## LETTER TO THE EDITOR

# Oxidative Stability of Biodiesel in Blends with Jet Fuel by Analysis of Oil Stability Index

Sir:

Recently, concern among biodiesel fuel suppliers and terminal operators has focused on determining the effects of long-term storage on the quality of biodiesel/petroleum middle-distillate fuel blends. Under most realistic storage conditions, methyl soyate (SME) was reported to be significantly more susceptible to oxidation or autoxidation than hydrolytic degradation in blends with jet fuel (JP-8) (1).

This work was conducted to measure oxidation induction period of neat SME (Interchem, Overland Park, KS) and SME in 10–30 vol% blends with JP-8 jet fuel (Air National Guard, Peoria, IL) by analysis of the oil stability index (OSI; oxidative stability instrument from Omnion Inc., Rockland, MA) at block temperature (T) = 50, 60, 75 and 90°C (± 0.1°C). The experimental method, adapted from the AOCS method Cd 12b-92 (2), apparatus, and preparation of SME samples prior to blending with JP-8 fuel were described previously (3).

Table 1 is a summary of the OSI results. In general, this work shows that the relative resistance to oxidation of SME/JP-8 fuel mixtures with blend ratios up to 30 vol% SME may be assessed by analysis of OSI under certain conditions. Timeliness is an important factor in reliable measurement of OSI data. Method Cd 12b-92 recommends identifying block temperatures to allow total measurement times in the range 4–24 h to increase the reliability of the results (2). Within that context, this work recommends the following block temperatures for measurement of OSI: neat SME, T = 50–60°C; 30 vol% SME blend in JP-8 fuel, T = 75–90°C; 20% SME blend, T = 90°C; and 10% SME blend, T >90°C. The results in Table 1 also indicate that conditions favoring measurement times exceeding ~50 h (low T or vol% SME) tend to increase variance of the mean OSI values.

Increasing blend ratio (vol% SME) decreased OSI. Straight-run (neat) jet fuel does not readily oxidize under most conditions unless high-pressure hydrotreating or hydrocracking occurs to destroy sulfur- or nitrogen-containing heteroatoms that otherwise act as oxidation inhibitors (4). This means oxidation of SME/JP-8 fuel blends likely did not cause significant degradation of jet fuel, under the conditions of this study. Thus, increasing blend ratio decreases relative resistance to oxidation, resulting in a decrease in OSI. Nevertheless, results indicate that the 30 vol% blends were significantly more resistant to oxidation than neat SME with respect to constant T. As noted above, decreasing the blend ratio to levels where total measurement time exceeds ~50 h increased variance in measurement of OSI.

**TABLE 1**
**Oil Stability Index (OSI [h]) of Methyl Soyate (SME)/JP-8 Blends**[a]

| Blend ratio | Block temperature (T), °C | | | |
|---|---|---|---|---|
| vol% SME | 50 | 60 | 75 | 90 |
| 10 | 285 ± 65 | $158^b$ ± 34 | 104 ± 15 | 45 ± 1.9 |
| 20 | $225^b$ ± 50 | 100 ± 4.6 | 40 ± 2.6 | 16 ± 1.5 |
| 30 | $187^b$ ± 18 | $65.3^b$ ± 0.25 | 22.88 ± 0.035 | 8.1 ± 0.25 |
| 100 | 17.2 ± 0.42 | 7.2 ± 0.30 | 1.55 ± 0.087 | $0.81^b$ ± 0.032 |

[a] Mean values are from two replicates for (i) 10 vol% SME blends at T = 50, 60, and 75°C, (ii) 20% blend at 50°C, and (iii) 30% blend at 60 and 75°C; otherwise, mean values are from three replicates.
[b] Mean value from measurements analyzed by onset time method.

Increasing T also decreased OSI. For the 10–30 vol% SME blends, decreasing T increased total measurement time and tended to make acquisition of reliable OSI results problematic. In addition to increasing variance in mean OSI data, decreasing T increased the likelihood that individual OSI measurements reported by the oxidative stability instrument analyzer were unreliable. In most cases (11 of 16 OSI values reported in Table 1), all replicate measurements for a given sample were taken as reported by the computer-based analyzer (inferred numerically by calculation of the maximum in the second derivative of the conductivity-time curve). In the five remaining cases, analyzer results did not agree with graphical evidence shown in the data curves, and OSI data were determined by applying the onset time method recommended as an alternative analytical method conforming to guidelines outlined in Cd 12b-92 (2,5). The onset time method determines OSI from the intersection of lines drawn tangent to the conductivity curve before and after transition from a relatively small to an advancing rate of oxidative degradation. For the 10–30% SME blends, four of the five OSI-values determined by the onset time method occurred at a T below those recommended above for obtaining reliable results (that is, at T = 50–60°C).

For the neat SME samples, increasing T to 75–90°C decreased total measurement time to less than 4 h. Although variances were relatively low (<0.008), reducing the measurement time decreased the total number of data points collected (the analyzer records the conductivity data every 0.05 h), an effect that may decrease the reliability of the results. Decreased reliability in shorter measurement times may partially explain why the onset

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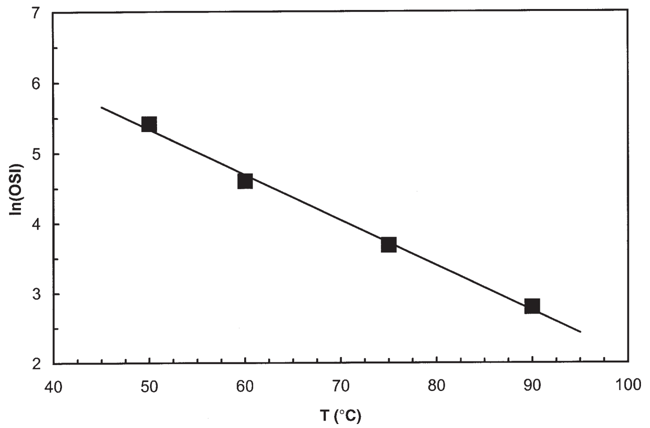

**FIG. 1.** Plot of ln(OSI) vs. T for 20 vol% SME/JP-8 fuel blends. Error bars (±0.10) for OSI data (h) = ±110 at T = 50°C; ±5.0 at 60°C; ±2.9 at 75°C; ±1.7 at 90°C. OSI, oil stability index; SME, methyl soyate.

**TABLE 2**
**Results from Least-Squares Regression Analysis of Data for SME/JP-8 Blends[a]: ln(OSI [h]) = *A* + *B*(T [°C])**

| Blend ratio vol% SME | *A* | *B* | $R^2$ | $\sigma_y$ |
|---|---|---|---|---|
| 10 | 7.8 | –0.0442 | 0.97 | 0.13 |
| 20 | 8.57 | –0.0646 | 0.99 | 0.094 |
| 30 | 8.9 | –0.0768 | 0.99 | 0.15 |
| 100 | 6.7 | –0.0787 | 0.96 | 0.28 |

[a] Two DF for each regression line. *A* = intercept; *B* = slope; $R^2$ = adjusted regression coefficient; $\sigma_y$ = standard error of *y*-estimate. See Table 1 for other abbreviations.

time method had to be applied for neat SME at 90°C, the fifth such point alluded to in the preceding paragraph where analyzer results disagreed with graphical evidence. Application of the onset time method to infer OSI data for neat SME was demonstrated previously (3).

Nakatani *et al.* (6) studied the effects of T on OSI of methyl linoleate blends in silicone oil and reported a linear relationship between log(OSI) and T. Similar results were reported by Jebe *et al.* (5), Hasenhuettl and Wan (7), Mendez *et al.* (8), and Reynhout (9). Figure 1 is a plot of ln(OSI) vs. T data for the 20 vol% SME in JP-8 fuel blends studied in this work. Results from linear least-squares regression analyses of data for 10–30% SME blends in JP-8 fuel plus neat SME are summarized in Table 2.

With the exception of the 10 vol% SME blend, slopes (*B*) listed in Table 2 were similar (–0.065 to –0.079), suggesting that the actual relationship between ln(OSI) and T data for SME and its blends with JP-8 fuel could be linear and parallel. Preliminary statistical comparison indicated a good probability ($P = 0.86$) that the lines for neat SME and a 30% blend in JP-8 fuel were parallel. However, similar comparison of 20 and 30% blends yielded $P = 0.12$, and of 20% blend and neat SME yielded $P = 0.24$, showing only that the hypotheses of equivalent slopes could not be rejected. Clearly, more detailed studies will be necessary to clarify these results.

Nevertheless, the aforementioned similarity between slopes inferred for 20 and 30 vol% SME blends in JP-8 fuel plus neat SME yielded an average value $B \approx -0.07$. This result compared well with those reported in the aforementioned study by Nakatani *et al.* (6), where $B = -0.069$. Results from this work also compared well with those from similar studies on the oxidation of soybean and fish oils, where $B \sim -0.07$ for both studies (5,8).

Finally, results from the present study preliminarily indicate that, with respect to only two DF, a linear relationship likely exists between ln(OSI) and T for SME and its blends in jet fuel. Further investigations will be necessary to confirm this observation. Should such confirmation be made, those results may be useful in developing a means for timely determination of the relative oxidative stability of SME under more realistic long-term storage conditions such as lower temperatures.

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