



Quality Improvement of an Acid Treated Fuel Oil

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Abstract

The work on the quality improvement of fuel oil using acid treatment was carried out. The improvement of the fuel oil was done using sulphuric acid to remove contaminants. Sulphuric acid at different concentrations were mixed with the oil and kept at 45°C for four hours in the agitator vessel to allow reaction to take place. Acidic sludge was then drained off from the agitator and the oil was neutralized with sodium hydroxide. Centrifugation operation was used to extract the sulphonate dispersed in the oil. The treated and untreated oils were characterized for various properties and the results showed that the viscosity, total sulphur of fuel oil decreased from 6.0 to before 5.0 cst after acid treatment and 2.57 to 1.2225% w/w respectively while the flash point increased from 248 to 264°F. The water and sediment content increased from trace before to 0.6 after treatment. In addition, the calorific value increased from initial value of 44,368 to 44,805 and 44,715 kJ/kg at 50% and 75% conc. H₂SO₄ while decreasing with 85% and 90% conc. H₂SO₄. However, both carbon residue and ash content decreases with an increase in acid concentration.

Keywords

Fuel oil; Contaminants; Acid treatment and Characterization.

Introduction

The world fuel energy and raw material balances have experienced many changes in the past 100 years until 1940 when the basic type of fuel energy used in the industries was obtained from coal. However, over the years, this has given way to cheaper, easy to process; easy to transport; easy to mine liquid and gaseous fuel called petroleum and natural gas respectively. These raw materials are treated and separated into fractions to cater for the world energy needs. Fuel oil, a fraction of this separation with high thermal efficiency, has served many purposes in the aspect of firing of process equipment such as furnaces and heaters [1]. Although crude treatment has been considered before separation into fraction commenced, the deterioration in the life span of process equipment by the use of fuel oil has been attributed to impurities contained in fuel oil. Fuel oil is a very heavy/viscous fraction of petroleum crude oil containing mostly the carbon element in the range of C_{16} to C_{20} hydrocarbons, boiling point of 250-350°C and an average molecular weight between 300-1000. It consists of liquid residues from cracking processes and fractions with suitable boiling point obtained by distillation of crude oil. Fuel oils are classified by their properties such a viscosity, flash point, distillation temperatures, and sulphur content. These properties are determined by standardized tests developed under the auspices of the ASTM [2].

Fuel oil is a very important liquid fuel for both industrial and domestic uses for power generation, steam generation, raising the temperature of a process stream, in large ships etc. They can also be used as blending components for asphalt production. The major among the fuel oil burning plants are steam boilers, coke ovens, blast furnaces, cement kilns and refinery heaters/furnaces. Since the properties are characteristic of fuel oil in the worldwide industries, the improvement in these properties through the removal of impurities will be necessary. For instance, some improvement techniques are carried out at the blending site but they still remain unsatisfactory. Such techniques include the blending of gas-oil or kerosene into the high viscous fuel oil to lower the viscosity.

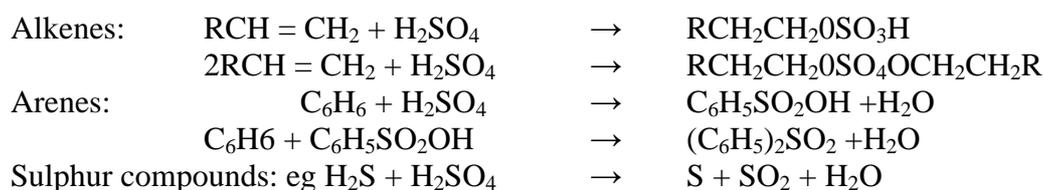
As petroleum product emerges from processing units, fuel oil needs purification treatment because it carries all kinds of impurities impairing its quality and rendering it unstable. For instance, the difficulty in pumping too viscous oil from the tank to the burner results in irregular combustion, incorrect atomization, and considerable carbon deposits, thereby causing faults in installation. Also the presence of water and sediments causes



complete breakdown of combustion, flames in impulses with sparks, loss in heat and sulphur which causes not only corrosion but produces toxic gases SO_2 and SO_3 that contaminate the atmosphere and if cooled and condensed form H_2SO_4 . Sulphur also decreases the calorific value of the oil. Other impurities such as the ash content and aromatics cause a lot of damages to equipments such as refractory materials, burner openings, pumps, valves to mention but few.

Literature Review

Industrial researchers, oil burning equipment manufacturers, and oil companies frequently liaise to find ways of applying oil firing to the best advantage over a wide range of industrial applications. They are concerned with the characterization of fuel oils, their transport, and storage and handling; such findings include the compatibility of blending components and the effects of prolonged storage of oils in heating storage tanks. These also include means by which the ash and sulphur contents of heavy fuel oil can be economically reduced. Sulphuric acid treatment is the most economical and effective method for removal impurities from petroleum products among the various purification techniques. The acid would react with alkenes, resinous, nitrogen and partly sulphur compounds in the following manners:



An article reporting the work on how to hydro treat waste lube oil disclosed that commercial oil reprocessing involves an acid treatment to remove gums, grease etc [6], followed by clay contacting to bleach oil and absorb impurities, finally filtering and blending operations were carried out. Hall and Chapman, 1986 described the acid/clay refining process of waste oil in which the acid treatment was completed by addition of grounded activated clay to absorb any remaining acid, [3].

Composition and properties of untreated fuel oil

Fuel oils have boiling point between 250 - 350°C, average molecular weight 300 - 1000 and carbon atom in the range of C₁₆ - C₂₀ [4]. Fuel oil of different types were chemically examined by standardized tests developed under the auspices of the American Society for Testing and Materials and the studies illustrated various constituents and properties of the oil. This was confirmed by Kaduna Refinery Petrochemical Company (K.R.P.C) earlier laboratory analysis that the fuel oils composition and properties could be as presented in Table 1.

Table1. Laboratory test values of fuel oil before treatment

TEST	TEST METHOD		LIMIT	RESULT
	IP	ASTM		
Specific gravity at 15.4°C, kg/cc	160	D1298	0.995 Max	0.8974
Pour point, °F	15	“97	70 max	70
Flash point, °	34	“93	150 Min.	248
Kinematic viscosity at 100 °F, Cst	71	“445	26 Max	6.30
Ash content, %wt	4	“482	0.1 Max	0.06
Carbon residue, % wt	13	“189	15 Max	5.03
Water & sediment, % wt	53	“473	0.5 Max	Trace
Total sulphur, %wt	-	“1552	6 Max	2.57
Calorific value, kJ/kg	Calculated	Calculated	-	44,368

Source of impurities and their treatment

Impurities in fuel oils are produced because of blending of various petroleum fractions (such as cracking residues, fractions from crude oil distillation etc) due to contaminants carried along by petroleum from boreholes (oil filed). Such impurities include aromatics, sulphur, sediments and ash as indicated by Institute of petroleum (IP). The maximum permissible values in wt% of aromatics, sulphur, water and sediments, and ash are 12; 0.5; 0.5 and 0.1 respectively.

Acid base treatment theory

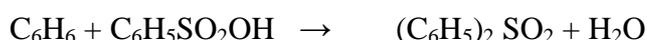
The process to effectively remove the impurities in fuel oil involves initial treatment with concentrated sulphur acid (H₂SO₄) to remove aromatics, soot (carbon residue), sulphur content, metallic compounds (Ash content) and other non-hydrocarbons, followed by treatment with caustic soda (NaOH) to neutralize excess acid either sulphuric or carboxylic, water washing/centrifugation and steam stripping.



Acid treatment

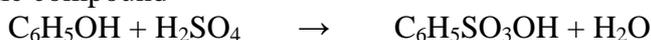
Due to the high stability of aromatic rings [5], concentrated sulphuric acid is usually employed in the purification of fuel oils for the reaction to proceed and continue and is known to extract such contaminants as aromatics, soot metals, sulphur etc. The following reactions are presumed to take place:

Sulphonation of reaction of arenes can be represented by:

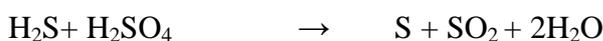
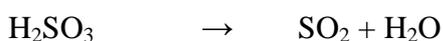


The sulphoacids and sulphones are soluble in sulphuric acid.

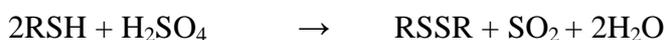
Phenolic compound



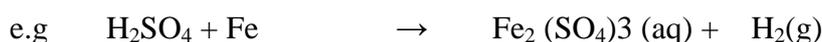
The hydrogen sulphide is oxidized with the formation of elemental sulphur and sulphur dioxide:



The mercaptans react with sulphuric acid to form disulphides and sulphur dioxide:



Reaction with metals (Ash content):

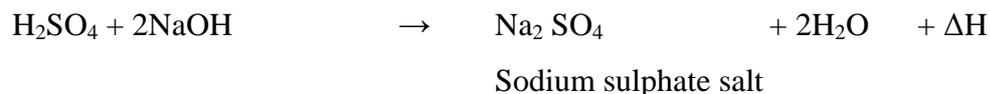


The acid sludge is formed at the bottom. It is a black, viscous layer of substance containing the spent acid and the impurities, which the acid has removed from the oil while the acid oil is the layer on top and contains the treated oil with some amount of acid entrained in it.

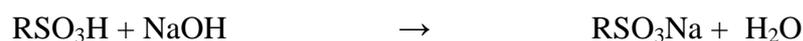
Caustic soda treatment

The acid is decanted and treated further with caustic soda to neutralize excess acid

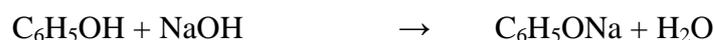
entrained in the oil.



The sodium salts are dissolved in water and dispersed in the neutralized oil. It also converts carboxylic acids and sulpho acids to sodium salts (soaps and detergents)



Phenols react with NaOH to form phenolates;



Methodology

The experiment was carried out using common laboratory reagents such as sulphuric acid and sodium hydroxide to extract contaminants from light fuel oil (L.P.F.O). The sample was collected from Kaduna Refinery and Petrochemical Company, Kaduna, Nigeria. Fuel oil and a sulphonating agent (H_2SO_4) were mixed and kept in the agitator batch vessel to react – Acidic sludge was then drained off from the bottom of the vessel and the top oil layer was neutralized with sodium hydroxide. Reactions are carried out at temperature 45°C for four hours. The temperature was maintained constant to enhance proper mixing in the vessel and allow for layers to be formed at the end of the reaction. Centrifugation was then carried out to extract the sulfonate dispersed in the oil [6]. The extent of the treatment depends on the strength, quantity of the acid and the degree of mixing. The reaction was monitored by making use of available laboratory analysers such as sulphur-in-oil analyser, viscometer, hydrometer; Pensky-marten's closed tester, Test jar, Sherman and Kropf empirical equations;

$$\text{H.H.V.} = 13,500 + (5600/\text{sp gr}) \times 2.3$$

Results

The table 2 shows the results of L.P.F.O when treated with 50% concentrated sulphuric acid.

Table 3 shows the results of L.P.F.O when treated with 75% concentrated sulphuric acid.

Table 2. L.P.F.O. Treated with 50% conc. H₂SO₄

TEST	UNIT	TEST METHOD (AST M)	LIMIT	TREATMENT	
				BEFORE	AFTER
Specific Gravity at 15.4°C	kg/cc	D1298	0.995 Max	0.8974	0.8708
Pour Point	°F	“97	70 Max	70.0	68.0
Flash Point	°F	“93	150 Max	248.0	250.0
Total Sulphur	% wt	“1552 x- RAY	6 Max	2.57	2.5633
Kinematic viscosity at 180°F (82.2°C)	Cst	D445	26 Max	6.30	6.10
Carbon Residue (conradson)	% wt	“189	15 Max	5.03	4.50
Ash Content	% wt	“428			0.04
Water & Sediments	% wt	“473	0.5 Max	Trace	0.5
Calorific value or Higher heating value (HHV)	kJ/kg	Calculated	-	44,368	0.1 Max

Table 3. L.P.F.O. Treated with 75% conc. H₂SO₄

TEST	UNIT	TEST METHOD (AST M)	LIMIT	TREATMENT	
				BEFORE	AFTER
Specific Gravity at 15.4°C	kg/cc	D1298	0.995 Max	0.8974	0.8762
Pour Point	°F	“97	70 Max	70.0	60.0
Flash Point	°F	“93	150 Max	248.0	258.0
Total Sulphur	% wt	“1552 x- RAY	6 Max	2.57	1.2225
Kinematic viscosity at 180°F (82.2°C)	Cst	D445	26 Max	6.30	5.81
Carbon Residue (conradson)	% wt	“189	15 Max	5.03	2.00
Ash Content	% wt	“428		0.06	0.02
Water & Sediments	% wt	“473	0.5 Max	Trace	0.30
Calorific value or Higher heating value (HHV)	kJ/kg	Calculated	-	44,368	44,715

Table 4 shows the results of L.P.F.O when treated with 85% concentrated sulphuric acid.

Table 4. L.P.F.O. Treated with 85% conc. H₂SO₄

TEST	UNIT	TEST METHOD (AST M)	LIMIT	TREATMENT	
				BEFORE	AFTER
Specific Gravity at 15.4°C	kg/cc	D1298	0.995 Max	0.8974	0.9156
Pour Point	°F	“97	70 Max	70.0	58.0
Flash Point	°F	“93	150 Max	248.0	260.0
Total Sulphur	% wt	“1552 x- RAY	6 Max	2.57	1.2901
Kinematic viscosity at 180°F (82.2°C)	Cst	D445	26 Max	6.30	5.67
Carbon Residue (conradson)	% wt	“189	15 Max	5.03	1.50
Ash Content	% wt	“428	0.1 Max	0.06	0.025
Water & Sediments	% wt	“473	0.5 Max	Trace	0.4
Calorific value or Higher heating value (HHV)	kJ/kg	Calculated	-	44,368	44,082

Table 5 shows the results of L.P.F.O when treated with 90% concentrated sulphuric acid.

Table5. L.P.F.O. Treated with 90% conc. H₂SO₄

TEST	UNIT	TEST METHOD\ (AST M)	LIMIT	TREATMENT	
				BEFORE	AFTER
Specific Gravity at 15.4°C	kg/cc	D1298	0.995 Max	0.8974	0.9480
Pour Point	°F	“97	70 Max	70.0	52
Flash Point	°F	“93	150 Max	248.0	264
Total Sulphur	% wt	“1552 x- RAY	6 Max	2.57	1.9572
Kinematic viscosity at 180°F (82.2°C)	Cst	D445	26 Max	6.30	5.00
Carbon Residue (conradson)	% wt	“189	15 Max	5.03	1.8
Ash Content	% wt	“428	0.1 Max	0.06	0.03
Water & Sediments	% wt	“473	0.5 Max	Trace	0.6
Calorific value or Higher heating value (HHV)	kJ/kg	Calculated	-	44,368	43,601

Discussion

The value of viscosity decreases with an increase in acid concentration as observed in Tables 2-5. For instance, at 6.10 cst for 50% acid concentration it decreases to 5.81 cst at 75% acid concentration. Similarly, this was observed for acid concentrations of 85% and 90%, which gave a value of 5.67 and 5.00 respectively. These values were attributed to the removal of aromatic contents that are normally responsible for the high viscosity value. In the same vein, like the viscosity, a uniform decrease in pour point was observed for all acid concentrations. Thus, a value of 11.76% decrease in pour point was observed for an increase of 25% in acid concentration[7]. This implies that considerable amount of paraffin responsible for the initial high pour point has been removed, thereby reducing the difficulty of pumping the oil to burners.

Both carbon residue and ash contents mark considerable changes with an increase in acid concentration. For instance the carbon residue with a value of 4.50 at 50% acid concentration was reduced to 2.0 wt% at 75% and 1.50 at 85%. However, the carbon residue increases from the to 1.8 at 90% concentration. This could be due to incomplete combustion of soot during the analysis, which in turn was responsible for a significant presence of water and sediment at this concentration. Similarly, the ash content decreases from 0.04 to 0.03wt% for a variation of 50% to 90% acid concentration.

In the case of sulphur, it was observed that the total sulphur decreases from 2.5653 to 1.2225wt% for a corresponding acid concentration of 25% increase. However, an increase in the sulphur was observed from 85 to 90%. This gave way to an important observation that there is a limit of acid concentration for sulphur removal, which was found to be at 75% acid concentration.

The specific gravity increases from 0.8708 to 0.9480 kg/cc with increase in concentration of 50 to 90% after treatment. All values are within the standard limit of the maximum, that is, 0.995. The water and sediment increases from trace before treatment to a value of 0.6%wt after treatment. This was attributed to large amount of water formed during the treatment, which was not effectively removed by the centrifugation process. The flash point was observed to increase with increase in acid concentration with a value of 250, 258, 260 and 264 for acid concentrations of 50%, 75%, 85% and 90% respectively. While the Higher Heating Value (HHV) or Calorific value according to the Sherman and Kropf empirical equation $HHV = 13,500 + (5600 / \text{sp.gr}) \times 2.3$ is inversely proportional to the specific gravity. Thus, since the specific gravity increases with acid concentration then the calorific value decreases from 44,895 to 43,601 kJ/kg with an increase in acid concentration of 50 to 90%.

Unlike the pour point, the flash point of the oil increases proportionally with the acid concentrations, 2.86%, 4.03%, 4.84% and 6.45% respectively, which gave an improvement of 76% over the untreated oil. However, the values, 68, 60, 58 and 52 were low when compared with ASTM value of 97°F for pour point.

Conclusions

The results have clearly showed that during purification of fuel oil, the sulphur content as major impurity is significantly reduced. Also, there is improvement in viscosity, specific gravity, pour and flash points. This has shown that aromatics, carbon residues, and ash of the oil have been reduced. Therefore, it was observed that the experiments yielded positive results. Impurities such as sulphur, aromatics, carbon residue etc. have been removed from the fuel oil by sulphuric acid treatment and properties such as viscosity, flash and pour points, specific gravity, total sulphur, etc have been improved.

The extent at which these impurities were removed depends upon the strength, quantity and the temperature of the acid and the degree of mixing. Sulphuric acid treatment requires bulky equipments and a large volume of reactants but the cost of treatment is relatively low when compared with the damages to the oil-burning equipments caused by contaminants.

Furthermore, the by-products from the process can be converted into valuable end products as raw materials for other manufacturing processes. These include acid-sludge to sulphuric acid, which can be used in the manufacture of organic fertilizer, explosives, dyes, printing ink, and chemical fibers. In addition, it is useful in the production of sewage and industrial detergents.

Finally, the process for treating fuel oil offers a lasting solution to pollution problems caused by the release of toxic gases into the atmosphere during its firing.

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