

## THE CHEMISTRY OF SEDIMENT FORMATION IN AUSTRALIAN MIDDLE DISTILLATE FUELS

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### Introduction

In earlier publications it was suggested that the formation of insolubles during storage of an unstable UK middle distillate fuel was caused at least in part by reactions of the chemical species indoles, phenalenes and acids<sup>1,2</sup>. The purpose of this present study was to determine whether reactions involving these species contributed to the storage instability of middle distillate fuels from quite different sources and to investigate the extent of correlation between fuel chemical composition and observed fuel storage stability.

The reaction sequence previously proposed is illustrated schematically in figure 1. The oxidation of phenalene and its alkyl homologues to the corresponding phenalenone species has been shown to occur both in model systems and in middle distillate fuels containing light cycle oils. The formation of indolylphenalenes, indolylphenalenones and 'indolylphenalene/acid salts' by acid promoted reactions of indoles and phenalenones has also been demonstrated by the isolation of these species both from model systems and from unstable fuel containing light cycle oil<sup>3,4,5</sup>. The role of acid in these reactions is not clearly understood. However it is known that at least catalytic amounts of acid are required for indoles to react with phenalenones and there is some evidence to suggest that acids become incorporated into the most polar components of insoluble fuel degradation products<sup>6</sup>.

The significance of this chemistry with respect to the stability of middle distillate fuels produced in Australian refineries has been investigated. The concentrations of phenalenone and alkylindoles were determined before and after storage of fuel samples for 13 weeks at 43C. Insoluble fuel degradation products were analysed by thin layer chromatography and compared with insolubles formed by degradation of fuels from UK sources.

### Experimental

Fuel samples were supplied directly from Australian oil refineries and generally consisted of one of five refinery stream types; straight run distillate (SRD), light cycle oil (LCO), hydrotreated light cycle oil (HT-LCO), hydrotreatment unit feed (LCO/SRD) or hydrotreatment unit product (HT-LCO/SRD). The samples from each refinery were combined to produce 12 blends containing 70% straight run distillate and 30% cracked components. The blend compositions are listed in table 1. Aliquots of both blended and unblended components were stored at -12C to minimise degradation before testing and analysis.

The stability of the blends was assessed by storage of 1 litre aliquots of fuel at 43C for 13 weeks, following the method detailed in ASTM D4625. Tests were carried out in duplicate. Filterable insolubles were determined using glass fibre filters (Millipore AP40). Adherent insolubles were determined by hotplate evaporation of gum solvent washings contained in disposable aluminium dishes. The chemical nature of insolubles formed during the storage tests was assessed using thin layer chromatography (silica gel stationary phase, 10% methanol in dichloromethane mobile phase). The concentration of phenalenone was determined using normal phase HPLC with UV detection at 384nm. The

detection limit for phenalenone was 0.5  $\mu\text{mol/l}$  with repeatability of  $\pm 10\%$ . The relative concentrations and distributions of alkylindoles were determined by a procedure which involved fractionation of fuel samples over silica gel, followed by addition of an internal standard (1-methylindole) and finally GC analysis with nitrogen specific detection.

GC peaks corresponding to alkylindoles were identified by reference to the published literature<sup>8,9</sup>. The relative concentration of alkylindoles in the fuel blends was calculated by assuming an equal detector response for all isomers and homologues. This method can also be used to determine the distribution and concentration of carbazole and its alkyl homologues:

### Results and Discussion

The stability of the 12 fuel blends was assessed by storage at 43C for 13 weeks. This test is widely believed to provide a realistic acceleration of degradation processes which occur at temperatures typically encountered in fuel storage facilities<sup>10</sup>. The relatively mild test conditions are considered to be approximately equivalent to one year of fuel storage at 18C to 24C. The results of this test are given in table 1. The filterable and adherent insolubles, produced during the storage period by all but the most stable fuels (samples 8,10,12,14), were analysed by thin layer chromatography and compared with insolubles produced during storage of unstable UK fuel. The isolation and characterisation of the UK insolubles has been described previously<sup>11,12</sup>. The chromatographic characteristics of the UK and Australian insolubles (both filterable and adherent) were found to be very similar. Subtle differences were noted amongst the most polar sediment components, but the degree of variation was within that previously observed for insolubles from different UK sources. Whilst not conclusive in itself, the similar characteristics of these fuel degradation products provided a positive indication that they may have been formed by common chemical processes.

The effect of chemical composition on observed fuel stability was addressed specifically in terms of the concentration of species highlighted in figure 1. According to this reaction scheme, unstable fuels would be expected to initially contain both phenalenes and indoles, with the concentration of phenalenes, indolylphenalenes and further reaction products (including insolubles) increasing with time. The acidic species required to promote these reactions may be present initially or may be produced during fuel storage. Stable fuels would be characterised by the absence of one or more of these chemical species.

In order to test this line of reasoning, specific chemical analysis was carried out on the fuel blends before and after thermal stress. The initial presence and subsequent reduction in concentration of phenalenes could have been determined in one of two ways; either directly, using reversed phase HPLC with electrochemical detection, or indirectly by determination of increasing phenalenone concentration using normal phase HPLC with UV detection. For simplicity of analysis, the latter approach was adopted in this study, with measurements being carried out before storage, after storage for 16 hours at 100C (to provide an initial indication of phenalene/phenalenone content) and after storage for 13 weeks at 43C. The results quoted in table 2 relate only to the concentration of the single species phenalenone. The total concentration of phenalenone species (alkyl- and benz- derivatives) in the fuel samples would of course have been higher. In addition it should be noted that the measured concentration of phenalenone was consistently lower than the initial concentration of phenalene<sup>2</sup>. Previous work has shown that phenalene is not quantitatively converted to phenalenone<sup>2</sup>. The total concentration of alkylindoles was determined in a limited number of the fuel samples before and after the 13 week storage test. The results of these measurements are given in

table 3. The remaining key species highlighted in the reaction scheme, namely acids, were not determined in this study.

The results of the storage tests, given in table 1, showed that the fuels tested covered a wide range of stability.

Four fuels (samples 8,10,12,14) proved to be extremely stable, all producing less than 1mg/l of total insolubles and not darkening in colour beyond 1.5 ASTM D1500 colour units. None of these fuels formed significant quantities of phenalenone during storage, indicating the virtual if not complete absence of phenalene species. The concentrations of alkylindoles in two of these samples were determined. Sample 8 initially contained alkylindoles at a concentration equivalent to 0.19mmols of 1-methylindole, and no significant reduction in concentration was observed during the storage period. The concentration of alkylindoles in sample 10 was an order of magnitude lower than in sample 8, essentially at the detection limit of the method. Again no significant change in concentration was detected during the storage period. The behaviour of these fuels was therefore entirely consistent with the reaction scheme illustrated in figure 1, i.e. stable fuels characterised by the absence of one or more of the key reactive species, phenalenes in the case of sample 8 and both phenalenes and indoles in the case of sample 10.

The four very stable fuels (8,10,12,14) all contained hydrotreated light cycle oil blending components. The beneficial effect of hydrotreatment on fuel stability is well known. This improvement in stability on hydrotreatment was clearly shown by the storage test results for the matched fuel pairs 7/8, 9/10, 11/12 and 13/14, where in each case the first sample contained light cycle oil and the second sample contained hydrotreated light cycle oil. The effect of hydrotreatment on the chemical composition of the fuel samples was also consistent with the observed improvement in stability. All the light cycle oil samples produced phenalenone during thermal stress, indicating the initial presence of phenalene species. However these species were removed during hydrotreatment to produce the stable 'phenalene free' fuels discussed previously. The effect of hydrotreatment on the initial alkylindole concentration was found to be variable. The light cycle oil samples all contained alkylindoles. There was no significant reduction in the initial concentration after hydrotreatment for sample pair 7/8, but a 25 fold reduction was noted for sample pair 9/10, indicating the use of much more severe hydrotreatment conditions.

The remaining fuel which contained hydrotreated light cycle oil was sample 16. Despite the hydrotreatment, this fuel was found to be moderately unstable, producing about 8mg/l total insolubles, and darkening significantly in colour during the storage period. It produced low but significant levels of phenalenone during storage, thus indicating the initial presence of phenalene species. The alkylindole content of this fuel was not determined. However it is reasonable to assume that alkylindoles were present, since high levels of alkylindoles were detected in fuel containing light cycle oil from the same refinery (sample 15) and it is unlikely that hydrotreatment conditions which left low levels of phenalene species would significantly reduce the concentration of alkylindoles. In addition, the insolubles produced during degradation of both samples 15 and 16 were clearly shown by ILC to be of the same type as those produced by fuels thought to follow the chemistry outlined in figure 1, which of course requires the presence of alkylindoles.

Other fuels which were found to be of similar stability to sample 16, producing 5 to 12mg/l total insolubles, were samples 6, 7 and 13. All these fuels contained light cycle oil and initially contained alkylindoles and phenalene species. The initial concentration of alkylindoles in sample 13 could not be measured because the fuel contained a high level of 'unidentified' nitrogen compounds which co-eluted and effectively masked the presence of alkylindoles. This was the only sample examined which contained these compounds. Further work is required in order to identify these species and investigate their

significance. The initial presence of phenalene species in samples 6, 7, 13 and 16 was indicated by formation of significant amounts of phenalenone (more than  $5\mu\text{mol/l}$ ) after storage of the fuels at  $100^\circ\text{C}$  for 16 hours with the measured level increasing further during the 13 week storage period. The amount of phenalenone present at the end of the 13 week storage test ranged from  $10\mu\text{mol/l}$  for sample 16 to  $230\mu\text{mol/l}$  for sample 6. This variation, which presumably also reflected differences in initial phenalenes concentration, clearly demonstrated that the degree of fuel instability cannot necessarily be extrapolated simply from the level of phenalene species. Indeed it is also worthwhile noting that the quantity of phenalene species and alkylindole species estimated to be present in fuel insolubles was always small in comparison to amounts potentially available in fuel solution. For example sample 15 produced approximately  $56\text{mg/l}$  of sediment but at the end of the storage period it still contained about  $95\text{mg/l}$  alkylindoles and  $35\text{mg/l}$  phenalenone (total phenalenones concentration would be several times this level). This observation tended to support previous conclusions that, given the presence of indoles and phenalenes, the amount of insolubles formed during storage is limited by acid concentration.

The fuels which proved to be the most unstable during the 13 week storage period were samples 5, 9, 11 (each producing about  $18\text{mg/l}$  total insolubles) and sample 15 (producing about  $56\text{mg/l}$  total insolubles). Chemical analysis of these samples indicated the presence of comparatively high levels of phenalene species and alkylindoles, consistent with their observed instability. Examination of the individual SRD and LCO components used in blending of samples 5, 9 and 15 showed as expected that phenalene species and alkylindoles originated entirely from the LCO components.

Significant reductions,  $>0.05\text{mmol/l}$ , in the overall concentration of alkylindoles were noted for the unstable fuel samples 5, 6, 7, 9 and 15 (concentration changes for the other two unstable fuels, samples 11 and 13 were not determined), thus providing strong evidence for reaction of alkylindoles during fuel storage. These changes represented reductions of between about 20% and 60% of the total initial alkylindoles concentration. The largest proportionate decrease was noted for the most unstable fuel, sample 15, and the smallest decrease for the most stable of these fuels, sample 7. Detailed examination of chromatograms showing the distribution of indoles in these aged fuel samples revealed that in all cases the concentration of certain isomers and homologues had decreased more than others. Figure 2 shows the chromatographic distribution of alkylindoles in sample 15 before and after aging. Very similar profiles were obtained for samples 5, 6, 7 and 9. Dorbon and Bernasconi have also recently noted that the distribution of alkylindoles in light cycle oils changes during aging at  $43^\circ\text{C}$ . In all cases the decrease in alkylindoles concentration during aging was greater than the quantity of these species estimated to have been incorporated into the insolubles collected at the end of the storage period. The amount of alkylindoles unaccounted for ranged from 3 to 10 times the amount estimated to be contained in the insolubles. The shortfall was probably associated with involatile but soluble fuel degradation products, such as for example the 'sediment precursor' compounds, indolylphenalenes, referred to in previous publications<sup>1,2</sup>. Soluble fuel degradation products of this type almost certainly contribute to 'fuel soluble gum' which may lead to deposits on hot engine and fuel system components.

#### Summary and Conclusions

The thin layer chromatographic characteristics of insolubles formed during storage of unstable middle distillate fuels from Australian refineries were found to be very similar to those of insolubles produced by the degradation of unstable fuel from UK sources, indicating that they may have been formed by similar chemical processes. All fuels which subsequently proved to be unstable during storage initially contained both alkylindole and phenalene species. Stable fuels were characterised by the absence of one or both of these

compound types. Phenalenes were either removed entirely or their concentration significantly reduced by hydrotreatment, which had the expected effect of improving fuel stability. In one case the initial concentration of alkylindoles was significantly reduced by hydrotreatment, but in all other cases no concentration change was noted. The reactivity of alkylindoles in unstable fuels was demonstrated by reductions in their overall concentration during fuel storage. In line with previous reports<sup>7</sup>, the distribution of alkylindole isomers and homologues was observed to change during fuel storage, indicating differences in reactivity amongst the species. Whilst the results of this study show that the absolute amount of insolubles formed during a storage period cannot be correlated directly with the concentration of alkylindole and phenalene species, it is clear that the stable fuels were characterised by the absence of one or both of these species and that both species were present in all the unstable fuels. These results therefore illustrate the potential for application of chemical methods to differentiate between stable and unstable fuels. However other factors clearly need to be considered when assessing the degree of fuel instability. From a chemical viewpoint, fuel acidity and fuel acidity potential are known to be important. Further work is required to identify the nature of acids in middle distillate fuels and to clarify their role in fuel degradation. In addition, physical parameters such as the solubility of fuel degradation products also need to be considered, particularly when fuel stability is assessed simply in terms of the weight of insolubles formed during fuel storage.

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Table 1. Results of fuel storage at 43 C for 13 weeks

Sample number	Sample type *	Initial colour	Final colour	Filtered insolubles mg/l	Adherent insolubles mg/l	Total insolubles mg/l
5	A(i)	0.5	4.0	9.9	8.0	17.9
		0.5	4.0	10.7	7.1	17.8
6	B(i)	1.0	4.5	4.7	7.0	11.7
		1.0	4.5	4.6	7.2	11.8
7	B(iii)	1.0	3.0	3.9	1.8	5.7
		1.0	3.0	3.0	1.9	4.9
8	B(iv)	0.5	<1.5	<0.1	0.1	0.1
		0.5	<1.5	0.3	0.4	0.7
9	C(i)a	<1.0	4.5	9.8	8.6	18.4
		<1.0	4.5	9.7	9.9	19.6
10	C(ii)a	0.0	0.5	0.2	0.2	0.4
		0.0	0.5	0.3	0.5	0.8
11	C(l)b	<1.0	<4.0	3.8	14.8	18.6
		<1.0	<4.0	2.5	15.0	17.5
12	C(ii)b	0.0	<0.5	0.8	<0.1	0.8
		0.0	<0.5	0.2	0.6	0.8
13	D(i)	<1.0	<3.0	2.0	7.4	9.4
		<1.0	<3.0	0.8	7.8	8.6
14	D(ii)	1.0	<1.5	1.0	<0.1	1.0
		1.0	<1.5	0.6	<0.1	0.6
15	E(i)	1.5	<7.5	23.4	33.2	56.6
		1.5	<7.5	23.4	32.4	55.8
16	E(ii)	2.5	<4.5	2.5	4.9	7.4
		2.5	<4.5	3.3	5.0	8.3

- X Refinery Code
- (i) 30% LCO in SRD
- (ii) 30% HT-LCO in SRD
- (iii) 30% LCO/SRD in SRD
- (iv) 30% HT-LCO/SRD in SRD

Table 2. Results of phenalenone measurements

Sample number	Phenalenone content $\mu\text{mol/l}$		
	(A) Initial	(B) After 16hrs @ 100 C	(C) After 13wks @ 43 C
5	4.4	42.0	150.1
6	12.7	87.8	230.8
7	6.1	30.7	52.6
8	ND	3.2	2.2
9	8.9	44.2	175.2
10	ND	2.0	ND
11	9.4	37.9	162.3
12	ND	ND	ND
13	ND	6.6	48.8
14	ND	ND	ND
15	15.6	107.2	193.8
16	ND	8.1	10.7

ND = not detected

Table 3. Results of indoles measurements

Sample number	Total indole content (mmol/l equivalent of 1-methylindole)		
	• (A) Initial	(B) After 13wks @ 43 C	( $\bar{A} - \bar{B}$ )
5	0.32	0.18 +/-0.02	0.14 +/-0.02
6	0.70 +/-0.05	0.39 +/-0.01	0.31 +/-0.06
7	0.23 +/-0.01	0.18 +/-0.00	0.05 +/-0.01
8	0.19 +/-0.05	0.17	insignificant
9	0.50 +/-0.02	0.25 +/-0.01	0.25 +/-0.03
10	0.02 +/-0.01	0.01 +/-0.00	insignificant
13	**	0.06 +/-0.00	
15	1.25 +/- 0.02	0.52 +/-0.03	0.73 +/-0.05

\* Average of duplicate results

\*\* Initial alkylindole concentration could not be determined because of interference from 'unidentified' nitrogen compounds

