Application News

Gas Chromatograph   Nexis™ GC-2030

Simulated Distillation GC Analysis of Biodiesel Blends by ASTM D2887 Procedure B

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User Benefits
◆ The distillation characteristics of fuels with boiling points from 55.8 to 538 °C can be investigated by accelerated analysis in accordance with ASTM D2887 Procedure B.
◆ Procedure B enables the measurement of biodiesel blends, such as B5, B10, and B20.
◆ LabSolutions™ simulated distillation GC software allows centralized management of data acquisition, distillation GC analysis, and report creation.

■ Introduction

Naphtha, gasoline, diesel, and other petroleum products derived from fossil fuels are used in different ways depending on the distribution of boiling points in their composition. In recent years, there has been a growth in petroleum product alternatives utilizing renewable energy sources such as biomass. The distillation method is typically used to measure the distribution of boiling points of components in such fuels. However, in the laboratory, the distillation method can require tedious and complicated operations, so methods that use gas chromatography to simulate the distillation method have been widely adopted.

ASTM D2887 is a test method that simulates the distillation method using capillary gas chromatography to analyze the distillation characteristics of fuels with boiling points ranging from 55.5 to 538 °C. Furthermore, Procedure B specifies analytical conditions that accelerate distillation analysis and can also be used to analyze biodiesel blends such as B5, B10, and B20.

This article describes an example of using the accelerated ASTM D2887 Procedure B to investigate the distillation characteristics of a biodiesel mixture.

■ Preparing Standard Solutions

Standard solution for checking system suitability and calibration was prepared by diluting each ASTM D2887-12 calibration standard 1 w/w% (20 components, Restek P/N 31674) by 40 fold with carbon disulfide. The ampoule was rinsed with solvent to prevent high-boiling components from remaining inside ampoules during calibration standard preparation. To account for the evaporation of the low-boiling components, a carbon disulfide mixture solution of about 0.025 w/w% containing C5, C6, and C10 was prepared separately. Low boiling point solution was prepared by cooling syringes and vials.

■ System Configuration and Consumables

The system configuration used for experiments is indicated in Table 1. To enable increasing temperature quickly, a high-powered GC model with a 230 V power supply is required. Heat-resistant septa were used to improve resistance to injection port temperatures. Plunger-in-needle type syringes suitable for injecting micro quantities and capable of on-column injection were used. An FID nozzle was used that is unlikely to cause flame extinguishment even at high column flowrates and has a 0.5 mm bore for resistance to contamination by high-boiling components.

Optional Simulated Distillation GC Analysis software that can be added to LabSolutions GC software was used for data analysis.

Table 1 System Configuration

Model:	Nexis GC-2030 (230 V model)/AOC™-30i
Injection Port:	OCI-2030 NX
Septum:	High Temp. septum (P/N: 221-48398-91)
Syringe:	0.5 µL NanoVolume on-column syringe (P/N: 227-35002-01)
Detector:	FID-2030 (with 0.5 mm dia. nozzle)
Column:	SH-MXT-1 7.5 m × 0.53 mm I.D., df= 1.50 µm (P/N: 227-36363-01)
Software:	LabSolutions Simulated Distillation GC Analysis Software

Table 2 Analytical Conditions

AOC-30i	
Injection Volume:	0.1 µL
Solvent Wash Times:	Pre 0, Post 3
Sample Wash Times:	1
Viscosity Comp. Time:	3.0 s
Sample Washing Volume:	0.3 µL

GC-2030	
Injection Temp. Program:	100 °C (0.5 min) → 35 °C /min→ 350 °C (2 min)
Carrier Gas:	He, 37 mL/min (Column flow mode)
Purge Flow:	3 mL/min
Column Oven Temp. Program:	40 °C → 35 °C /min → 360 °C
FID Temperature:	365 °C
Makeup Flow:	0 mL/min
Detector Gas:	H_2 32 mL/min, Air 200 mL/min
Filter Time Constant:	100 ms

■ Analytical Conditions

There are precautions to be taken when injecting samples with high boiling point components into the GC. For example, aspirating the sample at room temperature might cause high-boiling components to precipitate inside the syringe. Moreover, since the method requires aspirating and discharging ultra-micro sample quantities, it might not be possible to inject solution quantities accurately. Shimadzu AOC-30i autoinjectors enable sophisticated injection sequence settings for injecting samples in accordance with analytical objectives. Table 2 shows an example of AOC-30i analytical conditions for reducing high-boiling component residues inside syringes and achieving accurate injection volumes.

Analytical conditions for the GC unit were set in accordance with ASTM D2887 Procedure B. Due to the large column flowrate, the make-up gas flowrate was set at 0 mL/min. Typically, signal processing settings of the detector noise must be configured appropriately based on chromatogram peak widths. Suitable results were obtained for the given measurement parameters by setting the FID filter time constant to 100 ms.

■ System Suitability Test

As indicated in system suitability specifications, the prepared standard was used to confirm column resolution, skewness, and the relative response factor (RRF) for C10 (Fn). The chromatogram obtained from the standard solution is shown in Fig. 1. These results were obtained by subtracting a carbon disulfide blank from the sample. In Fig. 1, it was confirmed that the resolution calculated from the C16 and C18 peaks in accordance with ASTM D2887 was 8.0, which is within the 4 to 11 criteria specified. The skewness and RRF values for each peak are shown in Table 3. Skewness was within the 0.8 to 1.30 criteria for all alkanes except C5, and Fn values were within the 0.90 to 1.10 criteria. A retention time versus boiling point curve based on the results in Fig. 1 is shown in Fig. 2.
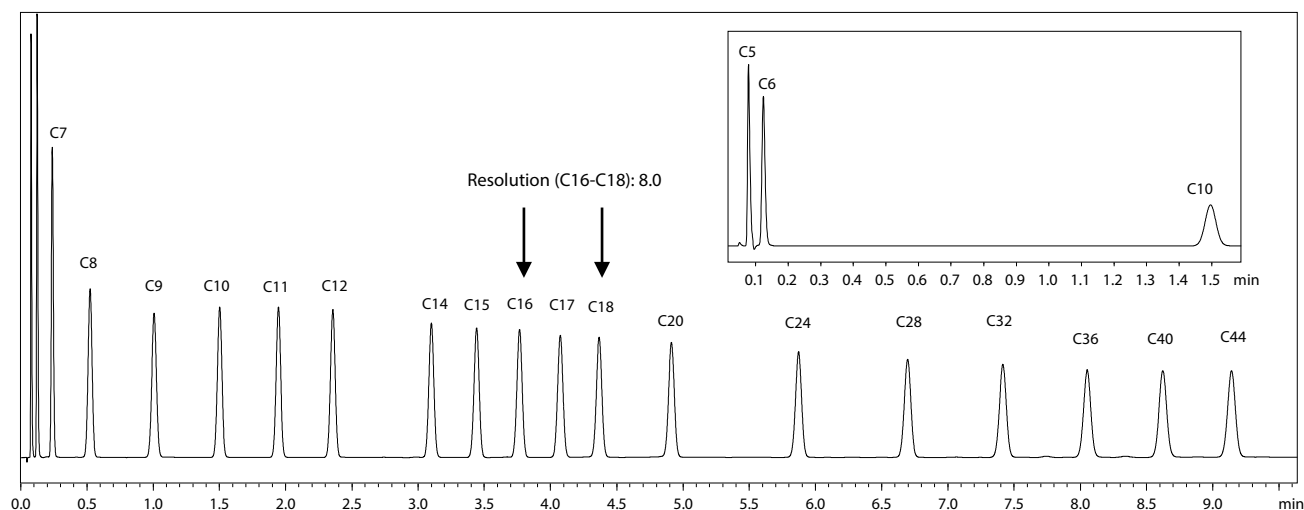
Fig. 1 Chromatogram of Calibration Standard Solution (Inset: Standard Solution for Low Boiling-Point Components)

Table 3 Confirmation of System Suitability

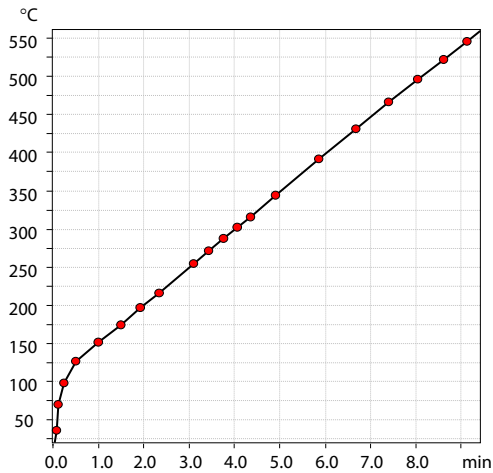| Alkane	Skewness	RRF: F_n
C5	-	1.06
C6	1.22	0.98
C7	1.13	1.04
C8	1.00	1.02
C9	0.97	1.01
C10	0.97	-
C11	0.97	1.00
C12	0.97	0.99
C14	0.97	1.03
C15	0.97	1.04
C16	0.98	1.03
C17	0.98	1.05
C18	0.98	1.04
C20	0.98	1.04
C24	0.98	1.06
C28	0.98	1.07
C32	1.02	1.07
C36	0.96	1.08
C40	1.00	1.03
C44	0.98	1.01

Fig. 2 Retention Time vs Boiling Point Curve

■ Reference Oil Check

Results from the reference oil check are shown in Fig. 3 and Table 4. The difference from the reference temperature and the within-laboratory accuracy values from 2 successive analyses were checked and good results were obtained.

Fig. 3 Chromatogram of Reference Oil (Lot 2)

Table 4 Example of Results from Reference Oil Check

Recovery (wt %)	Temp. (°C)	Criteria Temp. (°C)	Difference (°C)	Tolerance (°C)	Difference (n = 2) (°C)	Criteria Repeatability (°C)
IBP	113.2	115.3	-2.1	7.6	0	1.2452
5	151.2	151.2	0	3.8	-0.1	0.804
10	175.7	175.9	-0.2	4.1	-0.2	0.8
20	225.9	223.7	2.2	4.9	-0.1	0.8
30	261.3	259.2	2.1	4.7	-0.1	0.8
40	290.3	288.9	1.4	4.3	-0.1	0.8
50	312.8	312.1	0.7	4.3	-0.1	1
60	331.9	331.7	0.2	4.3	0	1
70	354.1	353.7	0.4	4.3	0	1
80	378.2	377.9	0.3	4.3	-0.1	1
90	407.1	406.8	0.3	4.3	0	1
95	428.8	428.3	0.5	5	-0.1	1.2
FBP	474.9	475.2	-0.3	11.8	-0.1	3.2

LabSolutions simulated distillation GC software can also be used to determine whether the reference oil check results passed or failed the criteria (Fig. 4).

Fig. 4 Results from Using LabSolutions Simulated Distillation GC Software to Check a Reference Oil

■ Measuring a Biodiesel Blends

The chromatogram in Fig. 5 was measured from a mixture of diesel oil with 20 % biodiesel derived from palm oil (National Institute of Advanced Industrial Science and Technology, P/N: 636-32071). In addition, distillation characteristics determined using the retention time versus boiling point curve in Fig. 2 are graphed over the chromatogram in light blue. Similar to the reference oil, good reproducibility was also obtained when measuring actual samples.
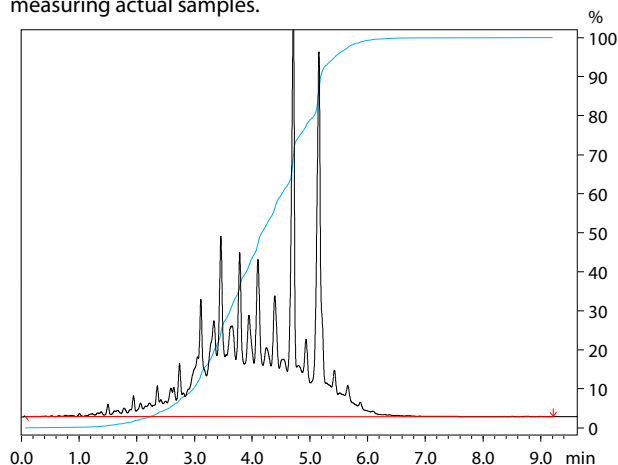

Fig. 5 Chromatogram and Distillation Characteristics (Light Blue)
of Biodiesel Blends

■ Measurement Using N_2 as an Alternative Carrier Gas

In Procedure B, N_2 can be used as an alternative carrier gas under the same system and analytical conditions. Fig. 6 compares standard sample chromatograms obtained with each carrier gas. As evident in Fig. 6, using an alternative carrier gas changes the retention times and peak shapes, even at identical flowrates, so particular care is required when checking system suitability and handling data.

System suitability test results using N_2 as the carrier gas are indicated in Table 5. Equivalent results were also obtained using helium. There were no problems with the reference oil check either.
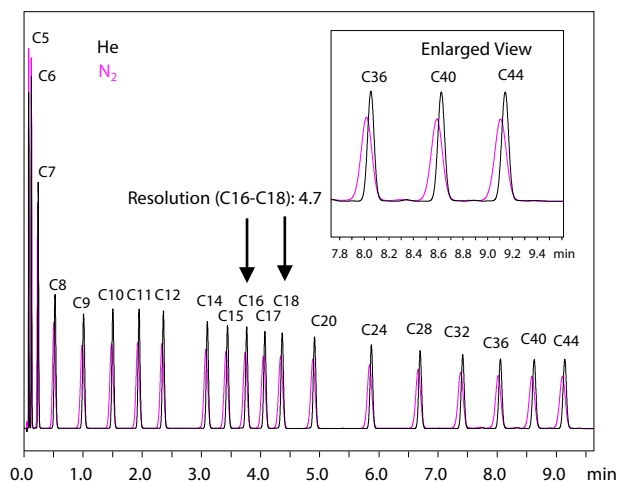

Fig. 6 Comparison of Standard Solution Chromatograms (Black: He; Pink: N_2)

Table 5 System Suitability Check Using N_2 Carrier Gas

Alkane	Skewness	RRF: F_n
C5	-	1.08
C6	1.30	1.00
C7	1.15	1.02
C8	1.02	1.01
C9	0.98	1.01
C10	0.97	-
C11	0.95	0.99
C12	0.97	0.98
C14	0.98	1.00
C15	0.98	0.99
C16	0.96	0.98
C17	0.93	1.00
C18	0.96	0.98
C20	0.93	0.98
C24	0.96	1.00
C28	0.94	1.02
C32	0.94	1.02
C36	0.95	1.04
C40	0.95	1.01
C44	0.96	0.99

Fig. 7 compares the distillation characteristics measured of biodiesel blends measured using alternative carrier gases. In this example, the graphs of distillation characteristics obtained using He and N_2 carrier gases are approximately identical, which indicates that the type of carrier gas resulted in a minimal difference for the given measurements. On the other hand, because alternative carrier gases can be expected to change peak patterns, it is necessary to be aware that the distillation characteristics obtained might differ from those obtained conventionally.
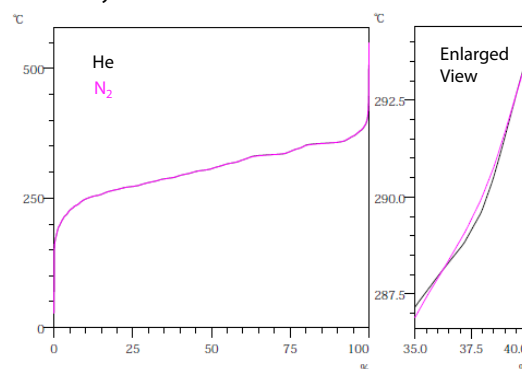

Fig. 7 Comparison of Biodiesel Blends Distillation Characteristics
(Black: He; Pink: N_2)

■ Conclusion

A Nexis GC-2030 system was used to investigate the distillation characteristics of biodiesel blends in accordance with the accelerated analysis method ASTM D2887 Procedure B. LabSolutions simulated distillation GC software was used to perform all steps from checking a reference oil to analyzing distillation characteristics centrally.

In addition, good measurement results were also obtained using N_2 as an alternative carrier gas. However, using an alternative carrier gas requires additional care because distillation characterization results might differ from the results using a conventional gas.

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