

USE OF PETROLEUM COKE AS AN ADDITIVE IN METALLURGICAL COKE MAKING

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Abstract

The use of petroleum coke as an additive in coal blends has been tested and established successfully to produce metallurgical coke of acceptable quality at JSW. The performance of coke produced from coking coal blends containing petroleum coke was successfully tested in Blast furnaces.

The amount of petroleum coke that may be incorporated in the blend without impairing the coke quality considerably depends mainly on the particle size and the rheological properties of the coal blend. The addition of petroleum coke produces a decrease in Maximum Fluidity (MF) in the blend due to the liberation of low molecular weight substances during heating within the plastic range and hydrogen containing species available to generate fluidity in co carbonization system. The use of low volatile petroleum coke as an additive resulted in better yield and reduction of coke ash.

The ability of petroleum coke to interact with coal during plastic stage to impart good bonding between components and maintain the coke quality to match the Blast Furnace requirements is well established through laboratory studies.

Key words: Petroleum coke, additive, MF, Plasticity, Carbonization

1.0 Introduction

Dwindling world's hard coking coal resources and with their concentration limited to a few countries has made the situation critical for continuous and smooth running of blast furnace based integrated steel plants. There has been high volatility in the pricing front because of demand and supply gap. Also due to the inconsistent Iron Ore quality, more emphasis was laid on Coke Quality i.e. to produce coke of better physical and high temperature properties so as to enhance the productivity and reduce the Coke rate of its blast furnaces making JSW one of the best profit making organizations. At various times we have experimented with additives such as coke breeze, petroleum coke, Semi soft coals etc.,. Semi soft coals usages hamper the coke quality In terms of Coke Ash and also shall impact Coke Production. Coke breeze content might substitute for a portion of the low-volatile coal normally used in blends, but neither material is considered suitable for total replacement of the low-volatile constituent. Of the materials tried, only petroleum coke is left as a possible replacement. Under these circumstances, JSW has taken an initiative to demonstrate the usage of Petroleum Coke in Coal Blend and its impact on Coke quality by using the pilot coke oven facility at its R&D and SS Centre.

Petroleum coke and its production

Petroleum coke (pet coke) is produced through the thermal decomposition of heavy petroleum process streams and residues. The three most common feed stocks used in coking operations are 1) reduced crude (vacuum residue), 2) thermal tar, and 3) decant oil (catalytically cracked clarified oil) These feedstocks are heated to thermal cracking temperatures and pressures (485 to 505°C at 400 kPa) that create petroleum liquid and gas product streams. The material remaining from this process is a solid concentrated carbon material, petroleum coke. The world's major oil refineries, including ExxonMobil,

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ConocoPhillips, Chevron, Shell, Valero, BP, CITGO, and Marathon, all produce varying quantities of Pet Coke. Petroleum coke can serve as either an energy source or carbon source.

Petroleum cokes can be categorized as either Green or calcined coke. Petroleum coke (both green and calcined) is a black-colored solid produced by the high pressure thermal decomposition of heavy (high boiling) petroleum process streams and residues. Green coke is the initial product from the cracking and carbonization of the feed stocks to produce a substance with a high carbon-to-hydrogen ratio. Green coke undergoes additional thermal processing to produce calcined coke. The additional processing removes volatile matter and increases the percentage of elemental carbon, which results in a lower potential for toxicity for calcined coke. Calcined coke is produced when green coke is treated to higher temperatures (1200 to 1350°C). The primary use of calcined coke is in making carbon anodes for the aluminum industry. Other uses include making graphite electrodes for arc furnaces, titanium dioxide, polycarbonate plastics, steel, carbon refractory bricks for blast furnaces, packing media for anode baking furnaces, and material for cathodic protection of pipelines. The principal difference is the amount of residual hydrocarbon (also termed volatile matter) in the two products.

Coking Processes and Terminology

Petroleum coke is formed from two basic reactions, dealkylation and dehydrogenation

Dealkylation: High molecular weight compounds such as asphaltenes and resins are subject to elevated temperatures in the coker unit, the resulting carbon residue is a highly disordered and cross-linked structure. This is marked by a significant difference in the concentration of hydrogen atoms measured in the resin- asphaltene feed and the formed coke. The carbon to hydrogen ratio increases from a range of 8-10 in the feed to 20-24 in the coke. This amorphous character, combined with high concentrations of impurities, render the coke produced from resin-asphaltene compounds unsuitable for special applications.

Dehydrogenation: This mechanism depends on the dehydrogenation of heavy oils with subsequent condensation of free radicals to form high molecular weight compounds with high carbon-to-hydrogen ratios. The coke thus produced contains fewer cross-linkages and has a more crystalline appearance than the resin-asphaltene based coke. Coke formed from feedstocks such as thermal cracker tars, catalytic cracker slurry, and decant oil, which are high in aromatics and low in resin-asphaltenes, is a premium grade product suitable for calcining and graphitization.

Green coke can be produced by one of three processes: delayed, fluid or flexi-coking. Delayed process coke is produced by a semi-continuous batch process and accounts for more than 92% of total coke production in the United States. Fluid coke is produced by a continuous fluidized bed process. Fluid coke typically contains less volatile matter than delayed process green coke but more than calcined coke, and occurs as spherical grains less than 1 cm in diameter. Flexi-coke is produced by a variant of the fluidized bed process in which most of the coke (up to 97%) is converted to a low heating value fuel gas for use at the refinery where it was produced. Solid flexi-coke has a smaller particle size than fluid coke and is dustier due to its lower volatile matter content.

Depending on its physical form, green coke produced in delayed cokers may also be classified as shot, sponge or needle coke. Shot coke occurs as small, hard spheres and is derived from low API gravity and high asphaltene and resin petroleum precursors via the dealkylation reaction mechanism. Sponge coke is the most common form of green coke and it

has a macroscopically amorphous appearance. Visibly, it has a dull black color and a porous consistency with walls and pores that vary in size. It is normally derived from virgin petroleum feedstocks, which contain large numbers of cross linkages. Gas bubble percolation inside the coke drum may also account for generation of some sponge coke. In reality, sponge coke is a mixture of shot and needle coke structures. Needle coke appears as silver-gray colored acicular structures (ribbon-like, crystalline needles) and is derived from feedstocks with high aromatic hydrocarbon content via the dehydrogenation reaction mechanism. Calcined coke is produced from green coke by a process of further heating at temperatures in excess of 1200°C). Most uses other than for fuel or gasification require green coke to be calcined in order to improve its properties. The process of calcining removes moisture, reduces the volatile matter to less than 0.4%, increases the density of the coke structure, increases physical strength, and increases the electrical conductivity of the material (Ellis and Paul, 2000a). When green coke is calcined, devolatilization of volatile matter occurs at 500 to 1000°C. Heating further to 1200 to 1400°C causes additional dehydrogenation, some desulfurization, and coke structural shrinkage (densification). The result is a hard, dense substance with low hydrogen content, a low coefficient of thermal expansion, and good electrical conductivity. These properties along with low metals and ash contents make calcined petroleum coke highly desirable for use in the aluminum smelting industry. Calcined coke is characterized as either anode-grade coke or graphite needle-grade coke depending upon its physical and chemical characteristics, with needle-grade coke having a higher purity (i.e., lower ash, sulfur, and metals contents than anode-grade coke, which is used in electric furnaces in aluminum and steel smelting. The physical characteristics of petroleum coke are important in determining the suitability of a coke sample for a specific use. These characteristics are typically the real and bulk densities and, in the case of anode and needle grade coke, the resistivity and coefficient of thermal expansion.

2.0 Literature review

2.1 Impact of pet coke addition on Plastic Nature of the blend

The plastic stage is the most important stage of coke making. Petroleum Coke was added at varying percentages to the base blend and changes in plastic properties were studied. The base blend fluidity was 1045 ddpm and all the trials suggested that there is a reduction in maximum fluidity after addition of Petroleum Coke but in different ways of addition of Pet Coke. The differences in the fluidity values were apprehended that it were due to the variation in their structural properties. As per the studies¹ on the activity of the Pet coke in Coke Making, the presence of unreacted pitch and “isotropic sacks” in green petroleum cokes has been considered a source of volatile matter evolution, and the extent of their movement within the coal particles may improve the caking ability of the blend. Although there is no relation between the amounts of unreacted pitch and partially reacted material present in green petroleum cokes, the use of different techniques like thermo gravimetric analysis, free-swelling index provides useful information about the different activities of the petroleum cokes during carbonization. Petroleum Cokes evolves a major part of their VM in the temperature range of 400- 500 °C, which is actually the plastic range of major coals that are used in Coke making. This property of a petroleum coke poses a positive activity of certain chemical changes during the plastic stage of the Coking coals. The calcined Petroleum coke in this aspect has no chemical activity due to the absence of any Volatile matter in it.

2.2 Impact of pet coke addition on Expansion and Contraction properties of the Blend

Pet coke addition can be considered as an effective additive in dissipating wall pressure developed during the carbonization process and reducing expansion of the system due to the partially inert nature of petroleum coke. As an inert, it is believed that it does not change in volume and the space available for the coal to swell/expand is therefore increased. The inert, by absorbing a certain proportion of tar, reduces the fluidity and the expansion of the coal and improves the permeability of the plastic layer and hence modifies its dangerous character two effects can take place in different extension. As an inert material it has a dilution effect, but the partially active material causes increased evolution of volatile matter, and then it contributes to less reduction in the expansion of the coal.

3.0 Experimentation

Based on the previous studies and available literature on usage of Pet Coke in Coke Making technology, Pet Coke Specifications were procured from different suppliers. After initial assessment of the specifications, Pet Coke samples from different suppliers were procured.

Table 3 shows the main properties of the Coals that are used as a basis in the preparation of blends. Table 4 shows the specifications of the petroleum coke that were used for the experiments.

Blends of Coal A, Coal B and Coal C with Petroleum Coke at varying proportions were prepared and were subjected to Gieseler Plasticity testing (ASTM D 2639 – 04) To evaluate the maximum fluidity, a modified constant torque Gieseler Plastometer was used, which is described in the ASTM D2639-74 procedure. The instrument measures the rotation of a stirrer in a compacted 5 g coal/blend charge (<424 μ m in size) while the coal is being heated from 300 °C at 3 ± 0.1 °C/min and records the fluidity in dial divisions per minute (ddpm). The sample of Coal Blend Prepared by using Coal A, Coal B and Coal C without petroleum coke was used as a reference. The variation in Max fluidity with addition of Pet Coke is shown in Table 5.

3.1 Carbonization Tests

Pilot Oven Carbonization tests were conducted using pet coke at varying percentages from 5-20% with low Sulphur pet coke of up to 20% and high Sulphur pet coke up to 10% in 120 kg capacity Electrical heated Pilot Oven of R&D centre of JSW Steel. The technical specification of Pilot Coke Oven is shown in Table 7 and the figure is depicted in Fig 1. Coal Blends were prepared according to the requirement and were crushed to a size of 3.15 mm. The crushing index attained was -3.15mm % 90% and -0.5mm% was 38%. Later the coal cake was prepared by stamping of cake. The Bulk density of the coal cake was 1110 kg /m³. The coal was then charged into the pilot oven. The coking conditions of the pilot oven during the set of trials were kept constant. After 24 hours of coking period, the coke was pushed out of the oven and was water quenched. Metallurgical coke obtained after carbonization and subsequent quenching were characterized in terms of Physical, Chemical, mechanical strength (M40 / M10 test) and high temperature properties (CSR / CRI test).

4.0 Results and Discussions

4.1 Influence of pet coke addition on Coke Quality

Pet Coke Addition in the coal blend resulted in no significant reduction in Coke Quality till 15% of Blend and further increase in the usage reduced the Coke Strength after reaction (CSR) and increased Coke Reactivity index (CRI). The results of the pilot oven trials are

tabulated in table 6. It can be observed that there was a significant reduction of coke Ash on addition of pet coke. Increase in Coke Sulphur was also observed. It is a known fact that Coke Ash and Coke S' play an important role in determining the Coke rate at Blast furnaces. Hence optimum Pet Coke can be used without much increasing the Coke Sulphur and significantly reducing the Coke Ash content. No much variation in Coke Ash chemistry was observed. The total alkali in the Coke was also within the range of acceptable Blast furnace operation norms. No negative impact on cold strength parameters like Micum Indices were observed till 15% of the pet coke and further increase of pet coke resulted in slight reduced of the Indices. This reduction in Indices shall have a negative impact on Coke Fines generation and shall in turn reduce the available BF grade coke, which is not desirable. The Coke yield increased with increase in Petroleum Coke addition. The coke yield at varying Petroleum Coke Addition is shown in table 6.

5.0 Conclusion:

Although the pilot oven studies on Petroleum Coke addition in coal blend revealed that there is no much variation in Coke Properties at lower percentage usages, further characterization of Petroleum Coke are required to come to a conclusion on usage of Petroleum Coke in actual plant scale trials. As per the fact that pet coke contains very high Sulphur levels when compared to coal, the impact on increase of coal blend Sulphur on Coke Oven Batteries and Byproduct plant and entire gas pipeline network in the long run needs to be analyzed thoroughly is a prerequisite. Also the impact of increase of Coke Sulphur on Blast Furnace performances needs to be analyzed prior to the usage.

7.0 References:

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Tables:

Table 1: Fuel grade pet coke properties

Parameter	Value	Significance
Fixed carbon %	85 - 90	High carbon indicates high calorific value.
Volatile matter %	10-12	Low VM indicates difficulty in igniting.
Ash, %	<2	Low ash is preferable for fuel grade
Gross calorific value, Kcal/Kg	7,500 - 8,000	Key from customer perspective. Significantly higher than coal.
Sulphur	2-8	Lower is better as it is less polluting. Important from regulatory point of view.
Hardgroove Grindability Index (HGI)	38 - 52	Low value indicates difficulty in grinding.

Table 2: Difference between fuel grade pet coke and coking coal

Pet coke	Coking coal
Low Volatile matter (10-12%)	High volatile matter (20-30%)
Very low ash content (<2%)	High ash content (10-20%)
High Fixed carbon (>83%)	Low Carbon content (50-70%)
High Sulphur levels (2-8%)	Low sulphur (<1.0%)

Table 3: Main Characteristics of Coking Coals used

	Coking Coals		
	Coal A	Coal B	Coal C
Ash,(wt% db)	10.2	8.8	7.3
VM,(wt% db)	19.5	24.0	34.2
S,(wt% db)	0.3	0.58	0.61
C,(wt% db)	79.2	79.8	77.3
H,(wt% db)	4.5	4.67	4.9
N,(wt% db)	1.7	1.79	2.1
Fluidity, ddpm	210	1382	4187

Table 4: Main properties of petroleum Cokes Used

	Petroleum Coke		
	P1	P2	P3
Ash,(wt% db)	0.33	0.45	0.74
VM,(wt% db)	10.6	11.6	12.4
Fixed Carbon, (wt% db)	89.1	87.9	86.8
S ,(wt% db)	1.67	2.22	4.12
C,(wt% db)	83.92	83.85	81.56
H,(wt% db)	4.06	3.88	4.12
N,(wt% db)	2.45	2.14	2.21

Table 5: Coal blend Properties

Test No.		VM, %	Ash, %	'S', %	MF,(ddpm)
T1	----	25.2	8.7	0.54	1045
T2	5% P1	24.5	8.3	0.58	850
T3	10% P1	23.5	7.8	0.65	625
T4	15% P1	23.0	7.2	0.72	425
T5	20% P1	22.0	6.7	0.79	390
T6	5% P2	24.8	8.5	0.61	965
T7	10% P2	23.8	7.9	0.71	695
T8	15% P2	23.0	7.2	0.80	495
T9	20% P2	22.0	6.7	0.90	410
T10	5% P3	24.9	8.5	0.71	745
T11	10% P3	24.3	7.9	0.90	620

Table 6: Properties Coke made in pilot coke oven

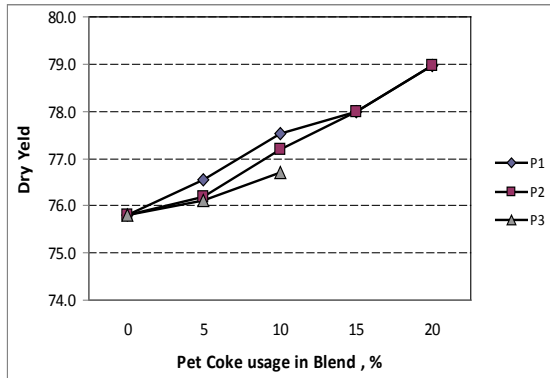
Test No.		Coke CSR	Coke CRI	Coke Ash	Coke S	Coke M40	Coke M10	Dry coke Yield, %
T1	---	68.0	22.0	11.5	0.53	86.5	5.5	75.8
T2	5% P1	67.0	23.0	10.8	0.57	86.2	5.8	76.6
T3	10% P1	65.0	25.0	10.0	0.63	85.1	5.9	77.5
T4	15% P1	65.0	25.0	9.2	0.70	85.2	6.1	78.0
T5	20% P1	63.0	27.0	8.4	0.75	84.2	6.2	79.0
T6	5% P2	67.0	23.0	11.2	0.60	86.4	5.7	76.2
T7	10% P2	67.0	23.0	10.2	0.69	85.8	5.8	77.2
T8	15% P2	65.0	25.0	9.2	0.77	85.2	6.2	78.0
T9	20% P2	64.0	26.0	8.4	0.85	85.4	6.4	79.0
T10	5% P3	66.0	24.0	11.2	0.70	85.2	5.9	76.1
T11	10% P3	64.0	26.0	10.3	0.88	84.2	6.1	76.7

Table 7: Details of Pilot Coke Oven

Type of Pilot Oven	Electrically Heated Oven
Capacity, Kg	120 Kg
Quenching system	Water Quenching
Coal Cake dimensions	
Length, mm	600
Width, mm	450
Height, mm	390
BD(t/m ³)	1.15
Coking time, hr	24
Temp. of Coke Bed, °C	1050
Temp. Control type	PLC
Heating wall	Silicon Carbide
Heating elements	Silicon Carbide

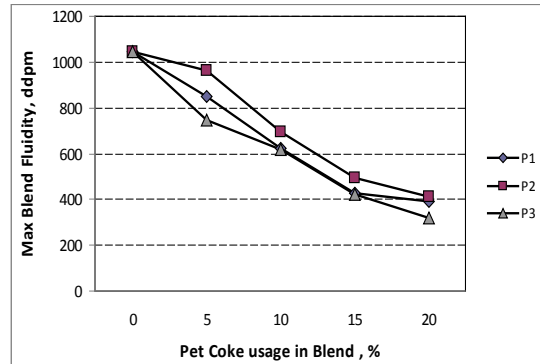
Graphs:

Impact of varying Petroleum Coke Addition on Various Coal and Coke Parameters



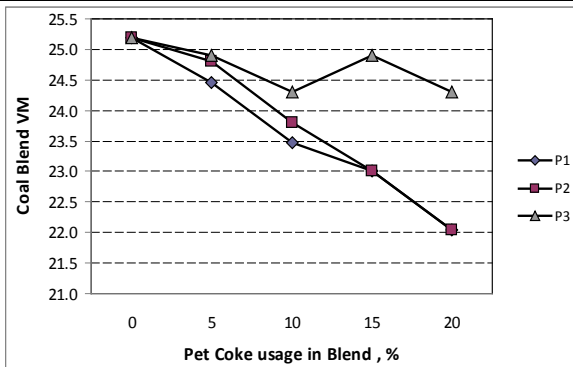
Graph 1: Impact on Dry Coke Yield

Observation: Dry coke yield increased 4.2% with increase in the pet coke %. Since pet coke contains VM in the range of 10-12% which will decrease the blend VM by which yield will improve.



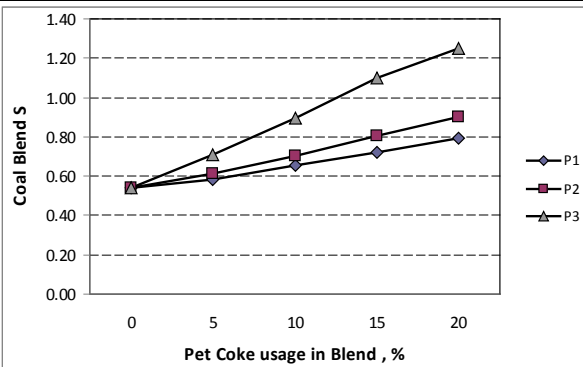
Graph 2: Impact on Max Blend Fluidity

Observation: Blend fluidity was decreased with increase in the %. Since pet coke is inert in nature and having no fluidity, blend fluidity will drop automatically.



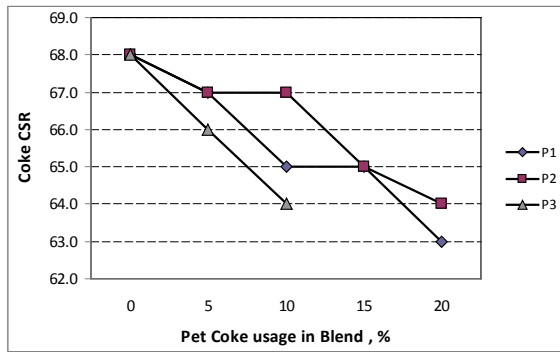
Graph 3: Impact on Coal Blend VM

Observation: Blend VM increased from 25.2% to 22.0% and 24.3% with 20% low sulphur pet coke and 10% high sulphur pet coke respectively.

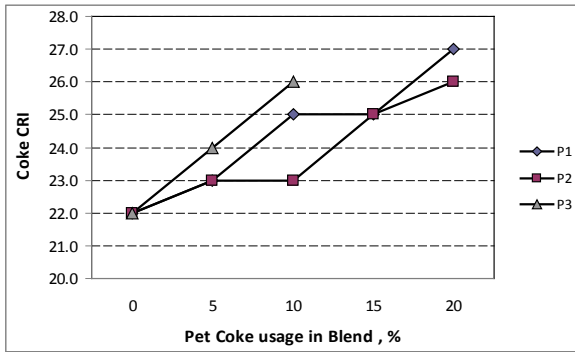


Graph 4: Impact on Coal Blend S

Observation: Since pet coke contains high sulphur content from 2-4%, blend Sulphur increased from 0.54 % to 0.9%

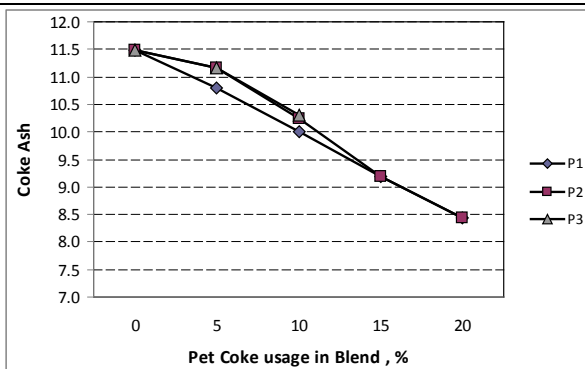


Graph 5: Impact on Coke CSR



Graph 6: Impact on Coke CRI

Observation: Drop in CSR and CRI of 3-4 points was observed with increase of pet coke percentage. This may be due to decrease in blend Maximum fluidity.



Graph 7: Impact on Coke Ash

Observation: Since pet coke contains negligible ash content coke ash was decreased drastically from 11.5 to 8.4% and 10.3% with usage of 20% low sulphur pet coke and 10% high sulphur pet coke respectively.

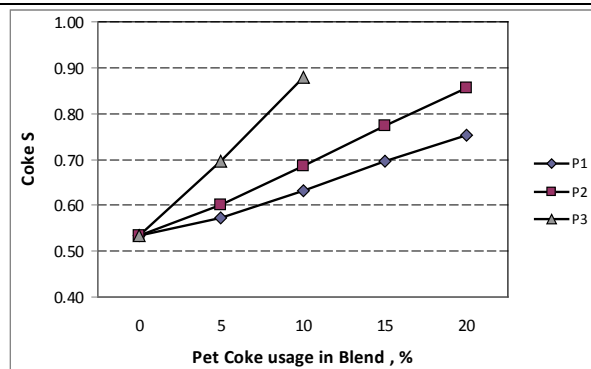
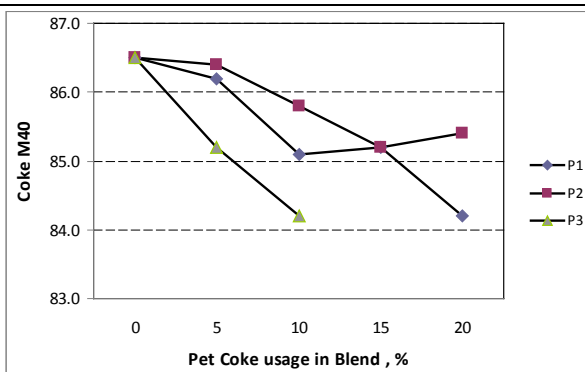


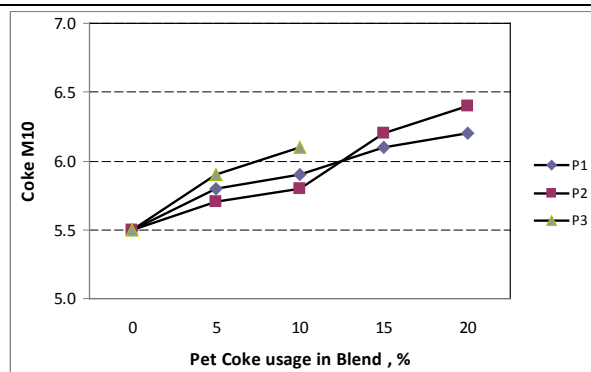
Chart 8: Impact on Coke Sulphur

Observation: Since pet coke contains sulphur in higher proportions Coke sulphur is increased from 0.5 to 0.88.



Graph 9: Impact on Coke M40

Observation: Drop of 2-3 points in M40 was observed.



Graph 10: Impact on Coke M10

Observation: Negligible rise (5.5 to 6.2) in M10 was observed with usage of pet coke.

Figures:

Fig 1: Pilot Coke Oven facility at JSW R&D and SS Centre



Fig 2: Green Delayed Petroleum Coke



Fig 3: Macrostructure of Petroleum Coke

