Republic of the Philippines
DEPARTMENT OF ENERGY

In line with the objectives of the Clean Air Act of 1999 and to the implementation of the Biofuels Act of 2006, the Department of Energy's Technical Committee on Petroleum Products and Additives (DOE/TCPPA) through its Technical Working Group 1 (TWG1) reviewed and revised the standard test method **DPNS/DOE TM 01:2015 - Determination of ester and lauric acid content in fatty acid methyl esters (FAME) by gas chromatography (Modified EN 14103).**

This standard test method is an update/review of PNS/DOE TM 01:2009 with revision made on the procedure to make the same applicable to any Gas Chromatography (GC) brands in general. Also the modified test method has been tested to verify blend higher than 2% (v/v%).

Enclosed is a copy of the draft standard for your comments. It is suggested that any proposed change to the specifications be supported with explanations/ justifications.

We appreciate receiving your comments/positions thru mail or email at products@doe.gov.ph on or before April 2, 2015 for it to be considered in the finalization of the standard. Non- receipt of your comments on the specified date shall be construed as an approval of the draft standards.

Thank you for your usual cooperation.

Very truly yours,

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DPNS/DOE TM 01:2015
ICS xx.xxx.xx

Determination of ester and lauric acid content in fatty acid methyl esters (FAME) by gas chromatography (Modified EN 14103)

Foreword

This Philippine National Standard PNS/DOE TM 01:2015 - Determination of ester and lauric acid content in fatty acid methyl esters (FAME) by gas chromatography was prepared by the Department of Energy's Technical Committee on Petroleum Products and Additives (DOE/TCPPA) through its Technical Working Group 1 (TWG 1).

Through its technical expertise, Chevron Philippines Incorporated again took the lead role in the review along with the other members of the TWG composed of oil and oleochemical companies. This standard test method is an update of PNS/DOE TM 01:2009 which was also prepared by a TWG headed similarly by Chevron Philippines.

This standard addresses the technical requirements of CME for a more suitable test method thereby ensuring a proper and effective fuel quality standard which is a continuing commitment of the Department. Specifically, this standard establishes further the method reliability for the determination of ester and lauric content of biodiesel (CME) and provides wider coverage for biodiesel blends higher than two percent (2%). Further, it made adjustment on the instrumental configuration for general gas chromatography application compared to a specific type of GC for the 2009 edition.

This standard test method cancels and replaces PNS/DOE TM 01:2009.

In the preparation of this document, BS EN 14103:2004 Fat and oil derivatives - Fatty acid Methyl Esters (FAME) - Determination of ester and linolenic acid methyl ester contents was considered.

This entire standard is subject for review and/or revision when necessary.

Introduction

The original test method, EN14103 has been modified to ensure the separation and detection of C6 to C18 methyl esters of CME or Coconut Methyl Ester.

The following modifications have been done on the original test method:

One-column system

1. Higher Final Temperature (200 °C vs. 310 °C);
2. Use of Temperature Programming; and
3. Use of Methyl tridecanoate/methyl undecanoate as internal standard.

The one-column system allows one to verify if the ester content is at least 96.5% (m/m%) and the methyl laurate content is at least 45% (m/m%).

Two-column system

1. The scope of the method has been expanded to cover both pure and blended CME;
2. Use of two columns, two kinds of stationary phase, to separate the CME or fatty acid methyl ester (FAME) portion of the sample from the non-FAME portion of the sample;
3. Cut part of the sample to the second column for better separation
4. Temperature programming; and
5. Use of Methyl tridecanoate/methyl undecanoate as internal standard.

The two-column system also allows one to verify if the ester content is at least 96.5% (m/m%) and the Methyl laurate content is at least 45% (m/m%). The modified method has been tested to verify blends of 2% (v/v%) and higher.

DRAFT PHILIPPINE NATIONAL STANDARD **DPNS/DOE TM 01:2015**

Determination of ester and lauric acid content in fatty acid methyl esters (FAME) by gas chromatography

1 Scope

This test method covers the determination of the percentage of methyl esters of fatty acids and lauric acid present in pure coconut methyl ester (pure CME) for a one-column system and both for pure coconut methyl ester and coconut methyl ester blended diesel oils for a two-column system.

2 Summary

Gas chromatography with a split/splitless inlet and FID is used to determine the ester and lauric acid methyl ester of fatty acid methyl esters (FAME) intended for use as pure biofuel or as a blending component for heating and diesel fuels. The method is suitable for FAME containing methyl esters between C6 and C24. Calibration is done by using methyl tridecanoate or methyl undecanoate internal standard. The analysis of fatty acid methyl ester (FAME) content is accomplished either by one-column or two-column system. The one-column system is used to separate the components of pure FAME as samples blended with Diesel will have interfering peaks or diesel components. The two-column system is used to analyze the fatty acid methyl ester (FAME) content in blended biodiesel samples by using gas chromatographic (GC) system wherein the primary column separates most of the petroleum hydrocarbons from the FAMEs. The FAMEs are selectively transferred to the secondary column, where they are resolved from the remaining hydrocarbon matrix. The instrument is calibrated using the total response of all separated FAME peaks.

3 Analysis

Since this modified method covers two types of GC analysis, the general requirement for both analytical approaches would be that the instrument be able to achieve and maintain the conditions listed in their respective class of analysis. Their respective analysis programs should be separate, detect and quantitate the ten major components of CME (C6, C8, C10, C12, C14, C16, C18:0, C18:2, C18:3).

4 Materials

4.1 Screw cap vials with PTFE-faced septa, 10-ml and 2-ml capacity

4.2 Volumetric flasks 50-ml capacity

4.3 Pipettes 1-ml and 5-ml capacity

5 Reagents

Use only reagents of recognized analytical grade, unless specified.

5.1 Heptane

5.2 **Methyl tridecanoate or methyl undecanoate,** 10 mg/ml solution

Accurately weigh approximately 500 mg of methyl tridecanoate or methyl undecanoate in a 50 ml volumetric flask and make up to mark with n-heptane.

5.3 **Methyl tridecanoate or methyl undecanoate,** 2 mg/ml solution

Accurately weigh approximately 100 mg of methyl tridecanoate or methyl undecanoate in a 50 ml volumetric flask and make up to mark with n-heptane

6 Apparatus

Usual laboratory Gas Chromatograph capable of achieving and maintaining the conditions listed for a one-column system or a two-column system below:

Analysis conditions for a one-column system:

Configuration	Single column, Split/Splitless injection
Equilibrium time	5 min.
Injector type	Split 2:1
Flow Rate	20 ml/min to 100 ml/min
Temperature	250 °C
Column	Capillary column, polar (Polyethylene glycol)
Length	30 m
Internal diameter	250 micrometers
Film Thickness	0.5 micrometer
Carrier Gas	Helium
Pressure	30 -100 kPa
Detector	FID
Detector temp	250 °C
Oven temperature	Temperature program: 20 °C/min to 210 °C
Internal standard	Methyl tridecanoate/methyl undecanoate

Analysis Conditions for a two-column system (with cutting):

Configuration	Double column, Split/Splitless injection, with switch
Equilibrium time	5 min.
Injector type	Split 2:1
Flow Rate	20 ml/min to 100 ml/min
Temperature	250°C
Column 1	Capillary column non polar (5%-Phenyl methyl polysiloxane)
Length	15 m
Internal diameter	250 micrometers
Film thickness	0.1 micrometer
Column 2	Capillary column, polar (Polyethylene glycol)
Length	30 m
Internal diameter	250 micrometers
Film thickness	0.5 micrometer
Carrier gas	Helium
Pressure	30 – 100 kPa
Detector	FID
Detector temp	250°C
Oven temperature	Temperature program 20°C/min to 210°C
Internal standard	Methyl tridecanoate/methyl undecanoate

7 Sampling

Sampling is not a part of this method. Please refer to PNS ASTM D 4057 for the correct sampling procedure.

8 Sample preparation

8.1 Accurately weigh 50 mg of sample in a 2-ml screw cap vial

8.2 Add 1 ml internal standard (2.0 mg/ml for FAME-blended diesel oils and 10.0 mg/mL for pure CME).

9 Chromatographic analysis

This standard covers at least four (4) different types of gas chromatographs and a detailed procedure cannot be provided. In lieu of an operating procedure, please refer to the particular instrument's documentation.

Refer to the instrument's documentation for the proper procedure for setting up the instrument so that the required conditions could be attained.

Refer to the instrument's operating manual for the proper procedure for conducting a test

10 Determination of Ester content

The ester content, expressed as mass fraction in percent, is calculated using the following formula:

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{(C_{EI})(V_{EI})}{m} \times 100\%$$

where:

$\sum A$ is the total peak area from the methyl ester in C6 to that in C18:3;

A_{EI} is the peak area corresponding to methyl tridecanoate/methyl undecanoate;

C_{EI} is the concentration, in mg per ml, of methyl tridecanoate/methyl undecanoate solution being used;

V_{EI} is the volume, in ml, of methyl tridecanoate/methyl undecanoate solution being used and;

m is the mass in mg of the sample.

Express the result to two decimal places.

To express the result in Volume %, calculate the individual volume percent of the methyl ester express as

Volume % = (conc in mass % x density of sample in kg/l) / density of individual methyl esters in kg/l)

Total volume percent is the sum of individual volume percent of all the FAMEs.

11 Determination of lauric methyl ester

The lauric acid methyl content, L, expressed as mass fraction in percent, is calculated using the following formula:

$$L = \frac{A_L}{\sum A - A_{EI}} \times 100\%$$

where:

$\sum A$ is the total peak area from the methyl ester in C6 to that in C18:3;

A_{EI} is the peak area corresponding to methyl tridecanoate/methyl undecanoate; and

A_L is the peak area corresponding to lauric acid methyl ester.

Express the result to one decimal place.

12 Precision

Initial Inter-laboratory testing has been done for pure CME and up to 5% biodiesel to verify, validate and improve the precision data. For future reference, a study should be conducted to determine the effect of increasing the concentration of internal standard C13 during B100 analysis since the peak area of C13 is small compared to the peak area of C12. Repeatability and Reproducibility values for pure CME and blended diesel are presented below.

13 Repeatability

The absolute difference between test results, obtained using the same method on identical test materials in same laboratory by same operators using same equipment, shall not be greater than:

For ester content		**For methyl laurate content**	
B5 biodiesel	0.11	B5 biodiesel	0.11
B100	0.57	B100	0.48

13 Reproducibility

The absolute difference between two single test results, obtained using the same method on identical test materials in different laboratories by different operators using different equipment, shall not be greater than:

For ester content		**For methyl laurate content**	
B5 biodiesel	0.45	B5 biodiesel	0.37
B100	2.74	B100	1.56

Annex 1

Results of the 2nd Biodiesel correlation

TWG 1 Interlaboratory Correlation
Samples: B100/B5

	B100 (Pure CME)		B5 (Blended ADO)	
	FAME	Methyl Laurate	FAME	Methyl Laurate
AVERAGE	96.7	46.1	5.2	2.5
STANDARD DEVIATION	0.9	0.6	0.2	0.2
T – Value	2.9	2.8	2.5	2.3
REPRODUCIBILITY	2.74	1.56	0.45	0.37
LOWER Rejection Value	94.0	44.6	4.8	2.2
HIGHER Rejection Value	99.5	47.7	5.7	2.9
OUTLIER	None	None	None	None
REPEATABILITY	0.57	0.48	0.11	0.11

References

PNS ASTM D 4057 (ASTM published 2006 reapproved 2011) Practice for Manual Sampling of Petroleum Products

EN 14103:2004 Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of esters and linolenic acid methyl ester contents

Abbreviations

PNS	-	Philippine National Standards
ASTM	-	American Society for Testing and Materials
EN	-	Euro Norm (Regional Standard European Countries)

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