



The effect of biodeterioration due to microbial growth in diesel, control using optimization of sulphur and consequences on Nigeria economy

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Abstract

Extended storage of petroleum product such as diesel enhances microbial growth resulting in sludge formation, diesel loss and corrosion in storage tanks. The use of biocides have been confirmed inappropriate due to high resistance to biodeteriorating agents, as well, high concentration of biocides have been confirmed to be hazardous to man. The research is targeted at the optimization of sulphur content in diesel in other to prevent biodeterioration due to microbial proliferation in storage tanks and pipes. The following concentrations of: 350, 400, 450 and 500 ppm of sulphur content were prepared to determine the corrosion frequencies and the degree of growth of *Hormoconis resiniae* in each sample by measuring the deterioration effects in the diesel. Graphs are plotted to show the growth and corrosion in terms of losses due to sulphur. Sulphur content optimizations were reach in other to struck a balance between the degree of corrosion to inhibition of *Hormoconis resiniae*. The optimized sulphur content came to be between 380-400 ppm after analysis. Results shows that; the higher the sulphur concentration, the higher the corrosion rates of storage tanks and pipes. Also the higher the concentration of sulphur the lower the proliferation of biodeteriorative agent *Hormonis resiniae*. This implies that the increase in sulphur concentration prevents the growth of *Hormoconis resiniae* which cause deterioration of diesel but increases corrosion. While the lower the concentration of sulphur the lower the corrosion rate of storage tanks and pipes but high microbial growth rate in the diesel. The total loss of diesel due to microbial deterioration, the cost of purchasing sulphur and cost of replacing storage tanks and pipelines is a sort of economic lost to Nigeria thereby depreciating its gross domestic product (GDP).

Keywords: Biodeterioration, *Hormonis resiniae*, sulphur optimization, corrosion

1. Introduction

The petroleum refining industry is one of the largest manufacturing industries in the world spending huge amounts each year on capital equipment, modernization and maintenance, including prevention and treatment of microbial contamination. The continual growth of diesel demand is driven by several factors: the superior economy and efficiency of diesel engines; advances in combustion systems and improvements in emission devices including filters for the removal of particulates and NO_x reduction systems (Sharafutdinov *et al.* 2012) [4]. The major microbial problem in the industry is the contamination of stored products, which can lead to loss of product quality, the formation of sludge and deterioration of pipelines and storage tanks, both in the refinery and at home (Gaylarde, 1998).

There are three types of fuels as discussed here, they includes aviation fuel, diesel and gasoline. Corresponding to increasing heavy petroleum fraction, Diesel is a hydrocarbon product boiling between approximately 150°C and 400°C, with carbon chain lengths of C15-C22 containing straight-chain and branched-chain. Microbial deterioration is an occasional problem. Microorganisms are constantly present in the fuel, however prompt quality control measures (removal of H₂O and addition of biocides) minimizes their growth (Hill & Hill, 1993). Furthermore,

reports of microbial growth in fuel tanks have increased in the last few years and the holding of strategic reserves for lengthy periods has always been a problem of concern (Hartman, 1991).

1.1 How Microbes Enter the Fuel

Biodeterioration agents such *Hormoconis resiniae* usually enter diesel from the soil, air, old pipelines, corrosive pipelines, and via biofilm present on the tank walls. The fungus are ubiquitous and are abundant in soil, they are also present in illegally refined petroleum products (Wiri, *et al.* 2019) [7].

1.2 Corrosion

Corrosion is the disintegration of an engineered material into its constituent atoms due to chemical reactions with its surroundings. This means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Diesel is a hydrocarbon with various specifications, for moisture content, sulphur content etc.

The tanks containing diesel are generally corroded and hence their internal stresses are elevated compromising the strength and safety of the personnel. Hence regular ultrasound checkups and welding is done, the values of stress at key points are kept minimum (Rajasekar, 2006).

2. Methodology

2.1 Preparation of Diesel Samples

Diesel, with no enhanced abilities, were purchased from the NNPC Fuel station (Adageorge Port Harcourt Nigeria). The sulphur powder was purchased from a chemical store in town Axis of Port Harcourt metropolis. It was prepared by varying the sulphur content in each from the range of Diesel taken in each of four conical flasks and calculated amount of sulphur were added. Samples were labelled: A, B, C and D. Flasks containing the samples were kept in a shaker at 200 rpm at room temperature for 2 hours. The sulphur completely dissolves in the samples to give the required concentration.

2.2 Determination of corrosion

Carbon steel were use, this is because most of the refinery storage tanks is made of carbon steel (0.6-0.99% carbon). Steel Pieces were wiped, clean and the weights and their dimensions were noted. Pour 50mL of A, B, C and D diesel samples into a Petri dish and label them. Dip those carbon steel pieces one in each of the Petri dishes and cover them with aluminium foil and keep in the incubator at 25°C for 5 days. After 5 days the Steel pieces are wiped with cotton and weighed. The Samples for corrosion rating are shown in Figure 1.

2.3 Preparation of Bushnell Haas Media

Chemicals required for the preparation of Bushnell Haas media were purchased from a chemical store in the Town area of Port Harcourt.

MgSO ₄	-	0.20g
CaCl ₂	-	0.020g
KH ₂ PO ₄	-	1g
KH ₂ PO ₄	-	1g
NH ₄ NO ₃	-	1g
FeCl ₃	-	0.050g
Agar	-	20g

Suspend the 23.27 g mixture in 1000mL of distilled water. Heat and boil to dissolve the medium completely. Sterilize by autoclaving at 15 lbs Pressure (121°C) for 15 min. A

white precipitate before sterilization turns to ceramic colour in the molten form at normal conditions. Petri dishes are cleaned with alcohol and are UV treated in a Laminar Flow Bench for 3 hrs. Molten media in the conical flask is poured into Petri dishes which are UV treated and allowed to set by cooling.

2.4 Cultivation of *Hormoconis resiniae*

Hormoconis resiniae is a fungus commonly found in Diesel storage tanks. The fungal strain was obtained from Nigeria refinery Eleme. Molten Bushnell-Haas was poured into a petri dish and allowed to cool in a laminar flow bench and the broth is inoculated on to the set media. Petri dishes covered with Aluminium foil are placed in an incubator at 20°C for 5 days, growth is observed for each Petri dish. 80mL of Diesel samples earlier prepared are filtered and poured to Tin coated metal cans and the cans are labelled as A, B, C and D representing different concentrations. The Can mouth is covered with Aluminium foils and placed in an incubator for 5-10 days. Growth is to be monitored from the 5th day onwards. Diesel samples from cans are each filtered and samples are weighed. The suspended solids are also weighed after drying the filter paper in an oven at 100°C for 16 hrs. The weight of filter paper before and after the filtration is obtained; now after the suspended solids are weighed the weight is reduced from dried filter paper.

3.1 Corrosion Assessment

When a Steel piece is dipped in diesel it gets corroded and it loses weight which will be measured by the difference of initial and final weights. As both, the sides of the metal are exposed to diesel the loss in thickness is halved. As the sulphur in the sample increases the corrosion also increases. Change in volume=change in mass/density

$$\text{Density} = 7.86\text{g/cm}^3$$

$$\text{Change in thickness (t)} = \text{change in volume/surface area}$$

As both, the sides of Steel pieces were in contact with diesel for 5 days

$$R = 365 t$$

All the Ratings are in mm/year

Table 1: Corrosion Assessment for diesel samples.

Sulphur Content (ppm)	Initial mass g	Final mass in g	Change in mass	Change in volume	Area	Thickness in cm	Rating in mm/year
250	40.2136	22.1808	20.0.053	0.004319	11.22	0.00038501	0.14053
300	100.4165	50.3502	50.076	0.008522	14.4	0.00059186	0.21603
350	150.06437	75.9684	75.12597	0.013483	13.6	0.00099142	0.36187
400	4000.9552	200.8183	200.1769	0.016697	12.25	0.00015263	0.55710

3.2 Loss Due to Corrosion

A tank of capacity 30000kL costs 120million US dollars excluding all the pumps and the piping costs. The average life of a commissioned tank is 20yrs according to a manufacturing company for the current specification of diesel. In general cases, every 10yrs the tanks are subjected to vigorous checkups and the welding and maintenance charges are fairly high, here the life is considered 20years for calculation (Turner, 1983) [6]. The corrosion ratings are used to obtain the corrosion losses per year. Diesel has a specification of 350ppm; it gives a corrosion rating of x mm/year

Thickness corroded in 20years $T = 20 X$ mm

Time is taken to corrode this thickness T for various

samples

$$Y_i = 20 X / X_i$$

X_i is rating for the diesel samples

Y_i is the time taken in years for the diesel samples to corrode the thickness T.

It is assumed that the Tank has to be discarded once the Regulation thickness is corroded.

Cost of a tank = 120million USD

Loss for 350ppm sample is = 120million

$$L = 6 (20 / Y_i) - 6$$

L is in millions/year.

As there is an estimate of about 36 Diesel tanks in a refinery, the total loss/year due to corrosion will be:

$$L_t = 36L$$

The summary results for the total Corrosion Losses for different diesel samples are shown in Table 2 and the results

of Microbial Growth Rating in terms of suspended solids are shown in Table 3.

Table 2: Determination of final Corrosion Losses for the samples.

Concentration in ppm	Time in years taken to corrode the thickness(Y _i) in years	Loss in millions/year For a tank/year	Total Corrosion loss in millions of USD/year
350	20	6.0	216.0
400	13	9.2	332.0
450	7.7	15.5	556.7
500	5	23.8	857.1

Table 3: Microbial Growth Rating in terms of suspended solids.

Sulphur Content (ppm)	The volume of the sample (mL)	Mass of the sample	Weight of suspended solids(g)	The final loss of diesel
250	80	47.6	0.0655	0.2451
300	80	47.6	0.0412	0.1736
350	80	47.6	0.0314	0.1058
500	80	47.6	0.0108	0.0273

3.3 Loss Due to Microbial growth integrated for a Refinery's Capacity

The loss in fuel for the experiment is integrated into refinery capacity to obtain the growth losses (Srivastava and Nandan 2012)^[5].

A Refinery has a capacity of 12MMTPA=12*10⁹kg of crude.

40% of Capacity is of diesel=4.8MMTPA of Diesel/year.

The density of the diesel sample is=0.845g/mL

Weight of the sample= 80*0.845=47.6g

Cost of diesel: 4.8*10¹² g/0.845=5.680*10⁹ L

Cost of diesel/L=USD 25.00

So total cost=1.42011*10¹¹USD/year

Consider the contaminated samples:

X g of loss in 47.6g of diesel so integrating for 4.8

$N=(47.6-X)/47.6$

$S=N*4.8*10^{12}$ g

The volume of contaminated sample (V)=S/0.845

Cost of sample(C)=(V/1000*0.845)*25

Loss/year=1.42011*10¹¹-C USD/year

Table 4: Microbial Growth Losses for diesel samples in Refinery capacity.

Sulphur content in sample n (g)	Mass of the diesel sample (g)	The actual mass of diesel present (g)	Loss in millions of US dollar/year
350	47.6	47.4545	514.9
400	47.9	47.5267	363.2
350	47.5	47.8944	221.0
450	47.6	47.8728	56.3

Table 5: Total Loss for diesel samples in Refinery capacity.

Sulphur content (ppm)	Corrosion losses in millions of USD/year	Microbial growth losses in millions of USD/year	The total loss in millions of USD/year
250	100	500	600
300	150	200	350
350	250	100	250
400	300	70	170

4. Discussion

4.1 Corrosion Loss with Varying Sulphur Content

The diesel samples with different sulphur content were prepared and the introduction of Carbon steel pieces into the sample gave the corrosion rating (bucker, 2011). As the sulphur content in diesel increases the acidic nature of diesel magnifies increasing the corrosion rate of the storage vessel in this case tank thereby increasing maintenance cost and the capital cost of the Unit.

4.2 Growth Loss with Varying Sulphur Content

Microbial growth decreases with increasing sulphur content, as discussed above, the higher the sulphur, the more acidic the medium becomes which affects the growth adversely (Hettige, 1989). Here as the sulphur increases in diesel

fungus growth decreases there by the sludge content formed is decreased. Sludge content decrease denotes less loss of diesel and less clogging leading to less maintenance cost and fewer product losses.

4.3 Total Loss with Varying Sulphur Content

The graph below denoted the variation of Corrosion, microbial growth loss, with sulphur content, these losses add up to a total loss. The nature of the plots is positive, as the corrosion loss increases at the same rate with sulphur content product and microbial growth rate decrease with the same rate with a total loss. (Rodriguez, 2010)^[3]. The plot of the variable indicates that the sulphur content with the lowest total loss which is termed optimum which ranges from 380-400ppm.

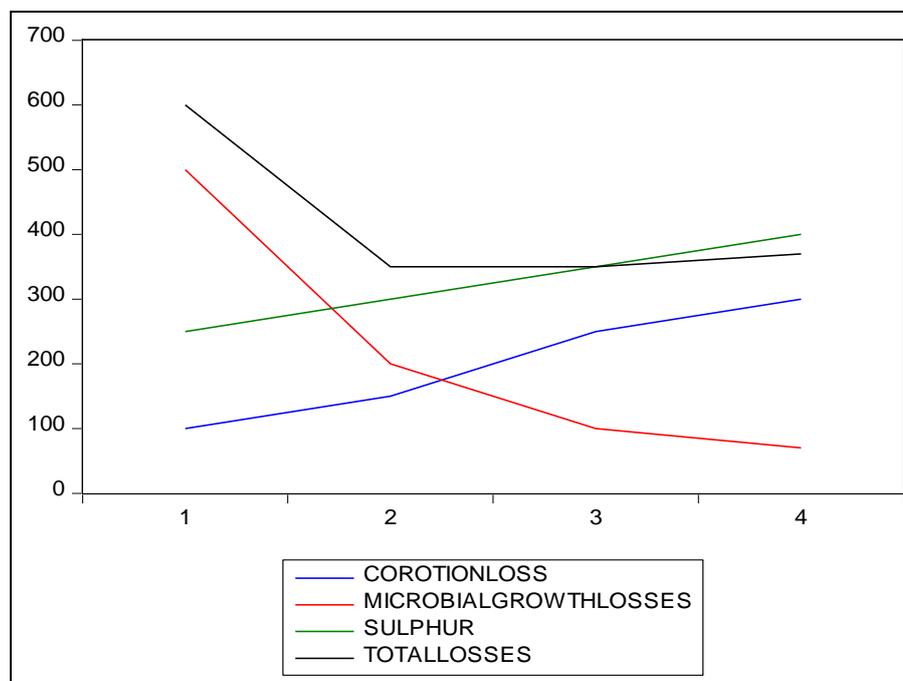


Fig 4: Graph Sulphur, Corrosion Losses, Microbial Growth losses and total loss Sample in Refinery all in US dollar/year.

It is observed that the two-variable should a positive trend and two-variable should negative trend. implying an increase in corrosion losses bring about an increase in

microbial growth losses, this result in an increase in total losses to Nigerian economy

Table 6: Relation among the Variables

	Corrosion	Microbial	Sulphur	Total losses
Corrosion	1.000	0.892588	0.98994	0.68821
Microbial	0.892588	1.000	0.91386	0.9414
Sulphur	0.9899	0.91386	1.000	0.729964
Total losses	0.68821	0.941404	0.729964	1.000

The relationship between the variable is significantly strong. The correlation between corrosion losses and microbial is had a positive value of 0.8925, these implied that every corrosion losses there is high microbial growth in the refinery lead to high rate loss of economic value to the country. The same is applied to microbial growth rate loss and sulphur content, the correlation between total losses and microbial

growth rate is 0.68821 which also positive and these well lead to increasing in economics losses in the refinery. The same applies to sulphur content and total losses their correlation is approximate 1, which indicate a strong relationship among the variable that leads to a high level of losses. The correlation of the same variable to its set is always one.

Table 7: Analysis of Variance of the Variables

Source of Variation	SS	Df	MS	F	P-value	F crit
Rows	59566.67	3	19855.56	0.947131	0.475041	4.757063
Columns	116816.7	2	58408.33	2.78614	0.139379	5.143253
Error	125783.3	6	20963.89			
Total	302166.7	11				

The test is used to assess the effect of one variable on the another. Microbial growth rate sample significantly affects the other variable as the F-statistics is greater than the tabulated value. This should a negative impact on the production of diesel in the refinery cause a great loss to the nation at large.

5. Conclusion

It is observed that by the increase in sulphur content, the Microbial Growth in diesel can be inhibited. But the increase in sulphur content favours the increase in corrosion of storage tanks and pipelines. Both measures are quite antagonistic. The ratings obtained from the experiments are

integrated to refinery capacity. Total loss is determined in refinery terms from the sum of corrosion loss and Microbial Growth loss. Optimum sulphur is that content in which the Total loss is minimal. It ranges from 380 to 400ppm as observed. If microbial growth is the crux, then Sulphur content can be kept as 400ppm, if Corrosion is given preference then the Sulphur content can be kept as 380ppm. This report is in agreement with the result of Srivastava and Nandan (2012) [5]. It causes the Nigerian government millions of USD to purchase sulphur in other to prevent microbial growth that enhances corrosion of diesel storage tanks. This in turns causes loss of diesel which were supposed to increase the GDP of the country.

6. References

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