

Assessment of the Oxygen Overpressure Test for Prediction of Middle Distillate Fuel Storage Stability

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ABSTRACT Gravimetric amounts of sediment produced by the oxygen overpressure test for ageing middle distillate fuels for 16 hours at 90°C with a pressure of oxygen of 794 kPa (100 psig) have been compared with that produced by ASTM D4625 conditions at 43°C for 13 weeks. Fifteen fuel blends comprising 30% light cycle oil or 30% hydrotreated light cycle oil were included in this study. Whereas approximately half of the fuel blends produced comparable amounts of sediments by the two procedures, there was no correlation overall for ranking fuels based on sediment produced. Comparison of gravimetric amounts of sediments produced by 12 months ambient ageing with that produced in the oxygen overpressure test of the ambient aged fuels again produced no correlation between the two procedures. The species separated by thin layer chromatography of the sediment produced in the oxygen overpressure test were compared with those produced under ASTM D4625 conditions. There was much similarity in the species observed for the standard oxygen overpressure conditions, but significant differences were noted as the temperature of stress used in the oxygen overpressure test was raised above 90°C. At the higher temperatures, brown species extending over all R_f values began to predominate in the thin layer chromatograms.

INTRODUCTION

World wide demand for middle distillate fuel continues to increase as at a greater rate than other fractions of the oil refinery barrel. This demand is being partly met by the greater use of cracking of the heavier distillation products and incorporation of this cracked stock in the form of light cycle oil (LCO) into automotive diesel fuel. The direct incorporation of LCO into automotive diesel fuel is one of the major, if not the most significant contributing factor, to the formation of insoluble particulate and gums on storage of the fuel.¹

With the decrease in fuel stability, the necessity for an accurate test to predict the storage stability of a distillate fuel is increased. Lower temperature bottle tests are generally the best indicators of storage stability and recently a 43°C test has been standardized as ASTM D4625. The length of time required to obtain significant amounts of sediment for reliable results by ASTM D4625 is a major drawback for quality control. The method of ASTM D2274 has been the most widely used rapid method for assessment of the fuel storage oxidative stability of a fuel.² However, it has been found that this test is a poor predictor for the storage stability of freshly refined fuel containing catalytically cracked stock.³ For many fuels, the amount of sediment produced in the 16 hour period at 95°C is too small to be measured accurately.⁴ Recently an oxygen overpressure technique has been proposed in which fuel is stressed for 16 hours at 90°C in an atmosphere of 794 kPa (100 psig) oxygen.³ This test has

the advantage that significant amounts of sediment were produced in a relatively short time period and good precision was obtained in replicates of gravimetric amounts of sediment.

For this oxygen overpressure technique to find widespread use as a predictive tool, it is necessary that it predicts the relative ambient storage stability of distillate fuels. This study was undertaken to correlate gravimetric amounts of sediment produced under both ambient and ASTM D4625 conditions with that of the oxygen overpressure technique. Reference fuels were chosen so as to include both freshly refined diesel fuel containing either thermally or catalytically cracked stock and aged commercial diesel fuels. Opportunity was taken of an associated study⁵ to compare the species present in sediments from oxygen overpressure conditions with those produced from the ASTM D4625 procedure. Correlation of both gravimetric amounts of sediment and chemical species present in the sediment would add to the confidence with which the oxygen overpressure technique could be used for predicting the relative storage stability of distillate fuels.

The role of reactions between alkylindoles and phenalene species to sediment formation in the reference distillate fuels is presented elsewhere.⁵ In this presentation, the initial concentration of alkylindoles in the reference fuels is considered in relation to the species observed in thin layer chromatograms of sediments produced by the oxygen overpressure technique and in correlations between total amounts of sediment produced by oxygen overpressure conditions and the ASTM D4625 procedure.

EXPERIMENTAL

Samples from automotive distillate refinery streams of straight run distillate (SRD), light cycle oil (LCO) and hydrotreated light cycle oil (HTLCO) were obtained directly from Australian refineries. All samples were reported to have being produced in less than one week of receipt. LCO was from catalytic crackers for all refineries except one, which has a thermal cracking unit. Samples were either blended upon receipt for immediate commencement of the ageing trial or stored as unblended components at -12°C. Experimental fuels were prepared by mixing 30% (volume/volume) LCO or HTLCO with SRD and filtering the mixture through glass fibre membranes (Millipore AP40) immediately prior to use. For all experimental samples, except FG1 and FG2 of Table 3, the sample components originated in the same refinery. Samples FG1 and FG2 were mixtures of 30% LCO and 30% HTLCO respectively from refinery F with SRD from refinery G.

Oxygen overpressure measurements were determined in the single bomb apparatus of ASTM D942 using 75 ml of fuel in 100 ml lipless borosilicate containers. The bomb containing the fuel sample was purged three times with 99.5% purity oxygen prior to being placed in a thermostated liquid bath which maintained the temperature to within 0.1°C. After being immersed in the bath for 15 minutes, the pressure was adjusted to 794 kPa (100 psig). During most runs the oxygen pressure decreased by 40-50 kPa. Upon completion of a run, the bomb was removed from the liquid bath and allowed to cool to ambient temperature prior to sediment determinations.

Suspended particulate matter in the samples was determined by filtration of the fuel through duplicate pre-tared glass fibre membranes (Millipore AP40). Adhered insolubles were determined by rinsing the containers with triple solvent (equal amounts of toluene, acetone and methanol) and hot plate evaporation of the solvent in disposable aluminium dishes and algebraic subtraction of a blank evaporation of equivalent amounts of solvent. Total sediment was the sum of the suspended particulate matter and the adhered insolubles. Data shown in the tables is the average of two duplicate fuel sample determinations.

The 13 week 43°C ageing was carried out according to the method of ASTM D4625 using 1 litre borosilicate containers thermostated in an air oven. The automotive diesel fuel samples listed in Table 4 were obtained directly from retail commercial outlets or sampled directly from user storage tanks in Northern Australia. Although the specific origin of this fuel is unknown, it is most likely that a significant proportion originated from refineries in Singapore. The fuel was stored in 1 litre plastic containers at ambient temperatures for 12 months after collection of the samples prior to the measurements. Total sediment measurements as described above were determined for the fuel prior to its use for the oxygen overpressure measurements.

Thin layer chromatograms of the sediments were obtained by dissolving the sediment directly from the glass fibre membranes with 10% methanol in dichloromethane. This solvent was then used as the mobile phase with a silica gel stationary phase. Alkylindoles were determined in the fuel samples after concentration of the polar species on a small column of silica followed by elution with dichloromethane. This solvent was evaporated with a gentle stream of nitrogen and the residue dissolved in toluene containing 1-methylindole as an internal standard. Separation of the constituents was achieved by injection into a gas chromatograph equipped with a BP1 capillary column (25 m x 0.5mm), a nitrogen specific detector and temperature programmed oven from 30°C to 280°C at 4°C per minute. Peaks from the nitrogen specific detector with a retention time between that for 1-methylindole and carbazole were considered to be alkylindoles with reference to previously published chromatograms⁶. All peaks in this range were summed and converted to a mole concentration by assuming an equal molar response on the nitrogen specific detector to that for 1-methylindole.

RESULTS AND DISCUSSION

The effect of oxygen pressure, temperature and time has previously been reported for the oxygen overpressure (OP) technique.³ Little variation was found when the oxygen pressure exceeded 350 kPa, so all measurements in this study were carried out with an oxygen pressure of 794 kPa (100 psig). With one of the refinery fuel blends in this study (A1), comparative measurements were made between a number of OP conditions and the ASTM D2274 and ASTM D4625 procedures. As may be seen from Table 1, sediment corresponding to medium instability was obtained for the ASTM D2274 and ASTM D4625 procedures for fuel A1. Similar amounts of sediment were obtained from 26 hr/80C and 16 hr/95C OP conditions.

FUEL	ASTM D2274 16 hr 95C mg/L	ASTM D4625 13 weeks 43C mg/L	OXYGEN OVERPRESSURE 794 kPa O ₂				
			26 hr 80C mg/L	16 hr 90C mg/L	16 hr 95C mg/L	64 hr 95C mg/L	16 hr 120C mg/L
A1	13	18	16	8	18	70	88
F1		15		33		119	

Table 1. Comparison of Total Sediment from ASTM D2274 and ASTM D4625 ageing with oxygen overpressure ageing for fuel A1 and F1.

Less sediment was obtained from 16 hr/90C OP conditions. A smaller number of comparative measurements was made for fuel F1. However, comparing only ASTM D4625 conditions with those for OP at 16 hr/90C, it may be noted that OP conditions produced 2.2 times as much sediment, whereas for fuel A1, the equivalent ratio was 0.4.

The total amount of sediment increased significantly as the temperature or time of ageing increased for OP conditions. The sediments produced by the experiments shown in Table 1 were separated into constituents by thin layer chromatography on silica gel. The results are shown schematically in Table 2.

A high degree of similarity in the species was observed in the sediment produced under ASTM D4625 conditions and OP conditions of 16 hr/90C. There was a higher degree of similarity in these chromatograms than those only for ASTM D4625 conditions from ageing the low and high alkylindole content blends of Table 3. Details of the ASTM D4625 sediments will be discussed elsewhere at this conference⁵ with rate process associated with the formation of the species.⁷

A major feature of the thin layer chromatograms was the increased intensity in the OP 16 hr/90C sediments of the pink material at an R_f value of approximately 0.45 and the orange material at approximate R_f 0.25. The intensity of this orange material was less on freshly chromatographed plates, but increased with age. If the orange band at R_f 0.25 was rechromatographed, an orange band at approximate R_f 0.90 was formed. Rechromatography of the pink material at R_f 0.45 again produced an equivalent pink band, but also an orange material at R_f 0.25. It is postulated that the pink material is the acid salts of indolylphenalenones, which partly disassociate on the thin layer plates to form orange indolylphenalenones.⁸ The increased formation of indolylphenalenone products under OP conditions is consistent with the increased oxidation environment.

The blue material at approximate R_f 0.30 is believed to be acid salts of indolylphenalenes.⁹ These salts are very pronounced in the high alkylindole fuel sediment under ASTM D4625 conditions. The proportion of the blue material decreased as the temperature and time of the OP conditions increased. At the longer OP times (64 hours) and temperatures (120°C), the proportion of brown streaking material on the thin layer chromatograms increased. This material extended over all R_f values and was the predominate material in the chromatogram of the OP 120°C sediments. As the formation of the brown material is accompanied by a decrease in the pink and blue materials on the thin layer chromatograms, it is postulated to be a polymeric material produced by further reaction of the indolylphenalene and indolylphenalenone salts. The formation of the brown material places an upper limit on the temperature of the oxygen overpressure test.

Comparison of the amount of sediment produced by ASTM D4625 conditions and the OP test at 16 hr/90C was extended to 15 fuels blends shown in Table 3. Whereas the ratio of sediment produced by the two procedures is within 1.0 ± 0.2 for a number of fuels, many fuels show a significant deviation from this ratio. No definite trend is obvious from the data in the table. The number of fuels in which significantly more sediment is produced by OP conditions is greater than the number of fuels in which significantly less sediment is produced. This may be the reason that these OP conditions have been postulated to be equivalent to three years ambient storage.³ However, this extrapolation would be very favourable to fuels such as A1 and E2 which produce significantly less sediment under the OP conditions. Attempts to correlate the total amount of alkylindoles in the fuels with agreement of the total amount of sediments by the two procedures did not yield any obvious relationship.

The comparative study was extended to some commercial automotive diesel fuels collected from Northern Australia which had been in storage for 12 months at ambient

temperatures. It may be noted that oxygen overpressure determinations and measurement of alkylindole concentrations were carried out on fuel which had been aged for at least 12 months and from which sediment produced by the ambient ageing had been removed. As may be seen from the data in Table 4, there does not appear to be any relationship between the gravimetric amount of sediment produced by the two procedures. The ratio of sediment produced by one year ambient ageing compared to OP conditions ranged from 0.3 to 2.8.

CONCLUSIONS

The oxygen overpressure test at a temperature of 90°C for 16 hours at 794 kPa pressure oxygen will produce comparable amounts of sediment for many fuels to that formed by ageing the fuel for 13 weeks at 43°C. However, there are a significant number of fuels which either produce greater or smaller amounts of sediment under oxygen overpressure conditions compared to lower temperature air environment ageing. As the difference in the relative amount of sediment is in both directions, it is unlikely that variation of the oxygen overpressure conditions will produce good correlation for all fuels. In this study, an attempt was also made to correlate the variation in relative amount of sediment with the total amount of alkylindoles in the fuel, but no relationship could be found.

Conclusions reached from the use of relative amounts of total sediment produced by oxygen overpressure conditions as the sole reference criteria for mechanistic studies of distillate fuel ageing processes should be interpreted with much caution.

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FUEL A1					
R _f RANGE	BAND COLOUR	ASTM D4625		794 kPa O ₂	
		13 weeks 43C	16 hr 90C	64 hr 95C	16 hr 120C
1.00-0.95	green	L	VL	VL	VL
0.92-0.84	orange	L	L	L	M
0.73-0.71	green	VL	VL	VL	VL
0.64-0.62	grey	VL	VL	VL	VL
0.56-0.55	grey	VL	VL	VL	VL
0.49-0.33	pink	M	L	L	NO
0.33-0.25	blue	M	M	VL	VL
0.25-0.19	orange	NO	M	L	NO
0.25-0.19	pink	M	NO	NO	NO
0.09-0.06	brown	M	M	M	D
0.05-0.02	yellow	M	M	M	NO

FUEL F1					
R _f RANGE	BAND COLOUR	ASTM D4625		794 kPa O ₂	
		13 weeks 43C	16 hr 90C	64 hr 95C	
1.00-0.96	green	L	L	L	
0.94-0.87	orange	M	M	M	
0.55-0.49	violet	L	L	L	
0.49-0.46	pink	L	M	M	
0.46-0.27	blue	D	M	L	
0.27-0.22	orange	L	M	NO	
0.10-0.08	brown	NO	M	D	
0.05-0.03	yellow	L	M	VL	
	NO	not observed			
	VL	very light			
	L	light			
	M	medium			
	D	dark			

Table 2. Thin layer chromatogram schematics of sediment from fuel A1 (low alkyindoles) and F1 (high alkyindoles).

FUEL SAMPLE	ASTM D4625 mg/L	OXYGEN OVERPRESSURE mg/L	RATIO	TOTAL ALKYLINDOLES* umol/L
A1	17.8	8.0	2.2	384
B1	11.8	19.5	0.6	632
B2	0.4	4.0	0.1	193
C1	19.0	19.9	1.0	506
C2	0.6	<0.1	>6.0	54
D1	9.0	10.0	0.9	nd
D2	0.8	1.0	0.8	nd
E1	56.2	47.0	1.2	1204
E2	7.9	1.0	7.9	nd
F1	14.6	33.2	0.4	1089
F2	18.6	21.3	0.9	904
G1	12.3	11.4	1.1	707
G2	0.2	2.0	0.1	49
FG1	12.4	24.5	0.5	nd
FG2	18.1	19.0	1.0	nd

* Assuming equal molar detector response to 1-methylindole

X1 30% LCO/SRD fuel blends

X2 30% HTLCO/SRD fuel blends

nd not determined

Table 3. Comparison of Total Sediment from ASTM D4625 (13 weeks at 43°C) with oxygen overpressure ageing (16 hours at 90°C with 794 kPa pressure oxygen) for 30% LCO/SRD and 30% HTLCO/SRD fuel blends.

FUEL SAMPLE	COLOUR ASTM D1500	AMBIENT mg/L	OXYGEN OVERPRESSURE mg/L	RATIO	TOTAL ALKYLINDOLES* umol/L
1	2.5	14	43	0.3	355
2	4.0	39	30	0.8	nd
3	1.5	14	16	0.9	44
4	2.0	11	4	2.8	129
5	1.5	11	24	0.5	17
6	1.5	5	5	1.0	<10
7	nd	11	<1	>11	223

* Assuming equal molar response to 1-methylindole

nd not determined

Table 4. Comparison of Total Sediment from one year ageing at ambient temperature with oxygen overpressure ageing (16 hours at 90°C with 794 kPa pressure oxygen) for commercial fuels from Northern Australia.