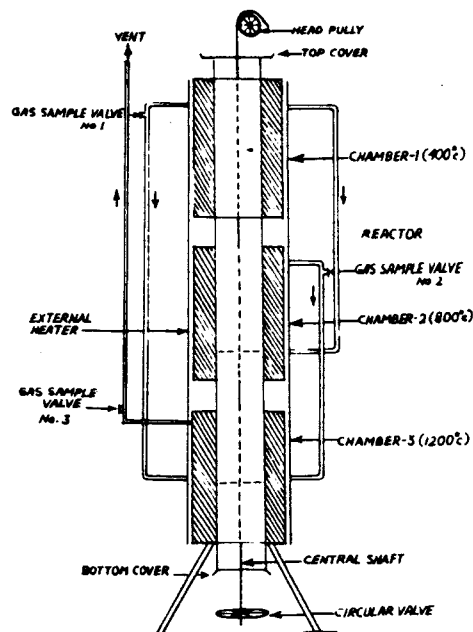


Figure 1. Reactor for calcination of RPC

Results and Discussion

Results in the Table indicate that cpc produced from rpc of different volatile level, significantly differ in physical properties, chiefly bulk density (BD) apparent density (AD) particle density (PD) and porosity. It can be assumed that BD, AD and PD, which depend on total porosity developed during calcination and the nature and amount of volatile matter determine the porosity development during escape. This is evident in Fig.2, where heat loss curves of a high volatile substance indicate elimination of v.m. more vigorously and at an early temp.

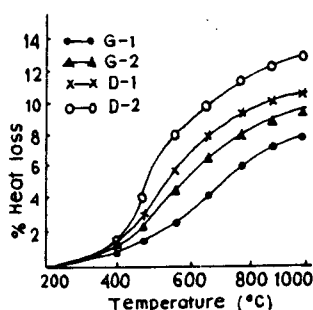


Figure 2. Heat loss curves of RPC

than a low volatile rpc, simultaneously determining pore size distribution pattern and total porosity as in Fig.3. It is estimated that 1% increase in v.m. increase porosity and decrease density by approximately 2% based on mercury intrusion.

The composition of v.m. in G-1 and D-1 sample are as follow. The escape of v.m. during heat treatment upto 1000°C are given in Fig.4.

		G-1	D-1
H2	%	11-12	11-12
CO	%	5	5-6
CO2	%	5-6	4
CH4 & C2H6	%	52	67
Other Hydrocarbons	%	21	6
Tar	%	5	6-7

It is seen that heat loss upto 300°C is chiefly due to entrapped air in both the samples, constituting 5-6% of total volatiles. Elimination of volatiles actually held within the micro and mesopores of the particles, takes place from 300°C and onward. Methane, Carbon dioxide and Hydrogen are the first permanent gases evolved at 300°C. Difference in nature of volatile in the two samples is evident from gases evolves at 400° and above. These are chiefly C3H8, C4H10, C5H10 and C5H12 in G-1 sample and C3H8 and C4H10 in D-1 sample grouped as other hydrocarbons besides CH4 and C2H6. These are also different from the gases as reported by others(6).

In the light of the above results it could be explained that, the upward trend in heat loss curve of D-1,2 rpc at an early temperature is due to high amount of lighter hydrocarbons, chiefly, CH4 and C2H6, which could also explain high porosity development because of bulk evolution constituting 73% of v.m., within a narrow range of temp. from 400-700°C. In comparison G-1, 2 rpc, containing low amount of CH4 and higher percentage of higher hydrocarbon undergoes less drastic thermal changes indicating slope in cruves (Fig.2 & 3). This signifies a loss of 51% of the total v.m. at 400-700°C range while 45% escape at higher temp. The gradual loss in v.m. give low porosity and reduction in macropore volume to give better said densities. It is also seen that nature of v.m. rather than amount is accountable for volatile release during heat treatment of rpc. The comparative amount of lower and higher hydrocarbons, determining cpc properties, may be due to interconvertible factors of coking parameter of the two refineries using identical crude.

Results in the Table are properties of cpc produced from G-1 rpc by different methods including the reactor designed. It is seen that improvement

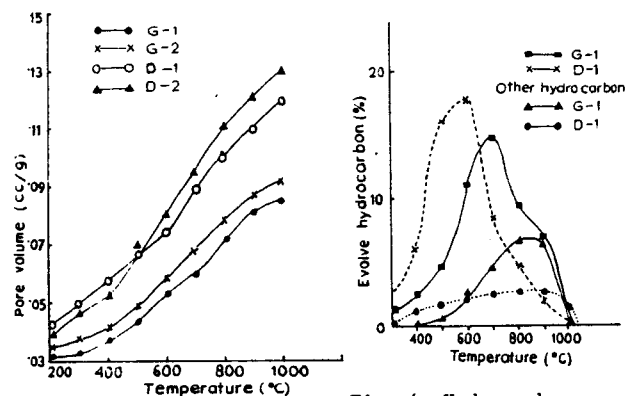


Fig. 3. Porosity curves at different temps.

Fig. 4. Hydrocarbon constituents at different temps.

in PD, BD and AD is significant in the reactor calcined material (RC) over the regular calcined and flash calcined (FC) material. Improvement in yield by 5-6% over the conventional calciner is the most economic aspects of the process. This could be explained either due to slow calcination(5) or decomposition of hydrocarbons, particularly CH4 and deposition on macropore which would affect the densities. This hypothesis is supported by continuous monitoring of gases obtained after passage through a column of cpc held at 1000°C as seen in the chromatograms (Fig.5) where peak No.2 is of CH4.

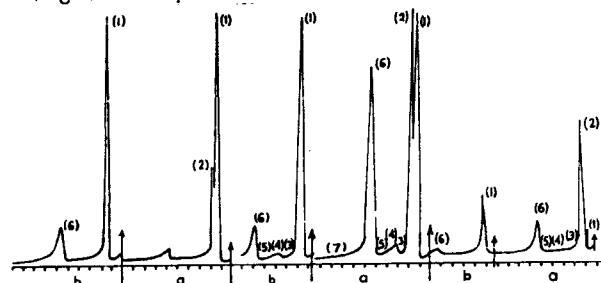


Figure 5. Hydrocarbon peaks of (a) RPC (b) after cracking

Conclusion

1. Amount as well as nature of volatile determine cpc properties under identical calcination parameters and they differ in different rpc of different refineries based on identical crude.
2. Development of porosity and total pore volume depend on relative amount of different v.m. constituent which affect densities of cpc.
3. The v.m. chiefly CH4 could be cracked and deposited at 1000°C on macropores of cpc particles to reduce porosity and increase density.

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