Process for Sulfur Reduction from High Viscosity Petroleum Oils

Sandeep Chavan, Harshad Kini, and Ranjan Ghosal

Abstract—**The petroleum heavy oils or residual oils are known to contain large amounts of sulfur, causing significant environmental concerns during the partial or complete combustion of these oils. The removal of sulfur species from such oil fractions is extremely difficult due to the recalcitrant nature of the sulfur species. The present work describes a novel process for sulfur removal from high boiling, high viscosity petroleum fractions, wherein a sulfur removal efficiency as high as 95% is observed. The process also sees a reduction in the asphaltene content of the treated oils by more than 50%. Further, the viscosity of the desulfurized oil was found to be significantly reduced by more than 90% as compared to that of the untreated or raw oil fraction. It is envisaged that utilization of this process for desulfurization of residual oils will result in much reduced SOx emissions, with accompanying environmental benefits.**

Index Terms—**Carbon black, environmental, sulfur, residual oil.**

I. INTRODUCTION

The composition of petroleum oil or crude oil is known to vary significantly from its origin or geographical location of the refinery. These crude oils can be differentiated into various individual fractions at different boiling ranges. The low boiling fractions ($< 170^{\circ}$C) are typically napthas, those between 180-250°C are kerosene and the ones boiling in the range of 250-350°C are termed as gas oils. The fractions boiling above 350°C are generally termed as residues and are obtained after most of the distillable products have been removed from the petroleum oil [1]. The use of this high boiling petroleum oil residue fraction includes heating (as a fuel), and as a feedstock for the manufacture of carbon black i.e. Carbon Black Feed Oil (CBFO). These residual petroleum oils are characterized by the presence of high sulfur content typically varying from about 1 – 4%. Some of these residual oils are known to contain up to 6-8 % Sulfur.

The presence of sulfur in the petroleum oil residue has a number of shortcomings, especially when using the oil as a fuel or in a process involving partial pyrolysis of the oil, such as the manufacture of carbon black by the furnace process. CBFO is a major source of feedstock for the manufacturing of carbon black, a vital component of tyres, inks and

colorants. Carbon black is produced by a process of controlled pyrolysis at temperatures of 1000-1800°C [2]. During the partial or complete combustion of a sulfur-containing residual oil, the sulfur gets converted to SO_2 and SO_3 (typically referred to as SOx). During the combustion or pyrolysis process, the sulfur emissions from a typical high sulfur residual oil can be extremely high; additional processes such as flue gas desulfurization are needed to clean up these emissions and bring the SOx content of effluent gases to acceptable levels. This requires an additional investment of capital, as well as additional operating expense, to continue operating industrial units that use the sulfur-containing residual oil.

Apart from the sulfur dioxide as the major emission, the Carbon Black manufacturing process causes additional sulfur based emissions such as carbonyl sulfide, carbon disulfide and hydrogen sulfide. These are in a varying proportion and arise from different source such as main reactor vent, dryer, incinerator, boiler etc. Most of these sulfur compounds get converted to sulfur dioxide during further processes at plant. These sulfur emissions have serious effects on our environment. The SOx (oxides of Sulfur) along with NOx (oxides of Nitrogen) gets adsorbed by the water molecules in the atmosphere resulting in acid rains. These acid rains have direct impact on vegetations, marine and aquatic organisms. The soil quality can be seriously damaged by acid rain by means of loss of essential nutrients and minerals. Some useful microbes in the soil are unable to tolerate the low pHs and get destroyed. Acid rain can also damage buildings and historic monuments and statues, especially those containing large amounts of calcium carbonate. Acid rain indirectly affects human health by the formation of fine particulate matter in the air causing heart and lung problems including asthma and bronchitis and is linked to various cardiovascular diseases. Even small amounts of sulfur dioxide can form secondary particles (sulphates) that cause haze and reduce visibility. Sulphur dioxide can cause problems over a whole urban area or more locally around a single or several industrial discharges. It can cause respiratory problems, irritation to nose, throat and lungs, irritation and burning sensation of the skin and eyes with possible eye damage. Repeated exposures may cause coughing, wheezing, phlegm and asthma attacks. Sulfur Dioxide may decrease fertility in males and females. Higher exposures may cause a build-up of fluid in the lungs (pulmonary edema), a medical emergency.

Thus, these adverse environmental and health issues caused by sulfur emissions are well known. Further, the sulfur content of residual oils is known to be a primary cause of corrosion in the process using the oil. In cases where the residual oil is used to produce carbon black, a part of the sulfur is retained in the final product and manifests itself in the final application. For certain applications of carbon black,

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the presence of sulfur is detrimental to product quality, and it is desirable to produce a carbon black with minimal or nil amounts of sulfur for these applications.

Thus, from the industry stand point, in addition to environmental concerns, the high sulfur content in residual oils can lead to corrosion of equipments as well as poor quality of products. The end result is greater environmental risk for the world at large, and additional expense on the part of the user of the residual oil. Hence it is well established that there is a need to desulfurize the available stocks of high sulfur residual oil to increase their value and reduce their environmental impact.

A number of techniques including catalytic transformation processes such as hydro-desulfurization [3]-[7] and physico-chemical processes such as solvent extraction [8]-[9], oxidation [10]-[16], adsorption [17]-[19], sodium metal reduction [20]-[21], bio-enzymatic [22]-[25], electrochemical [26]-[28] etc. mention about reduction in the sulfur content from various fractions of the petroleum oils. The hydro-desulfurization is by far the most studied process. This process is based on catalyst systems comprising of transition metals such as Ni, Co, Mo supported on Al_2O_3 and convert the sulfur species to into H_2S. The H_2S, again cannot be disposed off and needs to be further processed separately. Most of these technologies are more efficient towards the low boiling fractions such as gasoline, naptha, kerosene which themselves contain low boiling and less stable sulfur species. Their efficiencies however drops when treating high boiling fractions e.g. residual oil or CBFO. This is due to the fact that lower boiling oil fractions primarily contain sulfur in the form of mercaptans or lowered member ring compounds, which are relatively easier to desulfurize. In contrast, the high boiling fractions or resids contain sulfur species that are part of the more stable ring compounds such as substituted benzothiophenes and higher derivatives or large molecule ring compounds which are extremely difficult to desulfurize. Further the sulfur content in crude oils of low boiling fractions is much low in the range of 0.1 – 1%. Whereas, in case of resids the sulfur content can be as high as 4-5% and this sulfur thus appears to be essentially distributed over a majority of the molecules contained in the oil.

Thus, the focus of the present work is the desulfurization of high boiling, high viscosity residual petroleum oils, including CBFO. To the best of our knowledge, there is no such treatment for sulfur removal that is commercially available. The current process uses chemical reaction to modify the sulfur-containing species in the oil to hydrocarbons. The process has been able to achieve > 95% desulfurization, whereby the residual oil with high sulfur content of about 4% was reduced to a low sulfur content of <0.2%. Other advantages of the process include easier handling of the oil, improvement in processing issues, and improvement in the yield of the desulfurized oil. The viscosity of the desulfurized oil after desulfurization is reduced considerably, which provides benefits in processes utilizing the oil. The overall effect is substantial reduction in sulfur based environmental emissions, and improvement in the product quality.

II. EXPERIMENTAL

Varying quantities of (Carbon black feed oil (CBFO) are taken in the high pressure reactor (Anton-Parr) of 1 litre capacity. The CBFO was provided by Birla Carbon Company ltd. Different quantities of organic solvent is then added to the reactor vessel and stirred for a few minutes. Stoichiometric quantities of sodium metal (AR-grade) is then weighed separately and cut into small pieces of about 1 cm diameter. The exact quantities of the CBFO, solvent and the sodium metal taken are given in Table-I. The sodium metal pieces are then added to the high pressure reactor vessel. Nitrogen gas is purged through the reactor to displace any air and the reactor is then pressurized with hydrogen gas (100-500psi). The solution in the reactor is then mixed thoroughly under high mixing at 600-800 rpm. The system is then heated to a temperature of about 300°C for a period of about 4 hr. The pressure reactor system is then allowed to cool to ambient conditions and the remaining hydrogen gas vented out. The reactor is then again purged with nitrogen gas and the contents are then filtered. The filtrate is then subjected to solvent removal by means of a rotavapor and characterized for sulfur content based X-ray Fluorescence spectroscopy – XRF (Bruker) and compared with the sulfur content of the standard initial untreated CBFO. The viscosity measurements of the standard untreated oil and the desulfurized oil are carried by a viscometer (Brookfield).

III. RESULTS AND DISCUSSION

The initial experiments were carried by preparing standard solutions of CBFO:solvent mixture in the ratio 70:30 (weight:volume). The amount of CBFO taken was about 285 g. The sodium content was then systematically varied to determine the desulfurization efficiencies with respect to the sodium content in the system. In each of the cases the initial hydrogen pressure added to the system was kept as 300 psi. The reaction temperature was 300°C and the reaction temperature was maintained as 300°C. The sodium metal reacts with sulfur from the CBFO, resulting in the formation of Na_2S, which is a solid and is filtered out from the system. The processing conditions and the sulfur analysis results are tabulated in Table I below.

TABLE I: DESULFURIZATION EFFICIENCY FOR SODIUM CONTENT

Na amount	Desulfurization (%)
13.5	70
8.5	45
11.0	53
16.0	97

As seen in the table it was observed that the desulfurization efficiency increases with the sodium content. It may be noted that even by means of using stoichiometric sodium amount only about 70% desulfurization was observed. Thus, in order to achieve desulfurization about 90%, excess sodium concentrations were required. These results are plotted as desulfurization (%) vs sodium content (wt) in Fig. 1.
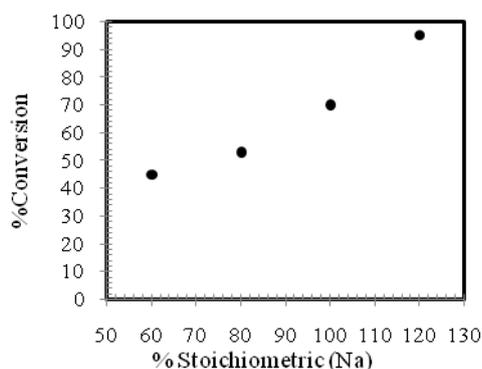
Fig. 1. Desulfurization as a function of sodium content.

Further to determine the optimum duration for the reaction or the residence time, similar experiments were carried, wherein the reaction time was varied from 10 min to 3 h. Thus, in this case also the CBFO: solvent ratio was taken as 70:30 and stoichiometric amount of sodium metal corresponding to 13.5g was added in each case. The reaction hold time was varied as 10min, 30 min, 45 min, 60 min and 180 min. The desulfurization was again measured by means of XRF and the results are tabulated in Table II below.

TABLE II: DESULFURIZATION EFFICIENCY AS A FUNCTION OF TIME

CBFO: Solvent	Processing Time	Desulfurization
70:30	180 min.	70%
70:30	60 min	70%
70:30	45min	68%
70:30	30min	59%
70:30	10min	50%

It was observed that the optimum residence time is about 45 min. The desulfurization values are considerably lower at lower hold durations. Similarly, the desulfurization doesn't appear to vary significantly even after hold duration of 3h. The plot of desulfurization (%) vs residence time is given in Fig. 2 below.
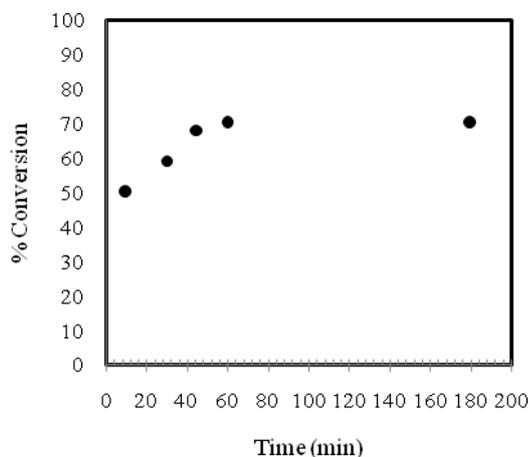

Fig. 2. Desulfurization as a function of reaction time

In Table III, the properties of the untreated and desulfurized residual CBFO are compared. The table shows that essentially complete removal of sulfur is attained by the process, resulting in conversion of sulfur-containing species to those containing carbon and hydrogen (hence an increase in carbon and hydrogen content of the oil is observed at the expense of sulfur).

TABLE III: COMPARISON OF PROPERTIES OF UNTREATED AND DESULFURIZED CBFO

Property	Untreated CBFO	Desulfurized CBFO
Specific Gravity @15.6 ºC	1.0982	1.0517
Mid-boiling point (ºC)	292.4	281.5
Asphaltenes (wt%)	10.6	4.65
Carbon (wt%)	89.4	91.1
Hydrogen (wt%)	7.5	8.3
Sulfur (wt%)	2.4	ND

The CBFO viscosity is an important parameter during the carbon black manufacturing process as it affects the carbon black properties in terms of particle size and structure. The sample thus obtained after desulfurization and solvent distillation in the present case appeared to be of reduced viscosity as compared to the original untreated sample. The viscosity measurements were then carried for the desulfurized sample and the untreated sample and compared as a function of temperature. Both the samples were thus initially heated to about 175ºC on a hot plate and the viscosity measurements were noted at different temperatures as the samples were being cooled, by a Brookfield viscometer. The results are tabulated in Table IV below.

TABLE IV: VISCOSITY CHANGE WITH TEMPERATURE

Temp (ºC)	Viscosity(cP) CBFO-Untreated	Viscosity(cP) CBFO-Treated
150	20	14
100	53	23
50	280	70
35	2800	120

It was observed that the viscosity of desulfurized oil has been reduced significantly especially at temperatures closer to ambient. Thus, the initial CBFO with a viscosity of about 2800 cP gets reduced to about 120 cP, which would also result in better handling and energy savings in terms of material pumping and transport. The reduction in viscosity may be associated due to breaking of large molecular species in the parent oils to lower molecular chains during the desulfurization reaction.

IV. CONCLUSION

A process has been developed which is capable of reducing the sulfur content of residual oils from an initial value of 4% to less than 0.2%. This implies substantial reduction in sulfur emissions- from about 2500-5000 ppm for the untreated residual oil, to the range of 100-250 ppm for the desulfurized residual oil, depending on the application. The process demonstrates considerable flexibility in conditions and raw material consumption, and can be tailored depending on the extent of desulfurization required. Stricter environmental regulations that cause an increase in the demand for low sulfur residual oil, coupled with a decrease in the actual

availability of the low sulfur oil, puts many industries in a difficult situation with increasing capital investment and/or operational costs needed to meet their requirements. The process presented here offers an alternative whereby high sulfur residual oils can be treated and used without violating present and future environmental regulations, at a relatively economical cost.

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