Boiling Point Range of Fatty Acid Methyl Esters Using the 7890A Gas Chromatograph, Low Thermal Mass (LTM) System, and 7693A Tower and Tray

Application Note

Hydrocarbon Processing

Author

Roger L. Firor
Agilent Technologies, Inc.
2850 Centerville Road
Wilmington, DE 19808
USA

Abstract

Two Agilent 7890A Series GC systems were used to determine the boiling point distribution of Biodiesel (B100 and B20). First, the standard oven was used to produce runs of about 16 minutes. This was followed by a 7890A equipped with an LTM system and 1 five-inch module which does an 8 minute run. Both systems used the Multimode inlet in temperature programmed split mode for sample introduction and a dual tower Agilent 7693A Automatic Liquid Sampler configuration with a 150-vial sample tray for sample prep and injection.

Agilent Technologies

Introduction

ASTM method D7398 describes procedures for determining the boiling point range distribution of pure biodiesel (B100) and biodiesel blends of B1 and higher. To ensure that unreacted triglycerides are detected, the gas chromatograph is temperature programmed to 400 °C. Only the procedures involving calibration and running of pure biodiesel and biodiesel blends will be demonstrated in this work. Some sample preparation is normally involved which includes dissolution of a Polywax 500 standard that involves heating, mixing, and sample dilution of the biodiesel. These sample preps can be largely automated using the Agilent 7693A Series injector and tray system. Simulated distillation software is then used to compute the boiling range distribution. A standard 7890A GC and a 7890A/Low Thermal Mass (LTM) was used to analyze the prepared samples.

Experimental

Standard 7890A System

Inlet:	Multimode, G3510, 325 °C (0 min) to 400 °C at 200 °C/min
Liner:	Single taper liner with glass wool, 5183-4647
7890A oven:	40 °C (0 min) to 400 °C at 15 °C/min
Column:	5M × 0.53 mm × 0.15 µm DB-HT SimDis, 145-1001
Flow:	Constant flow mode at 14 mL/min He
Injection:	0.1 µL split 4:1, PW500 standard, 1 µL

7890A/LTM System

Inlet:	Multimode, G3510, 220 °C (0 min) to 400 °C (2 min) at 300 °C/min
LTM column module:	5 m × 0.53 mm × 0.15 µm DB-HT SimDis
Module connections:	0.7 m deactivated ProSteel on inlet and outlet
7890A oven:	325 °C isothermal
LTM module program:	40 °C (0 min) to 400 °C at 50 °C/min
FID:	400 °C
Inlet pressure ramp:	2.5 psi (0 min) to 9.5 psi (1 min) at 1 psi/min
Injection:	0.1 µL, split 10 to 1, PW500 standard, 1 µL

Deactivated Ultimate Unions, part no. 3182-60580, are used with the LTM module for connection of the ProSteel retention gaps to the column ends.

The 7693A injectors are installed with the 150-vial sample tray which includes a mixer/barcode reader and heater compartment for the purpose of sample prep and injection. The front tower uses a 5-µL syringe and the rear tower uses a 250-µL syringe which requires the large syringe carriage G4521A.

Data is processed using ChemStation 4.01 and the Agilent SimDis software, part number G2887BA. Example sample preparation programs from the ChemStation are shown below for system calibration and biodiesel samples.

Sample Prep Programs Using the 7693A

Table 1. Sample Program for the Preparation of PW500 with C5-C18 Mix Added

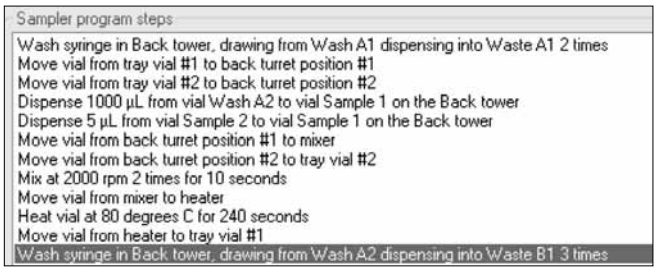
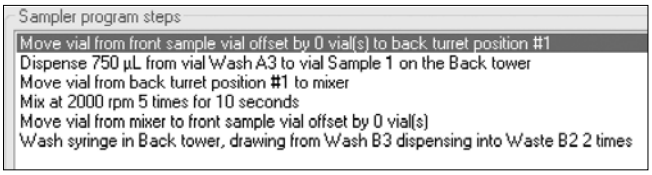


Table 2. Sample Program for the Dilution of a Biodiesel Sample Starting with 0.5 mL Biodiesel in a 2 mL Vial



Discussion

The calibration setup pane from the SimDis software is shown in Figure 1 for the LTM system. The mix of C5-C18 plus Polywax 500 gives a calibration from C_8 to C_{78}, covering the boiling point range of B100 (including unreacted components) and biodiesel blends. In Figures 1 and 2, calibration plot panes from the SimDis software with assigned carbon numbers are shown for the LTM and standard 7890A systems, respectively. Typical elution times for C_{70} are 7.5 minutes and 22 minutes for LTM and standard systems, respectively. Both show symmetric distributions indicating good inlet sample transfer with minimal discrimination. Figure 3 shows the chromatogram of a B20 soy-based biodiesel run on the LTM system. C_{16} and C_{18} fatty acid methyl esters can be seen above the diesel background.

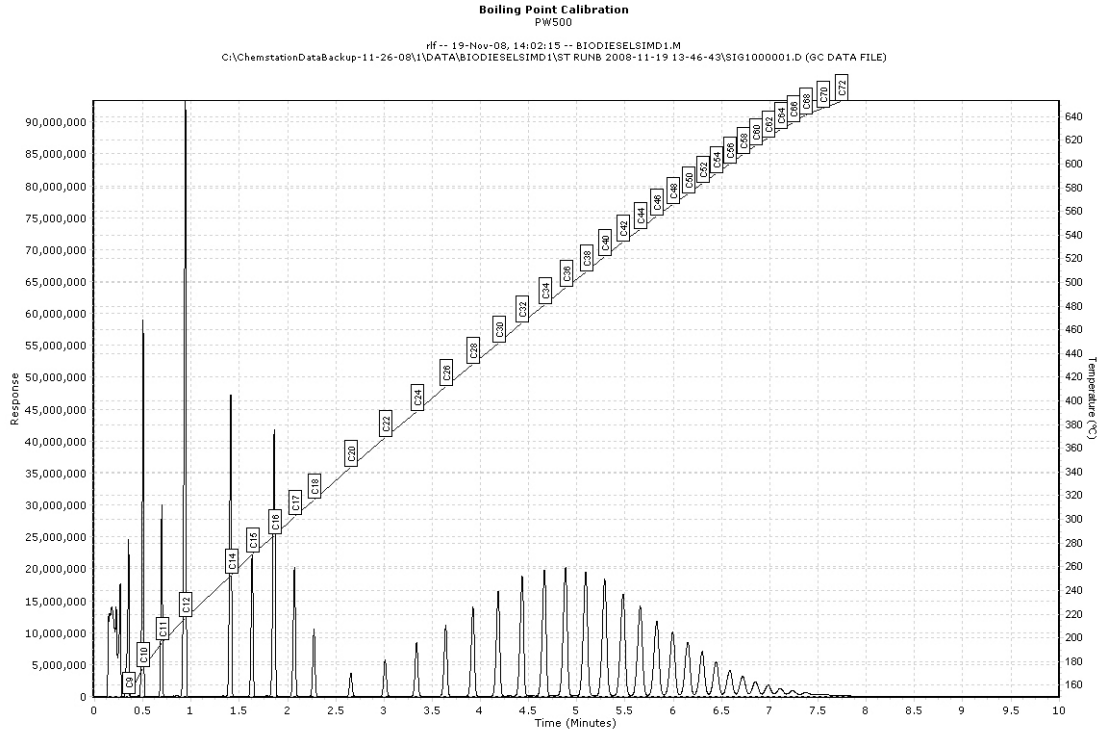


Figure 1. Calibration curve on LTM system from C9 to C72 prepared from PW500 and C5-C18 mix.

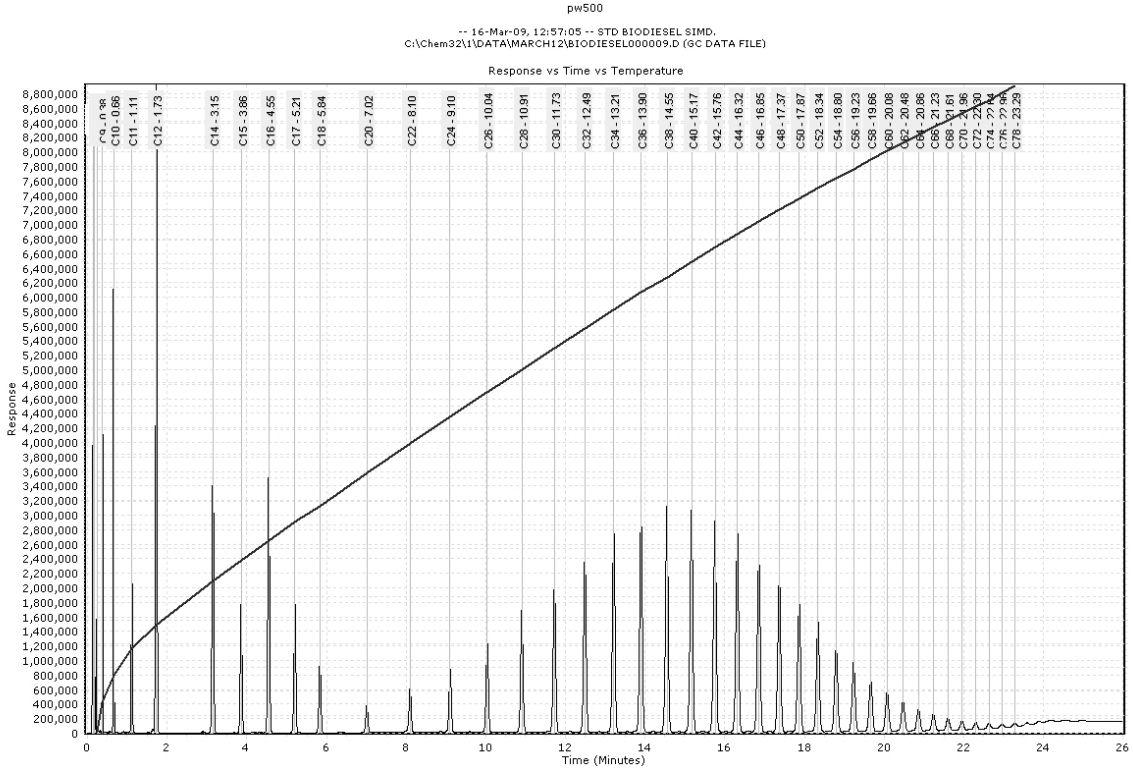


Figure 2. Calibration curve on standard 7890A GC.

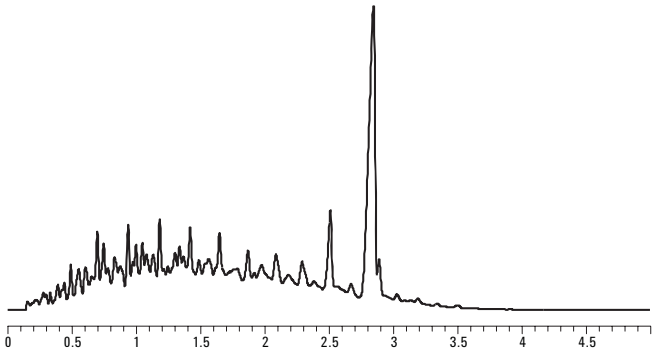


Figure 3. Chromatogram of B20 Soy based biodiesel using the LTM system.

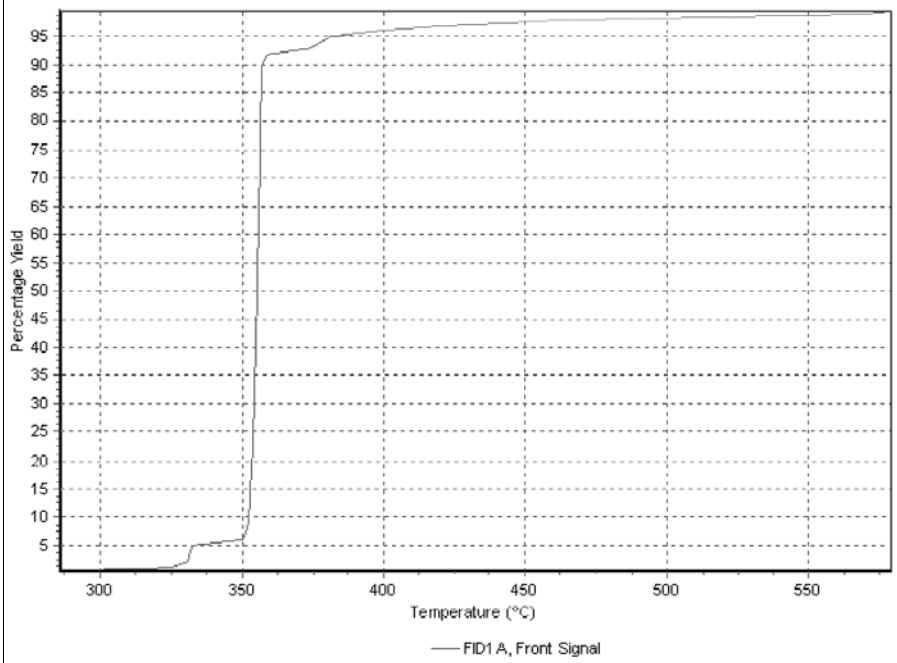
A boiling point distribution of B100 sourced from rapeseed is shown in Figure 4. In Figure 5, two chromatograms are shown in an overlay. These are both B100 production biodiesel from two different plants. Note the different ratios of the C_{16} group (6.6 min.) to the C_{18} group (7.5 min.) in these samples. Lastly, calculated boiling point distributions for both samples are shown in Figures 6 and 7.

Simulated Distillation Engineering Report

B100 rape

-- 16-Mar-09, 16:40:09 -- STD BIODIESEL SIMD
C:\Chem32\1\DATA\MARCH12\BIODIESEL000012.D (GC DATA FILE)

Simulated Distillation Report
Percentage Yield



Percentage Yield Table

	... Front Signa Temp. (Deg. C)
IBP: 0.5%	286.00
5.00%	332.00
10.00%	352.00
15.00%	353.00
20.00%	353.00
25.00%	354.00
30.00%	354.00
35.00%	355.00
40.00%	355.00
45.00%	355.00
50.00%	355.00
55.00%	356.00
60.00%	356.00
65.00%	356.00
70.00%	356.00
75.00%	356.00
80.00%	357.00
85.00%	357.00
90.00%	357.00
95.00%	381.00
FBP: 99.5%	579.00

Total ... Front Signa: (no RI

Agilent SimDis Report
3/17/2009 1:26:43 PM
Agilent Technologies

Calibration: C:\Chem32\1\DATA\MARCH12\BIODIESEL000009.D\FID1A.ch
Blank: C:\Chem32\1\DATA\MARCH12\BIODIESEL000008.D
No Qc Reference
SimDis Properties: custom properties

Figure 4. Boiling point distribution for rapeseed B100.

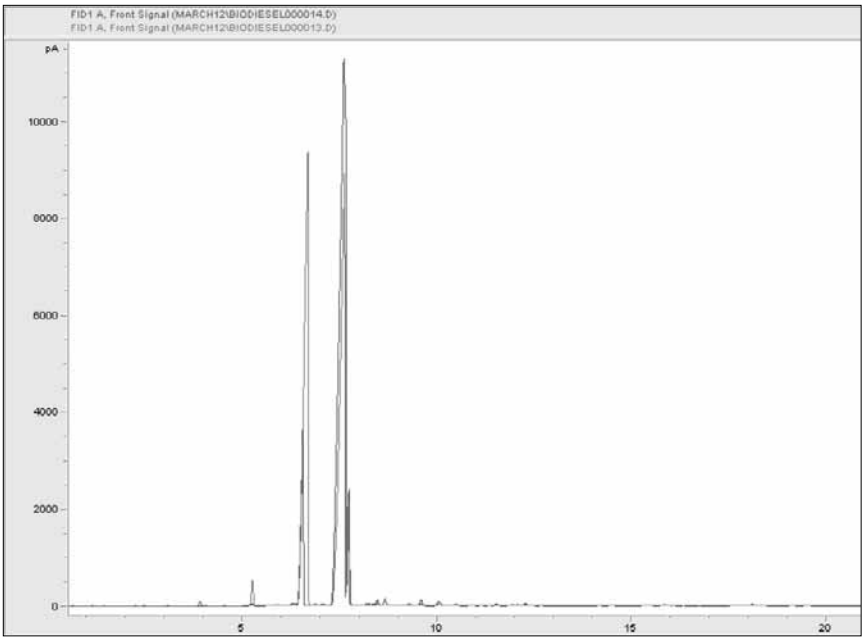


Figure 5. Overlay of two B100 samples from different producers. Both are soy based biodiesel. Producer A: signal 14, Producer B: signal 13.

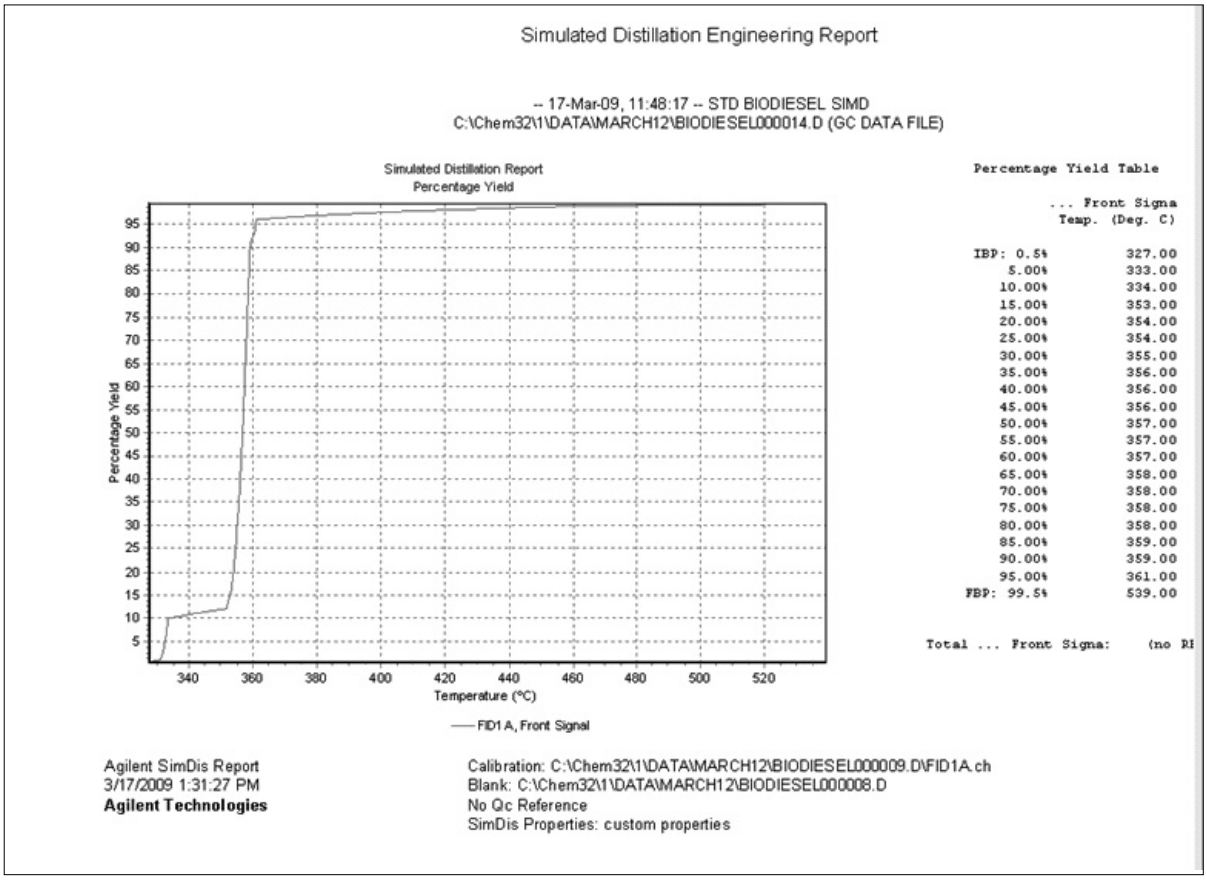


Figure 6. Boiling point distribution of B100, producer A.

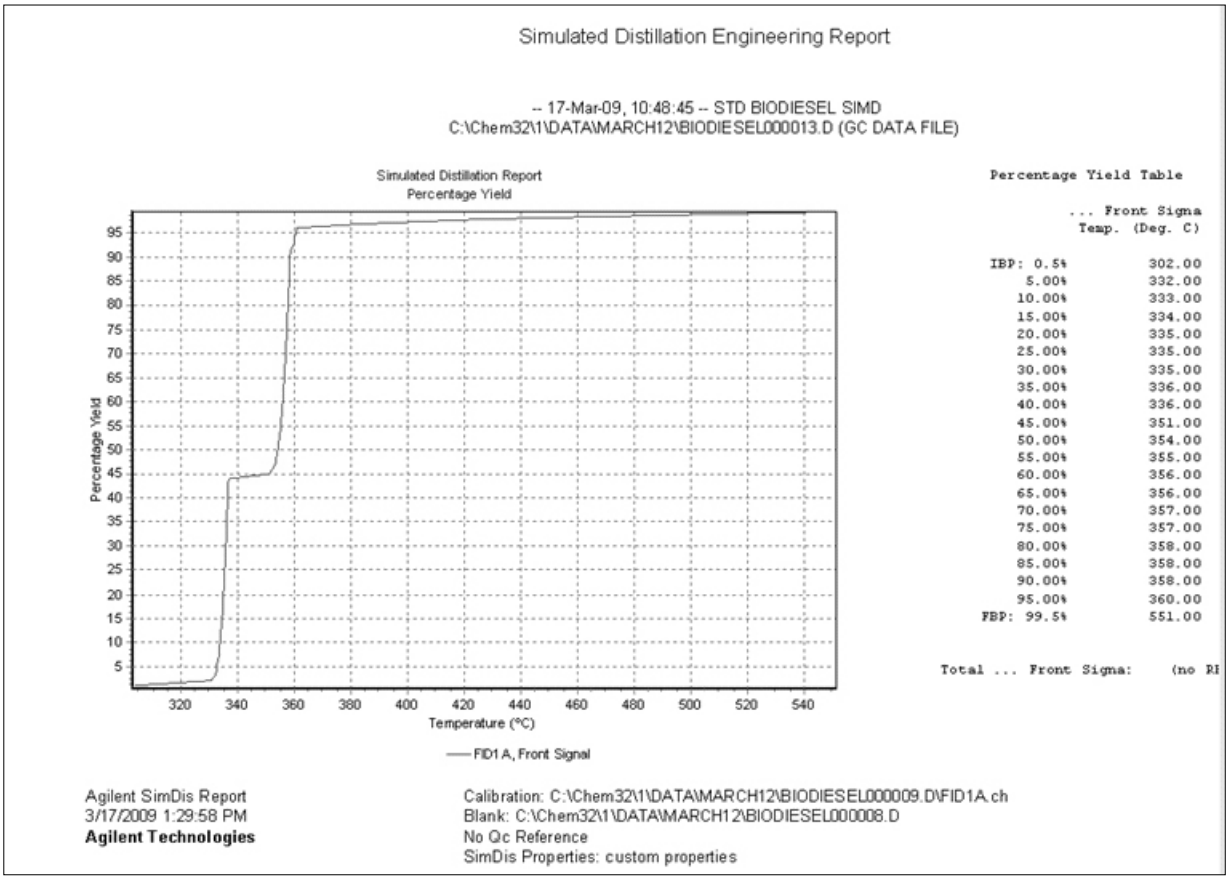


Figure 7. Boiling point distribution of B100 from producer B.

Summary

Simulated distillation is a powerful tool for characterization of biodiesel and biodiesel blends for a variety of starting oils. Besides determining the fatty acid methyl ester boiling point distribution, some information on the amount of un-reacted oil can be ascertained. The technique is also useful to determine authenticity and product consistency for quality control. The Agilent 7890A Series GC with the Agilent 7693A Automatic Liquid Sampler tower/tray system forms a complete analysis system from sample prep to boiling point distribution reporting using SimDis software integrated in the GC ChemStation.

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem.

www.agilent.com/chem

Printed in the USA
April 20, 2009
5990-3868EN

Agilent Technologies