BENEFICIATION OF PETROLEUM COKE FINES – PART I

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Beneficiation of petroleum coke fines containing 3.47% total ash has been attempted by (1) Wet screening (2) Simple acid leaching and (3) Heavy media separation processes. Beneficiation to eliminate silica and other impurities in the fine size range from 60 mesh (BSS) to 150 mesh (BSS) by simple wet screening of these fractions has not been successful. Acid leaching of + 85 mesh BSS fraction gave a product of 0.39% inherent ash content and yield of 82.20% from bulk. Heavy media separation of + 150 mesh (BSS) fraction increased the yield to 87.80% from bulk with an inherent ash content as low as 0.19%. Results from large scale sink and float tests have been very encouraging. The distribution of silica in the fine size range below 22 mesh (BSS) opens up further possibility of beneficiation of coke by heavy media separation and flotation process.

Petroleum coke, a by-product of the petroleum industry, is the residue from the distillation of crude oil. It consists largely of pure carbon with small percentage of ash, probably from impurities and fine sand in the crude. It is used as low ash fuel in power plants, as domestic fuel and in cement kilns. It is also used in the manufacture of electrodes and manufacture of silicon carbide and calcium carbide.

The present work involved the beneficiation of petroleum coke fines by (1) Simple acid leaching (2) Wet screening and (3) Heavy media separation, with a view to decrease the ash content well below 0.5%. Ash was contributed by the free silica particles which has to be removed below the specified limit for industrial use. With respect to size 10 + 150 mesh (BSS) was most useful with greater preference to coarser size. The beneficiated coke finds ready application in the manufacture of silicon carbide and calcium carbide.

EXPERIMENTAL

Sieve and Chemical Analysis :

A sample of petroleum coke fines was received from M/s Grindwell Norton Ltd., Bangalore for beneficiation trials. From this a sample was taken by scooping out equal amounts of material from different bags, thoroughly mixed and passed through a riffle sampler to get about a kilogram of material for sieve analysis. This was sieved after drying at 105°C, in small lots on 8 to 150 mesh (BSS) sieves for 15 minutes and the different sieve fractions were chemically analysed for ash content. Total ash was determined by igniting 5 gms of dry powdered coke at 900°C for 8 hrs to a constant weight. The results are shown in Table I.

TABLE I Sieve analysis of bulk coke and distribution of total ash in different sieve fractions

Mesh size B.S S.		% retained on each size	Cumulative % oversize	% Elementary ash in each size	Ash contributed by each size fraction	Cumulative ash in over size
	+8	9 69	9.69	0.19	0 0186	0.0186
−8	+10	5.78	15.47	2 17	0.1257	0.1443
−10	+16	20.63	36.10	0.72	0.1481	0.2924
−16	+22	14 32	50.42	1.09	0.1563	0.4487
−22	+30	7.64	58.06	1.22	0.0934	0 5421
−30	+44	11.06	69 12	2.44	0.2695	0.8116
−44	+60	8.77	77.89	5.91	0.5184	1.3300
−60	+100	7.81	85.70	9.34	0.7297	2.0600
−100	+150	4.14	89 84	11.34	0.4696	2.5293
	−150	10.15	—	9.08	0.9219	3.4512

The results of sieve analysis and total ash content of the bulk coke were checked by sieving at two intermediate sieve sizes i.e. 44 mesh and 100 mesh, finding out the ash contents of the respective oversize and undersize fractions and computing the cumulative ash for the bulk coke. Total ash content of the bulk sample was also determined separately and the results compared in Table II.

TABLE II Intermediate sieve analysis of bulk coke and distribution of total ash

Mesh size (BSS)	% yield	% Elementary Ash	Ash contributed by fraction
+ 44	69.69	0.917	0.662
— 44	30.31	9.020	2.733
Bulk	100.00	—	3.395
+ 100	86.90	2.525	2.195
— 100	13.10	9.60	1.258
Bulk	100.00	—	3.453
Bulk	100.00	3.565	3.565
		Average ash in bulk	3.47

Leaching with Hydrochloric acid :

The bulk coke sample was divided into + 22, + 30, + 44, + 60, + 100 and + 150 mesh fractions by individually fractionating at those sizes and the yield (% over size at each mesh sizes), total ash and "inherent ash" for each of the fractions were estimated separately. The "inherent ash" was determined by treating the total ash obtained by HF and H_2SO_4 to remove silica As the presence of silica in the total ash was not harmful in the final process, it was desirable to remove the metallic elements which would have contributed to the total ash in the coke by a simple leaching with dilute hydrochloric acid to convert the elements into their respective soluble chlorides.

To each cumulative sieve fraction of the coke from + 22 mesh to + 150 mesh (150 gms) and including the bulk, taken after proper sampling by coning and quartering, 250 cc of 20% hydrochloric acid was added, vigorously stirred and kept for 15 minutes. After the reaction, the coke was filtered, washed free of acid, dried, thoroughly mixed and a representative sample was taken for determination of total ash and inherent ash. The results are tabulated in Table III and indicated in Fig. 1.

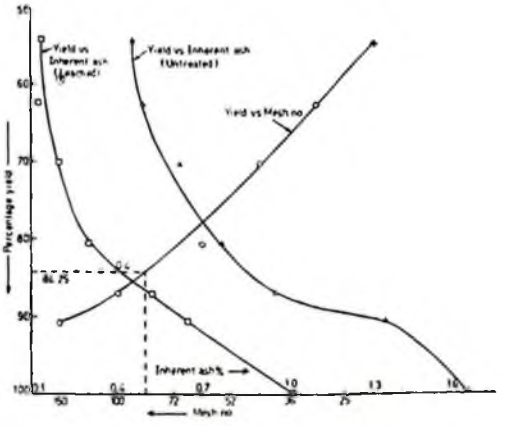


Fig. 1 Washability curve showing yield vs inherent ash for leached and untreated coke and yield vs mesh number.

Wet Screening

The impurities in the coke are present at a size below 44 mesh. To eliminate these impurities which might be adhering to the coke particles, wet screening of the sample below 44 mesh was carried out. Dry screened samples in the size range + 60, + 100 and + 150 mesh were studied. The samples were placed on the respective sieve and wet screened by spraying water for 5 minutes during sieving in a vibratory sieve shaker. The over size was collected, dried, mixed thoroughly and inherent ash determined. The results are indicated in Table III.

TABLE III Cumulative yields and inherent ash for untreated, leached and wet screened coke at different size fractions

Mesh size BSS	% yield	untreated			leached			Wet screened
		Total ash %	% Silica removed	% Inherent ash	Total ash %	% Silica removed	% Inherent ash	% Inherent ash
+ 22	53.96	0.465	8.90	0.424	0.298	55.71	0.132	—
+ 30	62.40	0.666	26.40	0.490	0.316	61.18	0.123	—
+ 44	69.69	0.813	23.66	0.621	0.517	67.41	0.169	—
+ 60	80.60	1.623	53.09	0 761	0.685	56.73	0.296	0.678
+ 100	86 90	2.117	55.01	0.952	1.699	69.05	0.526	0.731
+ 150	90 78	2.854	52 48	1.357	1.954	66.77	0.650	0.843
Bulk	100	3.433	52.77	1.622	3.169	66.46	1.063	—

Sink and Float

To improve the yield still further, it was desirable to remove all silica from the sample along with other impurities by heavy media separation method. The specific gravity of the coke being 1.28 and that of silica being 2.65, a calcium chloride solution of specific gravity 1.38 was used. The separation was carried out in a one litre capacity separating funnel on + 150 mesh fraction as well as the bulk sample. The suspension was vigorously stirred and kept undisturbed for some time for the two layers to separate out. The denser silica and other impurities settling at the bottom was drained off. The lighter coke floating at the top was vigorously stirred again to give further opportunity to any entrapped silica particles to settle at the bottom. This process was repeated until all the silica was removed. The coke from the top was removed, the calcium chloride solution was drained off and recovered. The wet coke was repeatedly washed until free from adhering calcium chloride solution. It was dried and the yield of coke along with the total ash and inherent ash was determined. The results are indicated in Table IV.

TABLE IV Heavy media separation of + 150 mesh and bulk samples of coke

Material	Description	+ 150 sample	Bulk sample
Coke	Feed (in grams)	132	129
	Recovery of washed coke (gms)	128	119
	% yield of washed coke	96.68	92.13
	% yield from bulk	87.80	92.13
	Amount of silica removed (gms)	2 7	4.1
	Losses during process (gms)	1 7	5.9
$CaCl_2$ solution	Specific gravity of the solution used	1.379	1.379
	Specific gravity of the solution recovered	1.368	1.372
	Amount of solution used (ml)	600	700
	Amount of solution recovered (ml)	560	610
	Percentage recovery of solution	93.3	87.1
Ash	% of total ash in the feed	2.854	3 433
	% of total ash in the concentrate	0 331	0.375
	% silica removed	43 19	42.99
	% inherent ash in the concentrate	0.188	0 214

Large scale sink and float test

To confirm the results, a large scale test was conducted on a 4 kg sample of coke of size + 150 mesh, in a cylindroconical vessel of capacity 10 litres, with 5 litres of calcium chloride solution of specific gravity 1.38. The test was conducted on 1 kg of coke sample at a time, removing the floated coke, draining off the silica and adding fresh calcium chloride solution to make up for the new feed. The results are indicated in Table V. Silica obtained as a sink product was dried and sieve analysed as shown in Table V.

TABLE V Large scale heavy media separation of coke at + 150 mesh.

Coke	Feed	: 4250 gms
	Recovery of washed coke	: 4100 gms
	% yield of washed coke	: 96.47
	% yield from bulk	: 86.88
	% total ash in feed	: 2.95
	% total ash in washed coke	: 0.32
	% inherent ash in washed coke	: 0 18
$CaCl_2$ solution	Specific gravity of solution used	: 1.380
	Specific gravity of solution recovered	: 1.375
	Amount of solution used	: 5700 ml
	Amount of solution recovered	: 4000 ml
	% Recovery of solution	: 70.18
Material Balance	Washed coke recovered	: 4100.00 gms
	Silica removed	: 81.75 gms
	Loss in process	: 68.25 gms
	Total	4250.00 gms

Discussion

From Table I it is seen that 89.84% of the bulk coke is in the desired size range of + 150 mesh. The + 22 mesh fraction representing 50.42% of the original sample and assaying 0.449% total ash is in the desired grade. The ash content of the fractions suddenly increase from — 44 mesh downwards indicating that most of the impurities present in the coke may be concentrated in this size range. From the ash contributed by each fraction, cumulative ash content was calculated to give an ash content of 3.45% for the

bulk coke. From Table II it is seen that the fractional yields at 44 mesh and 100 mesh compared favourably with the results in Table I. The ash contents calculated for the bulk sample from the fractional yields also compared favourably to give an average total ash of 3.47% for the bulk coke.

TABLE VI Sieve analysis of silica and other impurities obtained as tailings from heavy media separation at + 150 mesh

Mesh size BSS	Weight % retained	Cumulative % over size	Cumulative % under size
+ 16	10 24	10.24	89.76
+ 22	2.83	13.07	86 93
+ 30	3.24	16 31	83.68
+ 44	2.76	19.08	80.92
+ 60	20.67	39.75	60 25
+ 100	40.79	80.54	19.46
+ 150	16.06	96.6	3.40
— 150	3.40	—	

The maximum ash content desired in the coke is 0.5% which is contributed by the silica present in the coke as well as by the oxides of Ca, Mg, Al, and Fe. If SiO_2 is not considered as a major impurity, then the ash free from silica would be less than 0.5%. This inherent ash could be determined and hence enables the utilisation of a coke fraction containing a total ash of more than 0.5%. As seen from Table I, if total ash is taken into consideration, then the + 22 mesh fraction representing 50.42% of the bulk can be utilised without beneficiation by direct screening. By taking the inherent ash into consideration, it is possible to increase the yield of coke available for the process by direct screening as shown in Table III. This makes + 30 mesh fraction with a yield of 62.40% suitable without beneficiation by direct screening. But the fraction below 30 mesh containing higher percentage of inherent ash requires beneficiation before further utilisation in the process.

Thus the direct sieving of the bulk does not offer any solution to the problem. The presence of silica in the total ash being not deliterious in the final process, the removal of other elements, contributing to the total ash, as soluble chlorides by simple leaching has been attempted and results shown in Table III and Figure 1. From the table, it is evident that leaching the + 60 mesh fraction increased the yield to 80.60% to give a product of inherent ash content of only 0.296%. The + 100 mesh fraction improved the yield still further to 86.90% but the inherent ash content was above the limit at 0 53%.

From the results obtained in Table III the leachability curve was drawn as in Figure 1. From this curve it is possible to predict the best condition at which the coke of the required grade could be obtained by leaching in dilute hydrochloric acid. Thus at a sieve of + 85 mesh, it should be possible to get a yield of 84 25% containing an inherent ash content of 0.4% in the leached product. This was checked from actual experiment on + 85 mesh fraction when an yield of 84.65% was obtained with an inherent ash of 0.396% in the leached fraction thereby fully confirming the predictions from the leachability curve.

From Table I it was already found that most of the impurities present in the coke were in the size range below 44 mesh. Elimination of these fine size impurities by simple wet screening has not been successful as seen from Table III even though the results are better than obtained for dry screening. Leaching with the dilute hydrochloric acid limits the yield to only 84.65%. However this does not represent the true yield as it contained some free silica to the extent of 1.86%. The yield could be increased still further by heavy media separation of + 150 mesh fraction of the bulk sample of the coke as shown in Table IV, wherein a product with an inherent ash content as low as 0.188% was obtained compared to 0.396% obtained by acid leaching. The yield of washed coke which was free from silica was 87.80% from the bulk sample which was almost equal to the theoretical yield one could expect from this feed. The results were similar for the bulk sample of coke which included the — 150 mesh fraction also. Translation of the results on a large scale sample of + 150 mesh fraction of coke was very encouraging as shown in Table V. From a feed averaging 2.953% total ash, a washed coke of 0.323% total ash and 0 182% inherent ash was obtained with a yield as high as 96.47% of the feed and 86.88% from the bulk.

From the sieve analysis of the silica obtained as a sink product from large scale tests, it is seen that

nearly 87% of it is in — 22 mesh range. This shows a further possibility of beneficiation of coke by flotation process taking advantage of the natural flotability of coke Thus a combination of heavy media separation of a coarse fraction and flotation of fine fraction should give two concentrates which can be blended together to give a final concentrate of low ash and high recovery.

CONCLUSIONS

1. Dry screening and leaching the coke with the dilute hydrochloric acid gives + 85 mesh product with an inherent ash content of 0.396% and a yield of 84.65%.

2. Heavy media separation of + 150 mesh fraction of the bulk coke gives an yield of 96.68% on the feed or 87.80% on the bulk coke which is 5.0% greater than that obtained by the acid leaching process. Also the grade of the concentrate is better with a total ash content of 0.331% and an inherent ash content of 0.188% as compared to an inherent ash content of 0.396% obtained by the acid leaching process.

3. Results on large scale sink and float tests have confirmed the small scale laboratory tests. From a feed containing 2.953% total ash, clean coke of 0.323% total ash and 0.182% inherent ash has been obtained with a yield of 96.47% on the feed or 86.88% on the bulk coke.

4. From the point of view of beneficiation, the heavy media separation process with high yields and low ash contents of washed coke looks very attractive.

5. A combination of heavy media separation and flotation is possible as an alternative method of beneficiation.

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