STUDIES IN THE UPGRADING, ESPECIALLY DESULPHURISATION, OF WEST PAKISTAN COALS

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Most of the West Pakistan coals, as mined, have due to a number of unfavourable properties, e.g., high contents of volatile matter, ash and sulphur, a limited scope in regard to their utilisation as solid fuel for the generation of heat in industries and households. Upgrading, particularly by a reduction of volatiles, ash and sulphur is therefore highly desireable. In view of this, studies were undertaken to carbonise 8 West Pakitan coals in the presence of superheated steam in the temperature range of 300 to 600°C. The results show the favourable influence of steam with rising temperature on the reduction of volatile matter and on the various forms of sulphur in all the coals. At 600°C. the volatile matter was reduced to around 10% or less in the carbonised residue, for the production of a smokeless fuel, while, at this temperature, upto 95% of the pyritic sulphur, 60 to 70% of the organically bound and sulphate sulphur had been removed, resulting in an overall effect of 80 to 85% of the original total sulphur in the coals eliminated.

Introduction

Most of the mined coals of West Pakistan possess a number of properties which seriously limit their use as solid fuel for industrial and/or domestic purposes. The coals are comparatively young with respect to their geological age, and should be classified as sub-bituminous coals. It is because of their more recent origin that they contain a high amount of volatile matter, that most of them are soft and friable, easily disintegrating with the formation of slacks and fines, and that they do not give a hard coke on carbonisation. In addition, the contents of ash and sulphur is high in most of the coals.

Among the above-quoted properties, the reduction of volatiles, ash, and sulphur is most desirable. The high amount of volatile matter in the range of 40% — almost as high as the fixed carbon— causes the formation of smoke and soot on combustion, thus lowering the thermal effect. The same is true for high ash contents, particularly when the ash, due to the presence of pyrites, has low softening and melting points and does not permit of high combustion temperatures desirable for an economic boiler running. Sulphur dioxide formed from the combustible sulphur in coal, in the presence of condensed water and excess of air, is highly corrosive to the metallic parts of the boilers, and its discharge to the atmosphere is deleterious to human beings, animals, and vegetation.

The prospects of ash reduction by wet gravity separation, i.e. float and sink methods in a dense medium, are not too bad for a number of important West Pakistan coals. Preliminary laboratory experiments' have shown that, fori nstance, thea sh in a Sharigh coal sample could be lowered from 19.9% in the original coal to about 9% in the floats; in a sample of Om Parkash Makerwal coal from 15.9% to 8%; of Charles Mine Makerwal from 11.2% to 7%; in a sample from the Katha Mine in the Salt Range from 14.6% to even 5%, in all cases with a reasonable yield of lower ash floats. Further studies in this direction are in progress at the P.C.S.I.R. Laboratories.

The coal sulphur,[1] however, is hardly reduced by this physical method of coal cleaning. This is due to the fact that a considerable proportion of (often more than 50% of the total sulphur) is in an organically-combined from in the coal, and the inorganic, say pyritic sulphur which might go into the sinks due to its higher specific gravity, is so finely divided and intimately dispersed in the coal substance, that separation does not take place.

In view of this, chemical methods of removing sulphur naturally suggest themselves, e.g. thermal decomposition of the coal. It is known for a long time, and the results obtained in large-scale plants agree with laboratory experiments,[2] that 40 to 50% of the coal sulphur is distilled off in volatile form, mainly as hydrogen sulphide, during ordinary by-product coking. About 30 to 35% of the total sulphur is evolved during low-temperature carbonisation.[2,3] Carbonisation in the stream of gases like hydrogen, carbon dioxide, carbon monoxide, and nitrogen proved more effective than carbonisation alone.[4]

The application of steam instead of gases seemed to be a more economic proposition. With the intention to replacing solvents for the extraction of waxes and resins from coal, S. Siddiqui evolved a process of superheated steam treatment of coal

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at sub-carbonisation temperatures from 250 to 350°C. While resins are distilled off and recovered in a depolymerised form as well as waxes by this operation, the volatile matter of the residue is reduced, its fixed carbon correspondingly increased, the calorific value also improved, and another welcome effect is the partial desulphurisation of the steam-treated coal. For this process two patents have been obtained in Pakistan,[5] Australia, Great Britain, Canada, France, West Germany, U.S.A. and India.

Since the process, referred to above, has shown favourable influence of superheated steam in respect of a beneficiation of Pakistan coals, it suggested itself for application to a treatment of coal also in a higher temperature range, up to that of low-temperature carbonisation. It seemed of particular interest to investigate the effect of superheated steam on the various forms of sulphur. Therefore, the present study was undertaken with 8 different sub-bituminuos coals of West Pakistan, as discussed in the following.

Apparatus and Experimental Procedure

Steam raised in a small metallic boiler was passed on to a metallic, gasheated superheater where it was brought to a temperature of 300°C. and thereafter entered the tube of an electrically heated furnace. The tube at the other end was connected to a water cooled condenser and receiver. The coal to be tested was air-dried, of 72-100 mesh size, and spread on the bottom of the tube in a fine layer, 2″ apart from both ends of the furnace to maintain a uniform temperature at the desired level over the whole length of the layer. Twenty g. coal each were carbonised with addition of steam (about 200 g./hr.) for 6 hours each in separate tests at 300°, 400°, 500° and 600°C.

The original coals as well as the obtained residues were analysed for moisture, ash, volatile matter, total sulphur[6] and pyritic sulphur[7]. Organic and sulphate sulphur values combined were calculated as the difference of total and pyritic sulphur. Separate experiments had shown that the sulphate sulphur is only 1/5 to 1/6 of the organic sulphur, and that the action of steam on both is almost equal. Therefore, the sulphate sulphur in the reported tests was not determined separately. Tar/oil distilled from the coal was recovered along with the steam condensate in the receiver, and weighed after separation from water.

Results

The results of the carbonisation tests with addition of steam are shown in detail for the selected temperature range 300 to 600°C. for Makerwal coal (Table 1), Sharigh coal (Table 2), and Jhimpir coal (Table 3). For 5 more coals, i.e. from Mach, Dalwal, Chittidand, Pidh and Diljabba, though they were subjected to the same tests at 300 to 600°C. in an abridged table (Table 4), the results are given for 600°C. only, since the results obtained at 300°, 400°, 500°C. only slightly differed from those obtained for the first-mentioned 3 coals.

With increasing temperature upto 600°C. the weight of the residue decreases to 50 to 60% of the original coal, whereby the lower figures are influenced by a higher moisture content of the original coal. The yield of tar/oil increases with

TABLE 1.—SUPERHEATED STEAM TREATMENT AT VARIOUS TEMPERATURES FOR 6 HOURS OF MAKERWAL COAL (TRANSINDUS).*

Temp. of treatment °C.	Yield of: Residue g./100g. of coal	Yield of: Tar/oil g./100g. of coal	Analysis of coal resp. residue (moisture-free basis): Ash %	Vol. mat. %	Fixed carb. %	Total sulf. %	Pyritic S %	Sulfate + org. S %	In residue from 100 g. coal (m-free basis): Total Sulfur g.	Total Sulfur x %	Pyritic Sulfur g.	Pyritic Sulfur x %	Sulfate + org. S g.	Sulfate + org. S x %
	Untreated coal		8.7	44.0	47.3	3.55	1.70	1.85	3.55		1.70		1.85	
300	87.5	2.9	9.1	38.6	52.3	3.10	1.58	1.52	2.71	23.8	1.38	18.9	1.33	28.1
400	66.8	10.8	12.2	17.5	70.3	2.59	1.52	1.07	1.73	51.3	1.02	40.0	0.71	61.6
500	62.3	17.3	13.2	13.0	73.8	1.74	0.54	1.20	1.08	69.6	0.34	80.0	0.74	60.0
600	54.4	16.6	14.8	8.7	76.5	1.25	0.16	1.09	0.68	80.8	0.09	94.7	0.59	68.1

* Analysis of coal as received: moisture, 5.3; ash, 8.2; vol. matter, 41.6; fixed carbon, 44.9; total sulfur, 3.36; pyritic sulfur, 1.61; sulfate + organic sulfur, 1.75%;. x = % of coal sulfur removed.

temperature; for some coals at 500°C. slightly higher values were found than at 600°C., perhaps due to some decomposition or cracking of the tarry material at the higher temperature. The yield of tar/oil obtained at 600°C. corresponds to the quantity of bituminous matter contained in various coals; it is lowest for Jhimpir coal (5.2%) and highest for Makerwal coal (16.6%).

The effect of rise in temperature is evident in respect of the reduction of volatile matter from a level around 40% (m-free) in the original coals to about 6 to 12% in the residues obtained at 600°C., and the demand for a smokeless fuel with sufficient reactivity for easy ignition and proper combustion is fulfilled. Correspondingly the fixed carbon is increased at a very high rate in all of the residues.

An unavoidable effect of the carbonisation, up to 600°C. is the rise in the ash contents (by 55 to 70% of the value in the original coal). This drawback for high ash coals, however, may be overcome by cleaning prior to carbonisation.

The effect of the temperature on the reduction of all forms of sulphur by carbonisation in the presence of steam is quite favourable. The progress with rising temperature can be seen in Tables 1-3 for Makerwal, Khost-Sharigh, and Jhimpir coal respectively.

It is interesting to note that for Makerwal and Khost-Sharigh coal the reduction of organic and sulphate sulphur in the range of 300° to 400°C. (from about 30 to 60%) is favourable and not

TABLE 2.—SUPERHEATED STEAM TREATMENT AT VARIOUS TEMPERATURES FOR 6 HOURS OF KHOST-SHARIGH COAL (BALUCHISTAN).*

Temp. of treatment °C.	Yield of: Residue g./100g. of coal	Yield of: Tar/Oil g./100g. of coal	Analysis of coal resp. residue (moisture-free basis): Ash %	Vol. mat. %	Fixed carb. %	Total sulf. %	Pyritic S %	Sulf + org. S%	In residue from 100g. coal (m-free basis): Total sulfur g.	Total sulfur x %	Pyritic sulf. g.	Pyritic sulf. x %	Sulfate + org. S g.	Sulfate + org. S x %
	Untreated coal		13.0	41.5	45.5	8.59	3.20	5·39	8.59		3.20		5.39	
300	84.2	2.6	14.3	34.2	51.5	8.03	3.70	4.33	6.76	21.2	3.11	3.0	3.65	32.4
400	67.3	10.0	17.5	19.7	62.8	7.22	4.15	3.07	4.85	43.5	2.79	12.9	2.06	61.8
500	60.2	10.7	20.0	13.7	66·3	3.60	0.65	2.95	2.17	74.8	0.39	87.8	1.78	67.0
600	50.0	8.0	21.5	10.5	68.0	3.16	0.36	2.80	1.58	81.6	0.18	94.4	1.40	74.0

* Analysis of coal as received: moisture, 6.8; ash, 12.1; vol. matter, 38.7; fixed carbon, 42.4; total sulfur, 8.00; pyritic sulfur, 2.98; sulfate +, organic sulfur, 5.02%; x = % of coal sulfur removed.

TABLE 3.—SUPERHEATED STEAM TREATMENT AT VARIOUS TEMPERATURES FOR 6 HOURS OF JHIMPIR COAL (SIND).*

Temp. of treatment °C.	Yield of: Residue g./100g. of coal	Yield of: Tar/oil g. 100g. of coal	Analysis of coal resp. residue (moisture-free basis): Ash %	Vol. mat. %	Fixed carb. %	Total Sulf. %	Pyritic S %	Sulf + org. S%	In residue from 100 g. coal (m-free basis): Total Sulfur g.	Total Sulfur x %	Pyritic Sulf. g.	Pyritic Sulf. x %	Sulfate + org. S g.	Sulfate + org. S x %
	Untreated coal		22.2	41.2	36.6	7.49	4.20	3.29	7.49		4.20		3.29	
300	68.6	0.9	25.0	32.2	42.8	7.33	4.45	2.88	5.03	32.9	3.06	27.1	1.97	40.1
400	59.5	3.7	30.2	20.8	49.0	5.88	3.10	2.78	3.50	53.2	1.84	56.2	1.66	49.5
500	52.7	5.3	34.1	16.9	49.0	2.59	0.54	2.05	1.36	81.7	0.28	93.3	1.08	66.9
600	49.8	5.2	37.6	12.6	49.8	2.24	0.27	1.97	1.12	85.0	0.14	96.7	0.98	70.2

* Analysis of coal as received:—moisture, 13.4; ash, 19.2; vol. matter, 35.7; fixed carbon, 31.7; total sulfur, 6.49; pyritic sulfur, 3.64; sulfate + organic sulfur, 2.85%; x = % of coal sulfur removed.

much more thereafter at the temperature range of 400° to 600°C. when about 70% removal is reached. For Jhimpir coal the favourable range was found higher, between 400° and 500°C. At 600°C. also 70% elimination of these two forms of sulphur is achieved. Of the same order is their reduction at 600°C. for the other coals of West Pakistan (Table 4) except the Mach coal, for which only 58.8% was found.

Different from the observations made for the reduction of organic and sulphate sulphur are those in respect of pyritic sulphur. While at 300°C. the effect of steam is comparatively small in the range of 20% reduction, at 400°C. around 40%, the decomposition of the pyritic sulphur beyond 400°C. upto 500°C. becomes extremely vigorous, reaching values of a reduction of this form of sulphur from 80 to 90% at 500°C. At 600°C. its removal is almost complete (95% and more) for all the coals tested.

The figures obtained for the reduction of the total sulphur in the temperature range from 300° to 600°C. are, of course, the results of the removal of organic, sulphate, and pyritic sulphur combined. At 600°C. 80 to 85% of the original total sulphur was found to be eliminated from the residues, except for the Mach coal (73.6%) where the share of organic and sulphate sulphur is comparatively high, and the removal of these two forms low (58.8%).

Makerwal coal was also carbonised with the addition of steam at 700°C., but the results in respect of desulphurisation are only slightly better than at 600°C. On the other hand at 700°C. the water gas reaction already becomes quite strong, considerably reducing the quantity of residue. Therefore, this higher temperature is not advantageous enough to compensate for the loss of carbonaceous material involved.

At 600°C. the results for the reduction of total sulphur in the residues are quite satisfactory for most of the tested coals, as summarized below :—

Sample from	%Total sulfur (moisture-free basis) in: Untreated coal	Residue
Makerwal ..	3.55	1.25
Khost-Sharigh	8.59	3.16
Jhimpir ..	7.49	2.24
Mach ..	4.25	1.86
Dalwal ..	4.06	1.23
Chittidand ..	2.40	0.86
Pidh ..	3.78	1.10
Diljabba ..	2.60	0.73

TABLE 4(ABRIDGED).--RESULTS OF SUPLRHEATED STEAM TREATMENT FOR 6 HOURS AT 600°C. ONLY VARIOUS OF COALS OF WEST PAKISTAN

Temp. of treatment °C.	Yield of: Residue g./100g. of coal	Tar/oil g./100g. of coal	Analysis of coal resp. residue (moisture-free basis): Ash %	Vol. Mat. %	Fixed carb. %	Total sulf. %	Pyritic S %	Sulf + org. S %	In Residue from 100g. coal (m-free basis): Total Sulfur g.	x %	Pyrtic Sulf. g.	x %	Sulfate + Org. S g.	x %
	Mach coal:-		15.1	37.8	47.1	4.25	1.70	2.55	4.25		1.70		2.55	
600	60.2	6.3	23.3	9.2	67.5	1.86	0.12	1.74	1.12	73.6	0.07	95.9	1.05	58.8
	Dalwal coal:-		21.4	38.5	40.1	4.06	1.87	2.19	4.06		1.87		2.19	
600	58.3	9.5	32.7	6.2	61.1	1.23	0.16	1.07	0.72	82.3	0.09	95.2	0.63	71.2
	Chittidand coal:-		4.3	44.5	51.2	2.40	0.82	1.58	2.04		0.82		1.58	
600	53.5	13.7	7.4	6.9	85.7	0.86	0.06	0.80	0.46	80.8	0.03	96.3	0.43	72.8
	Pidh coal:-		19.9	38.6	41.5	3.78	1.98	1.80	3.78		1.98		1.80	
600	57.0	9.4	31.4	6.0	62.6	1.10	0.14	0.96	0.63	83.3	0.08	96.0	0.55	69.4
	Diljabba coal:-		24.2	35.9	40.9	2.60	1.33	1.27	2.60		1.33		1.27	
600	54.4	7.3	35.1	5.9	59.0	0.73	0.11	0.62	0.40	84.6	0.06	95.5	0.34	73.2

x = % S removed.

Unless the original sulphur values were extremely high, beyond 6%, as for Khost-Sharigh and Jhimpir coal, the total sulphur percentages of the residues were found below 2% and for most of them near or below 1%.

Conclusion

Series of tests undertaken on the carbonisation with addition of superheated steam of 8 West Pakistan coals in the range from 300 to 600°C. showed the favourable effect of the rise of temperature on the gradual reduction of volatile matter and sulphur. At 600°C. it was found that the volatile matter had been diminished to 6-12 % with corresponding increment of fixed carbon in the obtained residues, thus fulfilling the demand for a smokeless fuel, while 95% of the pyritic, 60-70% of the organic and sulphate sulphur, i.e. 80-85% of the total sulphur had been eliminated.

It appears from these results that carbonisation with addition of superheated steam at 550° to 600°C. of suitable coals offers a solution to the problem of producing a solid fuel for use in industries and households. The gas evolved in this operation, after remvoal of sulphur compounds by known methods, would serve as a source of heat for the process, while the liquid by-products, tar and oil, could be separated by distillation in various fractions of mineral oils and pitch, the latter to be used as a binder in briquetting the upgraded residues or for road construction.

The above mentioned superheated steam treatment at subcarbonisation temperatures could be combined with the proposed carbonisation process. In the first stage suitable coals, e.g. from Makerwal, would be processed below 350°C. for the recovery of resins and waxes, the residue from this operation thereafter being carbonised at 550 to 600°C. with the addition of steam for further reduction of volatile matter and sulphur.

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