

RAPIDLY MONITORING BIODIESEL PRODUCTION PROCESSES USING UPLC

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INTRODUCTION

Biodiesel is gaining significant interest as the replacement for petroleum-based diesel fuel since it is renewable and cleaner-burning. Besides these environmental factors, the increase in petroleum price and the government mandates have all contributed to its popularity. Biodiesel is fatty acid methyl ester (FAME) made from vegetable oil or animal fat, by transesterification with methanol in the presence of a catalyst. To maximize the yield of FAME and reduce non-volatile contaminants including unreacted feedstock (TAG), reaction intermediates (MAG and DAG), unwanted hydrolysis contaminants FFA, and glycerol (Scheme 1), the status of reaction and refining processes need to be monitored. Biodiesel samples can be analyzed by GC; however, the non-volatile contaminants (FA, TAG, MAG, and DAG) require derivatization prior to GC analysis, multiple injections with different GC experimental conditions are needed to characterize FAME and impurities, which are laborious. Analyzing biodiesel by conventional HPLC methods requires 30 to 80 minute run times and use halogenated solvents that are known carcinogens and restricted in laboratories.

This poster illustrates the application of a UPLC system equipped with photodiode array and evaporative light scattering detectors to analyze biodiesel samples without derivatization and halogenated solvents. Biodiesel related standards, biodiesel, and non-volatile contaminants were separated in 12 minutes.^{1,2} The method can be used to rapidly monitor biodiesel production to increase productivity. Compared with conventional HPLC methods, the UPLC solution shortens analysis time and reduces solvent usage, leading to cost benefits and aligning with the principles of green chemistry.

EXPERIMENTAL

Biodiesel was synthesized using the kitchen biodiesel method with soybean oil, MeOH and NaOH.³ Crude biodiesel was diluted to 12 mg/mL with 2-propanol (IPA) and the solution was filtered with a 0.45µm PVDF syringe filter for UPLC analysis. Standards (Table 1) were dissolved in IPA to make 0.5mg/mL solution for the analysis.

UPLC™ System and Operation Conditions^{1,2}
System: ACQUITY UPLC®/ACQUITY PDA/ELSD/Empower™ 2
Detection: PDA 195 to 300 nm; Weak Wash: IPA (600 µL)
Column Temp: 30 °C; Injection: 2 µL (full loop)
Column: ACQUITY UPLC™ BEH C18 2.1x 150 mm
Mobile Phase A: CH3CN; Mobile Phase B: IPA (Fisher, Optima)
Gradient Table

Time (min)	mL/min	%B	Curve
0	0.17	11	6
7	0.17	37.5	6
7.01	0.17	90	11
12	0.17	90	11

Scheme 1. Transesterification and hydrolysis reactions of esters involved in biodiesel production

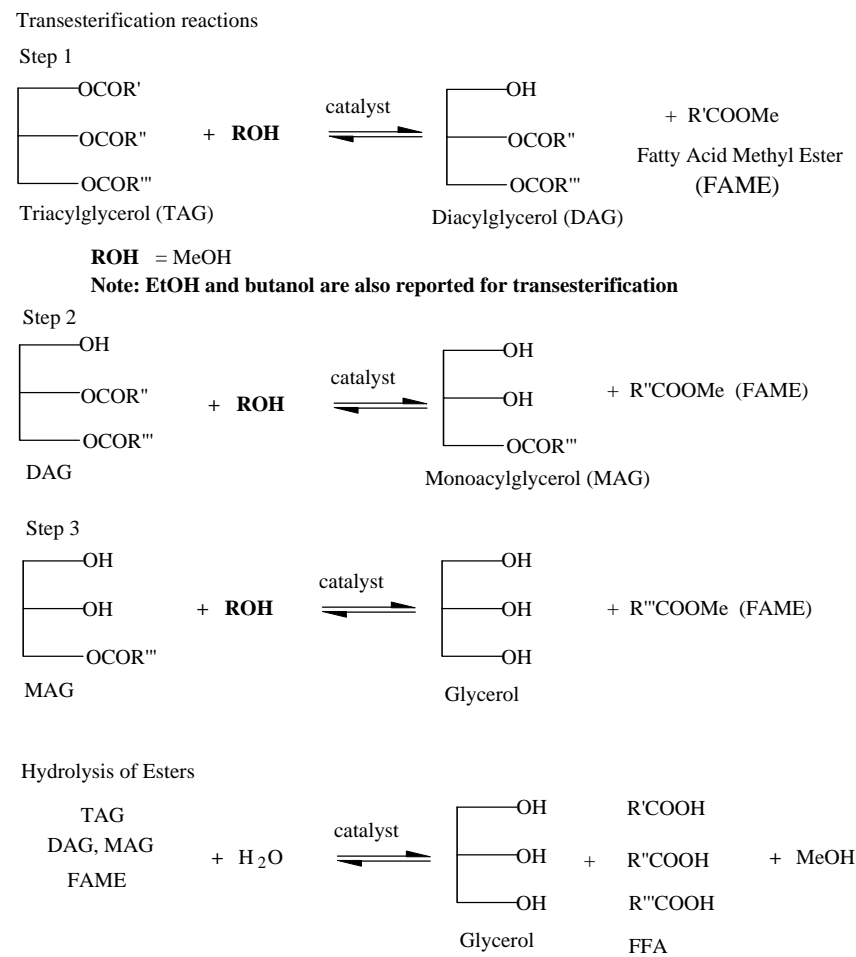


Table 1. Standards of FFA, FAME, MAG, DAG and TAG

ID	Name	CAS No.	Peak Label
1	Glycerol	56-81-5	a
2	Linolenic acid	463-40-1	b
3	1-Linoleoyl-rac-glycerol	2277-28-3	b
4	Methyl linolenate	301-00-8	c
5	Linoleic acid	60-33-3	d
6	1-Oleoyl-rac-glycerol	111-03-5	d
7	Methyl linoleate	112-63-0	e
8	Oleic acid	112-80-1	f
9	Palmitic acid	57-10-3	f
10	Methyl oleate	112-62-9	g
11	Methyl palmitate	112-39-0	g
12	Stearic acid	57-11-4	h
13	Methyl stearate	112-61-8	i
14	Arachidic acid	506-30-9	j
15	Methyl arachidate	1120-28-1	k
16	1,3-dilinoleoyl-rac-glycerol	15818-46-9	l
17	1,2,3-trilinoleoylglycerol	537-40-6	m
18	Glyceryl trioleate	122-32-7	n
19	Soybean oil	8001-22-7	

- Biodiesel components, FAME and non-volatile contaminants including TAG, reaction intermediates (MAG and DAG), hydrolysis and reaction byproducts (FFA, and glycerol) are separated in 12 minutes.
- UPLC enables rapid monitoring of production processes that can leads to the benefits of higher yield, lower contamination and higher quality products.
- By incorporating UV with the evaporative light scattering detection, more information per chromatographic run can be obtained, thus dramatically increasing productivity.
- The separation is several times faster than conventional HPLC, minimizes solvent usage and eliminates the use of toxic halogenated solvents, resulting in cost benefits and alignment with the principles of green chemistry.

REFERENCE

1. Lee, P. J. and Di Gioia, A. J. (2007) ACQUITY UPLC/ELSD/UV one methodology for FFA, FAME & TAG analysis, Waters application note 720002155en.
2. Lee, P. J. et al. (2009) Automating calculations for rapid seed oil quality control and Authenticity. Waters Corporation, application note 720002973en.
3. <http://kitchen-biodiesel.com/>

UPLC SEPARATION OF BIODIESEL & NON-VOLATILE CONTAMINANTS

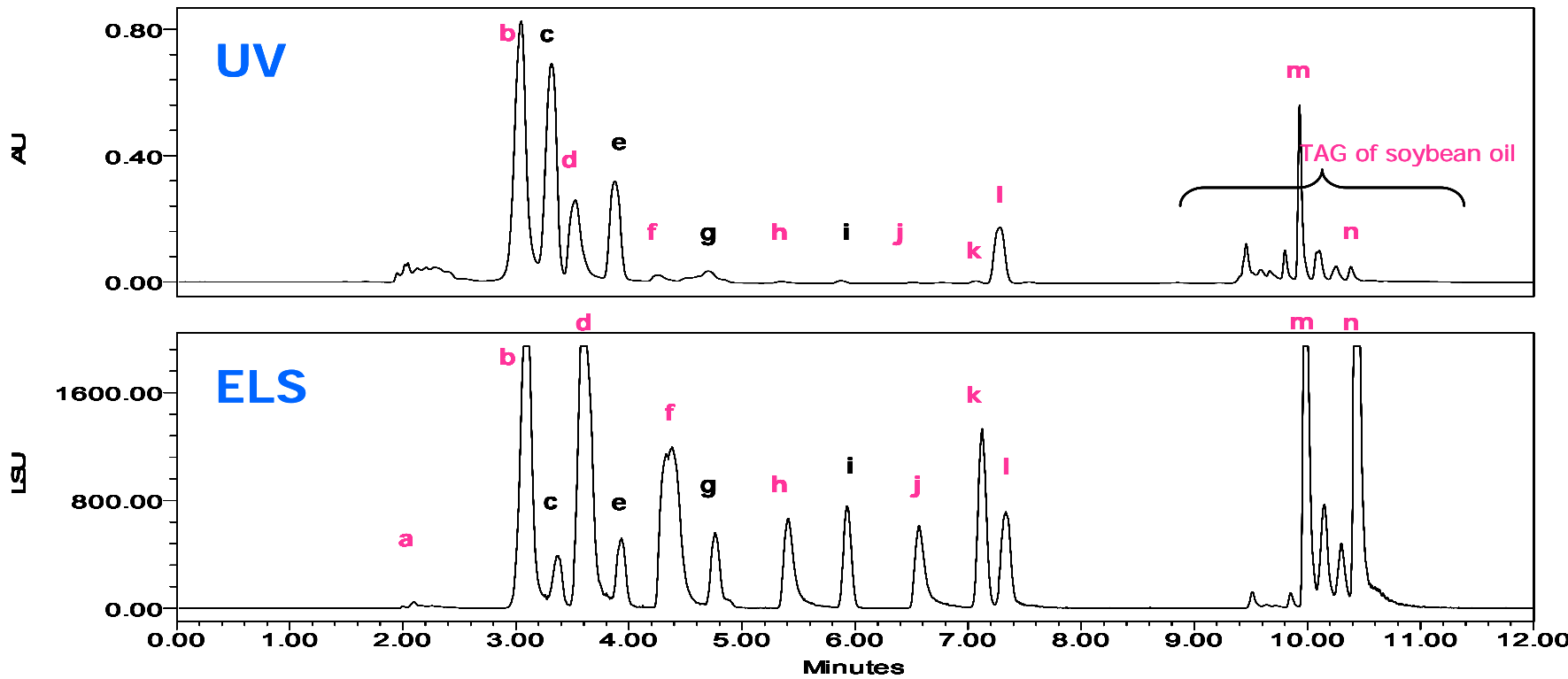


Figure 1. ELS and UV (210 nm) chromatograms of a solution containing soybean oil (0.7mg/mL) and standards of FFA, FAME, MAG, DAG and TAG (0.5mg/mL each, see table 1 for peak labeling).

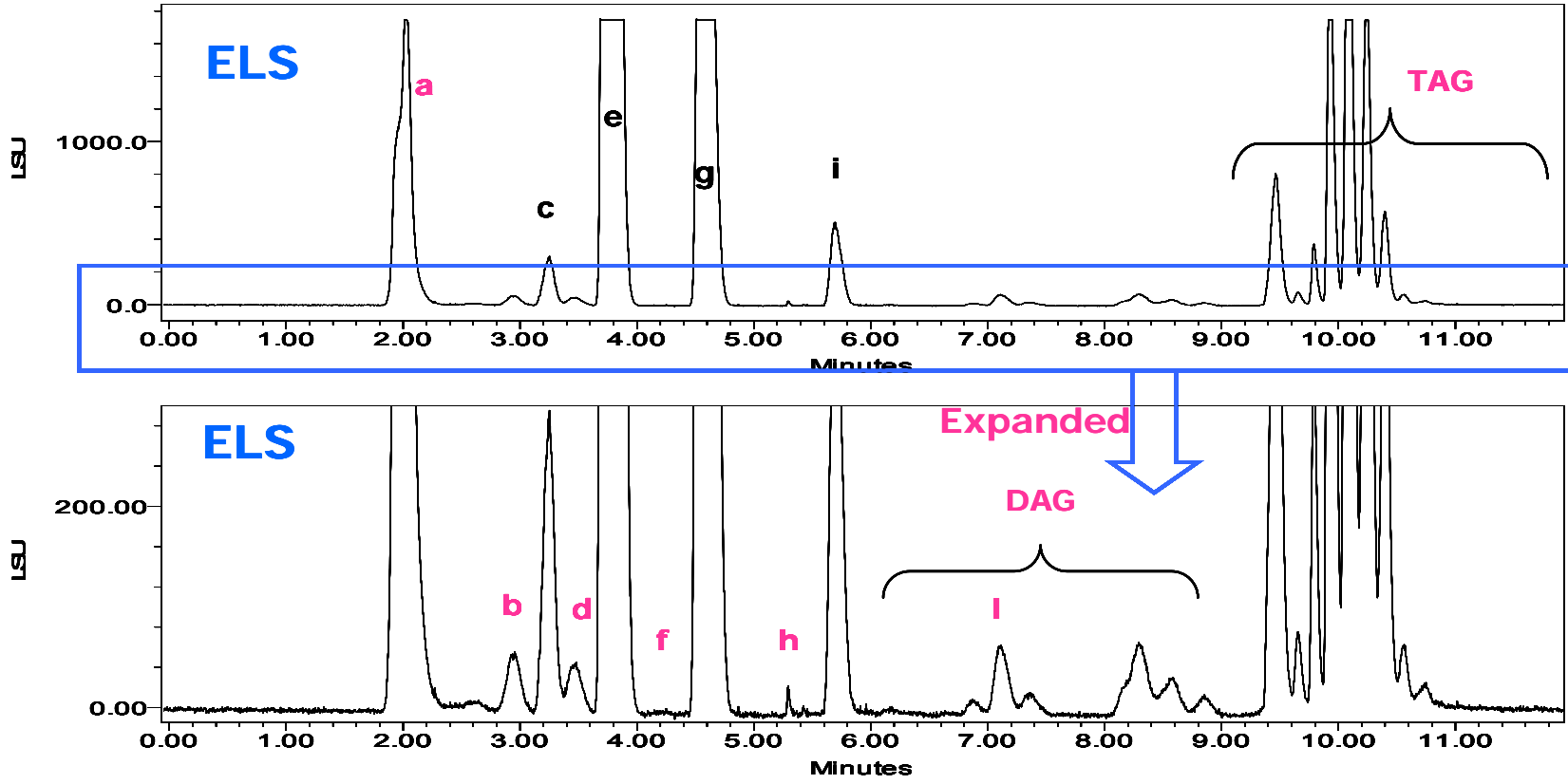


Figure 2. ELS chromatogram of homemade biodiesel (12mg/mL) made from soybean oil. Note: The lower chromatogram represents a baseline expansion.

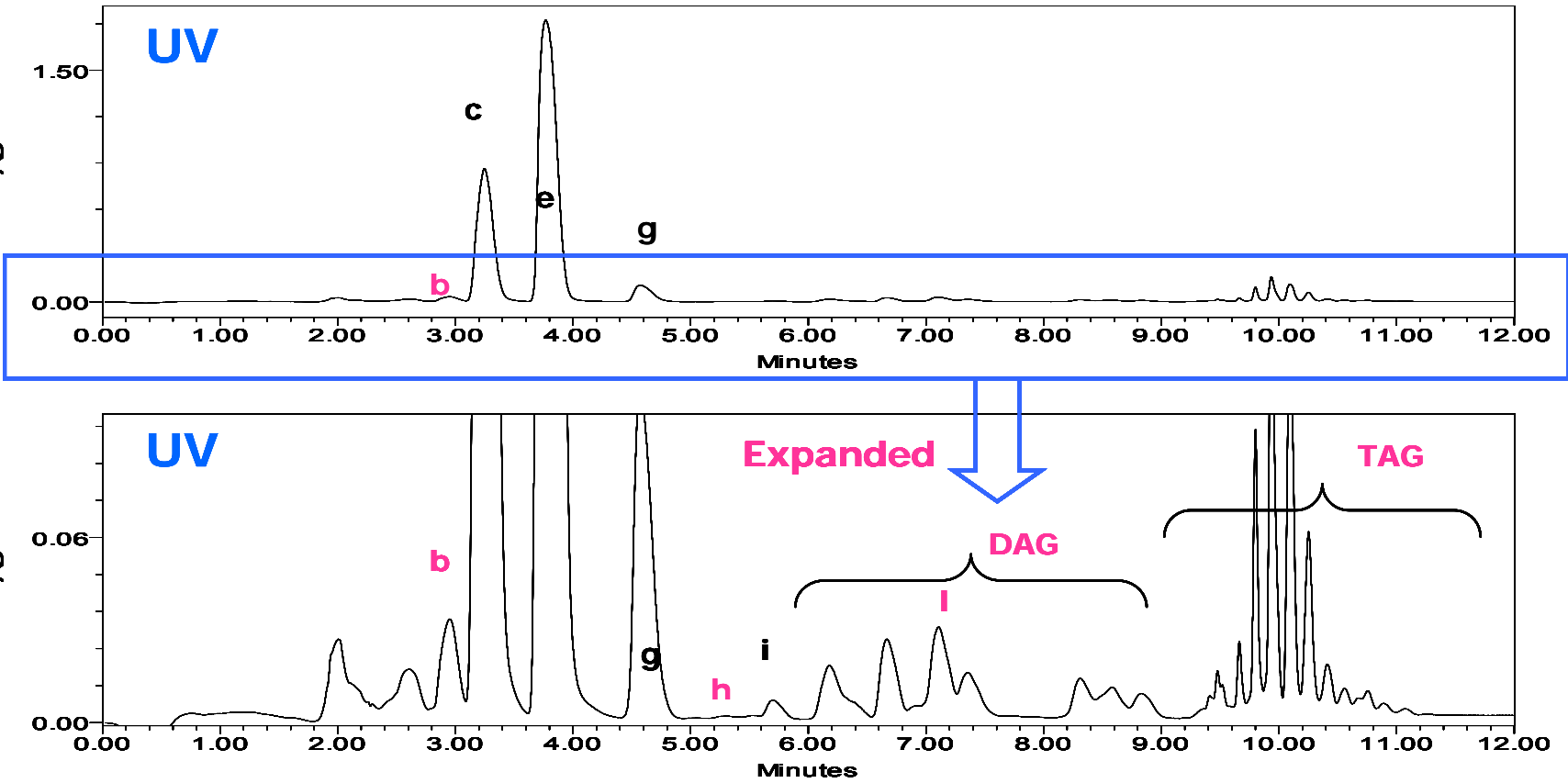


Figure 3. UV (210 nm) chromatogram of homemade biodiesel (12mg/mL) made from soybean oil. Note: The lower chromatogram represents a baseline expansion.

CONCLUSION