

STABILITY OF AUSTRALIAN AUTOMOTIVE DIESEL FUELS

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INTRODUCTION

The storage stability of automotive diesel (ADF) fuel can vary across a wide spectrum, depending principally on the properties of its parent crude oil and the refining processes employed in its production. Fuels with inadequate storage stability produce insoluble gums and organic particulates which result in engine operability problems due to blocked fuel filters. There is currently no precise definition of just what constitutes acceptable storage stability for automotive diesel fuel. As an approximate guide, a rate of formation of insolubles of 20 mg/L per year of ambient storage has been proposed as the maximum rate for 'stable' ADF.¹⁻³ The absence of an accelerated test which can reliably predict the storage stability of diesel fuels has contributed to the current unsatisfactory situation. However, a test developed by the US Naval Research Laboratory is showing considerable promise for satisfying this long-standing need.

RESULTS AND DISCUSSION

Stability of Australian ADFs The results of stability tests on 76 ADFs from the eight major Australian refineries are shown in Figure 1. These fuels were produced during the 15 month period from October 1987 to the end of December 1988. Most fuels were obtained during transfers of ADF from the refineries to terminal distribution tanks, so the fuels can be assumed to be less than one month old prior to being subjected to stability tests. The survey results in Figures 1 and 2 were obtained using the 43°C/13 week test, which simulates one year of storage at typical ambient temperatures. As discussed in the following section, this test is regarded as a reliable indicator of storage stability, and has recently been adopted as an ASTM Standard test method.

Figure 1 shows that the stabilities of Australian ADFs span a wide range. Of the 76 fuels tested, a majority (76%) yielded less than 10 mg/L of insolubles. A majority (67%) of those fuels which yielded insolubles >10 mg/L emanated from a single refinery, and all of the fuels with inadequate stability (>20 mg/L) came from that refinery. Figure 1 shows, however, that the same refinery produced batches of high stability ADF in addition to the low quality batches, resulting in average insolubles of 12 mg/L. This average level of insolubles is by far the highest of any of the eight refineries (see Figure 2). Three refineries consistently produced very high stability ADF, with average total insolubles <4 mg/L. The remaining four refineries produced ADF with average total insolubles of 6-7 mg/L, indicative of ADF with good storage stability quality.

From a similar though less extensive survey of Australian ADFs covering

the period 1982-86, it was concluded that Australian ADFs were exceptionally stable, and that ADF yielding more than 5 mg/L insolubles in the 43°C/13 week test was rarely produced by Australian refineries. The current survey shows a very different picture with approximately half of Australian ADF production yielding more than 5 mg/L of insolubles. However, judged by the <20 mg/L criterion for stable ADF, current Australian-produced ADFs (apart from refinery C) generally have high storage stability quality.

The very high stability observed in the 1982-86 period was attributed to the low heteroatom content of Gippsland Light (the principal crude feedstock for Australian refineries), and to the widespread use of diesel hydrotreating process or stabilizing additives. There have been many publications² warning that the stability of automotive diesel fuel must decline as refiners meet increasing ADF demands by inclusion of higher proportions of cracked blendstock (light cycle oil), and as refiners are forced to process crudes containing greater proportions of certain destabilizing heteroatom compounds. Furthermore, the stability of (untreated) cracked blendstock may have decreased as refiners direct heavier feedstocks to their cracking units. These trends are probably contributing to the lower storage stability revealed in the 1987-88 survey. Other factors may also have contributed. Some refiners may be seeking to reduce refining costs by reducing use of their highly effective but expensive hydrotreating units. This cost-saving approach is attractive because it has been demonstrated that storage stability can be achieved without hydrotreating, by careful selection of a stabilizing additive package.^{4,5} From results of the current survey of Australian ADFs, it is apparent that at least one refiner is either underdosing or making a poor selection from the range of commercially available stabilizing additives. Furthermore, an underlying cause for this situation may be the use of unreliable accelerated stability tests to assess the performance of commercially available additives.

Accelerated Stability Tests The formation of insoluble organic matter in diesel fuels during storage is the result of complex interactions among a range of reactive species in the fuel, and molecular oxygen. At least three classes of chemical reaction (eg oxidative gum formation, acid-base reactions and esterification) can occur.^{2,8,7} The more reactive compound classes include heteroatom⁶ compounds and olefins. Certain compounds eg alkyl pyrroles, indoles⁹ and thiophenols¹⁰ are known to be particularly potent destabilizers of diesel fuel. Recent years have seen a renewed interest in achieving a better understanding of the complex chemistry of diesel fuel degradation, leading to an improved understanding of the complex chemistry involved.^{11,12}

The complexity of the chemistry of diesel fuel degradation has been the principal barrier to the development of a reliable accelerated storage stability test. The methods used to accelerate the insoluble-forming reactions include higher temperature, higher oxygen concentration and copper catalysts. Certain insoluble-forming reactions, however, may be more sensitive to the accelerated reaction conditions. Hence, the overall chemistry occurring under the accelerated conditions may be quite different from that occurring under non-accelerated conditions viz. normal storage of ADF. Consequently, highly accelerated tests are likely to be the least reliable indicators of storage stability, unless they have been thoughtfully devised and carefully evaluated.

Based on American and European experience, there is general agreement that the mild acceleration involved in the 43°C/13 week storage stability test results in reliable assessment of storage stability at normal storage temperatures. Consequently, the American Society for Testing and Materials introduced the new standard test method ASTM D4625 "Distillate Fuel Storage Stability at 43°C" in 1988. For Australian ADFs, Figure 3 compares results from the 43°C/13 week ASTM test and one year storage of 700 mL samples in metal cans in a non-air conditioned shed in Brisbane, Australia (average temperature ≈25°C). While the experimental data show some scatter, it can be concluded that the quantity of insolubles formed during storage at ambient temperatures for one year is approximately equal to the quantity formed during 13 weeks at 43°C. Thus the 43°C/13 week test can be confidently employed for assessing the ambient storage stabilities of Australian ADFs.

Figure 4 shows the correlation between total insolubles formed in the more accelerated 80°C/7 day test and insolubles formed in the 43°C/13 week test, for a selection of Australian ADFs. The figure shows that the 80°C/7 day test can serve a useful predictive function for the more stable fuels, even though results do not correlate particularly well with results from the 43°C test. Those fuels which yielded less than 3 mg/L in the 80°C test also performed well in the 43°C test. However, fuels yielding 4-8 mg/L in the 80°C test yielded a very wide range of insolubles (3-32 mg/L) in the 43°C test. Hence, as a potential quality control test, the 80°C/7 day test shows inadequate correlation with the 43°C/13 week test if it is to be applied to fuels with a wide range of storage stabilities. Thus the acceleration of the processes of formation of filter-blocking insolubles has reduced the reliability of the accelerated test, even before the time required for the test has been shortened to the <24 hr period desirable for a refinery quality control test method.

Other studies involving attempts to accelerate ambient storage conditions by raising the temperature and shortening the test time suggest that 80°C/7 days may be much too severe to attempt a reasonable correlation to 43°C/13 week tests (Hardy et al, 1986). That work suggests that 80°C/4 to 5 day bottle tests should correlate much better with the 43°C/13 week tests for any given fuel. Unfortunately the precision of the test results obtained at 80°C/4 to 5 days is very poor and hence those conditions are not acceptable as a refinery quality control test for accelerated stability. Shortening the test time at 80°C below 4 days results in increasingly poor test precision or repeatability thus effectively barring the use of this test at the refinery.

One Australian refiner adopted an accelerated test based on a temperature of 100°C and the accelerating effect of soluble copper at a concentration of 10 mg/L. The test period of 2 h was short enough for the test to be used for quality control, and the test was used for acceptance/rejection purposes for ADF exchange between some Australian oil companies. Figure 5 shows that the test is clearly unsuitable for this application, even though there is a degree of correlation with the 43°C/13 week test. The problem is that some fuels which are stable (according to the <20 mg/L criterion for the 43°C/13 week test) are classed as unstable by the highly accelerated copper naphthenate test. Such a test is clearly unsuitable for quality control of large production batches of ADF, and in the light of evidence such as

presented in Figure 5, the test was abandoned in 1988. The possibility that similar situations may reoccur again highlights the need for a reliable short-term test for quality control of ADF storage stability.

While Figures 4 and 5 show that attempts to accelerate the formation of insolubles can result in unreliable storage stability tests, the combination of increased temperature and oxygen pressure may be more reliable. Figure 6 shows results for five US middle-distillate fuels, spanning a broad range of stability, when tested at 43°C for 18 weeks in atmospheric bottle tests and 43°C for 4 weeks at 100 psia oxygen. A linear least squares correlation gives $R^2 = 0.98$ for these two tests. The correlation between 43°C/4 weeks/100 psia and 80°C/64 hr/100 psia of oxygen is 0.97 for these same five fuels. This is a clear indication that a combination of increased temperature and increased oxygen pressure together should be quite useful for predicting ambient storage stability for most middle-distillate fuels.

The Oxygen Overpressure Stability Test A new oxygen overpressure method for predicting distillate fuel's tendency for forming deleterious fuel insolubles during ambient storage is rapid and precise and is predictive for up to 3 years of ambient conditions. For this test 100 mL samples of filtered fuel in 125 mL borosilicate bottles were placed in a low pressure reactor (LPR). The reactor was sealed and pressurized with 99.5% pure oxygen to 100 psig. The samples were stressed, while maintaining the oxygen pressure, under accelerated storage conditions for set temperatures and times. At the end of the stress period, the amount of filterable sediment and adherent sediment were determined gravimetrically and reported as total insoluble sediment weight. Samples were run in triplicate and the average values are reported in mg/100 mL.

Work at 43°C for up to 4 weeks at 100 psig (see Figure 6) and at 80°C for up to 64 hours at psia shows very good correlation with bottle tests done at 43°C (slight variation of ASTM D4625). In an attempt to make the test shorter, recent work has been done at 90°C for 16 hours at 100 psig for possible use as a new ASTM method.

Table 1 shows comparison gravimetric results for two accelerated storage stability tests using a variety of diesel fuels. Two of the fuels are blends of 30% cracked stock (LCO) and 70% straight run. One fuel is a blend of 30% diesel fuel containing 2% sulfur (HSD) and 70% straight run. The remaining fuels were US Naval Distillate fuels (NATO F-76). Very good correlation between the results of the lower temperature bottle tests and the oxygen overpressure tests is shown. When the pass/fail criteria at the bottom of the table is applied, it can be seen that, with the exception of one sample, the oxygen overpressure method correctly assessed the stability of these fuels when compared with the longer bottle tests. This fuel would be considered marginal by both methods.

This method has also been useful in assessing the relative effectiveness of middle-distillate fuel stabilizer (antioxidant) additives. Table 2 shows typical results for a slightly unstable fuel. The oxygen overpressure method correctly assessed the additive-free fuel in addition to evaluating the additives when compared to the lower temperature test. Additive 7 is a noteworthy exception when comparing the two test methods. This indicates the need to possibly extend the

test times of the 16 hour 100 psig test to exceed reaction induction times. Also, in two cases, additives 3 and 4, the 90°C test appears to be more severe than the 43°C test.

Figure 7 shows the gravimetric results obtained when the same six fuels, of various stabilities, were analyzed at NRL and at AMPOL using the oxygen overpressure method. Very good correlation between the results is shown, especially when it is considered that the samples were analyzed using reactors constructed separately at each of the labs. These results also show that the method has good reproducibility.

CONCLUSIONS

The storage stability of Australian automotive diesel fuels has decreased from the extremely high quality which existed five years ago. With the exception of one refinery, however, Australian refineries still produce ADF with good storage stability. Assessment of long-term storage stability by means of highly accelerated laboratory tests remains a challenge. Most highly accelerated tests have limited reliability when compared with the mildly accelerated 43°C/13 week test. The oxygen overpressure method, however, is showing promise of filling the long-standing need for a rapid, reliable test.

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TABLE 1. TOTAL INSOLUBLES (mg/L) FROM ACCELERATED STABILITY TESTS

| Sample Description | 43°C/18 wk Bottle Test | 90°C/16 hr/100 psig LPR Test |
|---------------------------|---------------------------|---------------------------------|
| 30%LCO/70%SR (Refinery 1) | 89 | 46 |
| 30%LCO/70%SR (Refinery 2) | 60 | 38 |
| 30%HSD/70%SR (Refinery 3) | 44 | 62 |
| NATO F-76 (1) | 39 | 39 |
| (2) | 5 | 7 |
| (3) | 7 | 13 |
| (4) | 11 | 7 |
| (5) | 12 | 14 |
| Pass/Fail | 40 | 30 |

TABLE 2. TOTAL INSOLUBLES (mg/L) FOR (30%LCO/70%SR) DIESEL FUEL FROM A U.S. GULF COAST REFINERY TREATED WITH VARIOUS STABILIZING ADDITIVES

| Sample Description | 43°C/18 wk Bottle Test | 90°C/16 hr/100 psig LPR Test |
|--------------------|---------------------------|---------------------------------|
| 2 | 19 | 7 |
| 3 | 28 | 38 |
| 4 | 39 | 52 |
| 9 | 43 | 31 |
| 6 | 45 | 28 |
| 8 | 47 | 24 |
| 1 | 52 | 34 |
| 5 | 56 | 31 |
| 7 | 56 | 14 |
| Neat | 62 | 45 |
| Pass/Fail | 40 | 30 |

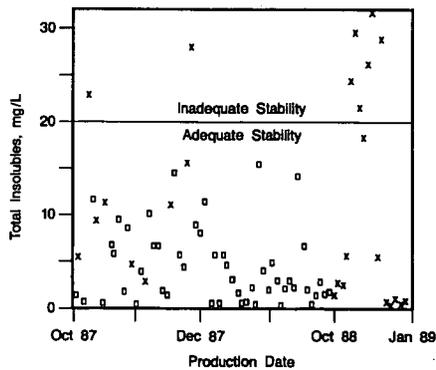


Figure 1. Total Insolubles Formed During Oven Storage at 43°C for 13 Weeks. Cross-Symbols - Refinery C; Square Symbols - Other Australian Refineries.

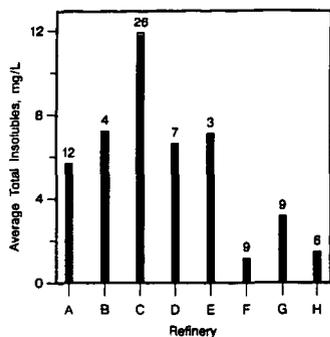


Figure 2. Average insolubles from 13 Weeks at 43°C for ADF from Australian Refineries. The Numbers of Samples Tested Are Indicated.

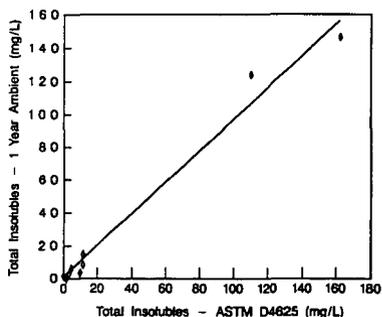


Figure 3. Correlation of Total Insolubles Formed During One Year at Ambient Temperatures and During 13 Weeks at 43°C (ASTM D4625).

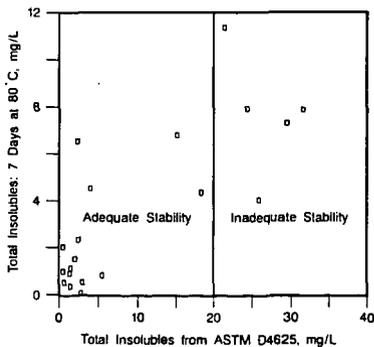


Figure 4. Correlation of Total Insolubles Formed During 7 Days at 80°C and During 13 Weeks at 43°C (ASTM D4625).

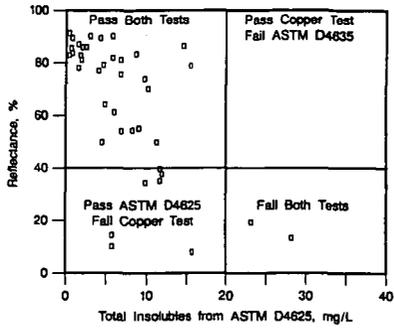


Figure 5. Correlation of a Stability Test Employing Copper as an Accelerating Agent with Insolubles Formed During 13 Weeks at 43 °C.

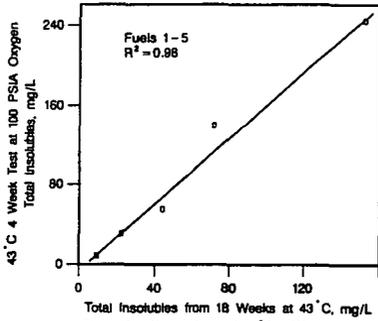


Figure 6. Comparison of 43 °C/4 Week/100 PSIA O₂ Test Results with 43 °C/18 Week Data.

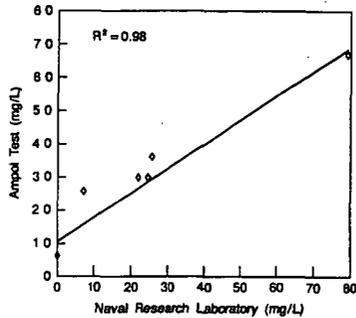


Figure 7. ASTM Round Robin Results for Oxygen Overpressure Stability Test (90 °C/16 Hr/100 PSIG)