Determination of glyceride and free fatty acid residues in biodiesel by thin layer chromatography combined with on-line THM-GC

[Background] Biodiesel is mainly produced from vegetable oils and animal fats via a transesterification reaction with alcohols (usually methanol) to form fatty acid methyl esters (FAME) which are renewable, biodegradable and nontoxic alternatives to diesel and petroleum fuels. However, the residual by-products formed during production such as monoglycerides (MG), diglygerides (DG), triglycerides (TG) and free fatty acids (FFA) can lead to severe problems for the engine, such as deposits, filter clogging, fuel deterioration and engine failures. In this note, thin layer chromatography combined with on-line pyrolytic methylation-gas chromatography (TLC-OPM-GC or TLC-THM-GC) was used for the determination of both residual glycerides and free fatty acids in biodiesel samples.

[Experimental] The system consists of a Multi-Shot Pyrolyzer (EGA/PY-3030D) coupled with a GC/MS system (Fig. 1).

TLC separation: 1 μL biodiesel samples were spotted onto TLC plates and developed in *n*-hexane/ethyl acetate/formic acid (90:10:2). Then the spots containing FAME, MG, DG, TG and FFA appeared as brownish after applying iodine vapors as a chromogenic reagent. Finally, the colored spots were cut into a size of 0.5 cm x 1.0 cm for OPM-GC analysis.

OPM-GC (/MS) analysis: The colored spots (obtained from the TLC plates) and 3 μL of trimethylsulfonium hydroxide (TMSH) were put into a sample cup. The sample cup was dropped into the the pyrolyzer furnace preheated at 350 ºC. The flow rate of nitrogen carrier gas was 30 mL/min and the column flow rate was 1.0 mL/min. The column temperature was increased from 50 to 230 ºC at 10 ºC/min (10 min hold). The injector and detector temperatures were kept at 250 ºC. A DB-23 column coated with 50 % cyanopropyl–50 % dimethylpolysiloxane was used for separation.

[Results] Typical chromatograms obtained by OPM-GC for the spots of glycerides and free fatty acids in a sample derived from a waste oil are shown in Fig. 2. Four kinds of fatty acids including C16:0, C18:0, C18:1, and C18:2 were all detected in the spots of glycerides and free fatty acids. The concentrations of glyceride and free fatty acid components as well as their distributions of fatty acid compositions were determined using the external standard and area normalization methods. The contents of glycerides or free fatty acids detected were above the maximum concentrations permitted in European Union (EU) (EN 14214:2008(E)). The results well demonstrates that TLC-OPM-GC is applicable not only to the quantitative determination of both residual glycerides and free fatty acids in biodiesel, but also the analysis of the distributions of the fatty acid compositions in these glycerides and free fatty acids .

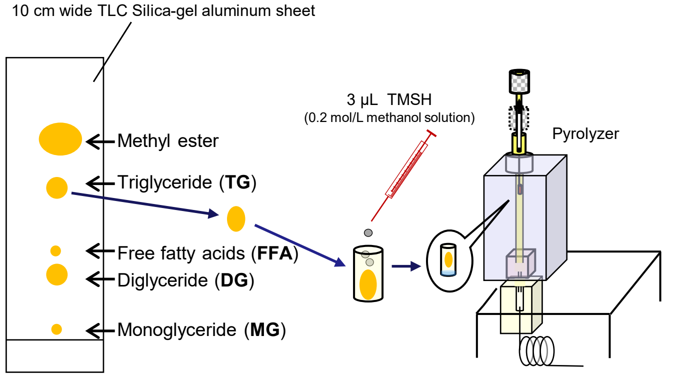

Fig. 1 Schematic diagram of a novel TLC-OPM-GC system.

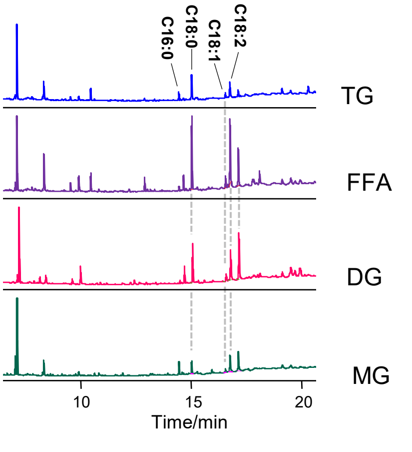

Fig. 2 Typical chromatograms of glycerides and free fatty acids derived from a waste oil, obtained by TLC-OPM-GC.

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Product used : Multi-functional Pyrolyzer

Applications : Simultaneous determination of glyceride and free fatty acid residuals in biodiesel

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