

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

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## Research

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# Abstract

Acid-catalyzed Fischer esterification of fatty acids with methanol as a reagent and solvent is used to prepare long chain alkyl methyl esters. Transesterification of palm oil in basic media using methanol is a synthesis route to prepare monoalkyl methyl esters of fatty acids. In this work, we report performing Fischer esterification of a sample of local palm oil sludge (rich in fatty acids) in the presence of methanol and obtaining ethyl esters of oleic and palmitic acids from transesterification reactions during extractions with ethyl acetate.

## 1. Introduction

Biodiesel, a mixture of monoalkyl esters of biodegradable long chain fatty acids, contains insignificant amounts of sulfur and is nontoxic and renewable [1]. Biomass conversion via the transesterification of palm oil sludge (POS) with methanol is a common route to synthesize fatty acid methyl esters (FAMES) [1]. Currently under study for potential applications as renewable oils and biofuels [2], fatty acid ethyl esters (FAEEs) can provide less toxic means to manage ethanol [3]. Our interest is modifying locally produced POS to produce fatty acid esters, and we hope to encourage others to build upon previous research in this field and eventually prepare substances of added value, e.g., surfactants.

## 2. Materials And Methods

POS used in this study was obtained from the third lagoon of the oxidation ponding system of Palmas del Cesar S. A. 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  $\text{H}_2\text{SO}_4$  (0.13 g) catalyst were added. The mixture was heated at  $60^\circ\text{C}$  at 300 rpm for 3 h according to Nata et al. [1] After cooling the reactor, the mixture was treated with 200 mL saturated  $\text{Na}_2\text{CO}_3$  solution to  $\text{pH} > 10$  to neutralize the  $\text{H}_2\text{SO}_4$  catalyst and poured into a continuous liquid-liquid extractor using 150 mL ethyl acetate (EA) as solvent and heating under reflux for 24 h. The organic layer was roto-evaporated, and solvents (methanol and ethyl acetate) were removed at  $40^\circ\text{C}$  under vacuum until a constant weight was obtained (4.78 g, 96 % mass). The resulting oily residue was purified by column chromatography (CC) on  $\text{SiO}_2$  using petroleum ether (PE):ethyl acetate (EA) (ratio 90:1) as the eluent. After purification, 1.65 g of a colorless oily sample was isolated (35 %),  $R_f = 0.33$  (PE:EA, ratio 90:1). Compounds in the sample 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 i.d.; 0.25 mm film thickness), analyzed 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 [4]. MS Interpreter version Beta 3.1a [5] (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

PE Soxhlet extraction separated the substances of interest from insoluble inorganic (sand) and organic material (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  $1697.5\text{ cm}^{-1}$  for carboxylic acids, where no ester band of glycerides is observed. Then, methanol-based esterification was performed according to Nata et al. [1] 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 [6], as corroborated by MS spectra of the less polar fraction obtained after CC. The FT-IR spectrum in Fig. 1 (bottom) shows the typical C = O stretching band for esters at  $1737.5\text{ cm}^{-1}$ .

GC-MS analysis of the isolated fraction (column chromatography, 35 % mass yield,  $R_f = 0.33\text{ SiO}_2$ , PE/EA 90:1) was carried out to identify the main compounds in that sample. Analyte MS spectra comparison using a mass spectral library search [7] corroborates the formation of ethyl esters of fatty acids instead of the expected methyl esters. Figure 2 presents the resulting gas chromatogram; the two main compounds in the fraction (91.7 %) were identified as ethyl palmitate ( $\text{C}_{18}\text{H}_{36}\text{O}_2$ , 53.6 %) and ethyl oleate ( $\text{C}_{20}\text{H}_{38}\text{O}_2$ , 38.1 %) with a higher match factor correspondence for its (*E*)-stereoisomer, in agreement with Nata et al. [1]. 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 [8]. 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 is shown in Fig. 3 (top) for ethyl palmitate and in Fig. 3 (bottom) for ethyl oleate.

Table 1

Match factors from the comparison of the mass spectra for the main analytes obtained in the CG-MS spectrum of the ester mixture and compounds in the NIST library.

Peak Name	tR (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 <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	1.0	Ethyl laurate	870
							[Ethyl dodecanoate]	
							Methyl tridecanoate	584
2	11.874	1.09	924	256.2	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	1.0	Ethyl myristate	910
							[Ethyl tetradecanoate]	
							Methyl pentadecanoate	632
3	13.717	1.59	1246	270.3	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	1.0	Methyl palmitate	947
							[Methyl hexadecanoate]	
							Ethyl pentadecanoate	605
4	14.758	53.54	1428	284.2	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	1.0	Ethyl palmitate	903
							[Ethyl hexadecanoate]	
							Methyl heptadecanoate	625
5	16.171	0.93	1675	296.3	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	2.0	Methyl oleate	926
							[Methyl (9Z)-Octadec-9-enoate]	
							Methyl (9E)-Octadec-9-enoate	922
6	17.316	38.13	1868	310.3	C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>	2.0	Ethyl (9E)-octadec-9-enoate	917

\* Ring and double bond equivalent

Peak Name	tR (min)	Area (%)	Scan No.	Molecular ion mass (g/mol)	Assigned formula	RDBE*	Assigned compound	Match Factor
							Ethyl oleate [Ethyl (9Z)-octadec-9-enoate]	892
							Methyl (10Z)-nonadec-10-enoate	726
7	17.562	3.84	1918	312.3	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	1.0	Ethyl stearate [Octadecanoic acid ethyl ester]	782
							Methyl nonadecanoate	671
* Ring and double bond equivalent								

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 IR spectra (Fig. 1, black spectrum), the POS contained predominantly carboxylic acids similar to compositions described in other reports [9], i.e., palmitic acid and oleic acid as the main components. Then, the POS sample underwent Fischer esterification (heating under reflux of 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<sub>x</sub>H<sub>y</sub>O<sub>2</sub> 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.

As reported by Dubé et al. [10], for our similar biphasic system, ester interchange should occur in the interphase, as shown in Fig. 4. The use of a weak base solution allowed the removal of the FFAs into the aqueous layer [11] as carboxylates, avoiding any interference in the reaction. Then, alkaline transesterification occurred in a similar way to the normal alkaline-catalyzed transesterification of vegetable oils to produce FAME and glycerol [11], considering that a small concentration of methoxide anion formed in the basic media through deprotonation of the residual methanol (used in the previous Fischer esterification) (Fig. 4, orange arrow). 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 ethoxide anion into the interphase where conditions allowed the ester to interchange from FAME to FAEE. The contact of the warm solvent with the aqueous layer provided the energy needed to

drive the reaction to form FAEE products, and the equilibrium was shifted by excess ethyl acetate and the extended duration of the process (24 h).

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 report. 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 palm oil sludge were unexpectedly converted into their ethyl esters (FAEEs) by a sequence of Fischer esterification and transesterification reactions. The transesterification process probably occurred during an extraction when warm ethyl acetate from the liquid-liquid extractor dropped continuously into the basic aqueous phase containing FAME. These were appropriate conditions to convert methyl esters into their corresponding ethyl ester derivatives, as demonstrated by mass spectra data comparison.

## Declarations

### Availability of data and materials

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

### Competing interests

The authors declare they have no competing interests.

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### Authors' contributions

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

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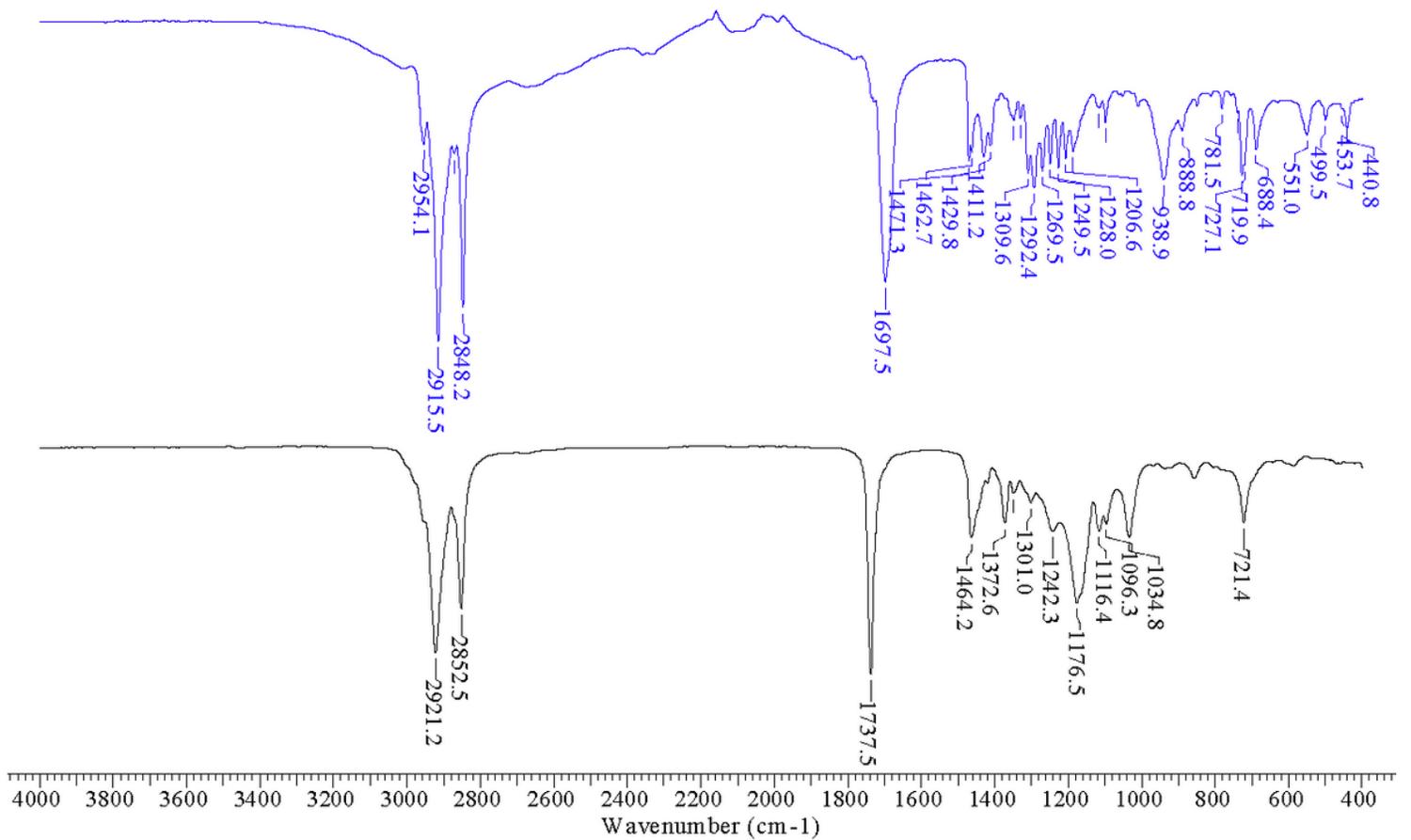
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J. Ch.-A. is a professional chemist with 5 years of experience in the industrial preparation of commercial liquid soaps. As a student in his final year of a Chemical Engineering M.Sc. program, he is developing his research about the use of palm oil sludge as a raw material for the preparation of surfactants. J.-M. U.-G. is lecturer in organic chemistry at the Universidad Industrial de Santander, and he is the supervisor of J. Ch.-A. in his M.Sc. research project.

## References

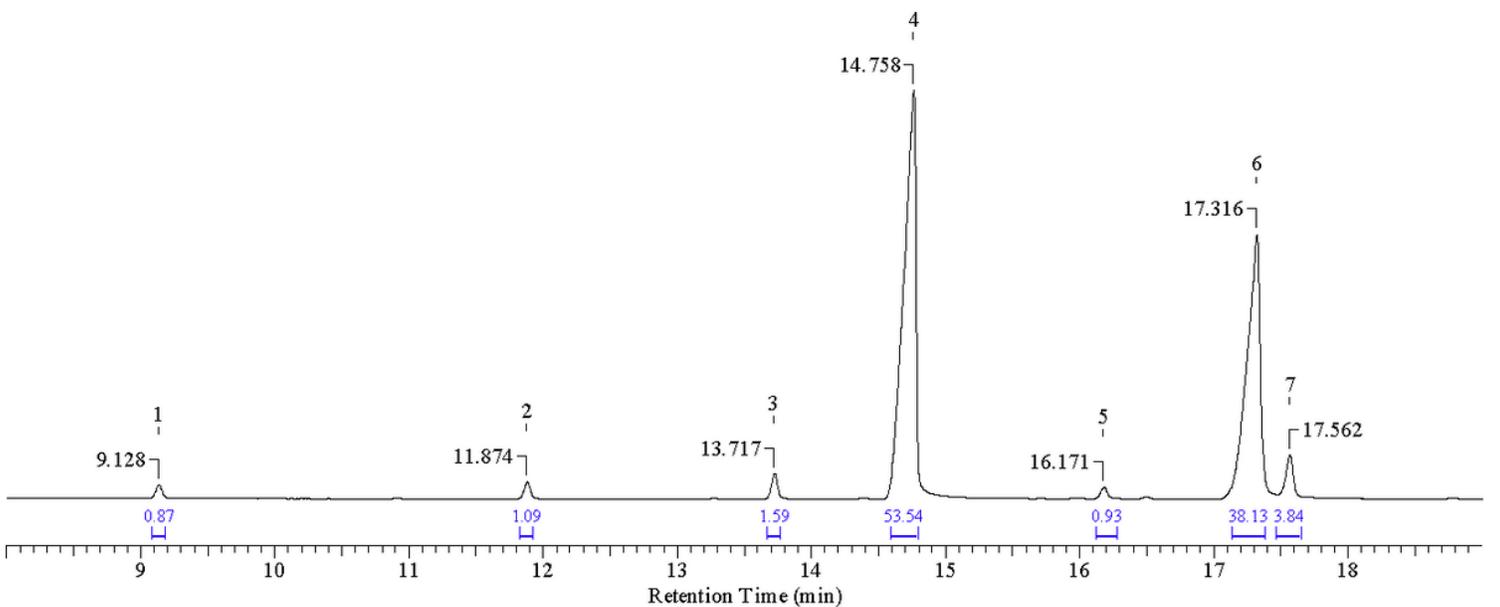
1. Abdullah, Rahmawati Sianipar RN, Ariyani D, Nata IF. Conversion of palm oil sludge to biodiesel using alum and KOH as catalysts. *Sustain Environ Res* 2017;27:291–5. <https://doi.org/10.1016/j.serj.2017.07.002>.
2. Nduwayezu JB, Ishimwe T, Niyibizi A, Munyentwali A. Biodiesel production from unrefined palm oil on pilot plant scale. *Int J Sustain Green Energy* 2015;4:11–21. <https://doi.org/10.11648/j.ijrse.20150401.13>.
3. Yusoff MFM, Xu X, Guo Z. Comparison of fatty acid methyl and ethyl esters as biodiesel base stock: a review on processing and production requirements. *J Am Oil Chem Soc* 2014;91:525–31. <https://doi.org/10.1007/s11746-014-2443-0>.
4. NIST/EPA/NIH Mass Spectral Library with Search Program - Data ver. 2.3. Gaithersburg, MD, USA: National Institute of Standards and Technology (NIST); 2017.
5. Y. Mirokhin, D. Tchekhovskoy, A. Mayorov, S. Stein. MS Interpreter Version BETA 3.1a. Gaithersburg, MD, USA: National Institute of Standards and Technology (NIST); 2017.
6. Dijkstra AJ. Revisiting the mechanisms of low-temperature, base-catalysed ester interchange reactions. *Ol Corps Gras Lipides* 2008;15:208–12. <https://doi.org/10.1051/ocl.2008.0200>.
7. Kind T, Fiehn O. Advances in structure elucidation of small molecules using mass spectrometry. *Bioanal Rev* 2010;2:23–60. <https://doi.org/10.1007/s12566-010-0015-9>.
8. Stein SE, Wallace W, Ji W, Little J, Markey S, Mallard WG, et al. Software user's manual for NIST Standard Reference Database 1A - NIST/EPA/NIH Mass Spectral Library (NIST 17) & NIST Mass Spectral Search Program (Version 2.3) 2017.
9. Aranda DAG, Santos RTP, Tapanes NCO, Ramos ALD, Antunes OAC. Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids. *Catal Lett* 2008;122:20–5. <https://doi.org/10.1007/s10562-007-9318-z>.
10. Ataya F, Dubé MA, Ternan M. Single-phase and two-phase base-catalyzed transesterification of canola oil to fatty acid methyl esters at ambient conditions. *Ind Eng Chem Res* 2006;45:5411–7. <https://doi.org/10.1021/ie060152o>.
11. Nitbani FO, Tjitda PJP, Nurohmah BA, Wogo HE. Preparation of fatty acid and monoglyceride from vegetable Oil. *J Oleo Sci* 2020;69:277–95. <https://doi.org/10.5650/jos.ess19168>.

# Figures



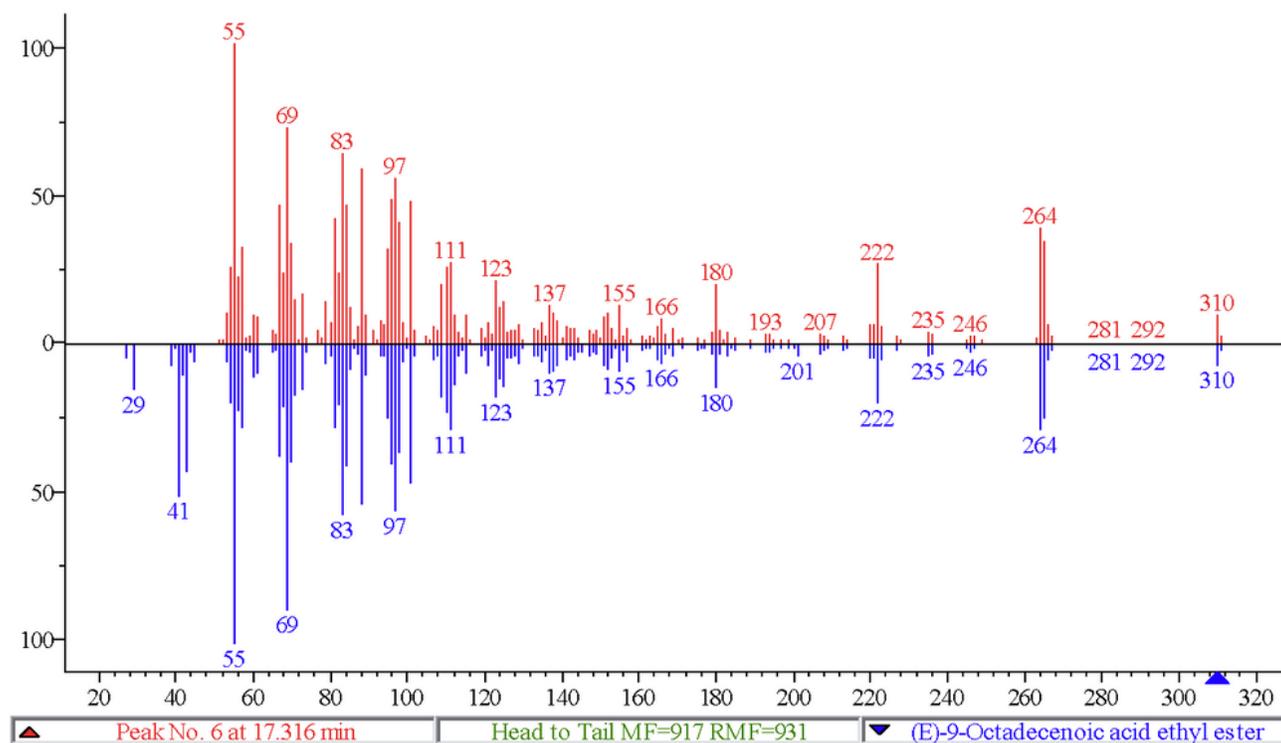
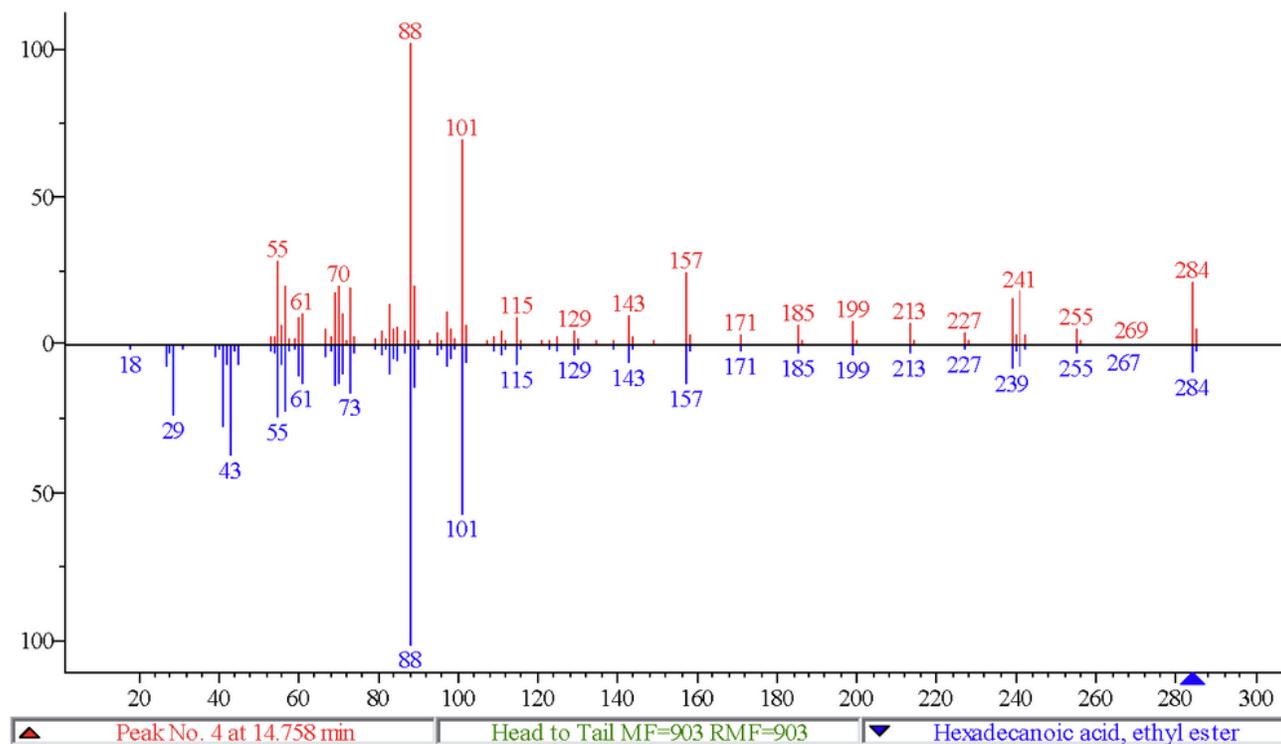
**Figure 1**

FT-IR spectra of the palm oil sludge after Soxhlet extraction (in blue) and the obtained ester mixture (in black). The C=O stretching signal appears at 1697.5 cm<sup>-1</sup> for carboxylic acids (top) and 1737.5 cm<sup>-1</sup> for the mixture of esters (bottom).



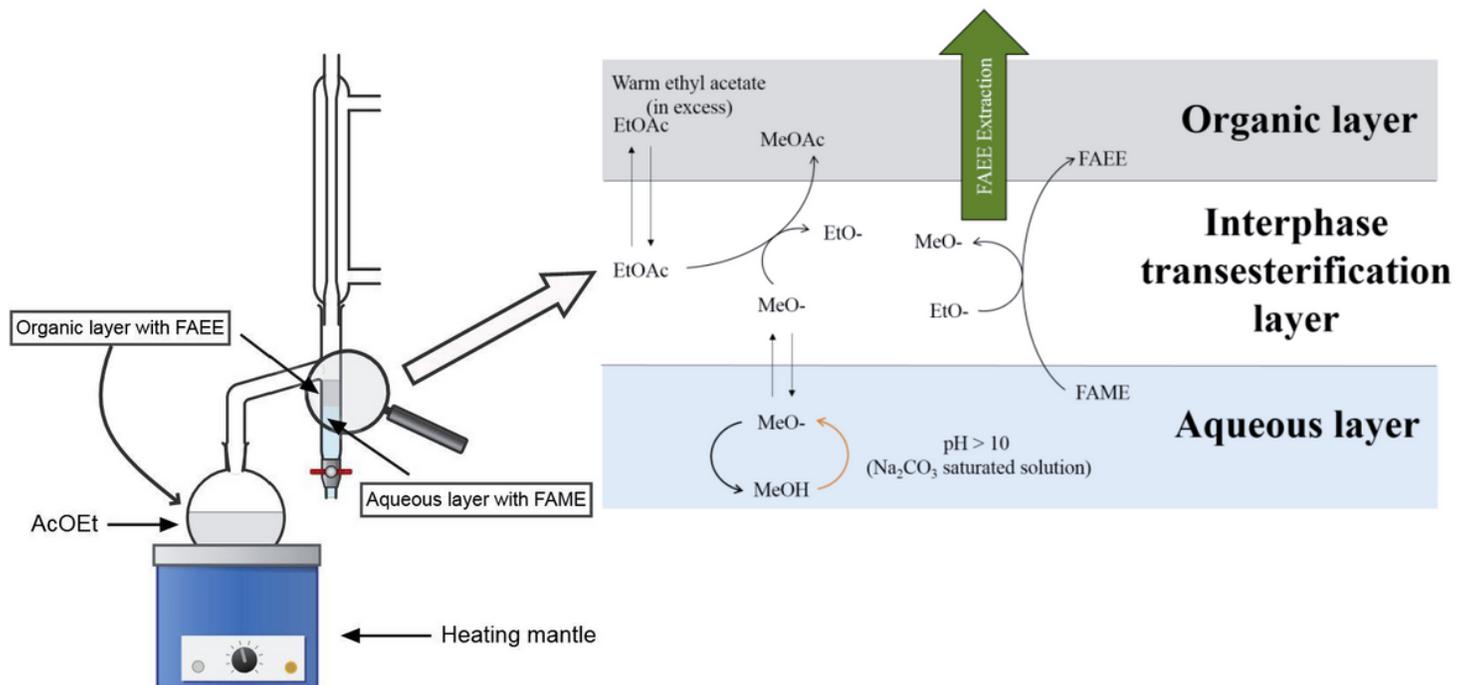
**Figure 2**

TIC obtained for the CG-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 identification of the other numbered peaks, see Table 1.



**Figure 3**

Results of the comparison of the mass spectra with the NIST library. The MS spectrum for peak No. 4 ( $m/z = 284.2$  g/mol, in red) matches the library spectrum for ethyl palmitate (in blue, top), and the MS spectrum for peak No. 6 ( $m/z = 310.3$  g/mol, in red) matches the library spectrum for isomeric ethyl oleate (in blue, bottom). The match factor (MF) and reverse match factor (RMF) for each comparison are also included.



**Figure 4**

Schematic diagram of the liquid-liquid continuous extractor used in the experiment and steps in the hypothetical sequence of reactions to convert FAMEs into FAEEs.