

## Reduction of Sulphur Content of Urals Crude Oil Prior to Processing Using Oxidative Desulphurization

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**ABSTRACT:** The presence of sulphur in crude oil poses enormous challenges as regards its negative environmental and economic impacts. As such, the safety of the personnel and the equipment is at high risk during the processing of Urals crude oil in Kaduna Refining and Petrochemical Company (KRPC) because of its sour nature. This study was aimed at reducing the sulphur content of the Urals crude oil prior to processing by subjecting it to oxidative desulphurization where peracetic acid was used as the oxidant in the actual mass-to-stoichiometric mass ratio ranging from 1 to 5. The oxidized sulphur compounds were thereafter extracted using acetic acid as the extraction solvent. Furthermore, atmospheric distillation was carried out on both the raw and the desulphurized crude oil samples. Finally, the sulphur contents of the various crude oil samples and their fractions were analyzed. The results showed drastic reductions in the sulphur contents up to actual mass-to-stoichiometric mass ratio of 2 but the reductions became progressively insignificant afterwards. Meanwhile, the highest reduction in the sulphur content of the crude oil was 61.6 % while those of the gasoline, kerosene, diesel and residue were 32.0, 45.1, 68.9 and 75.0 % respectively. Therefore, peracetic acid is an effective oxidant for oxidative desulphurization of the crude oil.

**Keywords:** Sulphur content, Crude oil, Oxidative desulphurization, Thiophenic compounds

### INTRODUCTION

The presence of sulphur has a very great influence on the value of the crude oils because of the negative environmental impact and the effect of the refined products on automotive and combustion engines. This has led to the stringent environmental regulations which place considerable pressure on refinery operators worldwide to reduce sulphur contents of crude oil products (Rasina and Rudin, 1988; James, 1999; Matar and Hatch, 2000; Germain and Herman, 2003; Prasad, 2006). In the past decades, more and more stringent legislations on the specifications of sulphur level in fuels have been passed in many countries and currently the production of ultra-low sulphur fuel oil has become an important task of oil refining industry (Zhang *et al.*, 2009).

Active sulphur includes elemental sulphur, hydrogen sulphide and mercaptan while the inactive ones include sulphide, carbon disulphide, thiophene (TH), and so on. It has been found that in fluid catalytic cracking (FCC) gasoline, more than 90 % sulphur exists in the form of thiophene and its derivatives, while in diesel, thiophenic sulphur accounted for 80 % of the total sulphur, and benzothiophene (BT) and dibenzothiophene (DBT) accounts for more than 70 % of this thiophenic category (Zhang *et al.*, 2009). As a result, removal of sulphur in

thiophenes is the main desulphurization focus of this study.

In addition, the current requirement of sulphur level in transportation fuels has shifted the attention of crude oil refiners from the conventional HDS to other processes. In recent years, industry has sought to develop less expensive desulphurization alternatives to hydrotreating. One of such alternatives that have been successful in meeting this requirement is the oxidative desulphurization which uses organic or inorganic peroxides as oxidants (McKinley, 2003).

It is known that contacting petroleum fuels with an oxidant converts the organosulphur and nitrogen compounds in the fuels into sulphones (or sulphoxides) and organic nitric oxides, respectively. These polar organic oxides can be removed from the fuels by solvent extraction and/or adsorption (Rang, 2006). More importantly, oxidative desulphurization can easily oxidize and remove thiophenic sulphur compounds, which cannot be readily treated by HDS due to the steric hindrance effect around the sulphur atom in the molecule (Zhang, 2009).

Different researchers have made tremendous breakthroughs in desulphuring crude oils fractions (Collins *et al.*, 1997; Cullen, 2004; Ali *et al.*, 2006;

Ranget *et al.*, 2006; Zhang *et al.*, 2009; Brown and Evans, 2009). An interesting process was worked out by desulphurizing petroleum oils with nitrogen oxides and oxygen to convert organic sulphur into sulphur trioxide which was absorbed with concentrated sulphuric acid (Guth *et al.*, 1975). The most desirable result was obtained by peroxy acid oxidation ( $\text{HCOOH}/\text{H}_2\text{O}_2$ ) after which the sulphones and the sulphoxides created during oxidation was carried out by extraction followed by adsorption with silica gel to reach sulphur content levels of 7.0 ppm and 0.00 %, respectively (Aida *et al.*, 2000). Another effective process has been suggested by Mei *et al.* (2003). Phosphotungstic acid, tetraoctyl ammonium bromide and ultrasound were used at 75 °C to complete the oxidation. The oxidized product was then extracted with acetonitrile. Under these conditions dibenzothiophene and its derivatives were removed from diesel fuel at a rate of more than 99 %. In recent years many desulphurization processes with peroxides have been patented: removal of sulphur from 250 to 5 ppm in diesel fuel (Rappas, 2002), sulphur removal in diesel fuel from 0.557 to 0.0008 % (Gunnerman, 2002), and from gas oil to 82 % (Gore *et al.*, 2003). In 2004, a patent application concerning desulphurization with oxidation was presented (Rang, 2006). Oxidation of crude oil was carried out by hydrogen peroxide in the presence of a catalyst, surface-active agent and radiation with sonic energy at 125 °C and 3 atm. The resulting sulphur content was reduced from 2.5 % to 0.7% (Cullen, 2004). Li *et al.* (2004) suggested an interesting oxidation catalyst which is also phase transfer agent. Oxidation was carried out using

## **MATERIALS AND METHODS**

### **Oxidation process**

Two conical flasks were each filled with half (0.5) litre of Urals crude oil which weighed 412.68 g with sulphur content of 1.12 wt %. According to the stoichiometric ratio of the oxidation of DBT by peracetic acid (PAA) which is 1:2 as represented by the equation in Figure 1, about 54.88 g of 40 wt % PAA solution was added to each flask.

The same 54.88 g of acetone was added to each mixture to minimize phase separation as the amount of acetic acid generated would be too high to keep the reaction in a single phase. The filled conical flasks were placed on a Stuart magnetic stirrer heater and the

hydrogen peroxide for 30 minutes at 60 °C and 8 minutes at 90 °C. The turnover number was estimated to be higher than 300. After the process the catalyst was separated by centrifugation, and oxidized sulphur compounds were removed with extraction by N-methyl-2-pyrrolidone. Ultra-deep desulphurization with sulphur content below 0.1 ppm in diesel fuel was achieved. The feed-stock was prehydrotreated diesel fuel, containing sulphur 0.053 wt %. In a patent application, it was shown that sulphone obtained from dibenzothiophene, created in oxidation process, was converted into biphenyl and hydrogen sulphide by hydrogenation (Levy *et al.*, 2003). Dibenzothiophene sulphone was hydrogenated under milder conditions than dibenzothiophene. A product containing 55 ppm sulphur was obtained from gas oil in a two-step process. Also recently, several patent applications concerning oxidation with ozone and oxygen have been presented (Rang, 2006). In another application, heterogeneous oxidation of transport fuel with oxygen in the presence of a solid catalyst at temperature of 160 °C and pressure of 14 atm, reduced sulphur content from 233 ppm to 12 ppm (95 % removal) (Hagen *et al.*, 2004). Lin *et al.* (2007) used non-aqueous peracetic acid solution and reduced the sulphur content of treated diesel from 198 to 5 ppm after oxidation at 60 °C for 20 minutes, water washing and adsorption with alumina. Using treated light gas oil(LGO), it was reduced from 307 to 88 ppm after oxidation at 50 °C for 15 minutes and extraction with acetic acid.

temperature was raised to 50 °C and maintained at this temperature for 20 minutes. Four other similar oxidations were carried out using 2, 3, 4 and 5 times the stoichiometric amount of the oxidant to obtain five different oxidized crude oil samples. These were respectively termed as 1:1, 2:1, 3:1, 4:1 and 5:1 crude oil samples.

Each of the oxidized crude oil was washed with water to remove the acetone added during oxidation. Acetic acid in oil-to-solvent ratio of 1:1 was mixed thoroughly and poured into separating funnel. The mixture was allowed to stand for 6 hours to ensure complete separation. The extract which contained the sulphones and the sulphoxides was drained off while the raffinate was collected as the desulphurized crude oil.

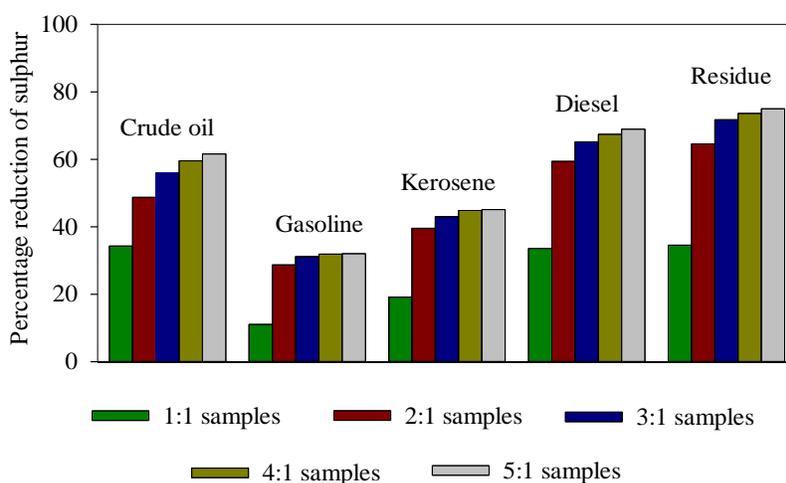


process was very effective up to three times the stoichiometric amounts of the oxidant as further

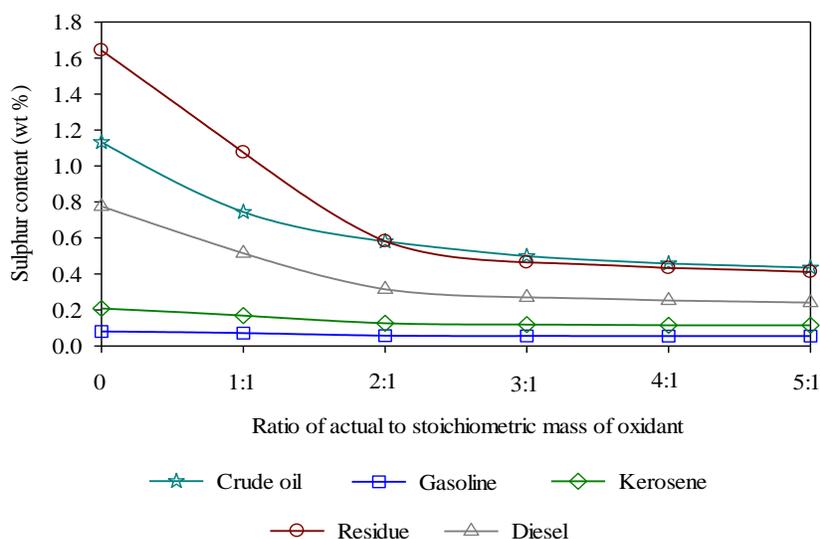
increase did not make significant reduction of the sulphur contents.

**Table 2:** Average Sulphur Contents of Crude Oil, Its Fractions and Extracts

Sample	Raw oil (wt %)	Desulphurized oil with different amounts of oxidant (wt %)				
		1:1	2:1	3:1	4:1	5:1
Crude	1.1326	0.7439	0.5806	0.4985	0.4580	0.4349
Gasoline	0.0805	0.0716	0.0574	0.0554	0.0548	0.0547
Kerosene	0.2086	0.1686	0.1261	0.1189	0.1150	0.1145
Diesel	0.7754	0.5150	0.3148	0.2698	0.2524	0.2408
Residue	1.6426	1.0701	0.5817	0.4643	0.4330	0.4110
Extract	-	0.0748	0.1635	0.1907	0.2147	0.2209



**Figure 2:** Relative level of sulphur reduction of crude oil and its fractions



**Figure 3:** Reduction of sulphur contents of treated crude oil and its fractions

## CONCLUSIONS

From the results obtained, it can be concluded that the difference in the product yields of the raw crude oil and those of the desulphurized crude oil samples were not very much. Therefore, oxidative desulphurization does not significantly affect the product yield. The sulphur contents of the raw crude oil and oxidant in the ratio of 1:1, 2:1, 3:1, 4:1 and 5:1 crude oil samples were respectively 1.1326, 0.7439, 0.5806, 0.4985, 0.4580 and 0.4349 wt %. This shows that the reduction in the sulphur content of the crude oil increased with increase in the amount of the oxidant. The sulphur content reduction of the fractions shows the same trend with that of the crude oil. The gasoline, kerosene, diesel and residue sulphur contents were reduced respectively from 0.0805 to 0.0548 wt %, 0.2086 to 0.1150 wt %, 0.7754 to 0.2698 wt % and 1.6426 to 0.4110 wt %. For economic reasons, the maximum amount of the oxidant that should be used is when the stoichiometric amount of the oxidant is doubled as no significant change was observed when higher ratios of oxidant were used. The qualities of the crude oil and its fractions were not very much affected by this desulphurization when compared with the crude oil assay and KRPC specifications. The KRPC specifications of sulphur contents for the crude oil fractions were reached after using twice the stoichiometric amount of the oxidant.

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