STUDIES ON RESINS FROM MAKERWAL COAL

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Makerwal coal is known to contain a high percentage of resins which are recoverable by solvent extraction. Alternative methods of recovery reported earlier [3,5] show a wide degree of variation in the yield of resins and the quality of coal residue. An attempt has been made to evaluate these methods, by studying separately the behaviour of original coal, solvent extracted resins and the coal residue from solvent extraction, on superheated steam treatment and carbonisation. It was found that on superheated steam treatment at 300-330°C these resins were only partially recoverable while on carbonisation extensive cracking of the resins was observed. The experimental data from the present work and critical review of the earlier work in this direction has clarified some of the hitherto reported anomalies of the behaviour of Makerwal coal.

Introduction

Makerwal coal of the Trans-Indus area is known to contain a substantial amount of solvent-extractable resins.[1] However, the yield and the nature of the extracted resins to some extent depends upon the nature of the solvent used. The most convenient solvents so far reported are *n*-propanol, benzene, or a 70:30 benzene-alcohol mixture.[2] Powdered Makerwal coal and other coals have been treated[3,4] with the superheated steam for the recovery of these resins in a depolymerised and chemically modified form with the simultaneous partial desulphurisation of coals below the sub-carbonisation temperature upto 330°C. Further work on superheated steam treatment of powdered Makerwal coal and other West Pakistan coals in the temperature range of 300-600°C had shown[5] that in the course of 6-hr treatment at 300°C only 2.9% of condensable volatile products, termed as "tar oil," were obtained. Moreover, the quality of coal residue from this treatment as shown by the yield and proximate analysis differed considerably from the one reported earlier.[3,4] The anomalous behaviour of Makerwal coal in the superheated steam treatment has also been mentioned by other workers,[6] who have attempted to explain this behaviour through the study of the chemical composition of ash without any conclusion. These differences and anomalies in the results of superheated steam treatment of powdered Makerwal coal necessitated the study of the behaviour of solvent extractable resins from Makerwal coal.

Experimental

200 g of Makerwal coal ground to pass 70- mesh B.S. sieve was exhaustively extracted using benzene-ethanol mixture 7:3 v/v as solvent in the Soxhlet extractor. The extracted material was recovered by distilling the solvent mixture and its last traces were removed by drying under vacuum. The material thus obtained was a dark brown powder. The coal residue left after solvent extraction was made free from solvent by vacuum drying. The results are given in Table 1.

The proximate analyses, and Gray-King carbonisation assays at 600°C of original Makerwal coal, coal residue from solvent extraction and solvent extracted resins were carried out by following the standard procedures.

Superheated steam treatment of 15-20 g Makerwal coal, coal residue from solvent extraction and solvent extracted resins was carried out separately at 300° and 330°C in a standard quartz tube used in the Gray-King assay. To hold the material in position a loose asbestos plug was introduced. The tube was placed in an electrically heated Gray-King tube furnace with precise temperature recording arrangement. The superheated steam from a boiler was passed to a gas-heated metallic superheater with temperature recording arrangement. The superheated steam (about 200 g/hr.) was then introduced through a perforated tube into the coal bed ensuring an intimate contact of steam with the material to be treated. The superheated steam at (320°C) was introduced into the retort heated to 150°C the temperature of the furnace was gradually raised (5°C/min and then maintained at 300±5°C until no more material distilled over with the steam (about 1.5 to 2.0 hr). In a separate experiment the original coal residue from solvent extraction was first treated at 300°C as before and then the temperature of the retort was raised to 330±5°C and further quantity of distillable material was collected. The superheated steam treatment was discontinued when no more material distilled over with the steam (about 1 to 1.5 hr). The results are shown in Table 2.

Results and Discussion

By the solvent extraction of original Makerwal coal (B.S.-70 mesh) it was found that the major

TABLE 1.—RESULTS OF BENZENE-ETHANOL, 7:3 v/v, EXTRACTION.

Sample extracted	% yield w/w of extracted resins						% total yield w/w on coal extracted (on dry original coal basis)
	1st 5 hr	2nd 5 hr	3rd 5 hr	4th 5 hr	5th 5hr	6th 5 hr	
Makerwal coal original, -70 mesh B.S.	8.10	0.77	0.39	0.20	0.11	Traces	9.57 (9.86)
Makerwal coal residue from superheated steam treatment at 300°C of original coal	5.27	0.50	0.13	Traces			5.90 (5.42)
Makerwal coal residue from superheated steam treatment at 330°C of original coal	4.40	0.65	0.10	Traces			5.15 (4.72)
Makerwal coal residue (char) from carbonisation (600°C) of original coal	Traces						

TABLE 2.—RESULTS OF SUPERHEATED STEAM TREATMENT.

Sample treated	% yield w/w on sample treated (on dry original coal basis)		Distillate (ml)
	Residue	Resins/ tar	
Makerwal coal original		2.04	470
-70 mesh, B.S., at 300°C	89.2	(2.10)	
	(91.2)	1.80	250
,, 330°C	84.7	(1.85)	
Makerwal coal residue after	(86.7)	0.40	340
solvent extraction, at 300°C	—	(0.37)	
,, 330°C	87.2	1.20	225
	(82.9)	(1.12)	
Resign from solvent extraction	58.3	25.00	480
of Makerwal coal, at 300°C	(5.7)	(2.54)	

portion of the resins present in the coal was extracted in the first 5-hour extraction (Table 1). The subsequent extractions yielded only a small amount of these resins. The extraction was stopped after 30 hr, as the amount of resins recovered from the sixth solvent extract was only in traces. The total yield of resins recovered from the coal was 9.57% w/w on as received basis. The yield of resins when compared to earlier work[2] is low. This is because of higher mineral matter (ash) content, Table 4 of the coal used for the present investigation.

The superheated steam treatment of the original Makerwal coal at 300°C yielded only 2.04% of resins and on further treatment at 330°C an additional 1.80% was obtained (Table 2). Thus the total yield of condensable volatile product obtained at 330°C was 3.84% as against the earlier reports of 9.7% of "depolymerised resins" obtained at 330°C and 2.9% of "tar oil" at 300°C. For the resinous material obtained at temperatures higher than 300°C the term, "condensable volatile product" is used. This is because, considering the quality of the indigenous coals it is difficult to state with certainty that at temperatures above 300°C the condensable volatile products obtained were entirely from the distillation of resins or were contaminated with tar from the decomposition of coal.

The results of superheated steam treatment at 300°C of the coal residue from solvent extraction, (Table 2), showed that only a small amount (0.4%) of the resins was recovered from the coal residue whereas at 330°C additional 1.2% of condensable volatile product was recovered. This 0.4% recovered at 300°C may be either partially due to recovery of solvent unextracted resins or due to the 'sweating' tar from this residue.

By the superheated steam treatment of solvent extracted resins at 300°C, only 25% of this material was found to be distillable (Table 2). The yield of distillable resins, in presence of superheated steam at 300°C, when calculated over the weight of coal is fairly close to the yield of resins obtained from the original Makerwal coal at 300°C.

From the above-noted results it was evident that only a part of resins present in the coal distilled over at 300°C with the superheated steam. This was confirmed by extracting the coal residue left from the superheated steam treatment at 300°C and 330°C of original Makerwal coal. As shown in Table 1, 5.90% of resins were extractable from the residue (300°C) and 5.15% from the residue (330°C).

From the above results the only plausible explanation for the higher yield of condensable volatile products reported earlier as "depolymerised resins"[3] may be found in the superheated steam treatment of coal at a higher temperature. This view was further substantiated by the comparison of the results of the yield of condensable volatile products and the proximate analyses of coal residue given in refs.3,4 and 5 with the results of the present investigations.

TABLE 3.—COMPARISON OF RESULTS OF SUPERHEATED STEAM TREATMENT OF POWDERED MAKERWAL COAL.

Temp. °C	% Residue on dry original coal	Dry ash-free basis % volatile matter	% fixed carbon	% resins/ tar	References
330	79.1	10.3	89.7	10.7	3
330	78.3	15.3	84.7	10.2	4
300	92.4	42.5	57.5	3.4	5
600	57.4	10.2	89.8	19.2	5
300	91.2	43.0	57.0	2.7	(Table 2 and 5)
330	86.7	38.4	61.6	5.0	(Tables 2 and 5)

from the original coal is calculated in the treated coal. The higher yield of condensable volatile 5 is not accounted for by the relative loss of volatile matter between 400° and 500°C. The loss of volatile matter in the above range is reported to be 4.5% whereas the increase in the yield of tar oil is reported to be 6.5%. If the figures reported in ref. 5 at 400°C are correct, the theoretical yield of tar oil could not have been more than 15.3% at 500°C presuming that all the volatile matter was condensed and no gases were formed due to cracking whatsoever.

In the low-temperature Gray-King assay of the original coal at 600°C a lower yield of only 11.5% (Table 4) of tar was obtained due to cracking.

TABLE 4.—RESULTS OF GRAY-KING LOW TEMPERATURE CARBONISATION ASSAY (600°C).

Sample carbonised	% yield on sample carboni ed (on dried original coal) Carbonised residue (char)	Resins/tar	Liquor	Gas in l at NTP	Remarks
Makerwal coal original, -70 mesh B.S.	65.7 (67.0)	11.5 (11.8)	11.0 (11.3)	10.6 (10.9)	Residue weakly coherent
Makerwal coal residue from solvent extraction of original coal	69.1 (63.8)	6.9 (6.4)	10.8 (10.1)	9.5 (8.8)	Residue pulverent
Makerwal coal resins from solvent extraction of original coal	43.2 (4.3)	30.4 (3.1)	8.0 (0.9)	12.5 (1.3)	Residue strongly coherent

TABLE 5.—RESULTS OF PROXIMATE ANALYSES ON DRY BASIS.

Sample analysed	% ash	% volatile matter	% Fixed carbon
Makerwal coal original, -70 mesh, B.S.	21.3	38.4	40.3
Makerwal residue from steam treatment at 300°C ..	24.6	32.4	43.0
Makerwal restidue from steam treatment at 300°C ..	26.1	28.4	45.5
Makerwal residue from carbonisation (600°C) ..	31.0	6.4	62.6
Makerwal coal residue from solvent extraction	26.1	34.6	39.3
Makerwal residue from steam treatment at 330°C ..	29.9	26.9	43.2
Makerwal residue from carboni sation (600°C)	37.0	6.6	56.4
Resins from solvent extraction of Makerwal coal original ..	0.2	88.5	11.3
Resins residue from steam treatment at 300°C	0.4	67.6	32.0
Resins residue from carbonisation (600°C)	0.5	9.8	89.7

It is evident that whereas the proximate analyses of treated coal at 300-330°C in ref. 3 and at 600°C in ref. 5 compare favourably in respect of volatile matter and fixed carbon, they widely differ in the yield of residue and the condensable volatiles. The higher yield of residue 3 does not hold good when the loss of moisture and volatile matter

It is highly probable that in superheated steam treatment at 600°C due to the sweeping action of steam cracking was avoided and a higher yield of condensable volatile products was obtained. The yield of resins and tar, in the coal residue from solvent extraction and in the extracted material, from Gray-King assay was found to be 6.9% and 30.4% (Table 4) respectively.

From these results it was noticed that the contribution of resins to the condensable volatile products on carbonisation at 600°C was about 5% when calculated over the weight of original coal since the remaining resins undergo extensive cracking during carbonisation as evident from higher yield of gas in the original coal than in the coal residue after solvent extraction (Table 4). There is a definite advantage of carbonising coal in the presence of superheated steam for due to its sweeping action the residence time of volatile products in the hot carbonisation zone is reduced and as a result the extensive cracking of condensable volatile products is avoided and more primary products are obtained. The use of superheated steam will, however, depend on economic factors. In view of our preliminary investigations on carbonisation by internal heating of West Pakistan coals with hot flue gases, we are of the opinion that with the beneficiation of coal extensive cracking of tar and resins could be avoided and the process would have definite economic advantage over superheated steam treatment.

Although no work is reported here from the point of view of desulphurisation it was noted that the results of desulphurisation at 300°C or 330°C in the presence of steam are not significant with respect to reduction in sulphur. This view is based on the consideration of results in ref.5 in which the reduction in total sulphur was claimed to be 23.8% at 300°C and 80.8% at 600°C calculated on 100 g. coal (m-free basis). The actual reduction calculated on the benificiated coal however comes to 12.6% at 300°C and 64.7% at 600°C. Considering the low yield of beneficiated coal (54.4%) at 600°C and the cost of steam raising and superheating, the reduction in sulphur no longer appears to be significant.

Conclusions

Of about 10% of resins present in the coal about 2.0 to 2.5% were found to be recoverable by superheated steam at 300°C. At higher temperatures more resins could be recovered but along with the products of decomposition of coal. The higher yield of resin in ref.3 was due to the higher temperature of steam treatment than what was claimed to have been employed. The solvent extraction method may therefore still be regarded as more suitable in so far as the recovery of the resins from coal is concerned.

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