# First Generation Biofuels: Simple Mixtures - Complex Analytics

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## Overview

The search for alternative fuels continues to be a hot political topic. Biofuels, in particular biodiesel, are controversial fuel sources and in many cases their use has been politically not scientifically driven. Here, different analytical approaches are presented to address the underlying analytical needs for identification of biodiesel (fatty acid methyl esters, FAMES) and related degradation products in different petrochemical matrices.

## Introduction

- First generation biofuels, *e.g.* biodiesel are made from trans-esterified natural triglycerides from vegetable oils or animal fats
- Biodiesel primarily refers to fatty acid methyl esters (FAMES)
- These can be used neat or blended with petrodiesel in normal diesel engines
- FAMES analysis by GC-MS is well documented and sources of neat biodiesel can readily be typed and detected at low levels in petrodiesel by this technique, Fig. 1 & Fig. 2
- Similarly fingerprints and LODs can also be obtained by flow injection and chromatography-API MS
- Once blended with petrodiesel and recirculated into lubricants the FAMES detection and their degradation products becomes a far greater analytical challenge, Fig. 3

## The Analytical Challenge

**Typification of Biodiesel**

- Aviation fuel must be B0
  - B0 defined as < 5ppm biodiesel
- UK legislation April 2008 all diesel 2.5% biodiesel (5% by 2010)
- FAMES source/origin
  - green, ethics, $$$, *etc.*
- FAMES purity
  - no free acids *etc.*
  - one source
- FAMES blends
- Biodiesel in complex matrices
  - biodiesel/petrodiesel
  - biodiesel in lubricants (crankcase)
    - dilution
    - thickening, Fig. 4

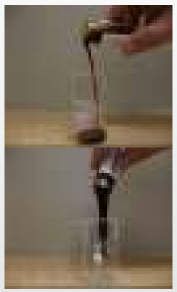
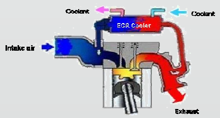


Figure 4. Post engine test crankcase lube without and with diesel/biodiesel mix




EGR fitted to meet emissions legislation
EGR introduces fuel and soot
Lube and fuel mix 'leak' past piston rings

Figure 5. Exhaust Gas Recirculation

## Results and Discussion

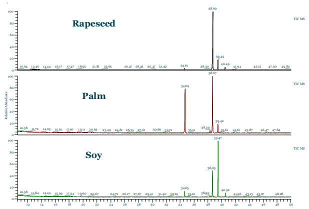



Figure 1. GC-MS of different biodiesel feedstocks (FAMES)

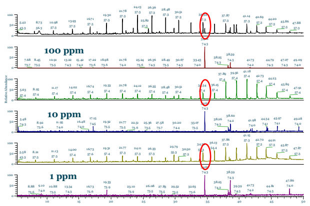



Figure 2. GC-MS TIC and EIC of biodiesel/diesel

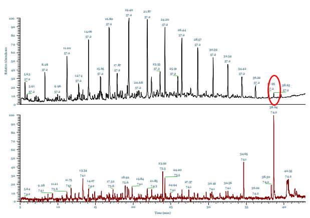


Figure 3. GC-MS of biodiesel/diesel in lube

Figs. 1, 2 & 3 show the ease of typification of FAMES sources by GC-MS and also their detection at low concentration in petrodiesel and petrodiesel/lubricant matrix. Lube dilution, see Fig. 5, is of interest because this can cause thinning and/or thickening of the lube matrix; thickening due to presence of biodiesel shown for post engine test lube, Fig. 4. The change in viscosity causes tribological issues. Understanding the chemistries in these samples is imperative, *e.g.* is it oxidative polymerisation of the FAMES?

Rapeseed methyl ester was used as a simplified model system for forced oxidation studies (bubbled air) and analysed by FIA-ESI, D-labelling, FT-ICR and HPLC-MS, Figs. 6-10.

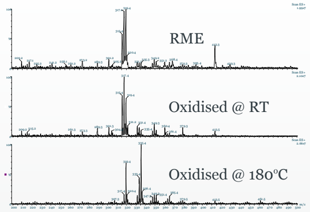



Figure 8. FIA-ESI-MS of force oxidised rapeseed methyl esters in crankcase lube

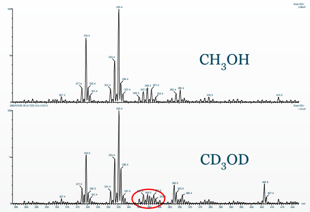



Figure 9. FIA-ESI-MS of force oxidised rapeseed methyl esters in crankcase lube

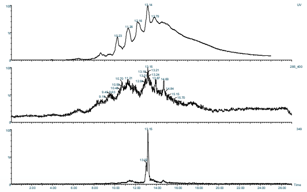


Figure 6. HPLC-MS of oxidised rapeseed methyl esters in diesel (500ppm)

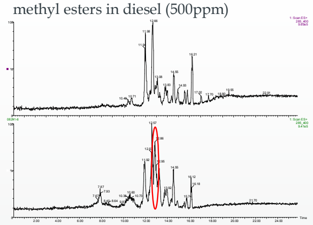


Figure 7. HPLC-MS of force oxidised rapeseed methyl esters in crankcase lube

GC-MS showed no change in FAMES profile. FIA, Fig. 8, showed subtle changes in population of sodiated molecules at RT and evidence of oxidation products at raised temperature. Deuterium exchange experiments suggest epoxidation and hydroxylation, Fig. 9. The latter confirmed by HPLC-MS, Fig. 7 and HPLC-FT-ICR MS, Fig. 10 & Table 1.

SFC shows great promise for analysis of diesel/biodiesel mixes, see Fig. 11, with separation of these species readily achieved with a run time of under 4 minutes *cf.* 30 minutes for the HPLC method and 75 minutes for the GC-MS assay.

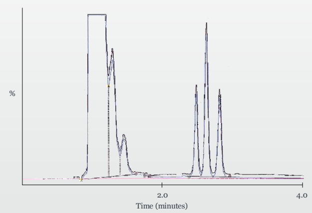



Figure 11. SFC-UV chromatogram of diesel/biodiesel

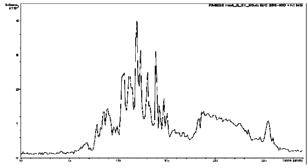


Figure 10. HPLC-FT-ICR MS of force oxidised rapeseed methyl esters in crankcase lube

| Formula | *m/z* | Error ppm |
|---|---|---|
| $C_{19}H_{32}O_2Na$ | 315.2295 | 3.22 |
| $C_{19}H_{34}O_2Na$ | 317.2451 | 0.22 |
| $C_{19}H_{36}O_2Na$ | 319.2608 | 2.86 |
| $C_{19}H_{32}O_3Na$ | 331.2244 | 3.59 |
| $C_{20}H_{38}O_2Na$ | 333.2764 | 0.48 |
| $C_{19}H_{36}O_3Na$ | 335.2557 | 0.62 |
| $C_{19}H_{32}O_4Na$ | 347.2193 | 3.23 |
| $C_{21}H_{40}O_2Na$ | 347.2921 | 4.62 |
| $C_{19}H_{34}O_4Na$ | 349.2349 | 2.66 |
| $C_{21}H_{42}O_2Na$ | 349.3077 | 4.36 |
| $C_{19}H_{36}O_4Na$ | 351.2497 | 2.47 |

Table 1. HPLC-FT-ICR MS accurate mass data of force oxidised rapeseed methyl esters in crankcase lube

## Experimental

Biofuel standards and samples supplied by BP Technology Centre Pangbourne UK

GC-MS: Trace-MS using a Restek Stabilwax® 30 m x 0.25 mm i.d., 0.25 μm, He carrier gas 1 mL min$^{-1}$ constant flow, 1 μL splitless injection

EI: 70 eV, source temperature 220°C

HPLC-MS: C18 Xterra™ 150 x 4.6 mm, 5 μm and 50 x 3 mm, 5 μm

Waters ZMD: ESI – HV 3.3 kV, CV 20 V, source temperature 250°C. APCI – HV 3.0 kV, CV 20 V, source temperature 250°C

FT-ICR MS: ApexIII 4.7 T: ESI – HV 4.5 kV, Capillary Exit 100 V

ESI infusion 3 μL min$^{-1}$, accumulation time 0.2 s, 1M data points, data acquisition *via* ApexControl, 4 scans summed

SFC-MS: Minigram SFC – LCZ Spherisorb® S10 $NH_2$ 250 x 4.6 mm, 5 μm. $CO_2$, 100 bar, MeOH modifier

## Conclusions

**GC-MS**
- ☺ FAMES straightforward
- ☺ Biodiesel/diesel quantitative to 1ppm
- ☺ Biodiesel in crankcase
- ☹ Degradation products (oxidised FAMES)

**API-MS**
- ☺ HPLC-MS
- ☺ APCI and ESI
- ☺ Biodiesel/diesel quantitative to 1ppm
- ☺ Biodiesel in crankcase
- ☺ Degradation products (oxidised FAMES)
- ☺ Deuterium labelling
- ☹ Limited chromatography resolution
- ☹ Need MS/MS

**FT-ICR MS**
- ☺ HPLC-MS
- ☺ Identify oxidation products
- ☺ Degradation products (oxidised FAMES)
- ☺ Ultra high resolution allows FIA
- ☹ Limited chromatography resolution
- ☹ Slow duty cycle

**SFC**
- ☺ Separation of biodiesel/diesel
- ☺ Fast analysis
- ☺ Couples to API
- ☺ "Green fuel by Green separation science"
- ☹ Too fast for FT-ICR MS
- ☹ Need MS/MS for structural determination

## Acknowledgements