THE EFFECT OF SULFUR – CONTAINING COMPOUNDS ON THE STABILITY OF DIESEL FUELS•)

By:
Zuhdan Fathoni, A *)
Batts, B.D. **)
Sprecher, R.F. ***)
Veloski, G. ***)

ABSTRACT

A high-resolution low-voltage mass spectrometric study has been carried out on the sulfur-containing fractions of fresh diesel fuel and on samples aged at 43°C in borosilicate bottles (ASTM D 4625 test) for periods of 6.5, 13, 19,5 and 26 weeks, and at 80°C for periods of 0.5, 1, 1.5, 2, 3, and 4 weeks. Homologous series of benzo-and dibenzothiophenes are the principal sulfur-containing components of these fractions and of the fresh diesel fuel. Trace amounts of oxygen and sulfur containing compounds were detected. The concentrations of all species present with aging were monitored and the role of each compound in the gum-forming process assessed.

I. INTRODUCTION

In any complete study of the stability of diesel fuels, the composition of the fuel in terms of the sulfur compounds present must be determined. It has been known for a long time that specific sulfur-containing compounds play an important role in diesel fuel stability problems[1-13]. Present knowledge is limited regarding the chemistry of autoxidation in complex fuel media. As a result, the role of sulfur-containing compounds in the oxidative instability of liquid fuels has been the subject of inconsistencies and considerable controversy in the literature[14]. There are many approaches to the study of this problem. One approach involves the examination of model sulfur compounds as dopants in otherwise stable base fuels. Another approach uses original unstable petroleum diesel fuels together with the characterisation of individual sulfur compounds present.

Several studies are reported and various methods and analytical instrumentation techniques have been used for the isolation and characterisation of specific sulfur-containing compound types in petroleum and synthetic fuels[15-20]. Jewell *et al.*[15] reported that in all petroleum distillates and most residual fractions studied, the sulfur compounds were

---

*) PPT Migas, Cepu, Indonesia
**) School of Chemistry, Macquarie University, Australia
***) Pittsburgh Energy Technology Center, Pittsburgh, USA.
•) Presented at the 4th International Conference on stability and Handling of Liquid Fuels – Florida Nov., 1991.

concentrated mainly in the polycyclic aromatic sulfur heterocycles (PASH). The use of low voltage mass spectrometry (LV–MS) to characterize the high boiling petroleum fractions has been reported by Thompson *et al.*[16]. Benz-hiophenes, dibenzothiophenes, naphthanothiophenes, naphthenobenzothiophenes and their homologs and isomers were the major sulfur compounds found. Wiley *et al.*[17] isolated fractions containing sulfur heterocycles from solvent-refined coal liquids (SRC I and SRC II) and from Paraho and Livermore shale oils, and identified the individual mixture constituents by using capillary column chromatography and mass spectrometry. They found that benzothiophenes, dibenzothiophenes, phenanthrothiophenes and several four-ring thiophene compounds are the major sulfur heterocyclic compounds in coal liquids and shale oils. Similar studies were carried out by Kong *et al.*[18]. They stated that PASH present in coal liquids and shale oils were mainly benzothiophenes and a dibenzothiophene series ranging from two to six rings. The use of low-voltage high-resolution mass spectrometry (LV-HR-MS) in analysis of individual components present in coal liquids[19,20,21] and petroleum-derived fuels and fractions of these fuels 22 has been reported.

In an effort to determine the effect of sulfur-containing compunds on the stability of diesel fuels, accelerated storage aging has been carried out at 43 and 80°C on stable and unstable petroleum diesel fuels. The sulfur heterocycles were then isolated and characterised. The methods used to isolate the sulfur-containing compound types included solvent extraction and elution chromatography, shown schematically in Figure 1. The characterisation techniques applied to the sulfur compound types included LV–HR-MS. The work presented here determines the role of the sulfur-containing compounds in controlling diesel oil stability, especially the role of the homologous series of compounds based on benzo- and dibenzothiophene. Those compounds are found as major constituents of sulfur compounds in petroleum-based diesel fuel, coal-derived liquids and shale oils. The roles of these compounds on fuel stability had not been determined in detail previously.

II. EXPERIMENTAL

A. *Storage test techniques*

The accelerated storage stability method used has been described in detail [23]. In summary, 400 mL filtered samples of fuel were stressed in the dark at 43± 1 and 80 ± 1 °C in 500 mL clear screw-cap borosilicate glass bottles covered with aluminium foil, in order to exclude light. Aging periods were 6.5, 13, 19.5 and 26 weeks for samples aged at 43°C and 0.5, 1, 1.5, 2, 3 and 4 weeks for samples aged at 80°C. At the end of each period, the prescribed sample was removed from the storage oven and allowed to cool in a dark environment for about 4-6 hours. After cooling, the sample was poured from the bottle into a clean separatory funnel and filtered through a tared Gooch crucible containing two glass fiber filters using a self-feeding system. The filtrate was saved for sulfur characterisation, and the filtration process was continued according to the ASTM D 4625 test method for analysis of insoluble (filterable and adherent) gums and, for soluble gum according to the ASTM D 381 test modified with nitrogen jet.

B. *Sulfur separation techniques*

The sulfur separation method which has been described in detail[17,18] was used with slight modification. The procedure is shown schematically in Figure 1.

C *Characterisation techniques*

The sulfur extracts were examined by LV–HR–MS. The instrument used was a

Kratos MS-50 high resolution mass spectrometer interfaced to a Kratos DS–55 data system. The samples were introduced into the mass spectrometer using the direct insertion probe. The samples were weighed into single closed-end melting point capillary tubes and contained there whilst the probe was inverted in the mass spectrometer source by a small plug of glass fibre filter paper. A source temperature of 200°C, ionizing voltage of 10 eV, static resolution of 30.000 and a scanning rate of 300 seconds per decade, were used. A useful calibration range of 455.8218 amu to 84.0034 amu was achieved for all experiments.

D. Elemental analysis

The elemental analyses were carried out using a Carlo Erba CHNS analyser at the CSIRO Divison of Coal and Energy Technology, North Ryde, NSW, Australia.

E. Fuels

Diesel fuels used in this study were obtained from the Caltex refinery, Kurnell, Sydney, Australia. The automotive diesel oil (ADO) was a commercial product, marketable on specification with sulfur content determined by X-ray fluorescent (ASTM D4294) of 0.21 mass % and the light waxy gas oil (LWGO) was a high sulfur (sulfur content = 1.723 mass %) diesel fuel component from the high vacuum unit (HVU).

III. RESULTS AND DISCUSSION

Accelerated storage stability tests of the ADO and LWGO were run at 43 and 80°C. Their complete gravimetric results are summarized in Table 1 and their total insolubles are shown in Figure 2. As is shown in Figure 2, the quantities of total insolubles produced in ADO at 80°C are always less than in LWGO. The total insolubles produced in ADO at 80°C became greater than 2 mg/100 mL after storage for two weeks and in LWGO after one week. It may therefore be concluded that the ADO is much more stable than the LWGO. It is generally agreed that 2.0 mg/100 mL of total insoluble gum formed over a one week period at 80°C or 13 weeks at 43°C[24,25] is the maximum level for pass/fail criteria for accelerated storage stability of diesel fuel. It is interesting to observe that not only did the ADO became unstable after storage for two weeks at 80°C but also it became unstable after storage for 26 weeks at 43°C which is equivalent to two years ambient storage[1,24-28]. Furthermore, Figure 2 also shows that the total insolubles in ADO produced after storage for 6.5 weeks at 43°C which gave 0.6 mg/100 mL of insolubles. The difference of 0.3 is within the repeatability for total insolubles measurement. The total for insoluble gums produced after one week storage at 80°C was 1.2 mg/100 mL, which was proportional to the levels of total insoluble sediments produced after 13 weeks storage at 43°C (which gave 1.2 mg/100 mL). In addition, approximately equal quantities of insolubles were obtained when the ADO was stored for 1.5 weeks at 80°C and 19.5 weeks at 43°C and also for two weeks at 80°C and 26 weeks at 43°C. These data indicate that the stress conditions used in these experiments (43 and 80°C) gave consistent behavior, parallel with the statement that 13 weeks storage at 43°C dark oven storage test gravimetrically equates with one week stress at 80° C[29].

Accelerated storage stability tests employing benzohiophene and dibenzothiophene as co-dopants in ADO were run at 80°C. The complete gravimetric results are summarized in Table 2. The total insolubles are shown in Figure 3 together with the results from LWGO doped with benzo-and dibenzothiophene. These results indicate that doping stable diesel fuel with benzo-and dibenzothiophene does not change significantly the stability behaviour of the fuel. The total insolubles produced from several concentrations of benzo and dibenzothiophene doped in ADO were less than 2.2 mg/100 mL in the original blank experiment. At one molar concentration of dopants a maximum level of 2.0 mg/100 mL of insolubles was obtained, which is different from the original blank by 0.2 mg/100 mL. This figure is still within the repeatability for total insolubles measurements. That benzothiophene and dibenzothiophene do not play a significant role in controlling diesel fuel stability may be concluded. They may, however, play a special role on interaction with other materials.

A different result is found for LWGO which is classed as an unstable diesel fuel as it contains more compounds likely to have deleterious effects. Accelerated storage tests employing benzothiophene, dibenzothiophene and 2,5-dimethylpyrole (DMP) as codopants in LWGO were run also at 80°C. The complete gravimetric results are summarised in Table 3 and the total weight of insolubles is shown in Figures 3 and 4. These results indicate that doping LWGO with benzo-and dibenzothiophene produces approximately twice the amount of total insoluble gums formed in the blank experiments. Huge amounts of total insolubles were produced with DMP used as dopant. A definite positive (synergistic) interaction exists between the DMP and the sulfur-containing compounds available (LWGO has a higher concentration of sulfur-containing compounds than ADO) under the conditions examined. This conclusion is also supported by the elemental analyses of the insoluble gum and oil raffinate as shown in Table 4 and Figure 5. Table 4 shows a complete elemental analysis of insoluble gums and the raffinate liquid. The percentage of sulfur content of the insoluble gum produced decreases with increasing DMP concentration as is shown in Table 4, because, as shown in Table 3, the number of total insolubles produced increases dramatically with the increase of DMPconcentration. The total weight of sulfur (in grams) produced as insoluble gum increases with the increase of DMP concentration is shown in Figure 5. Consistent results are shown in the elemental sulfur analysis of the raffinate liquid, which shows a decrease in percent sulfur with increasing concentration of DMP because this dopant is reacting with the sulfur containing compounds present in the liwuid and removing them as insoluble gum. The presence of DMP significantly increased the number of sulfur compounds in the insoluble sediment and decreased the sulfur content in the liquid phase.

The results of LV-HR-MS analysis of the sulfur extract from ADO stressed at 80°C and 43°C are shown in Tables 5, 6, 7 and 8 respectively. Tables 5 and 7 indicate that the sulfur extracts were relatively pure and contained only about 31 % on average of non-sulfur species. The sulfur species in all fractions studied belonged mainly (average of 98.81 %) to the $C_nH_{2n-z}S$ series of components. Homologous series of benzo-and dibenzothiophenes were the principal components of the $C_nH_{2n-z}S$ fraction as is shown in Tables 6 and 8. Table 6 presents a detailed description of the benzo- and dibenzothiophene series found in ADO after stressing at 80°C. The sulfur compounds found in ADO after storage at 80°C consist of at least 3% benzothiophene series and more than 91.8% dibenzothiophene series. Table 8 indicates that at least 3.1 % benzothiophene series and more than 91.8 % dibenzothiophene series were the main constituents of the $C_nH_{2n-z}S$ fraction at 43°C. It is interesting to observe that the total percentages of benzo- and dibenzothiophene in these fractions are constant with aging both at 80 and 43°C as shown in Figures 6 and 7. Figures 8 and 9 also indicate that the concentration of dibenzothiophene (Carbon number of 12) is relatively constant with aging both at 80 and 43°C.

The conclusion is similar to that obtained from the gravimetric results as discussed above which show that benzo-and dibenzothiophene do not play a significant role in oxidation instability of stable petroleum diesel fuel. Again, The results shown here, in terms of benzo- and dibenzothiophene in stable petroleum diesel fuel stored at 43°C are consistent with the LV-HR-MS results for analysis by the dark oven test at 80°C.

Interaction of benzo- and dibenzothiophene with other compounds such as nitrogen, oxygen, olefinic species and other sulfur-containing compounds are part of a continuing investigation.

IV. SUMMARY

Based upon the results described above, the following conclusions may be drawn:

1. As found by other researchers, accelerated storage stability of diesel fuel stored for 0.5 weeks at 80°C gravimetrically equates to 6.5 weeks at 43°C; 1 week at 80°C equals 13 weeks at 43°C; 1.5 weeks at 80°C is equivalent to 19.5 weeks at 43°C and 2 weeks at 80°C equates to 26 weeks at 43°C.
2. Not only in terms of insoluble gum produced, but also LV–HR–MS analysis of raffinates, the behaviour of benzo- and dibenzothiophene from ADO after storage at 80°C shows good correlation with the storage tests at 43°C.
3. Benzo- and dibenzothiophenes do not play significant roles in a stable petroleum diesel fuel instability process.
4. Positive synergistic interactions were found to occur between DMP and the sulfur-containing compounds available in LWGO under the conditions examined.
5. LV-HR-MS results indicate that the homologous series of benzo and dibenzothiophene were the principal components of sulfur compounds in petroleum diesel fuel as found by other workers.

Acknowledgements

We acknowledge funding support of the Indonesian State Oil Company (PERTAMINA) Marketing and Domestic Supply Directorate, Australian International Development Asistance Bureau (AIDAB) and Southern Pacific Petroleum, NL. Petroleum diesel fuel samples were supplied by Caltex Refinery Kurnell NSW Australia .

REFERENCES

1. **BATTS B.D.; FATHONI A. Z.** 1991, *Energy & Fuels* 1991, 5, 2-21.

2. **HAZLETT R.N., KELSO G.,** 1986, In *Proceedings of the 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels;* Stavinoha, L.L., Ed.; pp 541-555. Also Hazlett R.N., 1988, *Fuel Sci. Technol. Int.* 6(2), 185-208.

3. **MALHOTRAR. St JOHN, G.A.** In *Procedings of the 3rd International Conference on Stability and Handing Of Liquid Fuels.* Hiley R.W., Penfold R.E., Pedley, J.F. Eds; 1988; 515-537.

4. **HILEY R.W., PEDLEY J.F.,** 1988, *Fuel* 67, 469-473.

5. **HAZLETT, R.N., POWER A. J., KELSO, A.G., SOLLY, R.K.,** 1986, "The Chemistry of Deposit Formation in Distilate Fuels," *Department of Defence, Defence Science and Technology Organisation, Material Research Laboratories Report No. MRL–R-986.*

6. **MALHOTRA R., St JOHN G. A.,** 1986, *In* Proceedings of the 2nd International Conference on Long Term Storage Stabilities of Liquid Fuels; Stavinoha *L.L., Ed, pp* 327-325.

7. **LOEFFLER C.M., Li, N.C.,** 1985, *Fuel,* 64, 1047 - 1053.

8. **FRANKENFELD, J.W., TAYLOR W. F., BRINKMAN D.W.** 1988, *Ind. Eng. Chem. Prod. Res. Dev.,* 22,608-614.

9. **NIXON. A.C.,** 1962, Autocidation and Antioxidants of Petroleum. In *Autowidation and Antioxidants;* Lundberg. W.O. Ed., Inter-

science; New York, Vol. II Chapter 17, pp 696-856.

10. **CLINKENBEARD. W.**, 1959, *ASTM STP* 244, 32–40.11. **DUNN- F.R.; SAVER, R,W.** *ASTM STP* 1959, 244, 47-56.

11. **SAUER R.W., WEED A.F., HEADINGTON C.E.** Prepr-Am. *Chem. Soc. Div Pet. Chem* 3(3), 95-113.

12. **OFFENHAUER R.D., BRENNAN, J.A., MILLER, R.C.**, 1959, *Ind. Eng. Chem.*, 49 (8), 1264-1266.

13. **MUSHRUSH G.W., HAZLETT R.N, PEL–LENBARG R.E.** and **HARDY, D..R.**, 1991 *Energy & Fuels*, 5, 25-262.

14. **JEWELL D.M., RUBERTO R.G.** *and* **SWANSIGER, J.T.**, *Prepr-Am. Chem. Soc. Div Pet. Chem.* 1975, 20 (1). 19-29.

15. **THOMPSON C.J., FOSTER, N.G., COLE–MAN H.J.** and **RALL H.T.**, 1966, *Sulfur Compound Characterisation Studies on High Boiling Petroleum Fractions*, BuMines RI 6879, 17pp.

16. **WILEY C., IWAO M., CASTLE R.N, LEE. M.L.**, 1981, *Anal, Chem*, 53, 400-407.

17. **KONG R.C, LEE M.L., IWAO; TOMI–NAGA, Y., PRATAP, R, THOMPSON R.D.** and **CASTLE R.N.**, 1984 *Fuel*, 63, 702-708.

18. **BATTS B.D.** and **BATTS J.E.**, "1989, Mass Spectrometry of Coal Liquids." In *Spectroscopic Analysis of Coal Liquid*, Kershaw, J. Ed.; Elsevier; Amsterdam, Chapter 4, pp 68-128.

19. **SCHMIDT C.E.** and **SPRECHER, R.F.**, 1989, *ASTM STP*, 1019, 116-132.

20. **SHITE C.M.**, 1983, "Determination of Polycycyclic Aromatic Hydrocarbons in Coal Derived Material". In *Handbook of Polycyclic Aromatic Hydrocarbons*, Bjorseth, A.: Ed.; Marcel Dekker: New York, Chapter 13, 515-616.

21. **CHASEY K.L.** and **ACZEL, T.**, 1991, *Energy & Fuels*, 5, 386-394.

22. "Standard Test Method for Distilate Fuel Storage Stability at 43°C (110°F)", American Society For Testing and Materials, ASTM D 4625-86, *Annual Book of ASTM Standards*, Vol. 05,01, 1989.

23. **SMITH, R.J.; PALMER, L.D.**, 1986, In *Proceedings of the 2nd International Conference on Long Term Storage Stabilities of Liqueid Fuels;* Stavinoha, L.L., Ed, pp 875-886.

24. **HARDY, D.R., HAZLETT R.N.**, 1986, White, E.W. In *Proceedings of the 2nd International Conference on Long Term Storage Stabilites of Liquid Fuels; Stavinoha, L.L.; Ed.; pp* 887-901.

25. **STAVINOHA L.L; WESTBROOK, S.R.**, *ASTM STP* 1981, 751, 3-21.

26. **SCHREPFER M. W., ARNOLD, R.J., STANSKY, C.A.**, 1984, *Oil Gas J.*, Jan 16, 79-84.

27. **CHIANTELLA, A.J., JOHNSON J.E.**, 1959, "Comparative Studies of Some Acclerated Ageing Test for Distillate Fuels"; Naval Research Laboratory, NRL Problem C 01-03,

28. **STAVINOHA L.L, WESTBROOK R., BRINKMAN D.W.**, 1989, "Accelerated Stability Test Techniques For Middle Distillate Fuels"; U.S. Department of Energy Report No. DOE/BC/10043-12, Also "Optimization of Acclerated Stability Test Techniques for Diesel Fuels; U.S. Department of Energy Report No. DOE/BC/10043-25, 1981.

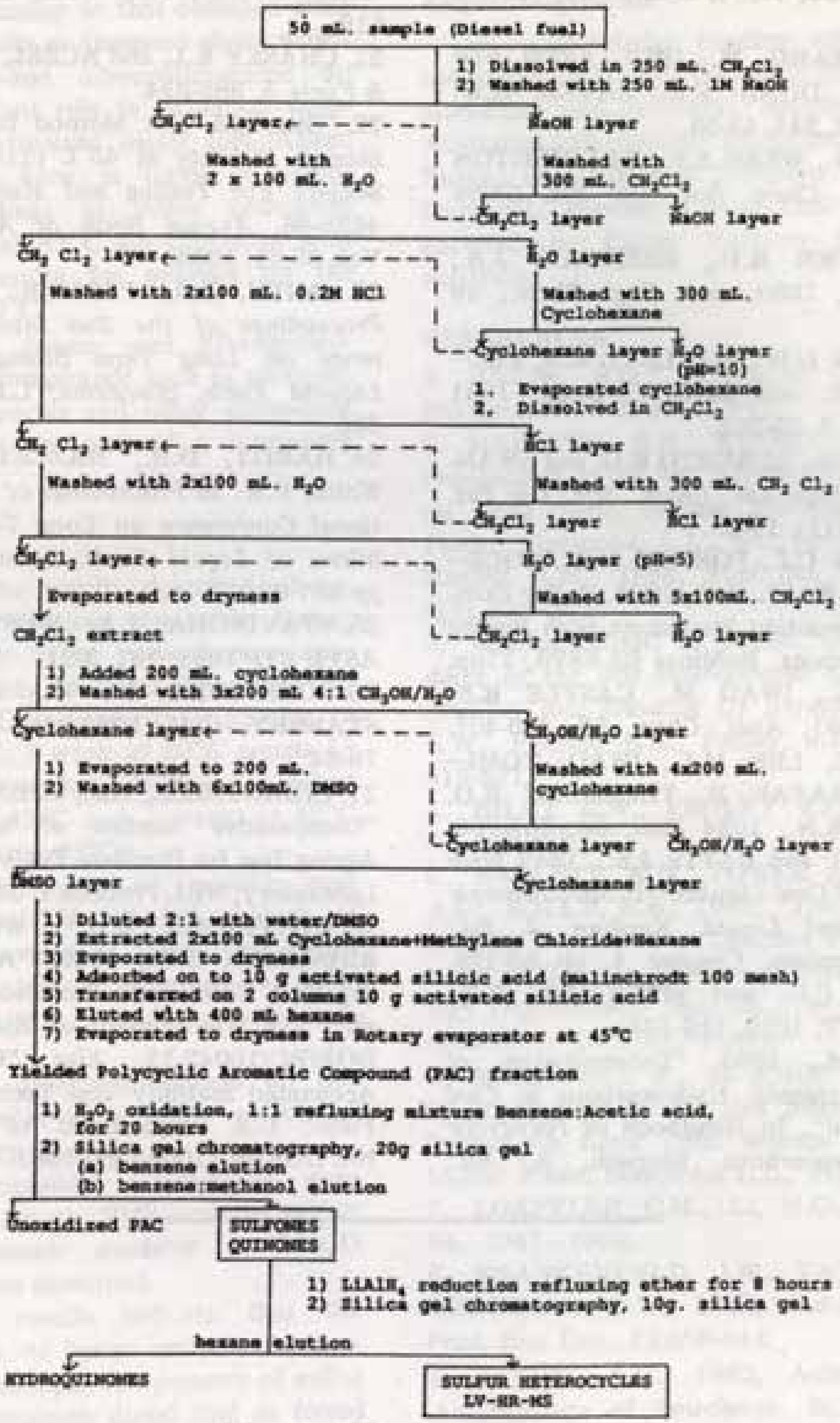

Figure 1. Sulfur separation scheme

Table 1. Storage stability of ADO and LWGO

Fuel	Condition	Insoluble gum			Soluble gum	Total gum
		Insoluble mg/100mL	Adherent mg/100mL	Total mg/100mL	mg/100mL	mg/100mL
ADO	6.5 week/43°C	0.4	0.2	0.6	20.4	21
	13 week/43°C	0.7	0.5	1.2	34.6	36
	19.5 week/43°C	0.9	0.9	1.8	44.8	47
	26 week/43°C	1.1	1.1	2.2	57.2	59
	0.5 week/80°C	0.4	0.5	0.9	21.8	23
	1 week/80°C	0.7	0.5	1.2	35.2	36
	1.5 week/80°C	0.9	0.8	1.7	45.6	47
	2 week/80°C	1.2	1.0	2.2	56.8	59
	3 week/80°C	1.3				
			1.6	3.2	91.6	95
LWGO	0.5 week/80°C	0.6	0.6	1.2	54.0	55
	1 week/80°C	1.4	0.7	2.1	59.6	62
	1.5 week/80°C	1.9	0.9	2.8	60.8	64
	2 week/80°C	2.3	0.8	3.1	104.0	107
	3 week/80°C	3.0	1.8	4.8	116.0	121
	4. week/80°C	3.9	1.8	5.7	125.0	131

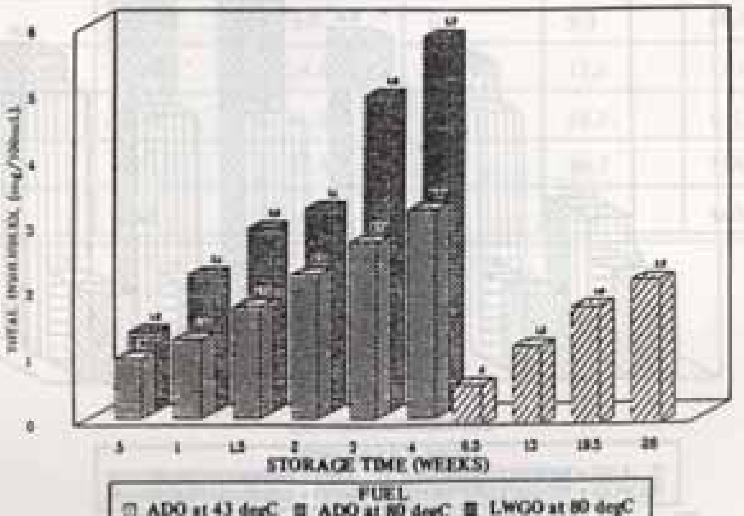

Figure 2. ADO and LWGO accelerated storage test result

Table 2
Storage stability of ADO in 2 weeks at 80 ° C employing benzothiophene and dibenzothiophene

Fuel+dopants	Dopants concentration	Insoluble gum			soluble gum	total gum
		Insoluble	Adherent	Total		
	M	mg/100vL.	mg/100mL	mg/100mL.	mg/100mL	mg/100mL.
ADO + BENZOTHIOPHENE	0	1.2	1.0	2.2	56.8	59
	0.01	0.6	1.3	1.9	58.2	60
	0.05	0,7	1.2	1.9	60.0	62
	0.1	0.7	1.3	2.0	61.0	63
	0,5	0.8	1.1	1.9	63.0	65
	1	0.9	1.1	2.0	62.0	64
ADO+DIBENZOTHIOPHENE	0	1.2	1.0	2.2	56.8	59
	0.01	0.7	1.2	1.9	67.4	69
	0.05	0.7	1.2	1.9	62.6	65
	0.1	0.8	1.2	2.0	66.4	68
	0.5	0.8	1.2	2.0	62.6	65
	1	0.9	1.1	2.0	66.6	69

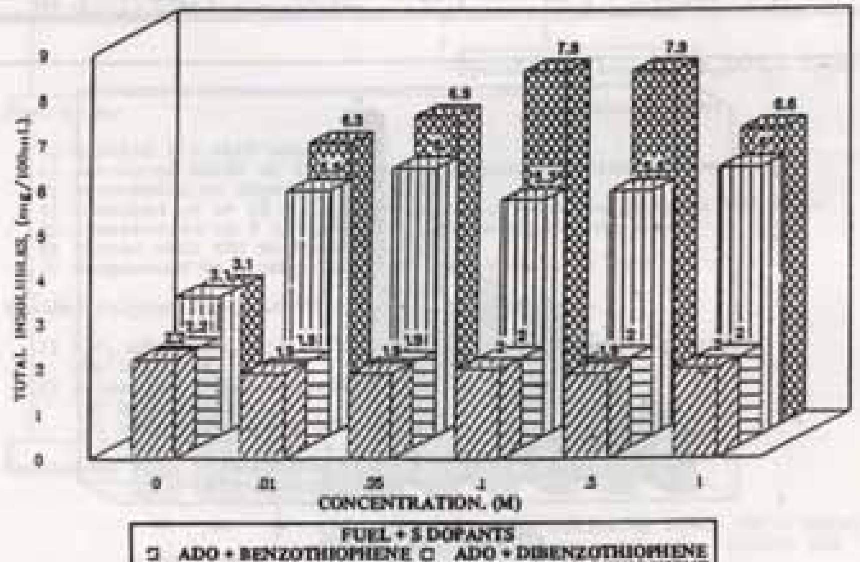

Figure 3. Diesel fuel+sulfur compounds as dopant
2 weeks storage at 80 degC
accelerated storage stability test result

Table 3. Storage stability of LWGO in 2 weeks at 80 ^oC employing benzothiophene, dibenzothiophene and 2,5 dimethylpyrrole (DMP

Fuel+dopants	Dopants concentration	Insoluble gum			Soluble gum	Total gum
	M	Insoluble mg/100vL	Adherent mg/100mL	Total mg/100mL	mg/100mL	mg/100mL
LWGO+benzothiophene	0	2.3	0.8	3.1	104.0	107
	0.01	2.2	3.3	5.5	85.4	91
	0.05	2.2	3.7	6.0	114.0	120
	0.1	2.0	3.3	5.3	83.0	88
	0.5	2.2	3.3	5.5	112.0	118
	1	2.3	3.7	6.0	87.0	93
LWGO+dibenzothiophene	0	2.3	0.8	3.1	104.0	107
	0.01	3.0	3.4	6.3	102.0	108
	0.05	3.5	3.4	6.9	104.0	111
	0.1	4.6	3.3	7.9	107.0	115
	0.5	4.6	3.3	7.9	114.0	122
	1	3.3	3.3	6.6	114.0	121
LWGO+DMP	0	2.3	0.8	3.1	104.0	107
	0.0005	9.0	0.3	9.3	88.0	97
	0.001	16.6	0.6	17.2	117.0	134
	0.005	51.2	1.0	52.2	121.0	173
	0.01	87.0	1.1	88.1	128.0	216
	0.05	261.0	1.1	262	143.0	405

Table 4. Elemental analysis of insoluble gum and raffinate liquid from LWGO + DMP after stressed in 2 week at 80°C

DMP concentration M	Insoluble gum					Raffinate liquid				
	%C	%H	%N	%S	gram S	%C	%H	%N	%S	gramS
0	57.9	5.10	1.73	5.1	0.0005	82.5	7.82	0.59	4.37	0.0184
0,0005	69.2	6.16	5.1	5.17	0.0019	76.8	7.24	0.92	4.32	0.0152
0,001	69.2	5.97	6.49	3.76	0.0025	83.5	10.6	0.4	3.74	0.0176
0,005	67.6	6.01	8.69	2.34	0.0048	83.7	11.5	0.39	3.7	0.0176
0,01	66	5.89	9.41	1.89	0.0066	81.8	11.8	0.3	2.97	0.0152
0,05	64.2	5.84	10.3	1.00	0.0104	36.0	3.2	3.85	1.81	0.0104

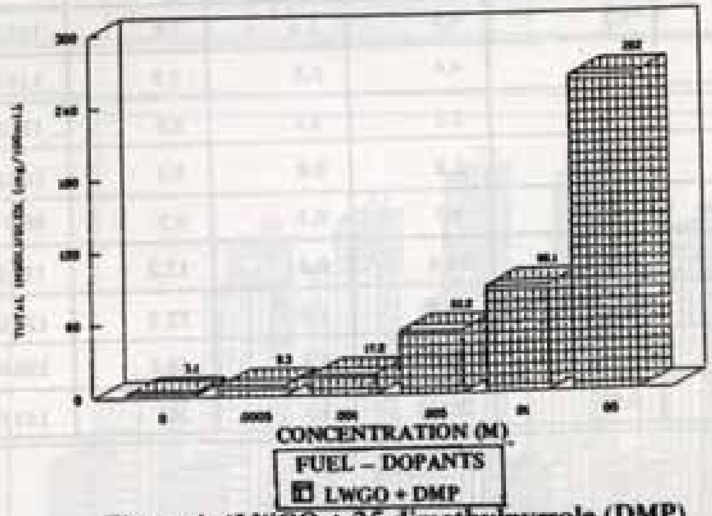

Figure 4. (LWGO + 25-dimethylpyrrole (DMP)
2 weeks storage at 80 degC
accelerated storage stability test result

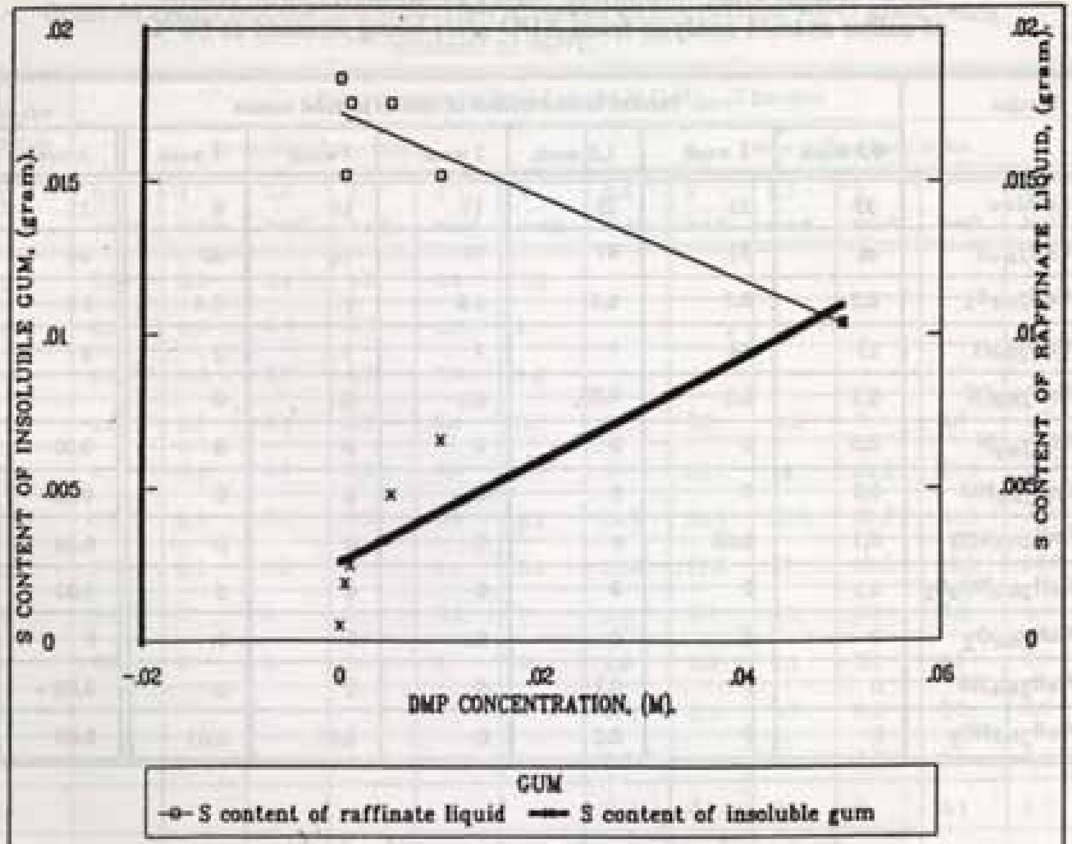

Figure 5. Sulfur compound elemental analysis
from liquid and insoluble gum produced
by aging LWGO + DMP in 2 weeks at 80 degC

Table 5

Low Voltage High Resolution Mass Spectrometry total results of sulfur extract analysis from ADO after being stressed at 80°C

Species	Percent concentration of species in total results						
	0.5 week	1 week	1.5 week	2 week	3 week	4 week	Average
C_nH2_{n-z}	39	35	25	17	16	8	23
$C_nH_{2n-z}S$	46	51	67	76	76	80	66
$C_nH_{2n-z}S_2$	0.5	0.3	0.6	0.8	1	0.4	0.6
$C_nH_{2n-z}O$	13	14	7	7	7	2	8
$C_nH_{2n-z}OS$	0.5	0.2	0.05	0.1	0.1	0	
$C_nH_{2n-z}N$	0.3	0	0	0	0	0	0.05
$C_nH_{2n-z}NO$	0.2	0	0	0	0	0	0.02
$C_nH_{2n-z}NOS$	0.1	0.06	0	0	0	0	0.03
$C_nH_{2n-z}NO_2S_2$	0.1	0	0	0	0	0	0.02
$C_nH_{2n-z}O_2$	0	0	0	0	0	0	0
$C_nH_{2n-z}NS$	0	0	0.1	0	0	0	0.02
$C_nH_{2n-z}NO_2$	0	0	0.2	0	0.01	0.03	0.03

Table 6
Low Voltage High Resolution Mass Spectrometry
detailed result in CnH2n-zS fraction of sulfur extracts from ADO after being stressed at 80°C

Species Carbon No.	Percent concentration of species in $C_nH_{2n-z}S$ fraction											
	Benzothiophene series						Dibenxothiophene series					
	0.5 week	1 week	1.5 week	2 week	3 week	4 week	0.5 week	1 week	1.5 week	2 week	3 week	4 week
9	0.1	0.2	0.4	0.2	0.2	0.8						
10	0.7	0.6	1.4	0.7	0.9	0						
11	0.6	1.3	0.9	1.2	0.9	1.8						
12	0.6	0.7	0.4	0.5	0.4	0.7	6	7.5	8.2	7	8.4	6.2
13	0.5	0.1	0.4	0.3	0.4	0.3	26	24.7	28.7	28.1	27.4	21.5
14	0.3	0.3	0.2	0.2	0.1	0.2	33.8	36.7	32.2	34.7	31.8	36.9
15	0	0.1	0.2	0	0.1	0.1	19.6	17.8	17	15.6	18.5	18.7
16	0.1	0	0	0	0.1	0	5.4	5.4	4.2	5.8	5.1	6.5
17	0.1	0	0	0	0	0	1.6	1.4	1.1	2.1	1.5	1.9
18							0.4	0.2	0.3	0.6	0.5	0.6
19							0.1	0	0	0.3	0.1	0.1
20							0	0	0.1	0	0.1	0.1
21							0	0	0	0.1	0.1	0
22							0.1	0	0	0.1	0	0
Total	3	3.3	3.9	3.1	3.1	3.9	93	93.7	91.8	94.4	93.5	92.5

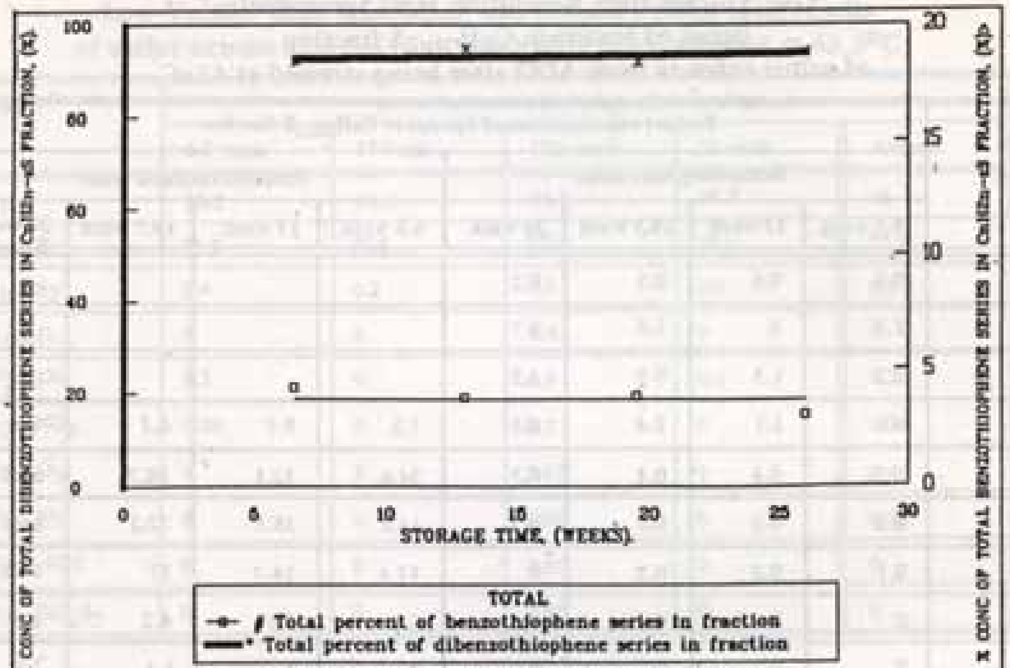

Figure 7. LV-HR-MS result, total % concentration of benzothiophene and dibenzothiophene series in fraction of S extract from ADO aged at 43 degC

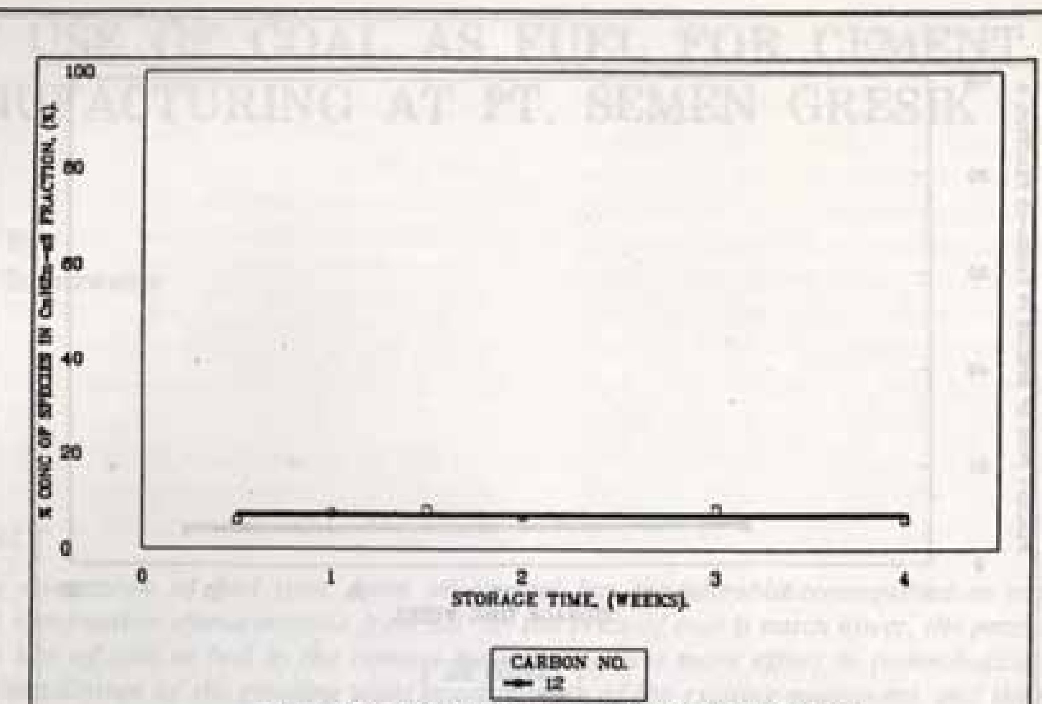

Figure 8. LV-HR-MS result, % concentration of dibenzothiophene (C 12) in CnH2n-zS fraction of sulfur extract from ADO after stressed at 80 degC

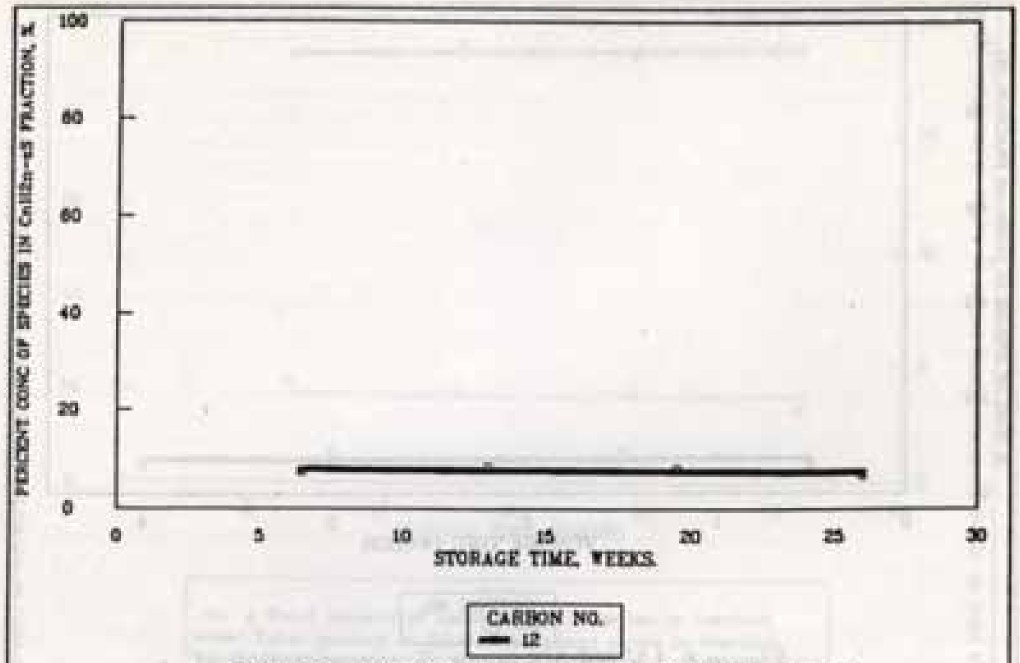

Figure 9. LV-HR-MS detail result, % concentration of dibenzothiophene (Carbon compare above) in CnH2n-zS fraction of sulfur extract from ADO aged at 43 degC