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The Novel Method for Measurement of Sulphur in Petcoke From Crude Oil

Dhiraj Gondaliya[1*], Kinjal Patel[2] and Ashok Maghodiya[3]

Research and Development Centre,
Nayara Energy Limited,
39 KM, Jamnagar-Okha Highway Vadinar,
Dist. Devbhumi Dwarka-361305, Gujarat, INDIA.
[1*]General Manager-R&D, [2 & 3] Manager R&D
email: Dhiraj.Gondalia@nayaraenergy.com,

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ABSTRACT

Petroleum coke (Petcoke) is marketed as per standard specification or in line with customer specification. There are different grades of petcoke like soft coke, granular, shot coke, fuel grade coke etc. The sulphur concentration in petcoke is a very important parameter for customers due to stricter environment norms. Most of petroleum the refiner estimate petcoke sulphur based on delayed coker unit feed sulphur multiply with fix factor or empirical formula based on the past experience. However many times refinery produce unplanned high sulphur petcock while processing more sour crude or quality give away in petcoke sulphur (very less sulphur compared to specification limit) while processing of sweet crude oil.

When unplanned high sulphur petcoke produced, refinery faces many problems like (a) material offtake when sulphur is beyond the specification limit resulting in shortage of committed product to the customers, (b) needs extra storage facility and more time for disposal. To avoid unplanned high sulphur petcoke production, refinery has to process low sulphur crude which is more costly leading to loss in profit margin.

The high sulphur in petcoke, quality give away in petcoke sulphur and dent in profit could be avoided if the advance information available on sulphur in petcoke, but there is no such method available or know to us.

Nayara Energy R&D team has addressed these issues innovatively and after comprehensive research work, team has developed a novel method for measurement of sulphur in petcoke from crude oil and petroleum residue samples using latest instrumental technique. The test results are accurate and correlate with actual sulphur in petcoke produce through delayed coker unit.
The advance information of sulphur in petcoke will be useful for,

a) Production of petcoke with very close to sulfur specification which will avoid unplanned high sulphur as well as reduce chance of quality give away.
b) Refiner can plan and produce low sulphur grade petcoke for better price realization.
c) Selection, procurement and processing of more sour crude oils which are cheaper.
d) Preparation of crude blends correctly.

Looking to the multiple benefits of research work, it is envisaged that, it will be highly useful for petroleum refining fraternity.

Keywords: Crude oil, Petcoke, Sulphur, Petcoke Sulphur, Delayed Coker Unit), Crude Distillation Unit.

I. INTRODUCTION

Petroleum refinery process different types of crude oils and produce valuable gaseous and liquid fuels, namely Liquefied Petroleum Gas, Motor Spirit, Aviation Turbine Fuel, Kerosene, Diesel, etc. and solid products like Sulphur and Petroleum Coke.

Petroleum refinery prepare & process blend of crude oils in different ratio considering distillation unit feed criteria, metallurgy of refinery processing units as well as profit margins. Bottom of the barrel mainly Vacuum Residue (VR) & Heavy Heavy Vacuum Gas Oil (HHVGO) from Crude Distillation Units (CDU) feed into Delayed Coker Unit (DCU) for further recovery of valuable distillates by thermal cracking. Post thermal cracking carbonaceous solid residue remains in the coke drum is called **Petcoke**.

Petcoke is marketed as per standard specification or in line with customer specification. There are different grades of petcoke like soft coke, granular, shot coke, fuel grade coke etc. The sulphur concentration in petcoke is a very important parameter for customers due to stricter environment norms. The sulphur in petcoke is measured at laboratory using test method ASTM D 4239 "*Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High- Temperature Tube Furnace Combustion"*.

Most of the refiner estimate petcoke sulphur based on DCU feed sulphur multiply with fix factor or empirical formula based on past experience and accordingly refinery

prepare crude blends to control sulphur in petcoke. Theoretically, sulphur concentration remains in petcoke purely depends on individual crude oil chemical composition, distribution of sulphur molecules, types and ratio of crude oils used in blend preparation, thermal treatments during refining process and ratio of VR & HHVGO in DCU feed. Hence, many a times refinery produce unplanned high sulphur petcock while processing more sour crude or quality give away in petcoke sulphur (very less sulphur compared to specification limit) while processing of sweet crude oils.

When unplanned high sulphur petcoke produced, refinery faces many problems like (a) material offtake when sulphur is beyond specification limit resulting shortage of committed product to the customers, (b) needs extra storage facility and more time for disposal. To avoid unplanned high sulphur petcoke production, refiner has to process low sulphur crude which is more costly leading to loss in profit margin.

The high sulphur in petcoke, quality give away in petcoke sulphur and dent in profit could be avoided if advance information available on sulphur in petcoke, but there is no such method available or know to us, hence needs arises to develop reliable technique to know sulphur in petcoke in advance.

II. HISTORICAL DATA OF SULPHUR IN PETCOKE

Most of the petroleum refiner process heavy crude oils with high sulphur due to better refining margins hence petcoke produced with high sulphur is being marketed at fuel grade petcoke. The fuel grade petcoke mainly categorised based on sulphur content namely low sulphur or high sulphur petcoke. The sulphur present in fuel grade petcoke is produce sulphur dioxide during combustion which pollute the environment while use as fuel, hence to protect environment some of Indian states are having legislation to use fuel grade petcoke with sulphur content less than 7.0 % wt.

The twelve months test results of sulphur in petcoke is presented in graphical form in figure-1. It is observed that, there is wide variation in sulphur content ranging from 4.2% to 7.3% during the period and many a times sulphur in petcoke crossing the target limit of 7.0% max.

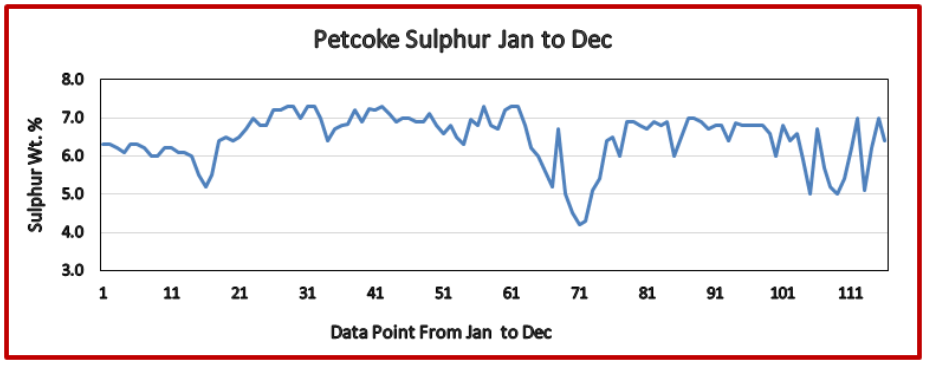

Figure 1

Opportunities: It is noticed that there is opportunity to produce low sulphur grade petcoke (<5%) as well as to process more quantity of sour crude oils, if the proper mechanism is available to control the sulphur concentration in petcoke.

III. METHOD DEVELOPMENT

Nayara Energy R&D team has addressed these issues innovatively and after comprehensive research work, team has developed a novel method for measurement of sulphur in petcoke from crude oil and petroleum residue samples using latest instrumental technique.

The invented novel method for measurement of sulphur in petcoke from crude oil or residue samples consist of two stages a) micro level petcoke generation at Lab and b) measurement of sulphur in micro level petcoke. The procedure is combination of two test procedures widely used in petroleum refinery laboratory for different applications viz IS 1448 P-122 *"Standard Test Method for Determination of Carbon Residue"* and ASTM D 4239 *"Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High- Temperature Tube Furnace Combustion"*. The basic process diagram of invented novel method is shown in figure-2.

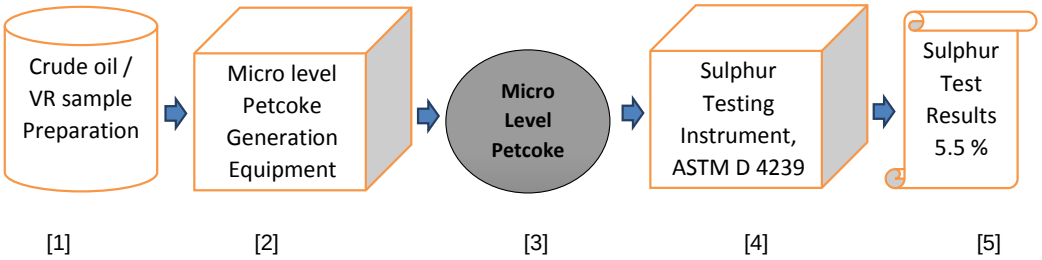

Figure 2

As described in figue-2 of method process diagram, stepwise process is explained below,

[1] Sample Preparation:

Analysis samples are collected in aluminum bottles or steel jars based on nature of sample. Shake the sample to make it homogeneous. In case of high viscus sample, heat the sample at 60 to 80 Deg C on hotplate and stir it using glass rod. Take appropriate sample in quartz glass vial or SS sample cell for micro level petcoke generation.

[2] Micro Level Petcoke Generation Equipment:

Nayara R&D team has developed 300 ml capacity coking equipment using SS vessel and digitally controlled electrical furnace. Carbon residue testing equipment confirming to test method IS 1448 P-122 or ASTM D 4530 requirements also can be used for this application.

The equipment consist of crucible, vial or SS vessel for sample coking, coking chamber or furnace, nitrogen purging and heating device to provide stable temperature of 500° C. Take appropriate sample according to coking cell capacity and kept inside coking chamber, close the coking chamber and set nitrogen flow. Start the equipment for petcoke generation. After coking program completion, stop the heater to reduce the heating. After reduction of coking chamber temperature below 50 Deg C, stop the nitrogen flow and open the lid, remove the sample cell and cool it up to room temperature. Collect the residual micro level petcoke generated in coking cell (crucible, vial or vessel). The petcoke generated can be calculate using below formula, if required.

Equation 1

% Petcoke = (Wt. of residual petcoke in gm X 100)/ Sample taken for coking in gm

[3] Micro Level Petcoke:

The micro level Petcoke generated by coking equipment will be collected either from single run or multiple run is mixed thoroughly and used for measurement of sulphur. Approximately 250 mg petcoke sample required to test sulphur in duplicate or triplicate measurement.

[4] Measurement of Sulphur:

The micro level petcoke generated is then tested for sulphur concentration using test method ASTM D 4239 "Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High- Temperature Tube Furnace Combustion".

Scope of Method: This test method covers the determination of sulphur in samples of coal or coke by high-temperature tube furnace combustion.

Instrumentation: Sulphur measurement instrument consist of high temperature combustion furnace, oxygen gas arrangement, sulphur sensing detector, sample boat and automatic software control system. Prepare the sulphur measurement instrument as per standard operating procedure and calibrate as per test procedure.

Precision of Test Method:

Table 1

Test Method Precision =>	Repeatability (r)	Reproducibility (R)
ASTM D 4239 @ 7.0%	0.22	0.52

Analytical Procedure: After verification of instrument performance by certified reference material or quality control sample, start the sample testing of petcoke. Take the appropriate petcoke sample weight (50 to 150 mg) in clean, dry and pre weight ceramic crucible. Insert the crucible with sample in furnace and start the analysis.

[5] Analysis Report:

After completion of analysis, the instrument software will automatically calculate sulphur concentration based on calibration graph & sample weight and test results will be display in software. Analyze all samples in duplicate and report average test results up to 0.1 % wt.

IV. EXPERIMENTAL TEST RESULTS AND DISCUSSION

Various laboratory experiments were conducted to establish the correlation between developed test method vs actual petcoke sulphur as well as verify performance of test method. The measurement of Sulphur is done using standard test method, hence precision data is not generated.

Experiment: 1

The aim of this experiment is to establish test method and develop sulphur correlation data between DCU feed, petcoke generated at lab from DCU feed and petcoke produced from DCU.

Test sample: DCU Feed sample (mixture of VR & HHVGO of CDU-1 and VR of CDU-2) were collected from coker battery limit sample point and respective petcoke product samples were collected from DCU coke fresh cutting area considering coking cycle time of 16 hrs. Five sets of samples were collected on different date for experimental work.

Sample Testing: The micro level petcoke is generated at laboratory from DCU feed samples using developed procedure. DCU feed samples are tested for sulphur concentration using ASTMD 4294 and petcoke samples are using ASTM D 4239 test procedure. The observed sulphur test results are tabulated in table-2.

Table 2

Sampling Date	DCU Feed Sulphur % (A)	DCU Feed Lab Petcoke Sulphur % (B)	DCU Petcoke Sulphur % (C)	Sulphur % Difference (B-C)	Ratio (C/A)
12.08.20	4.59	6.55	6.4	0.15	1.43
15.08.20	4.68	6.78	6.7	0.08	1.43
22.08.20	4.50	7.00	6.8	0.20	1.56
24.08.20	4.56	7.02	6.9	0.12	1.54
26.08.20	4.27	7.04	6.9	0.14	1.65

Observations: Following observations are derived from table-2 test results,

1. The sulphur test results of DCU feed Lab petcoke and actual DCU petcoke product are very close hence developed method can be useful for measurement of petcoke sulphur from DCU feed sample.
2. DCU feed to DCU petcoke sulphur ratio is found to be vary from 1.43 to 1.65 on day to day basis, this may be due to variation in feed composition or change in crude blend.

Experiment: 2

Aim of this experimental work is to establish the correlation between sulphur in lab petcoke generated from crude oil and 530+ Deg C residue (same as DCU feed) of same crude oil. Five different crude oils and its 530+ Deg C residue samples collected after true boiling point (TBP) distillation are used for this experimental work and test results are tabulated in table-3.

Table 3

Name of Crude Oil	Crude Oil		Residue (530+ Deg C)		Difference [B-D]
	Sulphur % [A]	Sulphur % in Lab Petcoke [B]	Sulphur % [C]	Sulphur % in Lab Petcoke [D]	
Vasconia	1.00	3.10	1.66	3.06	0.04
Castilla	1.89	3.90	2.58	3.88	0.02
Johan Sverdrup	0.78	2.15	1.33	2.10	0.05
Ural	1.54	4.03	2.45	4.07	-0.04

Observations: Sulphur in petcoke generated at lab from Crude oil and its 530+ Deg C residue found to be very close in all tested crude oils.

Experiment: 3

To generate data bank, more than 30 crude oils which are part of crude basket are tested for sulphur concentration in crude oil, its 530+ Deg C residue sample and petcoke generated in lab. Some of important data are tabulated in table-4.

Table 4

Name of Crude Oils	Sulphur % in Crude [A]	Sulphur % in 530+ Deg C Residue [B]	Sulphur % in Lab Petcoke [C]	Ratio [C/B]
RO1	0.60	1.0	0.7	0.8
MUR	0.77	2.2	4.5	**2.1**
CPB	0.60	1.7	4.7	**2.8**
AEL	0.81	2.6	5.0	**2.0**
OE4	1.38	2.8	5.7	**2.1**
DAS	1.13	3.1	6.5	**2.1**
CLB	3.43	**5.6**	**6.8**	1.2
KRL	3.64	**5.8**	**6.8**	1.2
FRH	3.52	**5.9**	**6.9**	1.2
QAL	1.28	**3.7**	**7.1**	**1.9**
AS2	2.22	**4.7**	**7.6**	1.6
KHA	2.88	5.6	8.6	1.5
KUW	2.62	5.5	8.8	1.6
BAL	2.77	5.3	9.2	**1.7**
BAG	4.02	6.9	10.5	1.5
KSR	4.92	7.1	11.0	1.5

Observations: Test results in table-4 are very interesting and indicates that sulphur increasing ratio widely vary from crude to crude oil and it is purely depends on inherent property of individual crude oil, hence advance information of sulphur in petcoke will be highly useful for selection, procurement and processing of crude oil.

Experiment: 4

The aim of this experimental work is to develop sulphur increasing ratio of DCU feed components (CDU-1 HHVGO & VR and CDU-2 VR) to understand the reason of day to day ratio variation observed in experiment-1.
Four sets of samples are collected from CDU-1 and CDU-2 units and tested for sulphur analysis before and after petcoke generation at laboratory. The observed test results of two sets of samples are tabulated in table-5.

Table 5

Sample Details	Date	DCU Feed Sulphur % (A)	Lab Petcoke Sulphur % (B)	Ratio (B/A)
CDU-1 VR	12.08.20	5.37	7.02	1.31
CDU-1 VR	17.08.20	5.39	7.40	1.37
CDU-1 HHVGO	12.08.20	4.83	6.72	1.39
CDU-1 HHVGO	17.08.20	4.73	7.20	1.52
CDU-2 VR (M72)	17.08.20	1.80	4.46	2.48
CDU-2 VR (M72)	24.08.20	1.77	4.40	2.49

Observations: Following observations are derived from table-5 test results,
1. DCU feed components are having different sulphur increasing ratio.
2. Also sulphur ratio vary from day to day may be due to change in crude blend.
3. Though CDU-1 VR and HHVGO having different sulphur, the sulphur in petcoke is found to be very close.
4. CDU-2 VR having very high sulphur increasing ratio compared to CDU-1 VR this may be due to CDU-2 operated mainly with Mangala crude oil.

V. CONCLUSION

From the experimental test results and observations, it is concluded as below,

1) The sulphur test results of experiments 1 & 2 indicates that, sulphur in petcoke generated at lab from crude oil and DCU feed is closely correlate with actual petcoke produced from DCU. The test results are very close and within repeatability limits of test method ASTM D 4239, hence developed method will be useful for measurement of sulphur in petcoke from crude oil and DCU feed sample.

2) Sulphur increasing ratio in DCU feed components found to be different however sulphur in petcoke generated from CDU-1 VR & HHVGO found to be very close.
3) Developed method can be useful to prepare estimation model from crude oil and or from DCU feed components.
4) Advance information of sulphur in petcoke from crude oil will useful to control sulphur in petcoke product, hence will reduce chance of unplanned high sulphur or low sulphur in petcoke product.
5) It will useful for selection, procurement and processing of sour & sweet crude oils lead to increase refinery margins.
6) It will also useful to plan and produce special grades (low sulphur < 5.0%) of petcoke for better prize realization.

VI. ACKNOWLEDGMENT

Author would like to thanks to M/s Nayara Energy management and Laboratory team for providing resource for this experimental work and granting permission to present in conference for benefits of global users.

VII. REFERENCES

Following reference test methods are used for development of test method,

1. IS 1448 P 122: Standard Test Method for Determination of Carbon Residue- Conradson Method.
2. ASTM D 4530: Standard Test Method for Determination of Carbon Residue (Micro Method).
3. ASTM D 4239: Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High- Temperature Tube Furnace Combustion".
4. ASTM D 4294: Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry".