

Methanol-Based Esterification of Palm Oil Sludge – Preparation of Palmitic and Oleic Fatty Acid Ethyl Esters via Ethyl Acetate Transesterification

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Acid-catalysed Fischer esterification of fatty acids with methanol as a reagent and solvent is regularly used to prepare long chain alkyl methyl esters. Transesterification of palm oil in basic media using methanol is also a synthesis route to prepare methyl esters of fatty acids. In this work, we report a Fischer esterification in methanol of a sample of local palm oil sludge (rich in fatty acids) where a column chromatography fraction analysed by gas chromatography-mass spectrometry matched an unexpected mixture of ethyl esters of oleic and palmitic acids, probably as result of a transesterification reaction that occurred during the extraction step using ethyl acetate in basic media.

1. Introduction

Biodiesel, a mixture of monoalkyl esters of biodegradable long chain fatty acids, contains insignificant amounts of sulphur and is nontoxic and renewable (Abdullah et al., 2017). Esterification and similar chemical reactions (transesterification and interesterification) for biodiesel production from renewable resources has been recently reviewed (Chuah et al., 2021). Biomass conversion via the transesterification of palm oil sludge (POS) with methanol is a common route to synthesize fatty acid methyl esters (FAMEs) (Abdullah et al., 2017). Similarly, and currently under study for potential applications as renewable oils and biofuels (Nduwayezu et al., 2015), fatty acid ethyl esters (FAEEs) are commonly prepared using ethanol, a less toxic solvent relative to methanol (Yusoff et al., 2014). The preparation and comparative characteristics of fatty acid methyl and ethyl esters has already been reviewed by Yusoff et al. (2014) as well as the most important catalysts used in FAMEs production (Nisar et al., 2021). Most used biodiesel technologies based on FAMEs production has also been compared (Ryms et al., 2013) and the use of innovative technologies simulated and its implementation on industrial scale highly encouraged (Petrescu et al., 2020).

Our interest is modifying locally produced POS to produce fatty acid alkyl esters, and during our experiments to prepare FAMEs an additional transesterification reaction was observed under basic conditions, and FAEEs were detected in gas chromatography-mass spectrometry analysis. As novelty of this work, we describe that local POS used in our experiments, coming from the third oxidation lagoon ponding system, contains mainly free fatty acids (FFAs) (glycerol or glycerides were not observed in the analysed products) and the conditions used during the reaction treatment by a continuous liquid-liquid extraction generated a transesterification that in situ converted FAMEs to FAEEs; with this work we hope to encourage others to build upon previous research in this field and eventually prepare substances of added value, e.g., surfactants.

2. Experimental

2.1 Materials and methods

POS used in this study was obtained from the third lagoon of Palmas del Cesar S. A. oxidation ponding system, at the plantation located in La Loma (San Martín municipality, Cesar Department, Colombia). The collected POS was purified by Soxhlet extraction with petroleum ether (PE). Then, 5.0 g of POS was poured

into a round bottom flask, and 10 mL of methanol and H₂SO₄ (0.13 g) as catalyst were added. The mixture was heated at 60 °C at 300 rpm for 3 h according to Abdullah et al. (2017). After cooling the reactor, the mixture was added to 200 mL saturated Na₂CO₃ solution to pH >10 to neutralize the H₂SO₄ catalyst; then, it was poured into a continuous liquid-liquid extractor using 150 mL ethyl acetate (EA) as solvent and heated under reflux for 24 h (schematic setup for the liquid-liquid extraction in Figure 4). The organic layer was rota-evaporated, and solvents (methanol and ethyl acetate) were removed at 40 °C under vacuum, until a constant weight was obtained (4.78 g, 96 % mass). The resulting oily residue was purified by column chromatography (CC) on SiO₂ (70-230 mesh, Merck) using petroleum ether (PE):ethyl acetate (EA) (ratio 90:1) as the eluent. After purification, 1.65 g of a colourless oily sample was isolated (35 % mass), R_f = 0.33 (PE:EA, ratio 90:1).

2.2 Gas chromatography-mass spectrometry (GC-MS) analysis

Compounds inside the obtained fraction (purified by column chromatography) were identified by gas chromatography-mass spectrometry GC-MS (Agilent 5977B GC/MSD, Santa Clara, CA 95051, United States) using an HP-5MS column (30 m; 0.25 mm internal diameter; 0.25 mm film thickness), analysed over a mass per charge (*m/z*) range of 50–550 and identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library. NIST MS Search 2.3 was used for mass spectra comparison (NIST Mass Spectrometry Data Center, 2017). MS Interpreter version Beta 3.1a (Mirokhin et al., 2017) (part of the NIST Mass Spectral Search program) was used to obtain the formula and RDBE (ring and double bond equivalent) for selected mass spectra.

3. Results and discussion

3.1 Sample preparation and Fourier Transformed Infrared (FT-IR) analysis

PE Soxhlet extraction separated the substances of interest from insoluble inorganic (sand) and organic material (mostly wood and cellulose). The FT-IR spectrum shows that the sludge contains mainly free fatty acids. Figure 1 (top) shows the main absorption signal of C=O stretching at 1697.5 cm⁻¹ for carboxylic acids, where no ester band of glycerides is observed. The FT-IR spectrum in Figure 1 (bottom) shows the typical C=O stretching band for the synthesized esters (fraction isolated by column chromatography) at 1737.5 cm⁻¹.

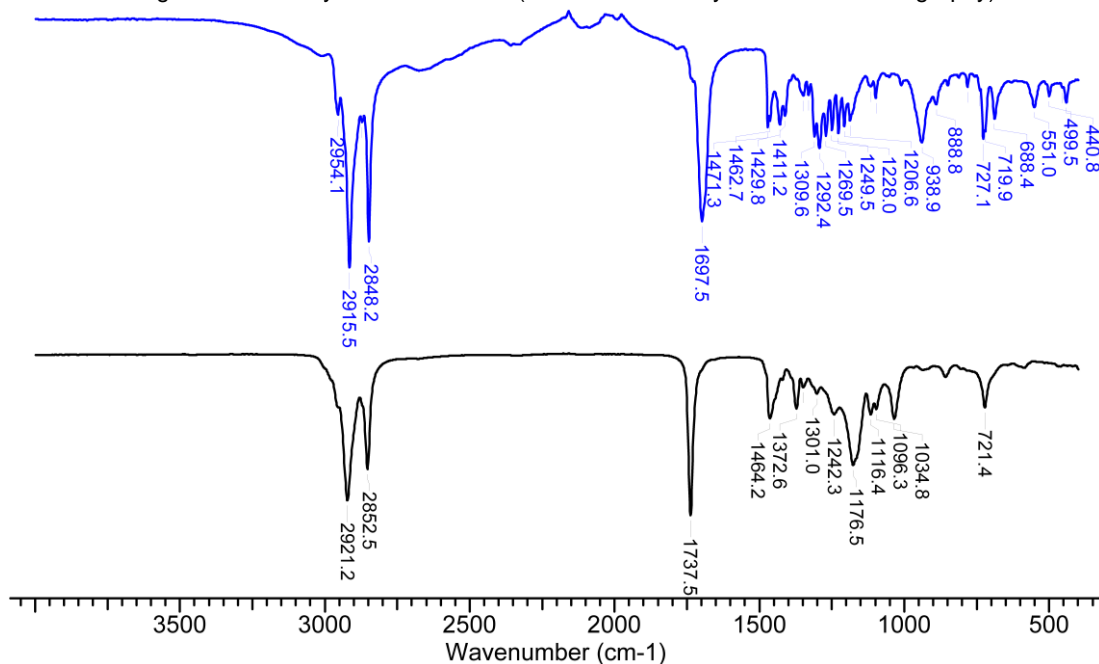


Figure 1: FT-IR spectra of the palm oil sludge after Soxhlet extraction (blue) and the obtained fatty acids esters mixture (black). The C=O stretching signal appears at 1697.5 cm⁻¹ for carboxylic acids (top) and for the esters mixture at 1737.5 cm⁻¹ (bottom).

3.2 Fischer esterification and solvent mediated transesterification determined by GC-MS

Methanol-based esterification was performed according to Abdullah et al. (2017). Due to the difficulty in performing a liquid-liquid extraction in a separatory funnel, a continuous liquid-liquid extractor with EA was

used. Then, the ester interchange reaction was carried out with continuous heating for 24 h (Dijkstra, 2008), as corroborated by MS spectra of the less polar fraction obtained after CC.

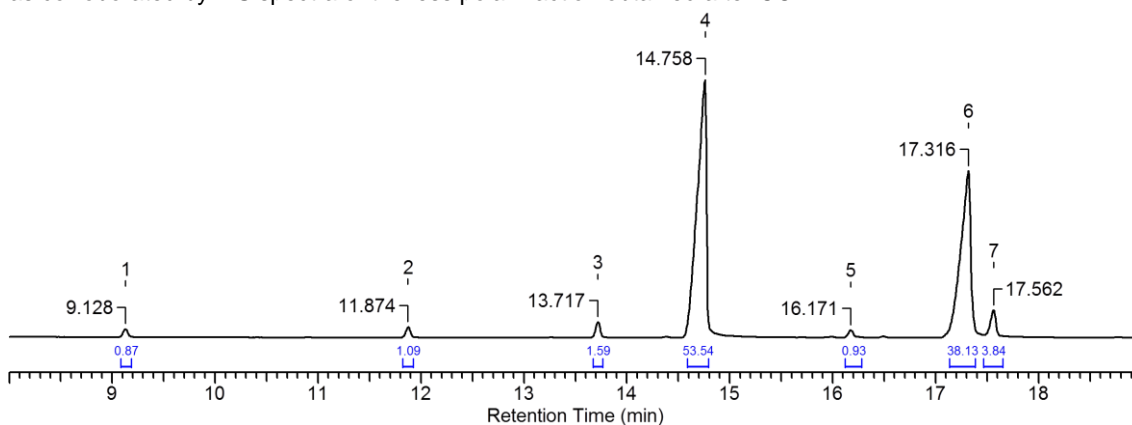


Figure 2: Total Ion Current (TIC) obtained for the GC-MS of the ester mixture. Approximately 53.5 % corresponds to ethyl palmitate (peak No. 4) and 38.1 % to ethyl oleate (peak No. 6). For the identification of other peaks, see Table 1.

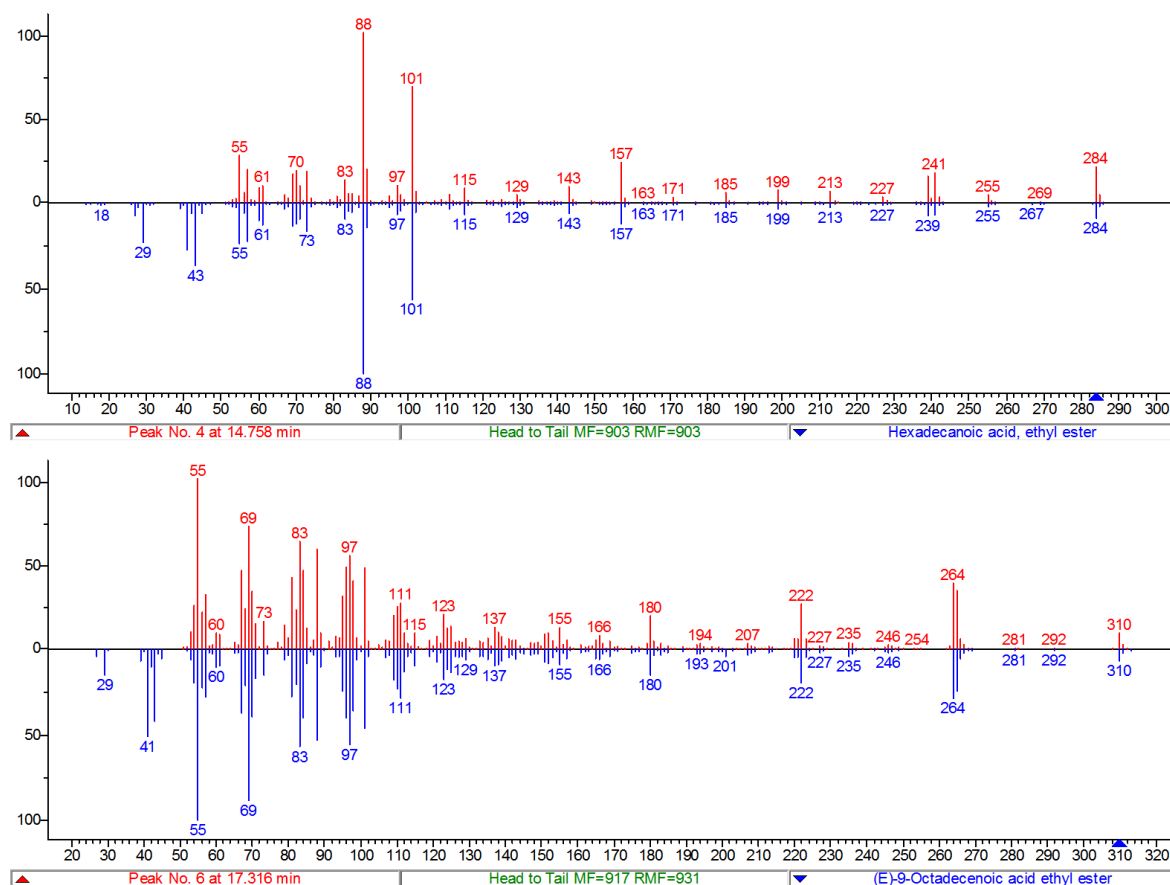


Figure 3: Mass spectra comparison for obtained GC-MS data with NIST library. MS spectrum for peak No. 4 ($m/z = 284.2$ g/mol, red) matches ethyl palmitate library spectrum (blue, top), and MS spectrum for peak No. 6 ($m/z = 310.3$ g/mol, red) matches isomeric ethyl oleate library spectrum (blue, bottom) [Match factor (MF) and reverse match factor (RMF) for each comparison are also included].

Analytes MS spectra comparison using a mass spectral library search (Kind et al., 2010) corroborated the formation of ethyl esters of fatty acids (FAEEs) instead of the expected methyl esters (FAMES). Figure 2

presents the resulting gas chromatogram; the two main compounds in the fraction (91.7 %) were identified as ethyl palmitate ($C_{18}H_{36}O_2$, 53.6 %) and ethyl oleate ($C_{20}H_{38}O_2$, 38.1 %) with a higher match factor correspondence for its (*E*)-stereoisomer, in agreement with Abdullah et al. (2017). The match factor is the measured value of the direct match of peak *m/z* values and relative intensities, while the reverse match factor ignores all peaks that are in the sample spectrum but not in the library spectrum (Stein et al., 2017). Clearly, a transesterification reaction occurred during the liquid-liquid extraction with EA and turned the methyl esters into their ethyl derivatives, as the MS spectra data comparison demonstrates. The MS comparison for ethyl palmitate is shown in Figure 3 (top) and in Figure 3 (bottom) for ethyl oleate.

NIST MS Search 2.3 was used to compare the mass spectra of methyl and ethyl ester derivatives with the same molecular ion mass (same molecular formula). Considering the absence of glycerides (as ester signals) in the sludge FT-IR spectra (Figure 1, black spectrum), the POS contained predominantly carboxylic acids similar to compositions described in other reports (Aranda et al., 2008), i.e., palmitic acid and oleic acid as the main components. Then, the POS sample (rich in FFAs) underwent a Fischer esterification (heating under reflux the carboxylic acid mixture in methanol), and the resulting reaction mixture was heated in basic aqueous media with ethyl acetate; under these conditions, the only expected derivatives of our POS were methyl and ethyl ester carboxylates. Based on that assumption, the molecular formula and ring and double bond equivalent (RDBE) assignments of the main signals in the chromatogram were calculated with MS Interpreter version Beta 3.1a considering only $C_xH_yO_2$ formulas. NIST MS Search 2.3 was used for the mass spectra comparison, and the results for the match factors are summarized in Table 1.

Table 1: Match factors from mass spectra comparison of main analytes from the ester mixture GC spectrum with compounds in the NIST library

| Peak number | GC retention time(min) | Area (%) | Scan No. | Molecular ion mass (g/mol) | Assigned formula | RDBE* | Assigned compound | Match factor |
|-------------|------------------------|----------|----------|----------------------------|-------------------|-------|--|--------------|
| 1 | 9.128 | 0.87 | 444 | 228.2 | $C_{14}H_{28}O_2$ | 1.0 | Ethyl laurate [Ethyl dodecanoate] | 870 |
| | | | | | | | Methyl tridecanoate | 584 |
| 2 | 11.874 | 1.09 | 924 | 256.2 | $C_{16}H_{32}O_2$ | 1.0 | Ethyl myristate [Ethyl tetradecanoate] | 910 |
| | | | | | | | Methyl pentadecanoate | 632 |
| 3 | 13.717 | 1.59 | 1246 | 270.3 | $C_{17}H_{34}O_2$ | 1.0 | Methyl palmitate [Methyl hexadecanoate] | 947 |
| | | | | | | | Ethyl pentadecanoate | 605 |
| 4 | 14.758 | 53.54 | 1428 | 284.2 | $C_{18}H_{36}O_2$ | 1.0 | Ethyl palmitate [Ethyl hexadecanoate] | 903 |
| | | | | | | | Methyl heptadecanoate | 625 |
| 5 | 16.171 | 0.93 | 1675 | 296.3 | $C_{19}H_{36}O_2$ | 2.0 | Methyl oleate [Methyl (9Z)-octadec-9-enoate] | 926 |
| | | | | | | | Methyl (9E)-octadec-9-enoate | 922 |
| 6 | 17.316 | 38.13 | 1868 | 310.3 | $C_{20}H_{38}O_2$ | 2.0 | Ethyl (9E)-octadec-9-enoate | 917 |
| | | | | | | | Ethyl oleate [Ethyl (9Z)-octadec-9-enoate] | 892 |
| 7 | 17.562 | 3.84 | 1918 | 312.3 | $C_{20}H_{40}O_2$ | 1.0 | Ethyl stearate | 782 |
| | | | | | | | [Octadecanoic acid ethyl ester] | 782 |
| | | | | | | | Methyl nonadecanoate | 671 |

* Ring and double bond equivalent

As reported by Ataya et al. (2006), for our similar biphasic system, ester interchange should occur in the interphase, as shown in Figure 4. The use of a weak base solution allowed the removal of the free fatty acids (FFAs) into the aqueous layer as carboxylates (Nitbani et al., 2020), avoiding any interference in the reaction.

Considering that a small concentration of methoxide anion was formed in the basic media through deprotonation of the residual methanol used in the previous Fischer esterification (Figure 4, orange arrow), an alkaline transesterification occurred in a similar way to the normal alkaline-catalyzed transesterification of vegetable oils to produce FAMES and glycerol (Nitbani et al., 2020). With that assumption, our hypothesis is that the methoxide anion initially transesterified the ethyl acetate used as extraction solvent, turning it into methyl acetate and liberating an ethoxide anion into the interphase, where conditions allowed the ester interchange from FAMES to FAEEs. The contact of the warm solvent with the aqueous layer provided the energy needed to drive the reaction to form FAEEs products, and the equilibrium was shifted by excess of ethyl acetate and the extended duration of the process (24 h).

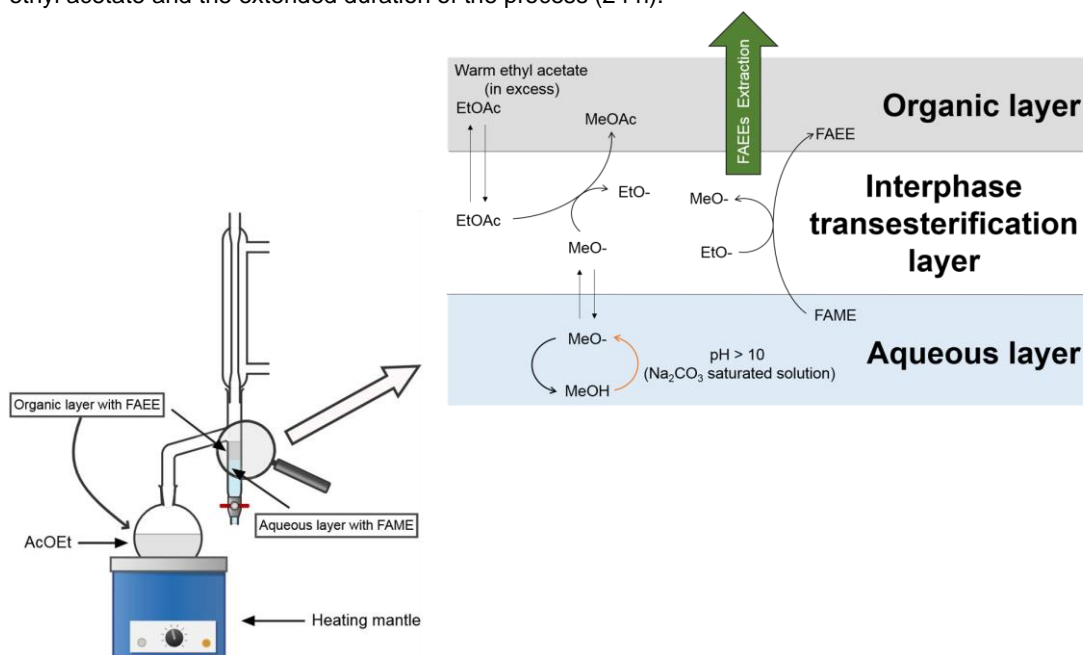


Figure 4: Schematic setup for the liquid-liquid continuous extractor used in the experiment and hypothetical sequence of reactions to convert FAMES into FAEEs.

Although very low amounts of ester derivatives of linoleic acid were expected, they were not observed. Work is in progress to increase the yield of the first separated fraction analyzed in this work and assess the repeatability, reproducibility in the observed transesterification. This research covered several aspects of green chemistry, and the main compounds obtained are expected to serve as surfactants in diverse oil/water systems.

4. Conclusions

In this study, free fatty acids (palmitic and oleic acids) contained in local palm oil sludge were unexpectedly converted from their methyl esters (FAMES) into their ethyl esters (FAEEs) by a sequence of Fischer esterification and transesterification reactions. The amount of palmitic and oleic acid ethyl esters in the analysed fraction was more than 90 % of the extracted FAEEs. The transesterification process probably occurred during the liquid-liquid extraction when warm ethyl acetate from the liquid-liquid extractor dropped continuously into the basic aqueous phase containing FAMES. The novelty of the work was the observation of these appropriate conditions to convert methyl esters into their corresponding ethyl ester derivatives, as demonstrated by mass spectra data comparison.

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J. Chaparro performed the laboratory experiments and reported the results from the FT-IR and GC-MS analyses. J.M. Urbina supervised the experiments, checked the data and wrote the final report. All authors read and approved the final manuscript.

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The data set (GC-MS file in *.ms format) generated and analysed during this study is available in the Zenodo repository [DOI 10.5281/zenodo.5142503 at <https://doi.org/10.5281/zenodo.5142503>]