

# Application Notes

## Gas Chromatography

### Analysis of Methyl Laurate Content In Low Concentration Biodiesel Blends (B1, B2) with Multidimensional Gas Chromatography System (Part I)

#### Introduction

The fossil fuels importing country like Philippines is actively implementing a long-term Alternative Fuels Program to develop indigenous and renewable energy fuels for long term energy security, which will be a pillar for the country's sustainable growth. Biodiesel Program, which is one sub-program of The Alternative Fuels Program, mandates a minimum 1% biodiesel blend (B1) in all diesel fuels sold in the country. It might be increased to 2% biodiesel blend (B2) within two years from the effective date of the Act.<sup>[1]</sup>

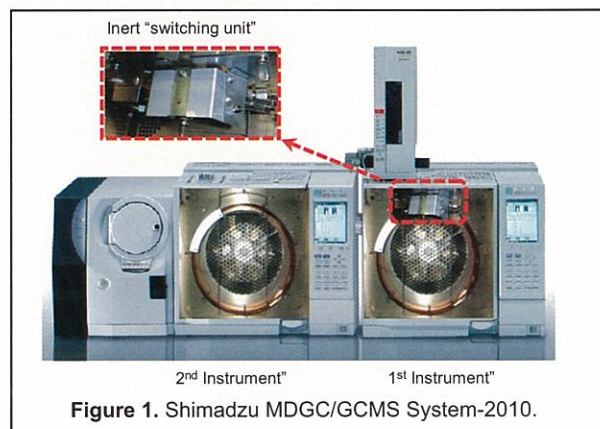
Biodiesel fuel is produced from renewable sources such as vegetable oil or animal fat through transesterification into fatty acid methyl esters (FAMES) mixture. Pure biodiesel is called B100. The Draft of Philippines National Standard DPNS/DOE QS 002:2007 specifies that the Methyl Laurate (C12ME) content in the pure (B100) biodiesel should be a minimum of 45% by mass.<sup>[2]</sup> This is a typical characteristic of biodiesel produced from coconut oil. Meanwhile, the standard DPNS/DOE QS 004:2008 requires that the B2 biodiesel blend (i.e. diesel fuel with 2% v/v biodiesel) that is sold in the country by 2009 should have a minimum of 0.8% by mass of C12ME.<sup>[3]</sup> This is to ensure that the B100 biodiesel used in the biodiesel blend is produced from the main local indigenous supply, the coconut oil. The FAMES mixture derived from coconut oil is called as "Coconut Methyl Ester (CME)" or "Coco-Biodiesel" locally.<sup>[4]</sup> The total FAME content of commercial B1 and B2 biodiesel blend could be easily determined by rapid analysis method with HATR-FTIR technique.<sup>[5]</sup> However, by only checking the C12ME content in these biodiesel blends, the use of CME in B1 and B2 biodiesel sold in the local market could be confirmed.

B1 & B2 biodiesel blends are complicated mixtures comprising of middle distillates (hydrocarbons range from C9~C23), FAMES and other minor impurities. At present, to analyze C12ME, the total

FAMES fraction is first extracted from diesel by atmospheric pressure liquid chromatography on a silica micro column. Then, only the isolated FAMES fraction is characterized by GC-FID.<sup>[6]</sup> Besides the target analyte extraction recovery issue, the sample preparation process is time consuming and significantly increases the consumables cost of the current analysis method.

C12ME is commonly co-eluting with other hydrocarbon peaks of diesel in single-dimension (1D) GC separation. Two-dimensional (2D) GC technique offers a superior separation and an alternative for this application. Shimadzu Multi-Dimensional Gas Chromatography system (MDGC) is ideal for this complex mixture. This dual-oven system is equipped with an inert "switching unit" and utilizes the mechanism of Multi-Deans Switching technology. The dual-oven characteristic allows 2D separation by using two columns of different characteristics, each operated under independent temperature programs.

The goal of this experiment is to develop a 2D GC method for direct injection of biodiesel blends employing a heart-cut technique to isolate C12ME from unresolved hydrocarbon components in the B1 and B2 biodiesel blends. The needs of 2D separation and dual oven 2D separation for this application were investigated.





## Experimental

### Samples and Standards

Four diesel samples named as SS, ES, PS and CS were obtained from different brands in the market and were used as matrices of the spiked samples. C12ME (Methyl Laurate) standard of 98.8% purity was purchased from ChemService, Inc, USA.

### Instruments and Analysis Conditions

An MDGC/GCMS-2010 equipped with a liquid auto-injector, AOC-20i and a set of GC/GCMS/MDGCsolution Workstation (Shimadzu Corporation, Kyoto, Japan) were used for this experiment. The system configuration is shown in Fig. 1. This system consists of a GC-FID (defined as 1<sup>st</sup> Instrument), equipped with an inert flow switching element (namely "switching unit") and linked with a heated interface (230°C) to a GC-qMS (defined as 2<sup>nd</sup> Instrument). A pair of column with combination of non-polar and polar columns were used in these methods development located in 1<sup>st</sup> and 2<sup>nd</sup> instrument respectively. The conventional MDGC methods with 0.25mm ID capillary capillary columns analysis conditions are listed in Table 1.

## Results

The upper diagram of Fig. 2 shows the chromatogram profiles obtained from the 1<sup>st</sup> column for 4 different brands of diesel and a particular diesel (CS) spiked with 1% C12ME. Diesel from different brand or sources are slightly different in its hydrocarbons composition. The lower diagram is an enlargement the upper diagram; the highlighted area shows the overlapping zone of C12ME with the matrix. This indicates that the target analyte might be able to be separated from the matrix with an optimized method in a particular diesel sample but it could co-elute with the matrix in other diesel samples. This means, it might not be possible to have a common analysis method by using single dimension separation that is optimized for various types of biodiesel blends.

To enhance the separation of C12ME in B1 and B2 biodiesel blend, the unresolved C12ME elution band from the 1<sup>st</sup> column (non-polar column) was selectively heart-cut by using the "switching unit" to the 2<sup>nd</sup> column (polar column) for further, 2<sup>nd</sup> dimension, separation. The details of the heart-cutting mechanism of the "switching unit" and its operation by MDGC solution software were described in the literature.<sup>[7,8,9]</sup>

The results of the analysis of CS diesel sample that was spiked with 0.5% C12ME are shown in Fig. 3; the upper diagram shows the chromatograms obtained from the 1<sup>st</sup> column, and the lower

diagram shows the TIC (total ion chromatograms) obtained from the 2<sup>nd</sup> column. The data were obtained by using four analysis conditions (listed in Table 1). The unresolved C12ME elution band was transferred to the 2<sup>nd</sup> column according to the cut time specified in the methods. TIC (a), (b) and (c) in Fig. 3 (lower diagram) were obtained by using analysis conditions (a), (b) and (c), where the oven temperature programming for the 1<sup>st</sup> and 2<sup>nd</sup> columns were identical. Under these conditions, C12ME could not be fully separated from the co-eluting hydrocarbons matrix components. This is because C12ME eluted close to the highest density of unresolved hydrocarbons complex mixture region of the diesel sample on a non-polar column. This demonstrates that it is very difficult to optimize the method to achieve the desired 2D separation for a real complex sample, by using a single-oven MDGC system.

On the other hand, TIC (d) in Fig. 3 shows that a perfect separation could be obtained by using a dual-oven system with independent oven temperature programming (see Table 1, conditions (d) for analysis conditions).

Another advantage of using a dual-oven MDGC system for this application is that the high boiling point components from biodiesel blends could be baked out from the non-polar column by using higher temperatures in the 1<sup>st</sup> oven (> 300°C), while keeping the polar column below its temperature limit (normally 230°C), thus preventing unnecessary column damage in the 2<sup>nd</sup> oven.

## Conclusions

Analysis of C12ME in low concentration biodiesel blends such as B1 or B2 is a great challenge due to the complexity of the sample matrix. Conventional 1D or even single-oven 2D separation could not provide sufficient resolution for the determination of C12ME content using a universal GC detector such as FID. However, it could be well separated by using a dual-oven MDGC system without sample preparation.



Table 1. Analysis Conditions of MDGC

|                       | Conventional MDGC (0.25mm I.D. columns)    |                                  |                                       |                                       |
|-----------------------|--|----------------------------------|---------------------------------------|---------------------------------------|
| Analytical conditions | a  | b                                | c                                     | d                                     |
| 1st instrument        |  |                                  |                                       |                                       |
| 1st Column            |  |                                  |                                       |                                       |
| type                  | Rtx-5SilMS; non-polar (Resteks Corp., USA) |                                  | Rtx-1; non-polar (Resteks Corp., USA) |                                       |
| dimension             | 15 m x 0.25 mm I.D., df=0.1 µm             |                                  | 30 m x 0.25 mm I.D., df=0.25 µm       |                                       |
| Oven temperature      |  |                                  |                                       |                                       |
| Initial temperature   | 50°C (0 min)                               |                                  | 70°C (0 min)                          |                                       |
| Program 1             | 50°C @ 20°C/min ~ 230°C (13 min)           | 50°C @ 10°C/min ~ 230°C (11 min) | 70°C @ 10°C/min ~ 250°C (13 min)      | 70°C @ 10°C/min ~ 220°C (0 min)       |
| Program 2             |  |                                  |                                       | 220°C@35°C/min ~ 300°C (6 min/11 min) |
| Carrier gas           |  |                                  | He                                    |                                       |
| flush inlet pressure  | 190 kPa                                    |                                  | 190 kPa                               |                                       |
| Switching gas         | He, 170 kPa                                |                                  | He, 120 kPa                           |                                       |
| heart cut time        | 7.97 ~ 8.11 min                            | 12.43 ~ 12.58 min                | 13.74 ~ 13.94 min                     |                                       |
| INJ temperature       |  |                                  | 250°C                                 |                                       |
| FID temperature       |  |                                  | 320°C                                 |                                       |
| Injection             |  |                                  |                                       |                                       |
| mode                  |  |                                  | Split                                 |                                       |
| split ratio           | 200  |                                  | 100                                   |                                       |
| volume                |  |                                  | 0.2 µL                                |                                       |
| 2nd instrument        |  |                                  |                                       |                                       |
| 2nd Column            |  |                                  |                                       |                                       |
| type                  | Stabilwax; polar (Resteks Corp., USA)      |                                  |                                       |                                       |
| dimension             | 30 m x 0.25 mm I.D., df=0.25 µm            |                                  |                                       |                                       |
| Oven temperature      |  |                                  |                                       |                                       |
| Initial temperature   | 50°C (0 min)                               | 50°C (0 min)                     | 70°C (0 min)                          | 50°C (15 min)                         |
| Program 1             | 50°C @ 20°C/min ~ 230°C (13 min)           | 50°C @ 10°C/min ~ 230°C (11 min) | 70°C @ 10°C/min ~ 250°C (13 min)      | 50°C @ 30°C/min ~ 220°C (2 min)       |
| GC I/F temperature    | 230°C                                      |                                  |                                       |                                       |
| DET, qMS              |  |                                  |                                       |                                       |
| I/f temperature       | 250°C                                      |                                  |                                       |                                       |
| IS, temperature       | EI, 200°C                                  |                                  |                                       |                                       |
| Acquisition           | Scan, M/Z 40~350                           |                                  |                                       |                                       |
| Scan speed            | 1666 amu/sec                               |                                  |                                       |                                       |

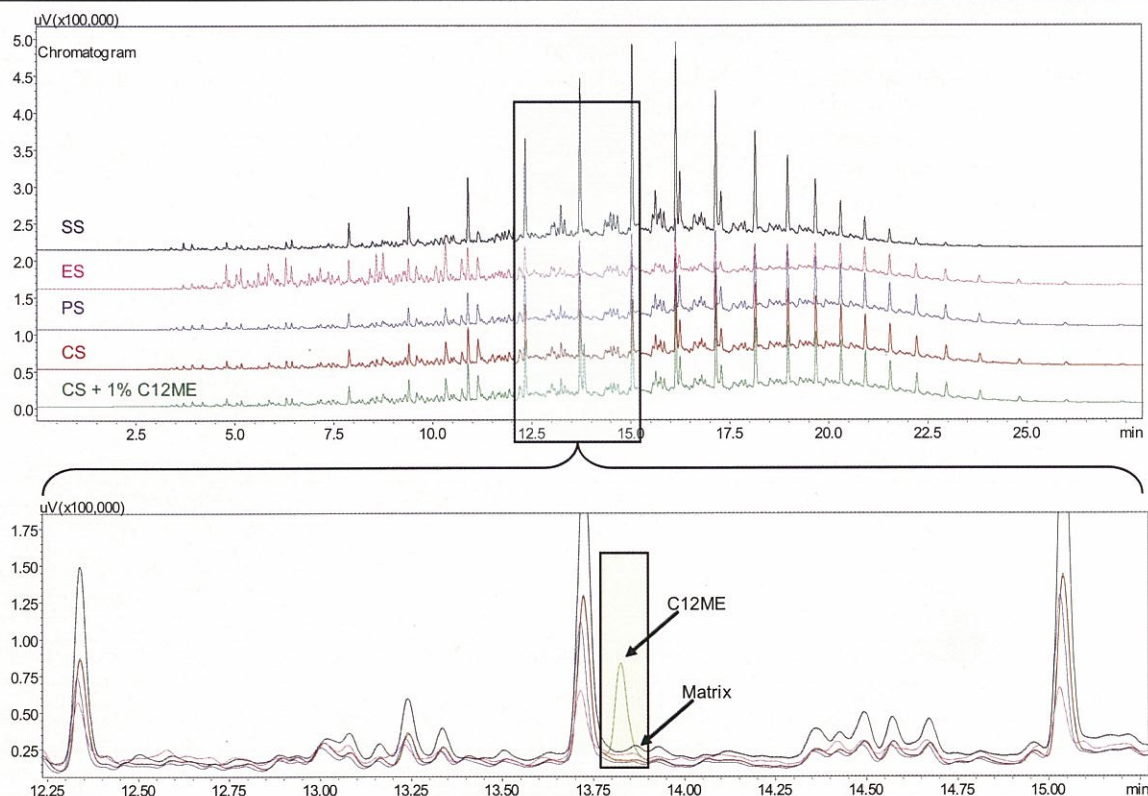
## References

- [1] <http://www.doe.gov.ph/Laws%20and%20Issuances/ra.asp>
- [2] Draft Philippines National Standard (DPNS/DOE QS 002:2007): Fuel – FAME (B100) -Specification.
- [3] Draft Philippines National Standard (DPNS/DOE QS 004:2008): Petroleum product – FAME blended diesel oil – Specification.
- [4] <http://www.doe.gov.ph/AF/Biodiesel.htm>
- [5] Joyce Lim, Takako Tokura, SAP FTIR Application Notes: Analysis of Biodiesel Blends by FTIR, AD-0020-FTIR (2008).
- [6] British Standard BSEN 14331:2004 (E)
- [7] MDGC/GCMS-2010 catalogue, C184-E015 (2008).
- [8] Shimadzu GC Application News: Introduction of MDGC System, G253 (2008).
- [9] Shimadzu GC Application News: Introduction of MDGCsolution, G255 (2008).

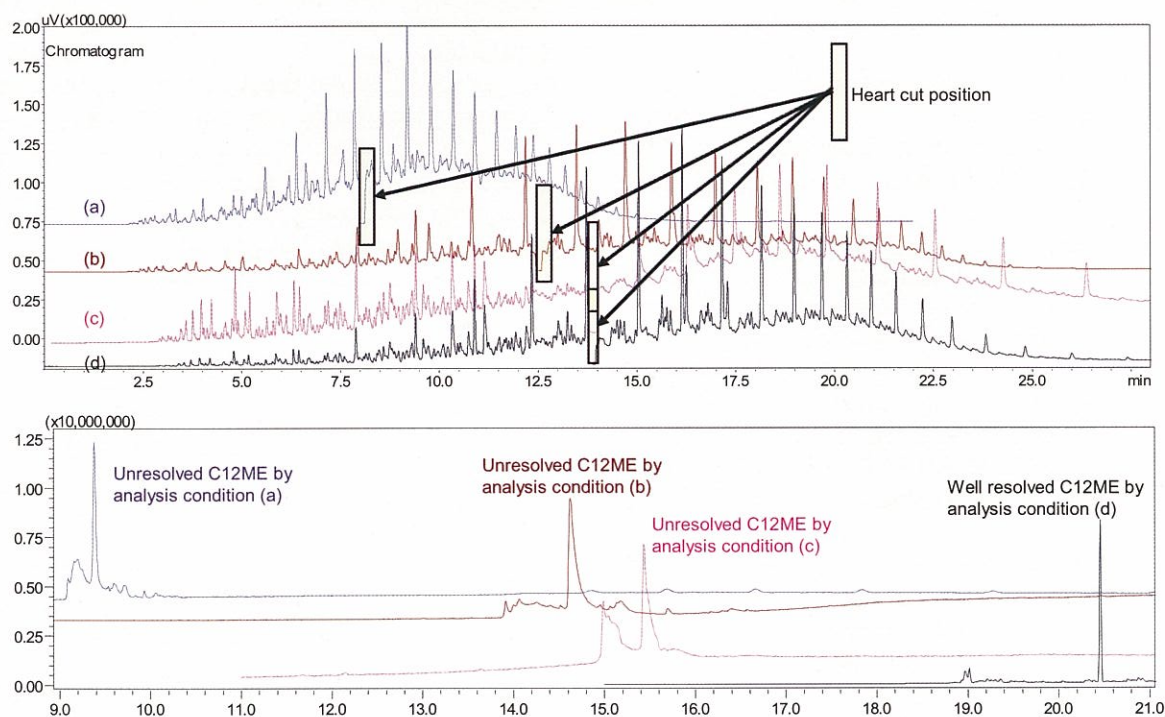
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**Figure 2.** Chromatograms obtained from 1<sup>st</sup> column by conventional MDGC analytical conditions (d) as per Table 1.  
**Upper:** Chromatograms of fuel diesels and a fuel diesel spiced with 1% C12ME. **Lower:** Enlargement of the upper diagram.



**Figure 3.** Data of 0.5% C12ME spiked in CS (diesel sample) analyzed by analysis condition (a), (b), (c) and (d) as per Table 1.  
**Upper:** Chromatograms from 1<sup>st</sup> column. **Lower:** TIC from 2<sup>nd</sup> column.