SHIMADZU

Application Notes

Gas Chromatography

Methanol Content in Palm Biodiesel by Headspace - Gas Chromatography

Introduction

The rising price of petroleum-based oil increases the world's interest in alternative fuels. Biodiesel is one of the more popular alternative fuels. The interest in biodiesel arises partly due to the fact that it is a renewable fuel source. Pure biodiesel is basically a group of compounds called Fatty Acid Methyl Esters (FAME), which is made from plant oils or animal fats through a process called *transesterification* (see **Figure 1**). In transesterification, the triglycerides from these natural oils are reacted with an excess amount of methanol in the presence of a catalyst.

In Europe and in the United States, there are standards that specify the minimum purity of, or the maximum levels of contaminants in, a pure biodiesel (called B100) before it can be deemed suitable for use as an automotive fuel. EN 14214 and ASTM D6751 are two documents that describe the standard specifications that a pure biodiesel must meet before being used as fuel. These standard documents also specify the analytical methods that can be used to test the purity of, or the impurity levels in, a biodiesel.

Gas chromatography (GC) is one technique that can be used to test three of the specifications of a pure biodiesel, namely: 1) the FAME contents; 2) the total gycerol contents; and 3) the methanol content.

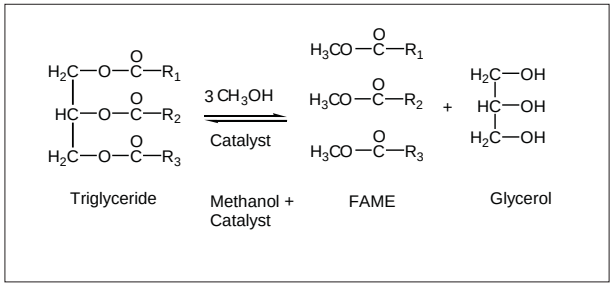

Figure 1. Transesterification process.

The amount of methanol in a biodiesel can be easily determined by using gas chromatographic (GC) method coupled with headspace extraction/sampling technique. EN 14110 standard method describes the procedure for this analysis. Here we describe the analysis of methanol in a palm olein biodiesel by using Shimadzu GC-2010 and AOC-5000 headspace autosampler.

Sample Preparation

The calibration standards were prepared according to the procedure described in BS EN 14110:2003. Basically, the calibration standards were prepared by dissolving a predetermined amount of methanol in a reference FAME (methanol-free FAME) and subsequently diluting this solution further by using the reference FAME. The concentrations of the methanol in the calibration standards are 0.01, 0.1, and 0.5% (m/m).

The reference FAME used in this experiment was prepared in our laboratory and purified through several cycles of washing with water. The washing cycle was repeated until the peak observed at

GC-2010AF Gas Chromatography for BioDiesel Analysis.

methanol retention time in the reference FAME chromatogram (obtained by using headspace-GC technique) showed an area count of 1500 or less or a height of 600 or less.

Analytical Conditions

GC	:	GC-2010AF
Headspace	:	AOC-5000
Column	:	Stabilwax-DA (Restek Corp.), 30m, 0.32mm i.d., 0.50µm df
Column oven temp.	:	60ºC (5 min) – 30ºC/min – 200ºC (4 min)
Injector temp.	:	150ºC
Carrier gas	:	Helium
Flow control mode	:	Constant linear velocity
Linear velocity	:	40 cm/sec
Injection mode	:	Split (split ratio 150:1)
Incubation temp.	:	80ºC
Incubation time	:	45 min (without agitation)
Injection volume	:	500µL
Syringe temp.	:	95ºC
Detector	:	Flame Ionization Detector (FID), 240ºC

Table 1. %RSD of peak area.

Run #	Level 1	Level 2	Level 3
1	46102	553167	2674695
2	45679	553585	2697961
3	45860	557018	2720603
4	46049	547544	2680439
5	45267	552410	2666259
Mean	45791	552745	2687991
%RSD	0.74	0.62	0.80

Table 2. %RSD of retention time.

	Level 1	Level 2	Level 3
1	2.73490	2.73307	2.73322
2	2.73483	2.73308	2.73273
3	2.73453	2.73290	2.73250
4	2.73455	2.73300	2.73270
5	2.73482	2.73322	2.73240
Mean	2.73473	2.73305	2.73271
%RSD	0.006	0.004	0.012

Results

Methanol was the only peak observed in the chromatogram of a palm biodiesel sample (see **Figure 2**). EN 14110 standard method recommends the use of automated headspace equipment for this analysis for achieving good repeatability and to allow the use of external standard calibration method. Compared to internal standard calibration method, external calibration method requires relatively simpler sample preparation. In this experiment, we obtained excellent linearity (r > 0.9999) for methanol in the specified calibration range (see **Figure 3**). Excellent repeatability for both peak area and retention times were also obtained, with an average %RSD of 0.72% and 0.007% for peak area and retention time, respectively. **Tables 2** and **3** show the repeatability of peak area and retention time, respectively.

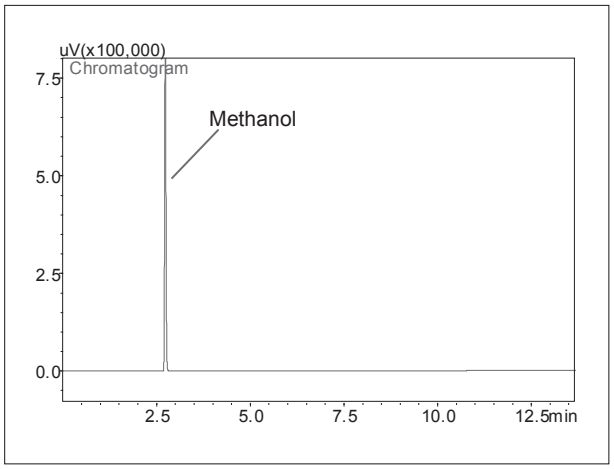

Figure 2. Chromatogram of a palm biodiesel sample.

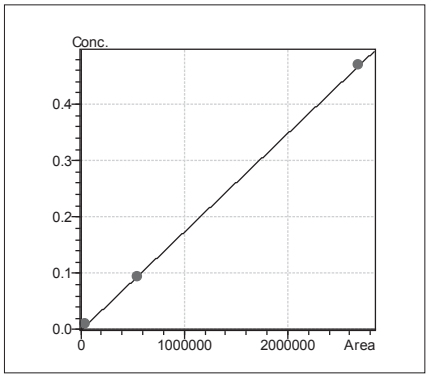

Figure 3. Calibration curve for methanol in biodiesel (r>0.9999).

Author: Hui-Loo Lai Chin, Novalina Lingga, Cynthia Lahey

SHIMADZU (Asia Pacific) Pte. Ltd.
Customer Support Centre
16 Science Park Drive #01-01, The Pasteur
Singapore Science Park I, Singapore 118227
http://www.shimadzu.com.sg
Tel: +(65) 6778-6280
Fax: +(65) 6778-2050

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