

# Determination of Total Biodiesel Fatty Acid Methyl, Ethyl Esters, and Hydrocarbon Types in Diesel Fuels by Supercritical Fluid Chromatography–Flame Ionization Detection

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## Abstract

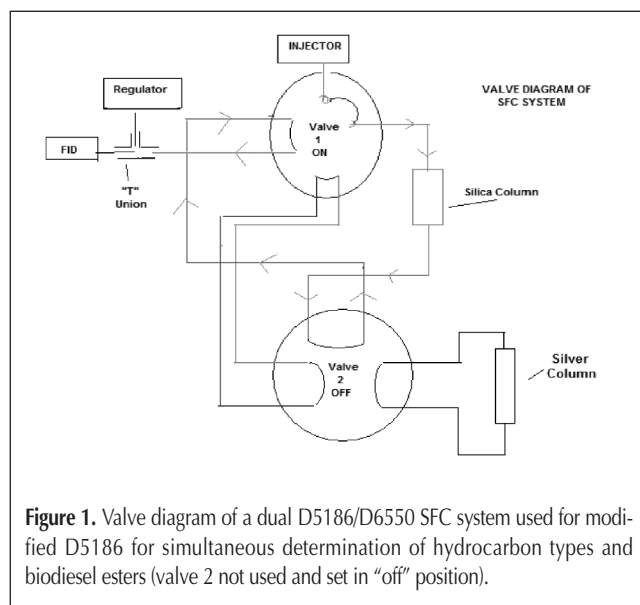
A method for determining total biodiesel methyl and ethyl ester content in diesel fuels by supercritical fluid chromatography–flame ionization detection (SFC–FID) is developed. A silica column typically used for determining aromatics in conventional diesel fuels by ASTM D5186 is back-flushed after separation of the hydrocarbons to allow elution of the various esters as a single “total biodiesel” distinct peak. The modification concurrently allows the determination of total aromatic hydrocarbons and their distribution as mono- and polynuclear compounds, as described in the current version of D5186. The instrument response is linear from 1.0% to 50% biodiesel esters with a signal-to-noise ratio of 25 at the 0.1% level. The short-term relative standard is 0.8%. Normalized percent quantitation using a hydrocarbon response factor of 1.00 and an ester response factor of 1.19 provide an average percentage error of 1.8% when measuring actual biodiesel/hydrocarbon fuel blends. The ester response factor is the average of the response factors of 10 pure ester compounds. These responses are calculated from respective solutions of each ester and the four compounds, hexadecane, toluene, tetralin, and naphthalene, as used for the D5186 response factor mixture.

## Introduction

The proposed use of biodiesel esters derived from a variety of biological sources, such as canola, corn, fish, and other oils, as diesel fuel blending components has led to the need within the petroleum industry to determine these compounds in the presence of the diesel fuel hydrocarbon matrix. Fatty acid methyl and ethyl esters ranging in carbon number from  $C_{10}$  through  $C_{26}$  would be produced by trans-esterification of the mono-, di-, and tri- glycosides in the oils with methanol and/or ethanol. The product of this reaction would then be blended with conventional hydrocarbon-based diesel fuels.

Currently, there are a limited number of easy and accurate

analytical methodologies for such an analysis. Methods based on Fourier-transform infrared spectroscopy (FTIR) may yield approximate values because it is difficult to obtain an accurate response factor (RF) for all of the potential esters that may be produced in biodiesels. Chromatographic separation of the biodiesel esters from the diesel hydrocarbons and detection with conventional universal mass detectors, such as the flame ionization detector (FID) is more desirable. Currently, D5186 (1) is a popular technique, used in regulation by California’s Air Resource Board for the determination of total aromatics and aromatic ring distributions in conventional diesel fuels. D5186 uses supercritical carbon dioxide, a normal phase silica column, and FID, but has not been fully evaluated for the analysis of the hydrocarbon types in the presence of co-blended biodiesel esters. The use of supercritical fluid chromatography in the analysis of hydrocarbons is well-documented in the literature (2–4). Presented here is the investigation into determining total fatty acid methyl and ethyl esters biodiesel in diesel fuels by supercritical fluid chromatography–flame ionization detection



**Figure 1.** Valve diagram of a dual D5186/D6550 SFC system used for modified D5186 for simultaneous determination of hydrocarbon types and biodiesel esters (valve 2 not used and set in “off” position).

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(SFC–FID), with the incorporation of “backflush” for analysis of biodiesel esters as well as hydrocarbon types.

## Experimental

An Analytical Controls (Rotterdam, The Netherlands) combination D5186 (1) and D6550 (5) SFC system (Figure 1) was configured as follows. (i) Injection volume: 0.5  $\mu$ L with a Berger Instruments (Thar, Pittsburgh, PA) Auto-sampler (all samples were injected neat). (ii) Supercritical fluid: carbon dioxide. In-house commercial source, filtered over silica gel scrubber ahead of pumping system, blank analysis yielded zero interference. (iii) Pressure control: downstream. (iv) Columns: 25 cm  $\times$  4.6 mm i.d.  $\times$  5  $\mu$ m silica (Analytical Controls). Columns meet D5186

**Table I. Response Factors Calculated for Each Ester**

Compound	Response Factor
Methyldecanoate	1.30
Methylundecanoate	1.30
Methyldodecanoate	1.18
Methyltridecanoate	1.25
Ethylmyristate	1.17
Methylpentadecanoate	1.13
Methylpalmitate	1.13
Methyloleate	1.14
Ethyloleate	1.12
Methylarachidate	1.13
Mean	1.19
RSD ( $n - 1$ )	6.0%

**Table II. Precision Data of a Methyloleate Spiked Diesel Fuel with the Average Ester Response Factor\***

Injection	Monoaromatics	PNA's	Total Aromatics	Methyloleate
1	25.5	4.2	29.7	10.1
2	25.6	4.2	29.6	10.0
3	25.6	4.2	29.8	10.1
4	25.6	4.2	29.8	10.0
5	25.5	4.1	29.6	10.0
6	25.4	4.3	29.7	10.0
7	25.4	4.3	29.7	10.0
8	25.5	4.2	29.6	10.0
9	25.5	4.2	29.7	10.0
10	25.5	4.1	29.6	10.0
% RSD <sup>†</sup>	0.3	1.6	0.3	0.4
Mean	25.5	4.2	29.7	10.0
Actual	N/A <sup>‡</sup>	N/A	N/A	10.0
% Recovery	N/A	N/A	N/A	100.0

\* Results are in mass %.

<sup>†</sup>  $N - 1$ ,  $n = 10$  over two days.

<sup>‡</sup> N/A = Not applicable.

specifications. (v) Column Pressure: 2176 psi (15.0 Mpa). (vi) Column flow: 2 mL/min. (vii) Run time: 45 min. (viii) Column oven temperature: 40°C isothermal. (ix) Detector: FID at 350°C. Air flow = 421 mL/min, H<sub>2</sub> flow = 66 mL/min, expanded CO<sub>2</sub> flow = 32 mL/min. Detector gas flows were set to provide analysis of

**Table III. Accuracy Tests of Pure Compounds in a Diesel Fuel with the Average Response Factor\***

Compound	Determined	Actual	% Relative Error <sup>†</sup>
Methyldecanoate	9.2 $\pm$ 0.1	10.2	9.8%
Methylundecanoate	9.2 $\pm$ 0.1	10.0	8.0%
Methyldodecanoate	9.8 $\pm$ 0.1	10.5	6.7%
Methyltridecanoate	0.3 $\pm$ 0.1	10.9	5.5%
Ethylmyristate	10.3 $\pm$ 0.1	10.5	2.9%
Methylpentadecanoate	10.3 $\pm$ 0.1	10.0	3.0%
Methylpalmitate	9.8 $\pm$ 0.1	9.8	0.0%
Methyloleate	10.0 $\pm$ 0.1 <sup>‡</sup>	10.0	0.0%
Ethyloleate	10.3 $\pm$ 0.1	10.2	1.0%
Methylarachidate	10.0 $\pm$ 0.1	9.8	2.0%

\* Results are in mass %.

<sup>†</sup> % Relative Error = [Absolute Value (Determined - Actual)/Actual]  $\times$  100. Average Relative Error = 3.9%.

<sup>‡</sup>  $\pm$  two times the standard deviation.

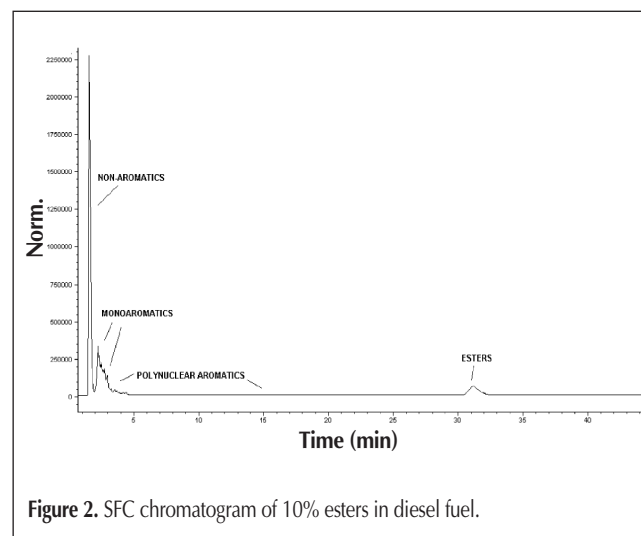


Figure 2. SFC chromatogram of 10% esters in diesel fuel.

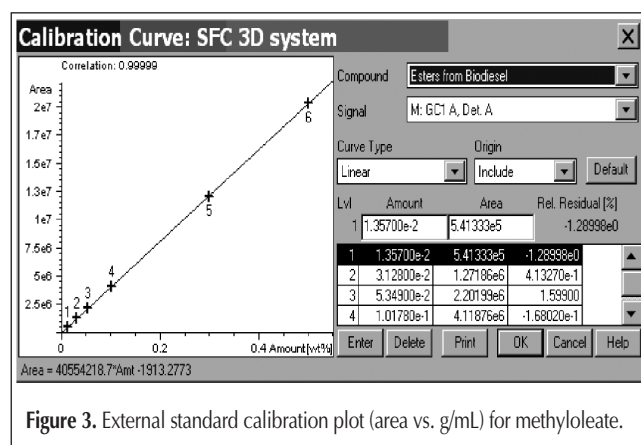


Figure 3. External standard calibration plot (area vs. g/mL) for methyloleate.

hydrocarbons as described in ASTM method D5186 (1). (x) Backflush valve time (valve 1 off): 30 min. Valve 2 remained off throughout the separation, keeping the silver column of D6550 isolated from the carrier stream. A valve diagram is shown in Figure 1. (xi) Linearity test: 0.10, 0.30, 0.50, 1.00, 3.0, and 5.00 g of methyloleate were weighed to the nearest 0.0001 g into respective 10.0-mL volumetric flasks, which were diluted to the mark with *n*-heptane and mixed 3 min on a vortex mixer. This process produced solutions ranging from 0.01 g/mL to 0.50 g/mL. The six solutions were injected, and a curve of area vs. concentration was generated. (xii) Calibration: pure compounds were purchased from Aldrich Chemical Co. (Milwaukee, WI). Ten mixtures similar to the performance mix required in ASTM D5186-3 except with an ester added were prepared as follows: 70.0 mass% hexadecane; 20.0 mass% toluene; 3.0 mass% tetralin; 2.0 mass% naphthalene; and 5.0 mass% ester.

The described mixtures were injected onto the SFC and response factors calculated for each ester as follows:

$$RF = \frac{[\text{gravimetric mass \% ester} \times \text{total area of hydrocarbons}]}{[\text{gravimetric mass\% total hydrocarbons} \times \text{area ester}]}$$

where: total hydrocarbons = sum of hexadecane + toluene + tetralin + naphthalene

## Results and Discussion

Initial studies using D5186 indicated that the biodiesel esters were not eluted from the silica gel separation column specified in D5186. The esters, which are more "polar" than the diesel hydrocarbons, are strongly adsorbed on the silica gel, and their elution times in the forward elution from the column were extremely long. As a result, a backflush of the silica column after the elution of the hydrocarbons was evaluated. For convenience, a combination commercially available D5186/D6550 instrument

(Figure 1) was programmed to perform this function. The silver loaded column used in the D6550 configuration was placed in by-pass mode and not used; that is, only the six port valve was used to backflush the esters.

Table I lists the RFs calculated for each of the 10 esters used in this work. Ethyl esters were included because trans-esterification with ethanol as well as methanol has been proposed for the production of biodiesels. The data in Table I shows a generally decreasing RF with an increasing ester carbon number. However, for esters in the range of C<sub>15</sub>–C<sub>20</sub>, the RFs are relatively constant and well within the precision of the determination. The average ester response factor was 1.19 with a relative standard deviation (RSD) of 6.0%. For further evaluation, the quantitative analysis was simplified as in D5186 by using normalized percent, with all non-, mono-, and poly-nuclear aromatics response factors set at 1.00 and the ester response factor set at 1.19.

Figure 2 shows a chromatogram of 10% (w/w) methyloleate spiked into a diesel fuel. The ester eluted in the backflush mode as an approximately symmetrical peak, and the hydrocarbons were separated into non-aromatics ("saturates"), monoaromatics, and polynuclear aromatics, as in conventional D5186. "Polynuclear aromatics" is defined as diaromatics + hydrocarbons. Figure 2 indicates that the addition of the backflush capability to the silica column in D5186 leads to the normal determination of the aromatic hydrocarbon types according to D5186 specifications in the forward elution, and also to the simultaneous determination of the biodiesel ester components by backflushing the column after the elution of the polynuclear aromatics. For instruments performing only conventional D5186, the single simplest modification required would be the installation of a four port instead of a six port switching valve to backflush the silica gel column.

Figure 3 shows the 1.0 to 50% (w/v) external standard calibration curve (Area of Ester vs. Concentration of Ester) for methyloleate. The curve was linear with a correlation coefficient > 0.999. The signal-to-noise ratio at 0.1% was 25.

Table II shows the repeated normalized percent analysis of 10% methyloleate in diesel with the 1.19 ester response factor. The short-term relative standard deviation (*n* – 1, *n* = 10 over two days) was 0.4%. For methyloleate, the mean recovery is was 100%.

The calibration was further tested with solutions of pure ester compounds gravimetrically spiked into a diesel fuel. These results are summarized in Table III. The average relative error of recovery was 3.9%. Table III indicates a similar pattern noted with the RFs of the individual esters in Table I. Generally, esters with a carbon number of C<sub>14</sub>–C<sub>20</sub> yielded reasonable results using the average RF = 1.19. An error of 3–4% is acceptable for most applications. Only esters with carbon number < C<sub>14</sub> exhibited the greatest deviation. Most current biodiesel esters used in diesel blending are in the carbon range of C<sub>14</sub>–C<sub>20</sub>, and reasonable accuracy by this SFC technique is expected. Accuracy could be

**Table IV. Aromatics Analyses of the Ester Test Solutions in Table III\***

Ester Spiked Fuel	Det. <sup>†</sup>	Calc.	Det.	Calc.	Det.	Calc.
	Mono-Arom.	Mono-Arom.	PNAs	PNAs	Total Arom.	Total Arom.
Diesel base fuel (no esters present)	29.5	30.4 (D5186)	4.5	4.3 (D5186)	34.0	34.7 (D5186)
Methyl-Oleate	25.6	26.5	4.2	4.1	29.8	30.6
Ethyl-Oleate	25.3	25.5	4.2	4.2	29.5	29.7
Ethyl-Myristate	25.4	26.5	4.3	4.0	29.7	30.5
Methyl-Decanoate	25.6	26.5	4.4	4.0	30.0	30.5
Methyl-Undecanoate	25.7	26.5	4.3	4.1	30.0	30.6
Methyl-Pentadecanoate	25.8	26.6	4.4	4.1	30.2	30.7
Methyl-Tridecanoate	25.4	26.3	4.3	4.0	29.7	30.3
Methyl-Dodecanoate	25.5	26.4	4.3	4.0	29.5	30.4
Methyl-Arachidate	25.7	26.6	4.3	4.1	30.0	30.7

\* Results are in mass % on a total sample basis.

<sup>†</sup> Det. = Determined. Calculated from the relative amounts of aromatics and the determined data for the mass % of esters (See Experimental section).

**Table V. Recovery Studies with Various Types of Biodiesels Spiked in Several Types of Conventional Hydrocarbon-Only Diesels**

Sample/Origin	Determined	Actual*	% Relative Error <sup>†</sup>
Diesel 1/Rapeseed	10.8 ± 0.1	10.6	1.9
Diesel 2/Tallow	10.4 ± 0.1	11.0	6.4
Diesel 3/Tallow	11.2 ± 0.1	11.1	0.9
Diesel 4/Soy Bean	10.8 ± 0.1	10.8	0.0
Diesel 5/ Rapeseed	10.7 ± 0.1	10.7	0.0

\* Actual = Calculated from the relative amounts of aromatics and the gravimetric data for the mass % of esters (See Experimental section).  
<sup>†</sup> Average % Relative Error = 1.8%.

improved further by calibrating with the actual esters or biodiesel used in blended diesel if this information were available.

Table IV summarizes the aromatic hydrocarbon analyses of the synthetic blends prepared with individual esters listed in Table III. The analysis of the ester-free “unspiked” starting diesel fuel using the backflush SFC system used for these solutions is included in the top line, and compared against results obtained from a second instrument with no backflush which met D5186 specifications. The overall data demonstrates that the determined values using the modified backflush SFC system and average RF are close to those calculated from the unspiked diesel corrected for dilution by the addition of the esters.

Table V summarizes accuracy data for a single diesel fuel spiked several times with different sources of “commercial” biodiesel esters. Generally, the results are reasonable, with a recovery relative average error of 4.2%. The diesel 2/tallow relative error is slightly higher, most likely due to preparation of blended diesel, because similar tallow biodiesel blended in diesel 3 yielded a lower error.

Tests with a variety of glycosides (e.g., mono-, di-, and tri-glycosides) of oils such as those derived from corn, soy bean, sunflower, pork (lard), and fish showed that these pre-trans-esterification feedstock materials did not interfere with the analysis. The latter pre-esterification materials are not likely to be present in significant amounts in the final esters used for blending, due to industry biodiesel specifications limiting the level of such components in the final ester product for blending.

## Conclusion

A precise and accurate SFC method for determining total methyl and ethyl esters in blended diesel fuels has been developed, with the simultaneous determination of hydrocarbon types. Such a technique should be useful in determining the final blend composition of blended commercial diesels. Furthermore, this technique can be implemented on existing instrumentation used for D5186 and/or D6550 analyses with simple modifications and calibration.

## Acknowledgment

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## References

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