

Biodiesel Identification: Distinguishing Individual Fatty Acid Methyl Esters and Identifying Oxidation Products Using MS Coupled to Chromatographic Techniques

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Overview

The need for a renewable source of fuel has prompted an increase in the search for alternate fuels. When rapeseed methyl ester (RME) is used as a fuel the lubricant oil can become more viscous. This thickening effect has been attributed to oxidation products. Research has been undertaken to identify the differences/changes in RME and in samples. These samples are simulated tests of what happens in an engine. ESI-MS and GC-MS have been used to identify fatty acid methyl esters (FAMES) and these oxidation products. Differences in the data have been identified and some of these differences are presented here.

Introduction

- Biodiesel, commonly referred to as FAMES, is used in different percentages with petro-diesel, *i.e.* B20 contains 20% biodiesel and 80% petro-diesel.
- FAMES are prepared from various feedstock sources *e.g.* vegetable oil and animal oil *via* transesterification.
- Feedstock sources come from many countries and can have varying ratios of individual methyl esters, producing a distinctive composition.
- FAMES can be saturated or unsaturated and be of chain length C₁₆-C₂₄ for the purposes of petro-diesel.
- Many techniques are available to analyse FAMES and identify trace impurities from manufacture *i.e.* HPLC-UV^[1], -ELSD^[1], -MS^[1], NMR^[2], IR^[3] and GC-FID^[4].
- Degradation of FAMES is an important area, however there are presently no methods to identify this.
- This work is based on oxidation products of FAMES which consist of a functionalised molecule mainly in a hydrocarbon mix.
- MS is an ideal candidate to identify these oxidation products.

Method

- RME of different ages and oil samples were provided from BP (Pangbourne, U.K.).
- FAME mix was added steadily at a rate of 5 mL/day to the oil samples.
- The oil samples were heated continuously at 165°C and sampled every 24 hours.
- Experiments continued until the viscosity at 40°C had doubled.
- Samples were analysed in cyclohexane and methanol in various concentrations.
- ESI-MS and GC-MS were used to analyse these samples.
- ESI-MS instrumentation: Micromass Platform LCZ equipped with an ESI z-spray source, single quadrupole MS. Introduced *via* infusion at 300 μL/hour.
- GC-MS instrumentation: Thermo TraceMS single quadrupole GC-MS (70 eV EI), fitted with a Stabilwax column 30 m x 0.25 mm *i.d.*, 0.25 μm film thickness.

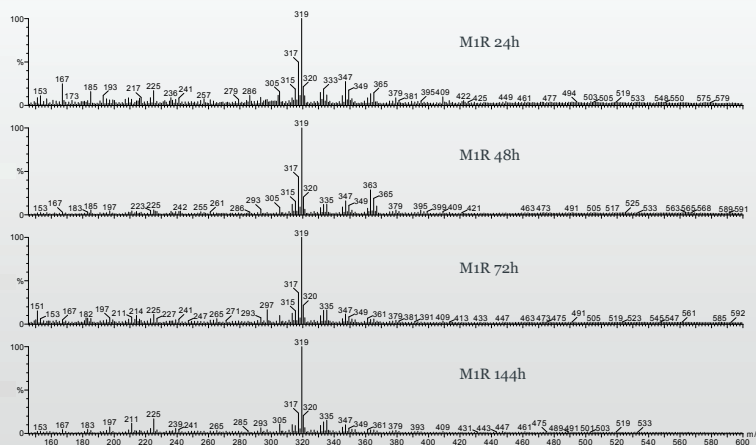


Figure 1: + ESI-MS spectra of M1R 24h, M1R 48h, M1R 72h and M1R 144h.

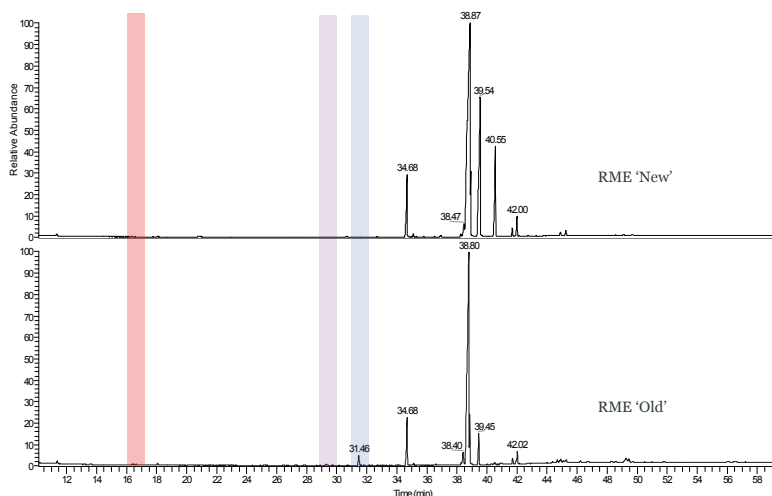


Figure 2: GC-MS TIC of 'new' and 'old' RME, highlights indicate Fig. 3, 4 and 5.

Results

- 18:1/18:2/18:3 species at *m/z* 319/317/315 are present in Fig. 1, this is also true for 'old' and 'new' RME.
- Peaks are present at *m/z* 331/333/335, *m/z* 345/347/349 and *m/z* 361/363/365 in all + ESI-MS data and are possible oxidation products.
- Oxidation products could include: ketones, aldehydes, longer alkanes and epoxides.
- Fig. 2 displays major differences, the most notable differences is the loss of 18:3 species (T_R 40.55/40.51 min.) and reduction of 18:2 species (T_R 39.54/39.45 min.).
- Other peaks are present in RME 'old' and not in RME 'new' most notable is a peak at T_R 31.46 min.
- This peak is attributed to 9-oxononanoic acid methyl ester (Fig. 5 and 8) it is present (in minute amounts) in M1R 48h, M1R 72h, M1R 144h and possibly M1R 24h.
- Smaller differences are also present: nonanal (Fig. 3 and 6) and 8-oxooctanoic acid methyl ester (Fig. 4 and 7); found in minute amounts in the later stages of the sample test (M1R 144h and M1R 72h/144h respectively).

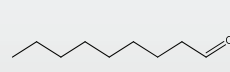


Figure 6: Structure of nonanal

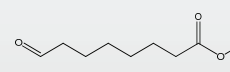


Figure 7: Structure of 8-oxooctanoic acid methyl ester

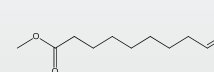


Figure 8: Structure of 9-oxononanoic acid methyl ester

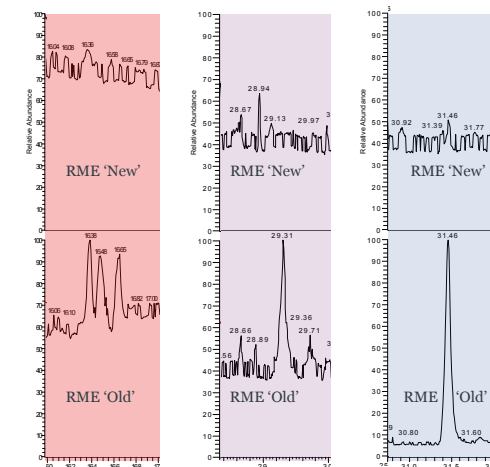


Figure 3: Expansion of Fig. 2 TIC displaying nonanal (T_R 16.48 min.) normalised to 'old' RME

Figure 4: Expansion of Fig. 2 TIC displaying 8-oxooctanoic acid methyl ester (T_R 29.31 min.) normalised to 'old' RME

Figure 5: Expansion of Fig. 2 TIC displaying 9-oxononanoic acid methyl ester (T_R 31.46 min.) normalised to 'old' RME

Conclusions

- 18:2 and 18:3 species decrease as time increases.
- Oxidation products are present in both RME and samples however are more prominent in RME as shown by ESI-MS and GC-MS.
- Oil samples only have small changes in GC-MS TIC's likely due to the testing conditions (5 mL/day of RME mix was added continuously) creating a build up effect therefore oxidation products (in comparison) will be small.
- Depletion of 18:2 and 18:3 species and identification of oxidation products suggest linked.
- 9-oxononanoic acid methyl ester present in 'old' RME and some samples – suggests possible compound to monitor oxidation.
- 8-oxooctanoic acid methyl ester and nonanal are present in 'old' RME and later stages of the sample test – suggests possible compound to monitor on-going oxidation.

Acknowledgements

RSC Chromatography and Electrophoresis Group



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References

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