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From ethyl biodiesel to biolubricants: Options for an Indian mustard integrated biorefinery toward a green and circular economy

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1 **From Ethyl Biodiesel to Biolubricants: Options for an Indian** 2 **Mustard Integrated Biorefinery towards a Green and Circular** 3 **Economy**

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5 *Jing Chen*^a, *Xiaoqiang Bian*^a, *Graeme Rapp*^b, *James Lang*^c, *Alejandro Montoya*^c, *Richard*
6 *Trethowan*^b, *Brice Bouyssiere*^d, *Jean-François Portha*^a, *Jean-Noël Jaubert*^a, *Peter Pratt*^e, and
7 *Lucie Coniglio*^{a*}

8
9 ^a Université de Lorraine - Ecole Nationale Supérieure des Industries Chimiques de Nancy,
10 Laboratoire Réactions et Génie des Procédés UMR CNRS 7274, 1, rue Grandville BP 20451,
11 54001 Nancy Cedex, France; jng.chen@univ-lorraine.fr (Jing Chen); xiaoqiang.bian@univ-lorraine.fr
12 (Xiaoqiang Bian); jean-francois.portha@univ-lorraine.fr (Jean-François Portha);
13 jean-noel.jaubert@univ-lorraine.fr (Jean-Noël Jaubert); lucie.coniglio@univ-lorraine.fr
14 (Lucie Coniglio)

15 ^b The University of Sydney, Plant Breeding Institute, I.A. Watson International Grains
16 Research Centre, PO Box 219, Narrabri, NSW 2390, Australia; graeme.rapp@sydney.edu.au
17 (Graeme Rapp); richard.trethowan@sydney.edu.au (Richard Trethowan)

18 ^c School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006,
19 Australia; james.lang@sydney.edu.au (James Lang); alejandro.montoya@sydney.edu.au
20 (Alejandro Montoya)

21 ^d CNRS / UNIV Pau & Pays de l'Adour, Institut des Sciences Analytiques et de Physico-Chimie
22 pour l'Environnement et les Matériaux, UMR 5254, 64000 Pau, France;
23 brice.bouyssiere@univ-pau.fr (Brice Bouyssiere)

24 ^e Ineos Enterprises France, Z.I. Baleycourt BP 10095, 55103 Verdun, France;
25 peter.pratt@ineos.com (Peter Pratt)

26
27 * To whom correspondence should be addressed. E-mail: lucie.coniglio@univ-lorraine.fr
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31 **Abstract**

32

33 This work aims to analyze whether Indian mustard can be harnessed within a biorefinery system
34 to generate energy carriers and high value-added products. Within this objective, two options
35 of harnessing Indian mustard seed oil (IMSO) were investigated, the first for the production of
36 ethyl biodiesel (IMSOEEs) and the second for the production of a biolubricant (IMSO2E1HEs)
37 by transesterification of the unpurified IMSOEEs with 2-ethyl-1-hexanol (2E1H). Furthermore,
38 low cost and environmentally-friendly conversion processes were targeted. The biofuel was
39 obtained under mild conditions of ethanolysis (35°C, atmospheric pressure, ethanol to oil molar
40 ratio of 8, 1.1 wt % KOH, and 50 min) carried out in two-stages separated by addition of
41 recycled glycerol, and followed by dry-purification with Indian mustard stems-based adsorbent.
42 In order to enhance biolubricant yield, reactive distillation with optimized operating pressure
43 was selected (0.05 bar, 70°C, 2 wt % KOH, 2E1H to IMSOEEs molar ratio of 2, 65 min),
44 followed by bubble-washing (assisted with citric acid) and then vacuum distillation (inferior to
45 0.01 bar). The produced IMSOEEs met the basic biodiesel properties with a satisfactory ester
46 content (95.8 wt %). Similarly, a high conversion of IMOEEs (93 wt %) was reached for the
47 biolubricant, leading to an IMSO2E1HE product that exhibited satisfactory properties, and thus
48 has the potential to act as a biolubricant. Nevertheless, these results could be improved with a
49 pre-treatment of the departure IMSO to remove species that are not glycerides, such as
50 glucosinolates. Thereby, ensuring that the produced ethyl biodiesel conforms strictly to industry
51 specifications.

52

53

54 **Keywords:** ethyl biodiesel; biolubricant; Indian mustard; biorefinery concept; low cost
55 production

56

57

58 **Abbreviations**

59	ALSI	Automatic liquid sampler injector system
60	AES	Atomic Emission Spectrometry
61	BET	Brunauer-Emmet-Teller
62	DGs	Diacylglycerides (or diglycerides)
63	EC	Ethyl cellulose
64	EDS	Energy dispersive X-ray spectroscopy
65	Ethyl C18:1	Ethyl oleate
66	Ethyl C18:2	Ethyl linoleate
67	Ethyl C18:3	Ethyl linolenate
68	2E1H C18:1	2-Ethyl-1-hexyl oleate
69	2E1H C18:2	2-Ethyl-1-hexyl linoleate
70	2E1H C18:3	2-Ethyl-1-hexyl linolenate
71	FAEEs	Fatty acid ethyl esters
72	FAMEs	Fatty acid methyl esters
73	FFAs	Free fatty acids
74	FID	Flame ionization detector
75	FIMS	Fine Indian mustard stems
76	GC	Gas-chromatography
77	IMSO	Indian mustard seed oil
78	IMSOy	Indian mustard seed oil obtained from yellow seeds
79	IMSO _b	Indian mustard seed oil obtained from brown seeds
80	IMSOEEs	Indian mustard seed oil ethyl esters (ethyl biodiesel)
81	IMSOyEEs	Ethyl esters of Indian mustard seed oil (ethyl biodiesel) obtained from yellow
82		seeds
83	IMSO _b EEs	Ethyl esters of Indian mustard seed oil (ethyl biodiesel) obtained from brown
84		seeds
85	IMSO2E1HE	Indian mustard seed oil 2-ethyl-1-hexyl ester (biolubricant)
86	IS	Internal standard
87	[KOH]	Potassium hydroxide concentration
88	MGs	Monoacylglycerides (or monoglycerides)
89	MHD	Methyl heptadecanoate
90	MR	Molar ratio
91	MS	Mass spectrometry

92	NEVO	Non-edible vegetable oil
93	S.I.	Supporting information
94	SEM	Scanning electron microscopy
95	STP	Standard temperature and pressure (T = 273.15 K; P = 10 ⁵ Pa)
96	TGs	Triacylglycerides (or triglycerides)
97	2E1H	2-ethyl-1-hexanol

98
99

100 1. Introduction

101

102 Biomass harnessed within the biorefinery concept that involves low cost and environmentally-
 103 friendly conversion processes to generate energy carriers and high value-added products is
 104 essential for a sustainable plant-based industry (Coniglio et al., 2014; Navarro-Pineda et al.,
 105 2016; Raman et al., 2018). Mustard is an important commercial plant across the world that is
 106 used for food and oil production and can naturally be integrated within a synergetic cropping
 107 system.

108 Indian mustard is a hardy, drought and disease resistant species with biofumigation
 109 properties that provides a chemical-free disease suppression in subsequent cereal crops, such as
 110 wheat and barley (Kirkegaard and Sarwar, 1999; Handiseni et al., 2012; Ngala et al., 2015).
 111 Cultivation of Indian mustard as a rotational crop for oil production is more versatile than other
 112 perennial plants, such as *Pongamia* trees, because the annual growth cycle is faster, reducing
 113 establishment costs, time to product delivery, and therefore, is ideal in climate change
 114 conditions (Boomiraj et al., 2010; Singh et al., 2018). The Indian mustard oil production and
 115 processing leave many valuable components which have potential to improve the commercial
 116 viability in an integrated biorefinery. For instance, pharmaceutical, veterinary, agricultural and
 117 animal food products can be obtained from the meal due to the high content of glucosinolates,
 118 proteins and fibre, and bioethanol and biogas can be obtained from the digestion of residues for
 119 energy generation. Mustard oils naturally contain a high erucic acid content which is harmful
 120 to human health (Tabtabaei et al., 2014). This has been reduced by selective breeding, enabling
 121 it to compete with canola as cooking vegetable oil (Rapp, 2018). Nevertheless in the context
 122 of a rotation crop for biofumigation, biodiesel and biolubricants can be obtained from the seed
 123 oil with limited environmental footprint, and it has been shown that high erucic acid varieties
 124 provide biodiesel with superior lubricating properties (Tabtabaei et al., 2014).

125 With reference to the production of biolubricants and biodiesel, vegetable oils (or any
126 lipid sources) require first chemical modifications to obtain the esters that meet the desired
127 properties and fulfill the standards in terms of performance. Regarding biolubricants (or bio-
128 based lubricants), the three main chemical routes currently used to enhance vegetable oil
129 properties targeted for this application, i.e. cold flow properties and thermal-oxidative stability,
130 are: (i) esterification or transesterification, (ii) estolide formation, and (iii) epoxidation followed
131 by ring opening and acetylation (McNutt et al., 2016; Syahir et al., 2017; Chan et al., 2018).
132 The first route requires high oleic base stocks to produce biolubricants meeting requirements
133 and high vacuum conditions to decrease the reaction temperature. The second route requires a
134 lower reaction temperature but often needs capping fatty acids which are expensive reactants
135 (Cermak et al., 2013; Syahir et al., 2017). Hence, to reduce the production cost by extending
136 the potential sales markets, de Haro et al. (2018) developed a three-step process leading to
137 methyl biodiesel and choline carboxylates (biosurfactants), in addition to estolide methyl esters
138 (biolubricant). The third route requires multiple reaction stages making it economically
139 unfavorable, although the final product exhibits ideal lubricant properties (McNutt et al.,
140 2016). Moreover, vegetable oil modifications by estolide formation or epoxidation followed by
141 ring opening and acetylation mainly occur under homogeneous acid catalysis, which involves
142 catalyst loss and potential corrosion issues during process operation. By contrast, the
143 transesterification of vegetable oils with long-chain alcohols (containing more than 5 carbon
144 atoms) or polyols (trimethylolpropane) may be carried out under homogeneous or
145 heterogeneous basic catalysis, with additionally a shorter reaction time compared with acid
146 catalysis (Zheng et al., 2018); the latest tendency being the enzymatic catalysis (Cerón et al.,
147 2018) extended to the esterification (Kim et al. 2019) to operate under mild conditions, but at
148 the cost of a longer reaction time. Regarding biodiesel production, transesterification with a
149 short-chain alcohol (methanol or ethanol) is the most widely used route to convert vegetable
150 oils into biodiesel, exhibiting much better engine performance and emission characteristics; not
151 to mention a much lower viscosity to avoid engine failure (Coniglio et al., 2013).

152 This work investigates two aspects of harnessing Indian mustard seed oil (IMSO), the
153 first for production of ethyl biodiesel (energy carrier) and the second for conversion of the
154 produced ethyl biodiesel into biolubricant (high-added value product). Both ethyl biodiesel and
155 biolubricant are produced via a common conversion process (KOH-based transesterification).
156 This flexibility is particularly suitable as crude oil prices fluctuate and the global demand for
157 lubricants is expected to increase by 2.0% per year to 45.40 million metric tons in 2020, with
158 the share of bio-based lubricant market projected to rise to 15-30%. This shift towards

159 biolubricants is mainly due to their high biodegradability, low aquatic toxicity, and
160 renewability, as they are mainly derived from vegetable oils (Karmakar et al., 2017; Panchal
161 et al., 2017; Hossain et al., 2018). Hence, thanks to their polar attraction to metals induced by
162 the chemical structure of their base stocks, biolubricants often perform better than conventional
163 mineral oil-based lubricants. Indeed, biolubricants exhibit higher adhesiveness, lubricity, and
164 thereby reduced frictional losses in engines and machinery, lowering energy or fuel
165 consumption, and subsequently decreasing harmful gases emissions (Syahir et al., 2017; Chan
166 et al., 2018; Hossain et al., 2018). The development of economic and green processes for the
167 production of biolubricants to replace mineral oil-based lubricants is thus critical (Karmakar
168 et al., 2017), especially from cheaper and reliable feedstocks (Wang et al., 2014; Syahir et al.,
169 2017).

170 While ethanol was selected to conduct the transesterification reaction leading to the
171 targeted biofuel, the alcohol commonly used to obtain the targeted biolubricant for
172 metalworking applications is 2-ethyl-1-hexanol (Habib et al., 2014; Kleinaité et al., 2014;
173 Trivedi et al., 2015; Geethanjali et al., 2016; Syahir et al., 2017; Zheng et al., 2018). Ethyl
174 biodiesel (fatty acid ethyl esters, FAEs) was preferred to the commonly commercialized
175 methyl biodiesel (fatty acid methyl esters, FAMES) for two main reasons: (i) apart from being
176 non-toxic, bioethanol may be produced from agricultural resources and residues, leading thus
177 to a 100% renewable biodiesel (Brunschwig et al., 2012; Coniglio et al., 2014; Navarro-
178 Pineda et al., 2016); (ii) FAEs have better biodegradability, higher flash point, improved
179 cold-flow properties and oxidation stability, and lower emissions of NO_x, CO, and ultrafine
180 particles than FAMES (Coniglio et al., 2013). Furthermore, fusel oil obtained as by-product of
181 ethanol fermentation and composed mainly of isoamyl alcohol has been used successfully to
182 produce biolubricant by transesterification of palm kernel oil (Cerón et al., 2018). Hence, a
183 major part of ethanol production industry could be integrated in the proposed process to yield
184 biodiesel (by using ethanol) and biolubricant (by using fusel oil), limiting material inputs,
185 production costs, and environmental impacts.

186 Apart from the development of a conversion process focused on a sustainable plant-
187 based industry, the novelty of this work is at two levels. Firstly, while the production of
188 biodiesel using the selected method (KOH-based ethanolysis with addition of recycled glycerol
189 followed by dry-purification with a natural adsorbent, the whole conducted under “ambient”
190 conditions) has proven to be efficient, low-cost, and environmentally-friendly for various non-
191 edible vegetable oils (NEVOs) (Nitièma-Yefanova et al., 2017), it has never been validated
192 with Indian mustard (*Brassica juncea*) by using the oil as a triglyceride source and the stems as

193 adsorbent. Ethanolysis of mustard (*Brassica nigra*) seed oil followed by dry-purification with
194 activated carbon from de-oiled cake was recently performed in the literature (Fadhil et al.,
195 2014), but under higher temperature. Secondly, regarding biolubricant production, the
196 combined effect of reactive distillation and reaction pressure (mainly investigated for
197 biolubricant synthesis by fatty acid esterification with polyols (Maurad et al., 2018; Kim et
198 al., 2019)) is revealed for the first time in this work (i.e. within the framework of ethyl biodiesel
199 transesterification with a long-chain branched alcohol such as 2-ethyl-1-hexanol).

200

201

202 2. Materials & Methods

203

204 A schematic representation of the catalyzed transesterification reactions that were
205 carried out in this work for the production of ethyl biodiesel and biolubricant are described in
206 Figures 1-2.

207

207 Figures 1-2

208

209 2.1. Materials

210

211 Reagents (citric acid, ethanol, glycerol, and potassium hydroxide), solvent (n-heptane)
212 and the chromatographic standards (methyl heptadecanoate, ethyl oleate) of analytical grade
213 were obtained from Merck, Acros Organics or Sigma-Aldrich. On the other hand, 2-ethyl-1-
214 hexanol (> 99 %) was provided by Ineos Enterprises France. For the lipid feedstock, yellow
215 and brown color Indian mustard seeds were used to obtain IMSOy and IMSOb samples
216 respectively, by mechanical crushing followed by filtration (Rapp, 2018). Characterization of
217 the oils in terms of fatty acid profiles and key properties with respect to ethanolysis, together
218 with the analytical techniques used, are summarized in Tables 1 and 2. The natural adsorbent
219 used in the dry-purification stage of ethyl biodiesel was prepared from Indian mustard stems,
220 previously sundried for 2-3 days, crushed and then sieved to a particle size of 100 to 710 µm.
221 Characterization of the obtained particles, designated FIMS, is detailed in Appendix B
222 (Mazivila et al., 2015; Feng et al., 2018; Rapp et al., 2018).

223

223 Tables 1-2

224

225 2.2. From *Indian mustard seed oils* to ethyl biodiesel

226

227 All experiments and analyses were conducted at least in duplicate (in triplicate when
228 disagreement was found). From each set of duplicates an average value was then calculated and
229 provided as result (for triplicates or more, results are given in terms of average \pm standard
230 deviation).

231

232 2.2.1. Conversion of *the Indian mustard seed oils*

233 The FFA and water contents of the departure lipid feedstocks (**Table 2**) confirm that the
234 alkali catalysis is a suitable route to produce the Indian mustard seed oil ethyl esters
235 (IMSOEEs). Similar to [Nitièma-Yefanova et al. \(2016-2017\)](#), a two-stage procedure with
236 intermediate addition of glycerol to enhance ethanolysis yields was adopted. However, the
237 various operating conditions were optimized for each lipid feedstock. The operating conditions
238 selected in this work (together with the corresponding IMSOEE content and ethanolysis-
239 separation yield) are summarized in **Table 3**. The catalyst and stirring parameters (speed and
240 duration) were **set** once and for all (respectively to KOH and 250 rpm during the first reaction
241 stage as this choice had showed to be the most appropriate for ethanolysis conducted in a
242 laboratory scale setup ([Nitièma-Yefanova et al., 2016](#))). By contrast, the other key variables
243 of the ethanolysis reaction, i.e. temperature, ethanol to oil molar ratio (MR), catalyst mass
244 concentration, mass fraction of glycerol added, were changed successively within ranges to
245 allow an optimum set of values to be reached while satisfying our constraints (biodiesel
246 production with low cost and high yields). In the same context, the possibility of reusing crude
247 glycerol by-produced from previous biodiesel production runs was also assessed.

248

248 **Table 3**

249 All ethanolysis reactions were carried out in a 250 mL three-neck round bottom flask
250 equipped with a thermometer ($\pm 0.5^\circ\text{C}$), a reflux condenser, a sampling **outlet, and** a
251 temperature-controlled magnetic stirrer system ($\pm 1^\circ\text{C}$) with a PTFE magnetic stir bar. After
252 weighing the desired amount of IMSO (60 g) in the dried reaction flask, the **system** was heated
253 to the **set** temperature **under constant stirring. Simultaneously, the** amounts of ethanol and KOH
254 defined for the experiment were mixed in another flask, preheated at the temperature of the
255 experiment, and then added to the IMSO. This addition **is taken** as time zero of the reaction.
256 After 30 min of reaction (end of the first stage), **glycerol was** added into the ethanolysis product,
257 showing as a single pseudo-homogenous phase (start of the second stage). Following 5 min of

258 vigorous stirring, the ethanolysis product was then allowed to stand at ambient temperature
259 until the end of the reaction time and subsequent phase separation. For experiments carried out
260 under ethanol normal boiling point, the reaction mixture was cooled to ambient temperature
261 prior to the addition of glycerol to reduce glycerol miscibility in the ester-rich phase. The
262 reaction time was set to a sufficient value for reaching the maximum conversion (60 min). Off-
263 line monitoring of ethanolysis was conducted by gas-chromatography coupled with a flame
264 ionization detector (GC-FID), at a given sampling frequency (2-min intervals up to 10 min of
265 reaction, and then 5-min intervals until the end of the experiment). The IMSOEEs were
266 preliminary identified by GC-mass spectrometry (MS). Information specific to the GC-
267 equipment and analysis of samples with preliminary neutralization are given in **Table A1**
268 (Appendix A) (EN-14103, 2011; Nitièma-Yefanova et al., 2016; Muhammad et al., 2017).

269 After the reaction, the ethanolysis product was transferred into a separating funnel. The
270 lower phase containing the introduced and liberated glycerol with entrained IMSOEEs was
271 withdrawn first, followed by the upper-phase consisting mainly of IMSOEEs with residual
272 glycerides and some glycerol. The ethanol remaining in each phase was then evaporated (70°C,
273 180 mbar, for 1.5 h) to further separate glycerol from the IMSOEEs (Zhou and Boocock, 2006;
274 Nitièma-Yefanova et al., 2017). The recovered fractions of IMSOEEs were then gathered to
275 determine the yield of the ethanolysis and separation steps according to:

276

$$277 \text{Yield (wt \%)} = \frac{\text{mass of crude IMSOEEs recovered}}{\text{initial mass of IMSO}} \times 100 \quad (1)$$

278

279 The IMSOEE samples of runs with high ester contents and yields were collected to
280 obtain a single pool from which a fraction was further purified by dry-washing (section 2.2.2);
281 the remainder was dedicated to biolubricant production (section 2.3).

282

283 2.2.2. Purification of IMSOEEs and fuel property evaluation

284 The IMSOEEs were mixed with a specified amount of the natural adsorbent to remove
285 residual catalyst, glycerol and other impurities. The procedure was modified from previous
286 work (Nitièma-Yefanova et al., 2015; 2017). A three stage dry-washing was conducted with,
287 for each treatment cycle, 4 wt % of adsorbent in the unpurified IMSOEE sample maintained
288 under stirring for 20 min at 35°C, followed by vacuum filtration. Details of the equipment and
289 operating conditions used to characterize the IMSOEEs before and after dry-washing on the
290 FIMS adsorbent are summarized in **Table A1** (Appendix A) (EN-ISO-12937, 2000; Pohl et

291 [al., 2010](#); [Caumette et al., 2010](#); [EN-14105, 2011](#); [EN-14103, 2011](#); [Nitièma-Yefanova et](#)
292 [al., 2015](#); [Muhammad et al., 2017](#)). Characterization was achieved by considering molecular
293 species such as triacylglycerides (TGs), diacylglycerides (DGs), monoacylglycerides (MGs),
294 free glycerin, water and IMSOEEs, and also potassium and heavy metals (brought into the
295 IMSOEEs via the catalyst used and the IMSO extraction stage). Some fuel properties of the
296 resulting ethyl biodiesel (acid value, color, density, viscosity, flash point, cloud point, and pour
297 point) were also evaluated in accordance to ASTM or ISO standards (**Table A1**, Appendix A)
298 ([EN-ISO-12185, 1996](#); [EN-ISO-3104, 1996](#); [EN-14104, 2003](#); [ASTM D1544-04, 2010](#);
299 [Carareto et al., 2012](#); [Bolonio et al., 2015](#)).

300

301 *2.3. From ethyl biodiesel to biolubricant*

302

303 The fraction of IMSOEEs that was not dedicated to purification (section 2.2.2) was
304 converted by alkaline transesterification with 2-ethyl-1-hexanol (2E1H) to obtain the targeted
305 biolubricant, i.e. IMSO-based 2-ethyl-1-hexyl esters (IMSO2E1HEs). As KOH used in excess
306 during ethanolysis was not removed from the IMSOEEs, the same catalyst was naturally used
307 for this additional transesterification step. The characteristics of the IMSOEEs used here as the
308 departure reactants (composition in molecular species including KOH content) are given in
309 **Table 4** for the IMSOEEs before purification.

310

Table 4

311

312 *2.3.1. Conversion of ethyl biodiesel*

313 Biolubricant synthesis was carried out in a laboratory scale batch reactive distillation
314 unit operating under low pressure. This option has two main positive features: (i) to reduce both
315 reaction temperature and reaction time leading to minimized energy costs; (ii) to remove
316 ethanol (by-product) by distillation from the reacting mixture, leading to increased biolubricant
317 yield by shifting the transesterification chemical equilibrium in favor of product formation. The
318 selected reactive distillation method (thus somewhat different to the commonly used method
319 with a reflux condenser ([Habib et al., 2014](#))) should help operating under a less severe vacuum.
320 Therefore, the impact of operating pressure on the transesterification (which has never been
321 investigated to the best of the authors' knowledge) was analyzed for three low pressure
322 conditions: 0.05, 0.1, and 0.5 bar. By contrast, the other key transesterification parameters were
323 kept constant (**Table 5a**): reaction temperature set at 70°C ([Habib et al., 2014](#)) (i.e. few degrees
324 under the boiling point of 2E1H at 0.01 bar), 2 wt % of KOH ([Habib et al., 2014](#)) (on basis of

325 the initial IMSOEE mass), MR (2E1H to IMSOEEs) = 2 (i.e. twice the stoichiometric value to
 326 shift even more the reaction chemical equilibrium towards products formation), with a reaction
 327 time long enough to promote conversion of IMSOEEs (65 min).

328 **Table 5**

329 Similarly to IMSO ethanolysis, all transesterification reactions of ethyl biodiesel to
 330 biolubricant were conducted in a 250 mL three-neck round bottom flask equipped with a
 331 thermometer ($\pm 0.5^\circ\text{C}$), a sampling outlet, and a temperature-controlled magnetic stirrer system
 332 ($\pm 1^\circ\text{C}$) with a PTFE magnetic stir bar. However, the reflux condenser was replaced by a
 333 Vigreux column surmounted by a second thermometer ($\pm 0.5^\circ\text{C}$) and connected, on the side, to
 334 a Liebig condenser. This was in turn connected to a vacuum take-off adapter for attachment via
 335 a three-way valve to the vacuum pump and to two flasks for collecting distilled ethanol. The
 336 Liebig condenser was cooled with a recirculating silicon oil bath (0°C) and the two collection
 337 flasks with an ice bath (for bulk reasons). In the procedure, crude IMSOEEs (50 g)
 338 corresponding to 44.06 g of FAEEs (content before purification: 88.1 wt %, **Table 4**; average
 339 molecular weight: 313, **Table 1**) were weighed directly in the dried reaction flask and were then
 340 heated to the selected temperature. Simultaneously, to generate the active species of the catalyst
 341 *in situ*, 2E1H (36.71 g) and KOH (0.8812 g) were mixed in another flask, preheated at the
 342 temperature of the experiment and then added to the IMSOEEs. The three-way valve was then
 343 switched for connecting the reactive distillation unit to the vacuum pump. This point was
 344 considered as time zero of the reaction which was monitored off-line by GC-FID at a given
 345 sampling frequency (10-min intervals until the end of the experiment, after a first sampling at
 346 4 min reaction time). Similar to IMSOEEs, preliminary identification of the IMSO2E1HEs was
 347 conducted by GC-MS, and information specific to the GC-equipment and sample analysis are
 348 given in **Table A1** (Appendix A) (**EN-14103, 2011; Nitièma-Yefanova et al., 2016;**
 349 **Muhammad et al., 2017**).

350 **The yield of biolubricant** was estimated by:

$$351 \text{ Yield (\%)} = \frac{(m_{\text{IMSO2E1HEs}})_{\text{actual}}}{(m_{\text{IMSO2E1HEs}})_{\text{theoretical}}} \times 100 \quad (2)$$

352 with: $(m_{\text{IMSO2E1HEs}})_{\text{actual}} = m_{\text{IMSO2E1HEs}}^{\text{crude}} \cdot \bar{x}_{\text{IMSO2E1HEs}}$ and

$$353 (m_{\text{IMSO2E1HEs}})_{\text{theoretical}} = \frac{\vartheta_{\text{IMSO2E1HEs}}}{\vartheta_{\text{IMSOEEs}}} \cdot \frac{m_{\text{IMSOEEs}}^{\text{crude}} \cdot \bar{x}_{\text{IMSOEEs}}}{M_{w_{\text{IMSOEEs}}}} \cdot M_{w_{\text{IMSO2E1HEs}}}$$

354

355 where ϑ_i is the stoichiometric coefficient of species i of molecular weight M_{w_i} and occurring
356 in the reacting mixture k of mass m_k^{crude} with a mass fraction \bar{x}_i . As illustrated in **Figure 2**,
357 $\vartheta_{IMSOEEs}$ and $\vartheta_{IMSO2E1Hs}$ are both equal to unity.

358

359 *2.3.2. Purification of IMISO2E1HEs and biolubricant property evaluation*

360 The crude IMISO2E1HEs were purified by batch bubble-washing conducted at 35°C, 1
361 atm, with a 4 wt% citric acid solution in distilled water at first, and then only distilled water.
362 Washing solution and esters (respective volume proportions: 1/3 and 2/3) were poured in a
363 separating funnel equipped inside with a fritted glass cannula connected to an air pump via a
364 control valve. Purification batches were carried out by replacing the contaminated washing
365 solution until potassium concentration in the aqueous phase remained constant (analysis by
366 Flame Atomic Emission Spectroscopy (Flame-AES), **Table A1**, Appendix A). After bubble-
367 washing to remove catalyst (with residual ethanol and potential traces of glycerol), excess 2E1H
368 and residual water-washing were recovered by vacuum fractional distillation (operating
369 pressure lower than 0.01 bar with a similar equipment as the one used for the batch reactive
370 distillation). Ester and potassium contents of the purified IMISO2E1HEs (distillation residue)
371 were respectively determined by GG-FID (**EN-14103, 2011; Nitièma-Yefanova et al., 2016;**
372 **Muhammad et al., 2017**) and ICP-AES (**Pohl et al., 2010; Caumette et al., 2010; Nitièma-**
373 **Yefanova et al., 2015**), while some key biolubricant quality requirements were evaluated
374 according to ASTM or ISO standards (**EN-ISO-12185, 1996; EN-ISO-3104, 1996; ISO-6618,**
375 **1997; ASTM D1544-04, 2010**) (**Table A1**, Appendix A).

376

377

378 **3. Results and discussion**

379

380 *3.1. Ethyl biodiesel production and main performance properties*

381

382 The fundamental aspects underpinning the following discussion are available in earlier
383 published works, both for the reaction & separation stages (supporting information-Appendix
384 A of (**Nitièma-Yefanova et al., 2016**)) and the dry-purification stage (**Nitièma-Yefanova et**
385 **al., 2015**). Consequently, results will be discussed on the basis of conclusive justifications
386 derived from these fundamental aspects.

387

388 3.1.1. Reaction and separation

389 The FAEE contents in percent mass fractions and the ethanolysis-separation yields
390 obtained for the most relevant experiments conducted in this work are presented in **Table 3**.
391 The FAEE contents as a function of time of the ethanolysis process monitored by GC-FID are
392 given in **Figures 3-6**.

393 **Figures 3-6**

394 As illustrated in **Figures 3-6**, for all operating conditions the FAEE content increases
395 rapidly during a short period, and then asymptotically approaches the first stage chemical
396 equilibrium imposed by the initial composition and temperature of the reacting mixture.
397 Furthermore, none of these FAEE profiles depict any mass transfer limitation at the early stage
398 of the reaction. Ethanol has a higher dissolving power for triglycerides than methanol.
399 Therefore, the sigmoidal profiles commonly obtained with methanolysis (under control of three
400 successive mechanisms: mass transfer, kinetics, and chemical equilibrium) are not observed
401 with ethanolysis (under control of the last two mechanisms, only). Then, after addition of
402 glycerol to initiate the second stage, the FAEE content increases sharply in the first few minutes
403 for asymptotically approaching a new chemical equilibrium state. The increment in the ester
404 content, generated during the 10 min after the glycerol addition, ranges from 3 to 9 wt %
405 depending on the initial operating conditions of the ethanolysis reaction. These increments
406 correspond to a glycerol recovery (after ethanol evaporation) of about 40 to 87 wt %, confirming
407 the two-stage procedure efficiency (glycerol performs as poorly as water for glyceride removal
408 (**Berrios et al., 2011**)).

409 Furthermore, temperature has a dual effect on IMSO ethanolysis. Indeed, when
410 ethanolysis is still under kinetic control (sharp rise of the ester profile), the temperature has a
411 positive impact, similar to catalyst concentration, by increasing the reaction rate constant
412 (Arrhenius law) thus accelerating glyceride conversion (**Figure 3**; exp. 11 vs 12 in **Figure 5**).
413 However, when ethanolysis comes under thermodynamic control (ester profile reaching a
414 plateau), temperature has a negative impact, particularly for MR approaching a critical value of
415 6:1 (plateaus of the 1st stage chemical equilibrium at 35 and 78°C far from each other in **Figure**
416 **3a**, much closer in **Figure 3b** with MR = 8:1). This behavior may firstly be explained by a
417 likely exothermicity of the IMSO ethanolysis as observed in the literature for soybean oil
418 (**Richard et al., 2013**) and some NEVOs (**Nitièma-Yefanova et al., 2017**); and secondly, by
419 the partial miscibility of glycerol into the ester-rich phase that is favored at higher temperature
420 (**Nitièma-Yefanova et al., 2016**). Nevertheless, IMSO ethanolysis should not be conducted at
421 temperatures lower than 35°C (i.e. 25°C, exp. 3 **Table 3** and **Figure 3**) although a decrease of

422 10°C in this temperature range does not seem to significantly impact the effect of glycerol
423 addition (ester content increment between the 1st and 2nd stage of chemical equilibrium when
424 reaction temperature is 35 or 25°C: 5 wt %; exp. 2 vs 3, **Table 3**).

425 In contrast, alcohol to oil MR had a positive impact on IMSO ethanolysis regardless of
426 whether the reaction was under kinetic or thermodynamic control (**Figure 4**). The effect is
427 however more significant when operating at a MR limiting value of 6:1. Indeed, at ambient
428 temperature (35°C) while rather similar ester profiles are obtained for MR ≥ 8:1, the deviation
429 is visible for MR = 6:1 by slowing the reaction rate and lowering the plateau of the 1st stage
430 chemical equilibrium (5 wt %, **Figure 4a**). This latter effect is even more important when
431 operating under higher temperature (78°C), with an ester content decrement of 15 wt %
432 observed when the MR decreased from 8:1 to 6:1 (**Figure 4b**). This result may be attributed to
433 the enhanced miscibility of glycerol in the reacting mixture under high temperature; within this
434 context, the relevant option to counterbalance this effect is to add ethanol in higher proportion
435 to shift the chemical equilibrium towards ester production.

436 Moreover, addition of glycerol involves a progress of the reaction all the more
437 substantial that glyceride conversion is incomplete (ester content increment of 8 wt % reduced
438 to 5 wt % when operating IMSO ethanolysis at 78°C or at 35°C) (**Figure 4**). Therefore for MR
439 = 8:1, addition of glycerol enhanced the plateau of the 2nd stage chemical equilibrium which
440 reached at 78°C the same level as the plateau reached at 35°C (**Figure 3**). Nevertheless, a larger
441 amount of glycerol than 25 wt % (up to 35 wt %) produced no significant rise in the ester
442 content at the 2nd stage (exp. 9, **Table 3**).

443 As could be expected, catalyst concentration has no effect on the chemical equilibrium
444 plateau, however in large excess it had a negative impact on glyceride conversion, with a slower
445 increment in the ester content after glycerol addition, likely by limiting liquid-liquid demixing
446 of the reacting mixture (exp. 12 vs 11 or 13, **Figure 5**).

447 The addition of recycled crude glycerol obtained as a by-product from previous
448 biodiesel production batches (ethanolysis & separation) yields as good results as the addition
449 of pure glycerol tested in the original procedure (**Nitièma-Yefanova et al., 2016-2017**) (exp. 2
450 vs 8; exp. 1 vs 10). Although this result is not surprising, since crude glycerol is rich in catalyst
451 and thus, can only increase even more the oil conversion, the recycling of glycerol is more
452 suitable for industrial purposes.

453 In addition of showing that the kinetics of ethanolysis is established by the major fatty
454 acid moiety of the departure lipid feedstock (i.e. oleic acid here), the results in **Figure 6** and
455 **Table 3** confirm that the two tested oils, IMSOy and IMSOb, have similar behavior; this is in

456 compliance with their very close chemical and physical properties (**Tables 1-2**), except for the
457 sulfur content that finally does not induce any difference. Therefore, the ethyl esters produced
458 from the two oils IMSOy and IMSOb will be designated in the following under a single
459 denomination IMSOEEs.

460 The key parameters of ethanolysis optimized in previous works for NEVOs (*Balanites*
461 *aegyptiaca* and *Azadirachta* oils (**Nitièma-Yefanova et al., 2016-2017**)) can be used for the
462 IMSOs **resulting in similar efficiencies** and guaranteeing satisfactory results (exp. 2, **Table 3**).
463 **Moreover**, the rather successful results obtained at a larger scale ($\times 3$) suggest a satisfactory
464 transfer at pilot scale (exp. 11 vs 13, **Table 3** and **Figure 5**). The recent work carried out on
465 ethanolysis of mustard (*Brassica nigra*) seed oil by using the traditional one-stage procedure
466 with similar operating conditions except for the reaction temperature (60°C) led to much higher
467 content in esters (98 wt %) (**Fadhil et al., 2014**); however, this value was obtained after
468 purification of the produced biodiesel.

469

470 3.1.2. Purification of IMSOEEs *and fuel properties*

471 The dry-purification yield (defined as Y_i (wt %) = $(m_i/m_o)\times 100$ with m_i and m_o the mass
472 of sample before and after treatment respectively) was 95 ± 1 wt %. Characterization results of
473 the produced IMSOEEs before and after dry-purification, along with of treatment efficiency,
474 are shown in **Table 4** for molecular species and chemical elements. As it can be observed, the
475 selected dry-purification procedure combined with the FIMS as adsorbent shows very good
476 performances. Indeed, the treated sample is concentrated in IMSOEEs with no retention of
477 specific esters while all contaminants are removed in whole (free glycerin, TGs, and K) or in
478 part (MGs, DGs, Sn), with the exception of water. This contamination from the FIMS suggests
479 that likely more care should be taken during storage (with a container tightly closed and
480 protected from moisture). Regarding the residual Sn in the purified IMSOEEs, it would difficult
481 to conclude whether this contamination brought during IMSO extraction by mechanical
482 treatment (**Table 2**) is an issue or not, since no standard-limiting requirement exists to date for
483 this metal. Also, it should be mentioned that the S atomic species initially observed by ICP-
484 AES in the departure IMSO (around 15 ppm on average, **Table 2**) is no **longer** detected in the
485 crude IMSOEEs; this reveals that the probably responsible glucosinolates are converted (into
486 other molecules than FAEEs) during the IMSO ethanolysis. Occurrence of other species than
487 glycerides (pool convertible into FAEEs) in the departure IMSO may explain the low IMSOEE
488 content obtained prior purification (88 wt %).

489 Although ester content does not meet the specifications after dry-purification (95.8
490 instead of the required 96.5 wt %), the resulting IMSOEE product shows very satisfactory
491 physical properties as biodiesel (**Table 6**). This makes it a good candidate to pursue further
492 investigations with thermal and emission analyses and thus get a significant **diagnosis**.
493

494 **3.2. Biolubricant production and main performance properties**

495

496 **3.2.1. Reaction**

497 Global results of IMSOEE transesterification with 2E1H for yielding IMSO2E1HEs
498 (biolubricant) are gathered in **Table 5a**. Unfortunately, the cooling system of the vacuum
499 reactive distillation unit has not been efficient enough to trap all ethanol produced during
500 transesterification. Consequently, overall material balance could not be done and **Figure 7**
501 depicts mass fraction vs time profiles for all reaction mixture species except ethanol. The whole
502 results highlights some important points discussed below.

503

Figure 7

504 Mass fractions vs time of the reaction mixture species verify the specific features of any
505 reversible reaction under successive kinetic and thermodynamic control, with no mass transfer
506 limitation. Thence, profiles of IMSO2E1HEs and IMSOEEs are very similar (**Figures 7 and 3**).

507 Furthermore, pressure has clearly a significant impact on IMSOEE transesterification
508 with 2E1H. The lower is the operating pressure, higher is the reaction yield, just as the IMSOEE
509 conversion and IMSO2E1HE mass fraction, if these are considered only at the end of reaction
510 (**Table 5a**).

511 Nevertheless, when considering evolution vs time, **Figure 7** clearly shows that the
512 chemical equilibrium state of the IMSOEE transesterification with 2E1H is reached faster when
513 increasing pressure, with however a plateau located lower. On the other hand, when the
514 operating pressure is too low, IMSOEE conversion (just as IMSO2E1HE formation) is slower
515 at the early stage of the reaction. This phenomena might be attributed to a partial vaporization
516 of 2E1H during reactive distillation. Indeed, assuming that transesterification of IMSOEEs with
517 2E1H (**Figure 2**) is of partial first order in each reactant, the initial reaction rate r_0 can be
518 written as (considering that reaction occurs in a closed perfectly stirred reactor of constant
519 volume):

$$520 r_0 = k_0 [IMSOEEs]_0 [2E1H]_0, \quad (3a)$$

$$521 \text{ with } r_0 = \left(\frac{d[IMSO2E1HEs]}{dt} \right)_0 \approx \frac{\Delta[IMSO2E1HEs]}{\Delta t} \text{ if } \Delta t \text{ small,} \quad (3b)$$

522 where k_0 and $[R_i]_0$ are respectively the initial kinetic constant and molar concentration of
523 reactant R_i . Thence, for two IMSOEE transesterification reactions carried out at different
524 pressures (P_2, P_3) all other operating conditions remaining constant, the ratio between their
525 initial reaction rates $r_0^{P_2}/r_0^{P_3}$ attributed to partial evaporation of 2E1H should be equal to
526 $[2E1H]_0^{P_2}/[2E1H]_0^{P_3}$. By taking as initial conditions the reacting mixture composition after 4
527 min reaction time, we obtain:

$$528 \left(\frac{\Delta[IMSO2E1HEs]}{\Delta t}\right)^{P_2} / \left(\frac{\Delta[IMSO2E1HEs]}{\Delta t}\right)^{P_3} = 1.08 \quad \text{and} \quad [2E1H]_0^{P_2} / [2E1H]_0^{P_3} = 1.11 \quad (4)$$

529 leading to the conclusion that assumption of partial 2E1H vaporization is valid.

530 Within a different context focused on hydraulic fluid synthesis by enzymatic
531 esterification of fatty acids with a polyol, **Kim et al. (2019)** also observed the importance of
532 applying a suitable vacuum level to reach good yields. Indeed, the issue was to inhibit
533 hydrolysis (by removing water formed during esterification) thanks to a high vacuum but the
534 latter could not be too high in order to keep enough water to ensure a significant enzymatic
535 activity. In a similar context of hydraulic fluid synthesis but here by autocatalytic esterification
536 followed by short-path distillation, **Maurad et al. (2018)** also highlighted the crucial role of
537 vacuum applied in the two stages (500 and 0.05 mbar respectively).

538 Similarly to the IMSO ethanolysis, kinetics of IMSOEE transesterification with 2E1H
539 is imposed by the major ethyl ester, i.e. ethyl oleate (**Figure 8**).

540 **Figure 8**

541 Moreover, the reactive distillation under low pressure proves to be a relevant option
542 allowing for shifting the chemical equilibrium towards formation of biolubricant by ethanol
543 removal from the reacting mixture and thus improving reaction yield and product purity. Under
544 the optimal pressure of 0.05 bar (other operating conditions: 70°C, MR (2E1H to IMSOEEs) =
545 2:1, [KOH] = 2 wt %) 93 wt % of the departure IMSOEEs were converted in less than 65 min,
546 with a reaction yield and an IMSO2E1HE content of respectively 91 and 71 wt % (**Table 5a**).
547 Here again, it should be noted that a higher content in IMSO2E1HEs would have been obtained
548 if the departure IMSO had been pre-treated to increase the glyceride pool, and thus the IMSOEE
549 content.

550

551 3.2.2. Purification of IMSO2E1HEs and lubricant properties

552 In order to simulate a worst case, efficiency of the purification method was evaluated
553 by selecting the sample of IMSO2E1HEs showing a poor content in esters (63.8 wt % obtained
554 under the reaction pressure of 0.10 bar).

555 As illustrated in **Table 5b**, purification of IMSO2E1HEs shows very good performance
556 once the catalyst is removed through bubble-washing and the excess of 2-ethyl-1-hexanol
557 (including the residual ethanol traces) through vacuum distillation. All esters are thus more
558 concentrated in the residue, of which the non-converted IMSOEEs could not be removed
559 successfully under 0.01 bar (minimum operating pressure reached with the equipment used).

560 Nevertheless, the resulting IMSO2E1HE product shows satisfactory behavior as
561 biolubricant (**Table 6**), at least regarding the basic properties (density, viscosity, and color)
562 (**Habib et al., 2014; Trivedi et al., 2015; McNutt and He, 2016; Zheng et al., 2018**). The
563 higher color Gardner observed for the IMSO2E1HEs compared with the RO2E1HEs is due to
564 the parent oil (orange for the IMSO, pale yellow for rapeseed oil RO). Moreover, the high acid
565 value of the IMSO2E1HE product might be reduced by operating with a less concentrated citric
566 acid solution during bubble-washing. This change should not be prejudicial thanks to the
567 demonstrated driving force efficiency of citric acid in removing the catalyst in the form of
568 potassium citrate. **The remaining traces of citric acid should not be prejudicial either since the**
569 **addition of this natural antioxidant proved to enhance the oxidation stability of biolubricants**
570 **(Sharma et al., 2016), similarly to biodiesel and vegetable oils (Serrano et al., 2013; Yaakob**
571 **et al., 2014; Bekkar et al., 2018).** This could also compensate for the rather high content of
572 polyunsaturated species encountered in the produced IMSO2E1HEs (linoleic and linolenic
573 esters: 37 wt %) compared to monounsaturated ones (46 wt %), containing however oleic like
574 esters in large part (35 wt %) (**Table 5b**). Indeed, a low degree of unsaturation is preferred for
575 better thermal-oxidative stability, as well as higher viscosity; however, it is also desirable to
576 keep a certain number of unsaturation sites to meet suitable cold flow properties. Moreover, an
577 increase in the fatty chain length increases the viscosity. Thence, high oleic acid vegetable oils
578 are considered optimal to produce high performance biolubricants (**Reeves et al., 2015; Chan**
579 **et al., 2018**). Thermal-oxidative stability of the produced IMSO2E1HEs could not be evaluated
580 in this work. Nonetheless, the obtained viscosity meeting the requirements (for metalworking
581 fluids), it can be assumed that the effect of the polyunsaturated esters (linoleic and linolenic
582 acid esters) is counter-balanced by the presence of monounsaturated longer chain esters (C20
583 to C22) (**Tables 5b-6**). Furthermore, should viscosity of the obtained IMSO2E1HE product
584 need to be enhanced for a specific application, ethyl cellulose (EC) which is able to boost this

585 property by two-fold in small amounts could be used as additive (Chan et al., 2018).
586 Additionally, EC could be derived from Indian mustard stems rich in cellulose (Rapp et al.,
587 2018), which would broaden even more the contours of a biorefinery system focused on Indian
588 mustard. Finally, it was observed that transesterification of fatty acid methyl esters with 2-ethyl-
589 1-hexanol instead of trimethylolpropane led to a biolubricant showing better cold flow
590 properties and, moreover, in a shorter reaction time (McNutt et al., 2016). As a result, all these
591 considerations suggest that the obtained IMSO2E1HE product is a potential candidate as
592 biolubricant, particularly as a metalworking fluid.

593 **Table 6**

596 **4. Conclusions**

597
598 The two routes investigated in this work for harnessing IMSO as an energy carrier
599 (IMSOEEs) or biolubricant (IMSO2E1HEs) via conversion of IMSOEEs led to positive results.

600 Although based on homogeneous catalysis, the alkali route selected for IMSO
601 conversion into IMSOEEs leads to an interesting alternative of low cost production of a 100%
602 renewable biodiesel. The main features of this alternative are firstly, simple operating
603 conditions (35°C, atmospheric pressure, ethanol to oil molar ratio of 8, 1.1 wt % KOH, 50 min);
604 and secondly, a two-stage procedure based on glycerol recycling followed by a dry-purification
605 method based on Indian mustard stems (FIMS). Moreover, a satisfactory ester content was
606 reached (95.8 wt %) and the produced IMSOEEs subsequently met the basic biodiesel
607 properties (acid value, color, density, viscosity, flash point, pour point, cloud point, and cold
608 filter plugging point). Nevertheless, a pre-treatment of the departure IMSO prior ethanolysis
609 would be beneficial by removing species that are not glycerides, such as glucosinolates, and
610 thus ensuring the produced biodiesel conforms to industry specifications (such as EN 14214
611 standard).

612 Regarding the IMSO2E1HE production via transesterification of unpurified IMSOEEs
613 with 2E1H, the selection of reactive distillation with optimized operating pressure (0.05 bar, at
614 70°C with 2 wt % of KOH and a 2E1H to IMSOEEs molar ratio of 2 in 65 min) allowed a high
615 conversion of IMSOEEs (93 wt %) to be reached and a IMSO2E1HE content of 71 wt %.
616 However, the latter value could be improved by increasing the glyceride pool of the parent
617 IMSO, and thus the ester content of the departure IMSOEEs. Nonetheless, after purification by
618 bubble-washing (driven by citric acid) and vacuum distillation (inferior to 0.01 bar), the

619 resulting IMSO2E1HE product exhibited interesting basic properties (density, viscosity, and
620 color) making it a good biolubricant candidate.

621

622

623 **Author contributions**

624 Jing Chen and Xiaoqiang Bian (executing of the biodiesel and biolubricant synthesis); Graeme
625 Rapp and Richard Trethowan (providing of the Indian mustard seeds, oil, and stems; review of
626 the manuscript); James Lang and Alejandro Montoya (Indian mustard oil analysis by GC;
627 review of the manuscript); Brice Bouyssièr (biodiesel analysis by ICP-AES); Jean-François
628 Portha (biolubricant purification and review of the manuscript); Jean-Noël Jaubert (financial
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630 (conceptualization, methodology, assistance during biodiesel and biolubricant production, and
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632

633

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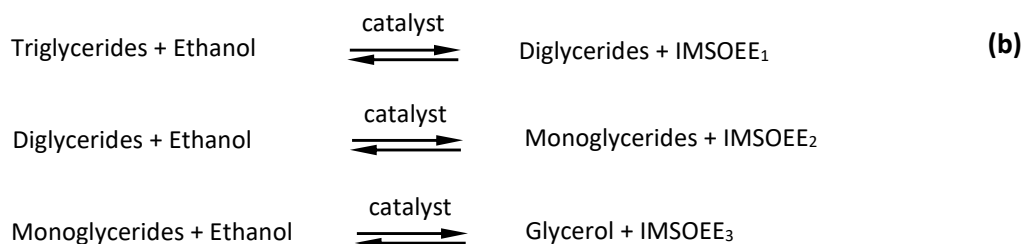
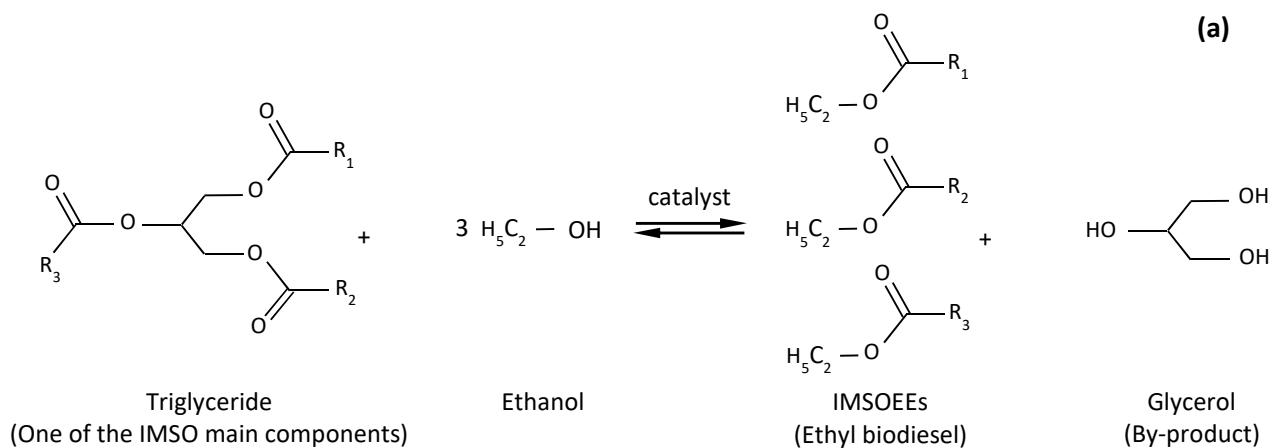
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FIGURES



848 where the active species is $[C_2H_5O^-, K^+]$ when KOH is selected as catalyst.

849

850 **Figure 1.** Catalyzed transesterification reaction of triglycerides involved in IMSO conversion

851 to ethyl biodiesel. (a) Overall chemical equation of triglyceride ethanolysis yielding IMSOEEs

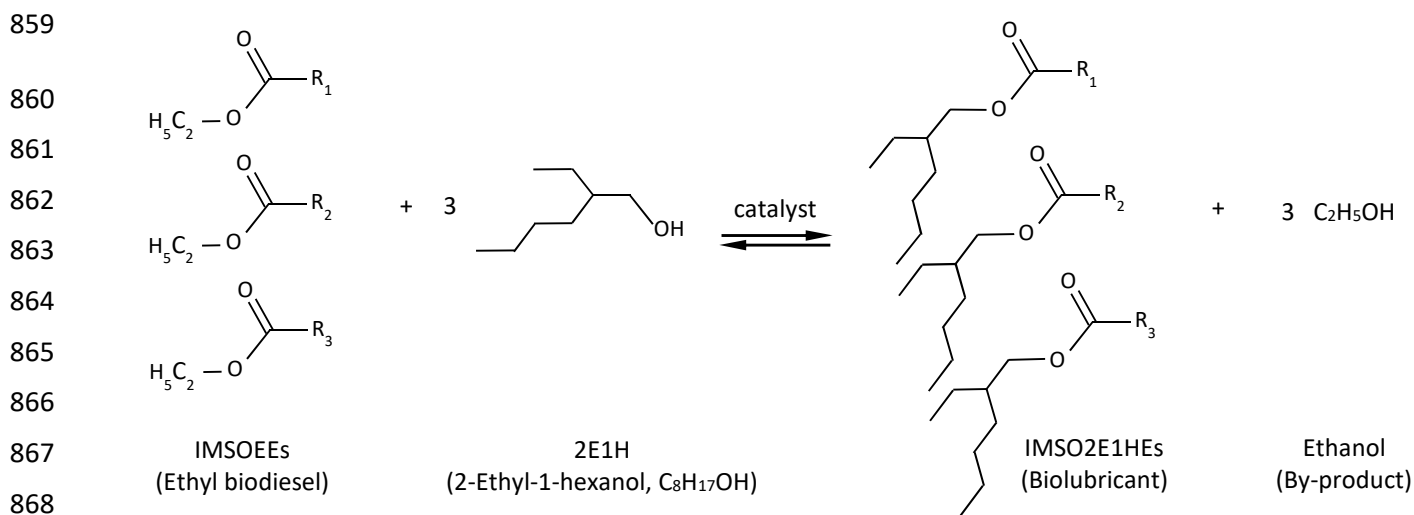
852 and glycerol (R_1, R_2, R_3 are identical or different aliphatic chains with zero to three unsaturated

853 bond(s): $CH_3-(CH_2)_m-(CH_2-CH=CH)_n-(CH_2)_k$ with $(m+k)$ ranging from 15 to 18 and $n = 0, 1,$

854 2 or 3). (b) Ethanolysis of triglycerides as a sequence of three consecutive and reversible

855 reactions (IMSOEE₁, IMSOEE₂, or IMSOEE₃ are identical or most likely different).

856 Stoichiometry of the overall reaction (a): 1 mole of triglyceride for 3 moles of ethanol.

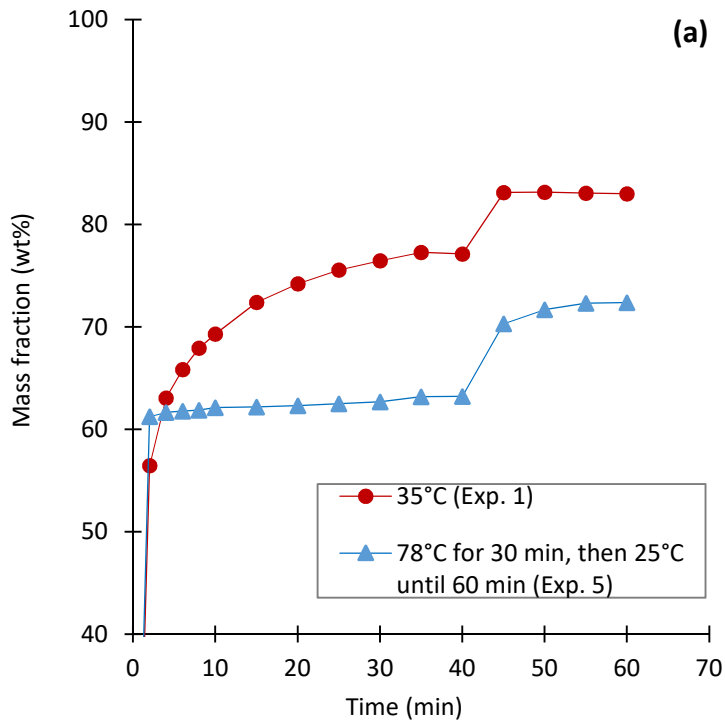


870 where the active species is $[C_8H_{17}O^-, K^+]$ when KOH is selected as catalyst.

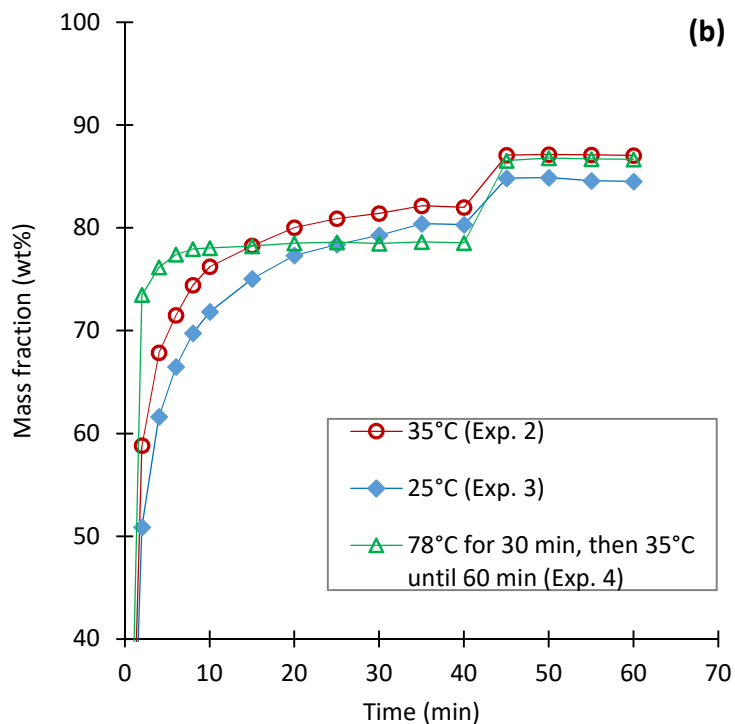
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872 **Figure 2.** Catalyzed transesterification reaction of IMISOEEs (ethyl biodiesel) with 2-ethyl-1-
 873 hexanol (2E1H) yielding IMISO2E1HEs (biolubricant). R₁, R₂, R₃ are different aliphatic chains
 874 with zero to three unsaturated bond(s): CH₃-(CH₂)_m-(CH₂-CH=CH)_n-(CH₂)_k with (m+k)
 875 ranging from 15 to 18 and n = 0, 1, 2 or 3. Stoichiometry of the reaction: 1 mole of IMISOEE
 876 for 1 mole of 2E1H.

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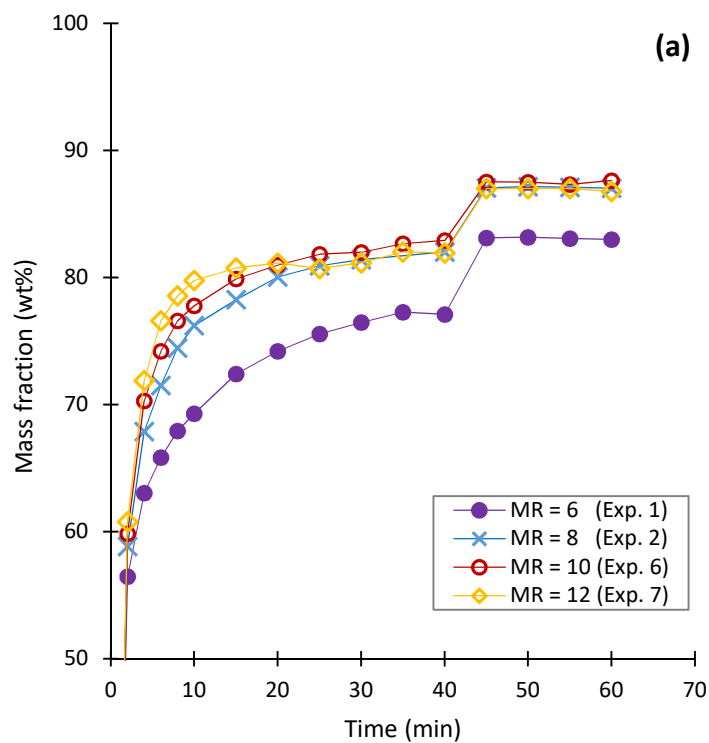


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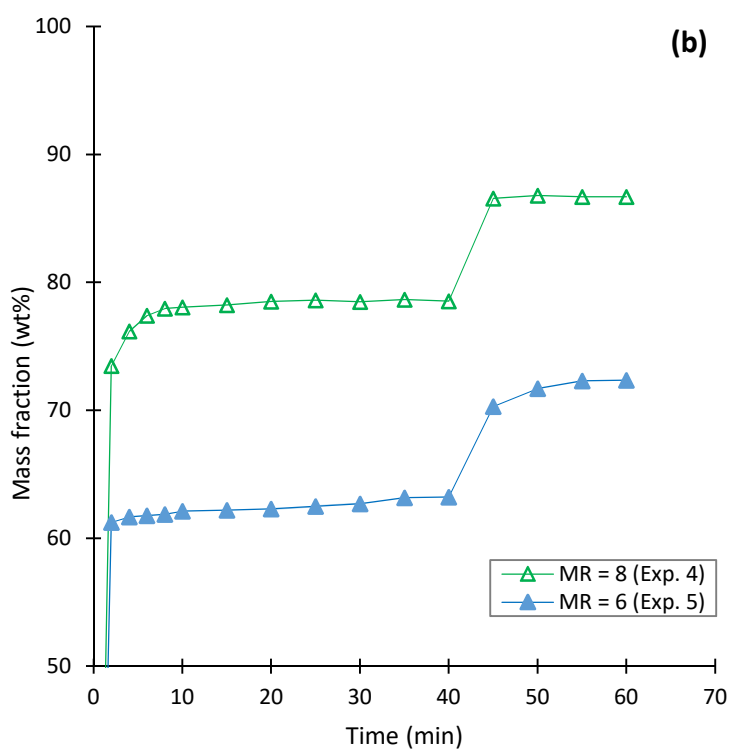


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Figure 3. IMSoyEE mass fractions as a function of reaction time at different reaction temperature (mass fraction of pure glycerol added: 25 wt %); (a) MR (ethanol to oil) = 6, (b) MR (ethanol to oil) = 8.



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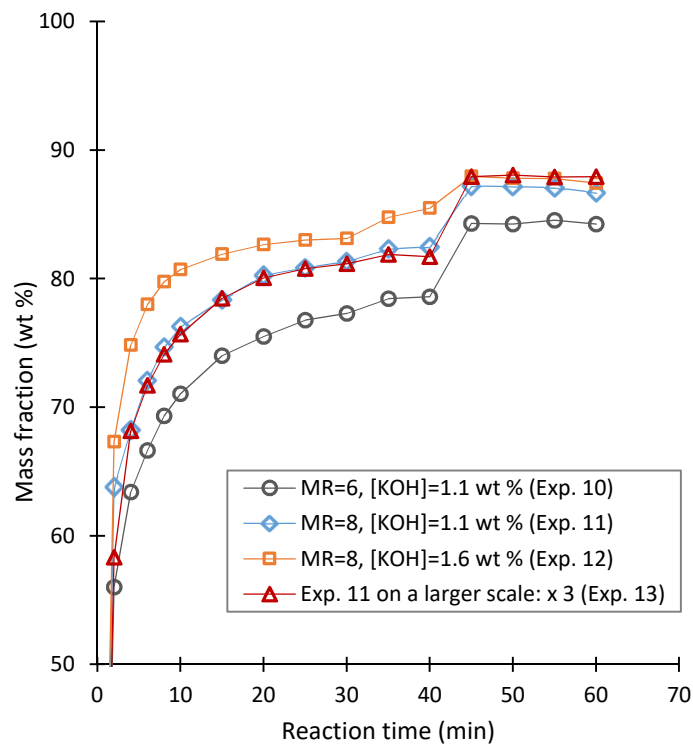


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890 **Figure 4.** IMSOyEE mass fractions as a function of reaction time at different ethanol to oil
891 molar ratio (MR) (mass fraction of pure glycerol added: 25 wt %); (a) 35°C, (b) 78°C for
892 30 min, then 35°C (Exp. 4) or 25°C (Exp. 5) until 60 min.

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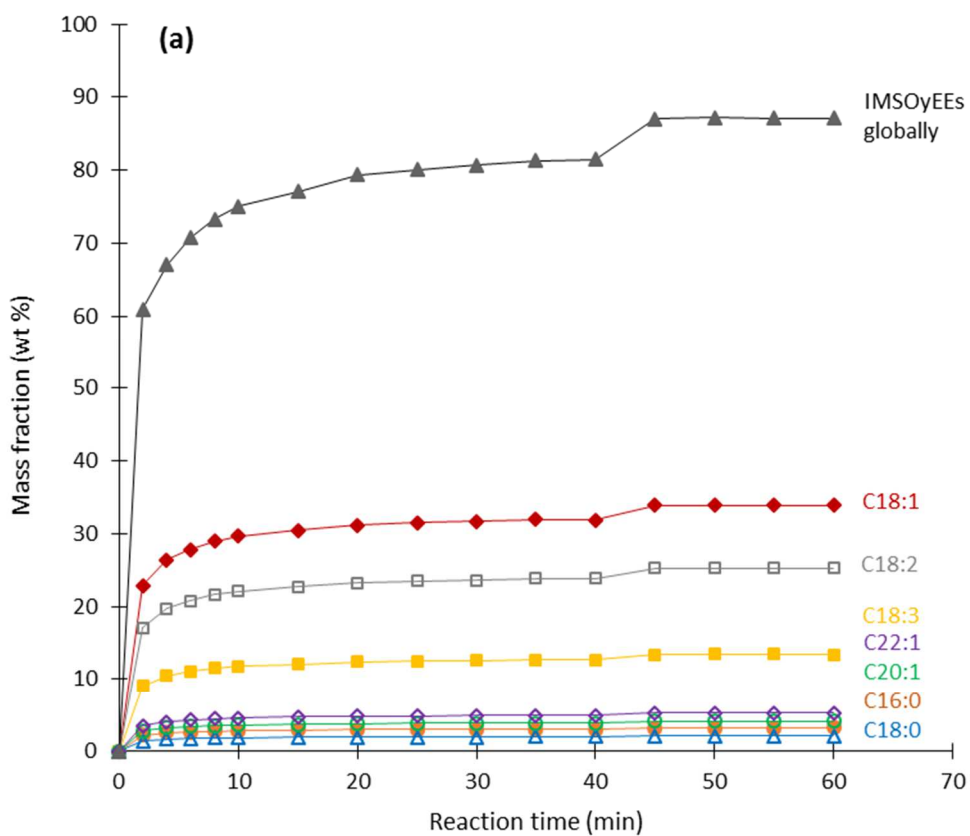
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897 **Figure 5.** IMSObEE mass fractions as a function of reaction time for different key parameters
898 analyzed separately: ethanol to oil molar ratio (MR), KOH concentration, and a larger scale of
899 reactor ($\times 3$) for a given reaction temperature of 35°C (mass fraction of recycled glycerol added:
900 25 wt %).

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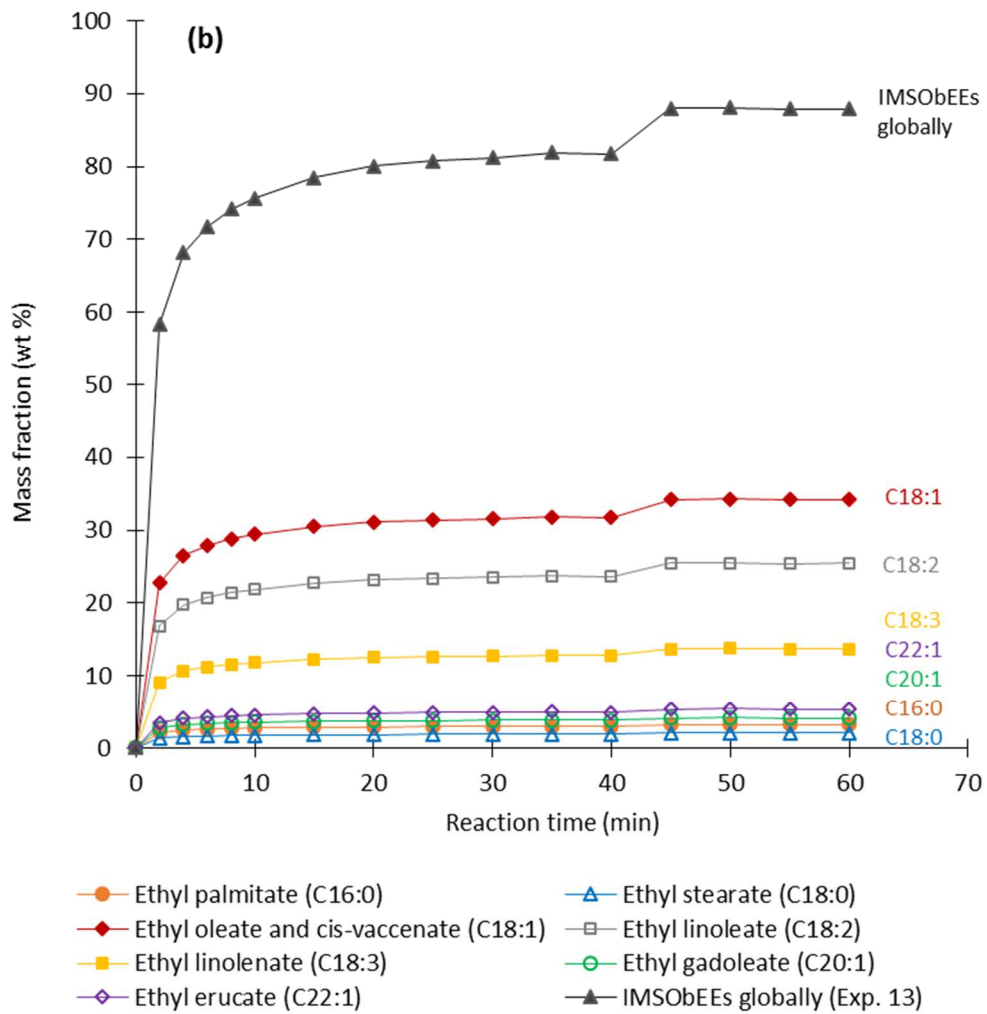
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- Ethyl palmitate (C16:0)
- ◆— Ethyl oleate and cis-vaccenate (C18:1)
- Ethyl linolenate (C18:3)
- ◇— Ethyl erucate (C22:1)
- ▲— IMSOyEEs globally (Exp. 2)
- △— Ethyl stearate (C18:0)
- Ethyl linoleate (C18:2)
- Ethyl gadoleate (C20:1)

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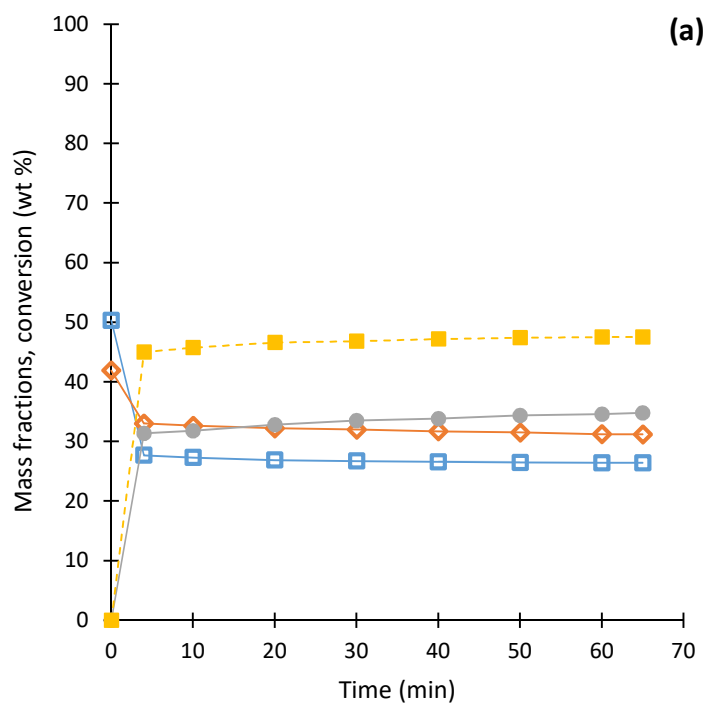
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908 **Figure 6.** IMSOEE mass fractions as a function of reaction time (a) Results for IMSOyEEs
 909 globally and distribution of major IMSOyEEs (Exp. 2), (b) Results for IMSObEEs globally and
 910 distribution of major IMSObEEs (Exp. 13).

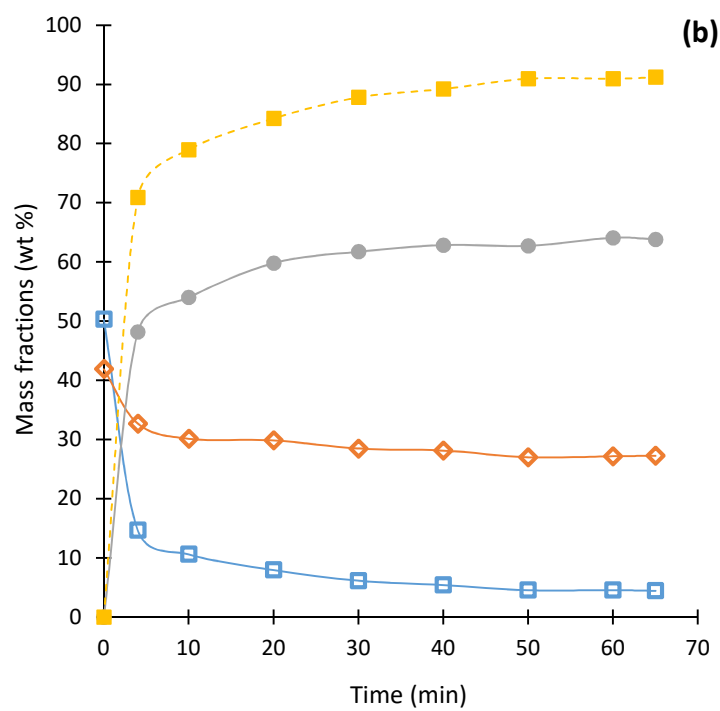
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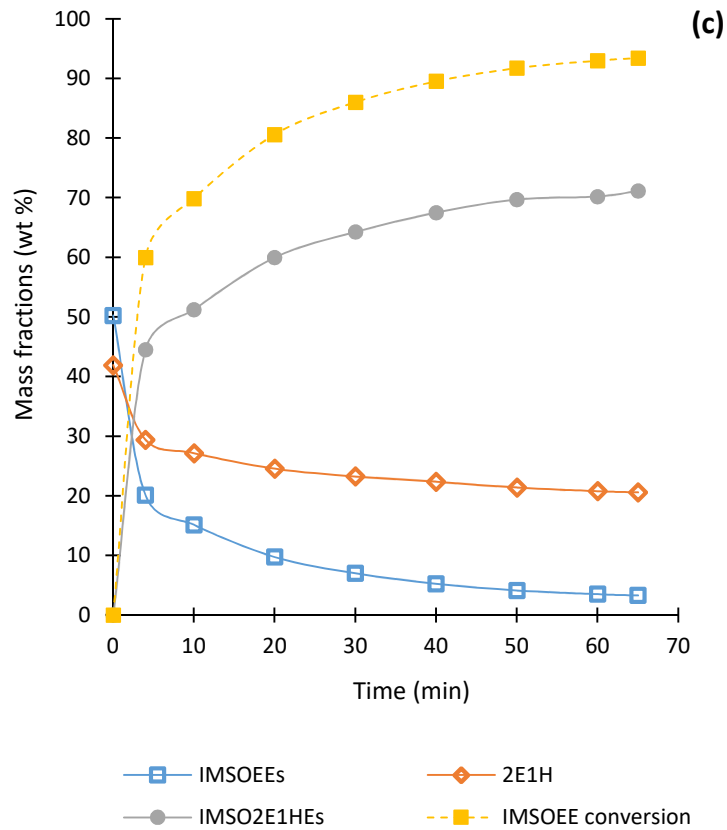
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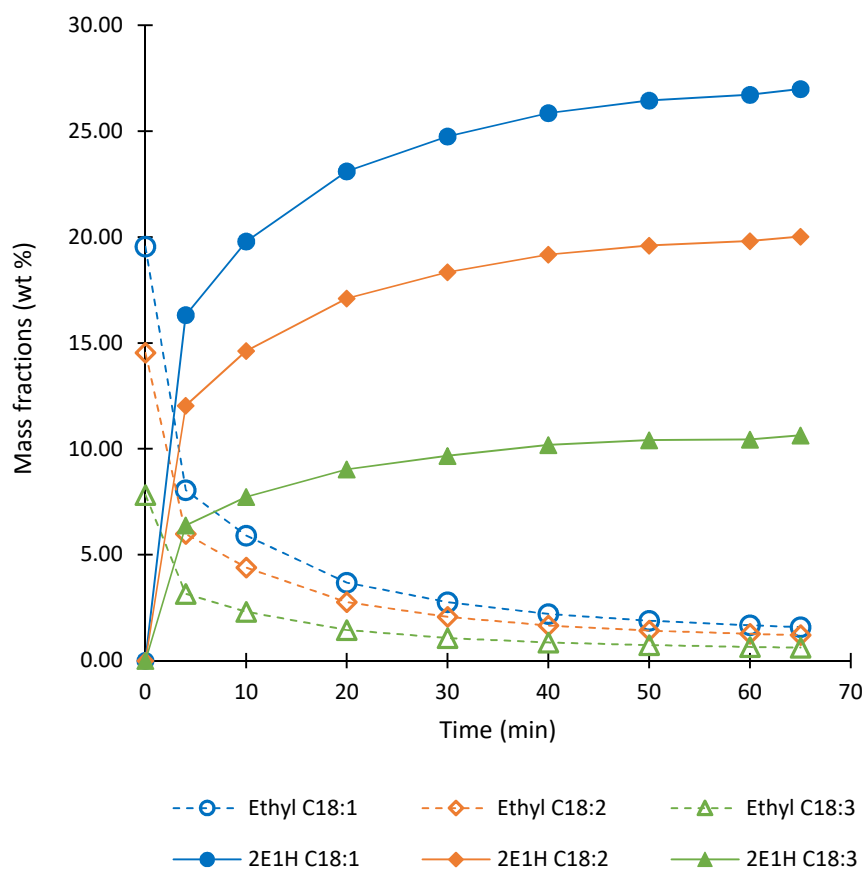


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919 **Figure 7.** Species mass fractions and conversion as a function of time during transesterification
 920 of crude ethyl biodiesel (IMSOEEs) to biolubricant (IMSO2E1HEs). Operating conditions:
 921 70°C, [KOH] = 2 wt %, MR (2E1H to IMSOEEs) = 2, and pressure (in bar) = 0.5 (a), 0.1 (b),
 922 0.05 (c). The residual KOH content due to previous IMSO conversion into IMSOEEs was not
 923 included.

924



925

926

927 **Figure 8.** Major ester species mass fractions as a function of time during transesterification of
 928 crude ethyl biodiesel (IMSOEEs) to biolubricant (IMSO2E1HEs). Operating conditions: 70°C,
 929 [KOH] = 2 wt %, MR (2E1H to IMSOEEs) = 2, and pressure (in bar) = 0.05. The residual KOH
 930 content due to previous IMISO conversion into IMSOEEs was not included.

931

932 **TABLES**

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Table 1. Fatty acid composition (molar fractions %) of the **IMSOy** and **IMSOB** samples. Major components are indicated in bold. ^a

Fatty acids - Formulae (<i>name</i>) ^a	IMSOy	IMSOB
C16:0 (<i>Palmitic acid</i>)	3.8 ± 0.1	3.7 ± 0.1
C18:0 (<i>Stearic acid</i>)	2.6 ± 0.1	2.4 ± 0.1
C18:1c9 (<i>Oleic acid</i>) + C18:1c11 (<i>cis-Vaccenic acid</i>)	38.8 ± 0.3	39.0 ± 0.2
C18:2c9c12 (<i>Linoleic acid</i>)	28.9 ± 0.2	28.9 ± 0.2
C18:3c9c12c15 (<i>Linolenic acid</i>)	15.1 ± 0.1	15.3 ± 0.1
C20:1c9 (<i>Gadoleic acid</i>)	4.7 ± 0.1	4.7 ± 0.1
C22:1c13 (<i>Erucic acid</i>)	6.1 ± 0.1	6.0 ± 0.1
Total	100.0	100.0
Saturated species	6.5 ± 0.2	6.1 ± 0.1
Monounsaturated species	49.5 ± 0.2	49.8 ± 0.1
Polyunsaturated species	44.0 ± 0.1	44.1 ± 0.1
\overline{M}_w as FFAs	284.6 ± 0.1	284.6 ± 0.0
\overline{M}_w as FAEEs (2E1H esters)	312.6 (396.8)	312.6 (396.8)

937 ^aFatty acid profiles were determined by methanolysis according to the ASTM-D1983 standard
938 (**ASTM D1983-90, 1995**) for a complete conversion of the IMISO glycerides into FAMEs which
939 were further quantified by gas chromatography (**Table A1**, Appendix A) (**EN-14103, 2011;**
940 **Nitièma-Yefanova et al., 2016**); the standard deviations report the cumulative errors made
941 during methanolysis and quantification. ^b For example, C18:1c9 means an 18 carbon fatty acid
942 chain with one *cis* double bond (c) located at carbon 9 (starting from the carboxylic group).
943

944 **Table 2.** Key properties of the **IMSOy and IMSOb samples used** as feedstocks for ethanolysis.
 945

Key properties	IMSOy	IMSOb
Average molecular weight ^a	891.7 ± 0.4	891.9 ± 0.1
Water content (wt %) ^b	0.044 ± 0.002	0.045 ± 0.002
Acid value (mg KOH/g) ^c	0.91 ± 0.01	0.90 ± 0.01
Acidity (%) ^c	0.46 ± 0.01	0.45 ± 0.01
Sulfur content (mg/kg) ^d	21.42 ± 0.04	8.03 ± 0.04
Tin content (mg/kg) ^d	32.01 ± 0.02	36.28 ± 0.02

946 ^a Calculated from the oil molar composition in terms of fatty acids. ^b Determined by Karl-
 947 Fischer titration method (**EN-ISO-12937, 2000**). ^c Determined by following the standard EN-
 948 14104 (**EN-14104, 2003**). ^d Determined by ICP-AES (**Table A1**, Appendix A) (**Pohl et al., 2010**;
 949 **Caumette et al., 2010**; **Nitièma-Yefanova et al., 2015**).

950

951 **Table 3.** Operating conditions of the most relevant experiments and corresponding ester contents obtained. Each operation variable (temperature,
 952 ethanol to oil molar ratio, catalyst mass concentration, mass fraction of glycerol added) were changed sequentially (when changing one variable,
 953 the others were remained constant). Optimal operating conditions are indicated in bold. ^a

Experiment	T/°C	Ethanol to oil molar ratio	[KOH] (wt %) ^b	Mass fraction of glycerol (wt %) ^c	Ester content (wt %) 1 st stage (30 min)	Ester content (wt %) 2 nd stage (50 min)	Ethanolysis & Separation Yield (wt %)
<i>IMSOy (Yellow seeds)</i>							
1	35	6: 1	1.1	25	77	83	88
2	35	8: 1	1.1	25	82	87	95
3	25	8: 1	1.1	25	80	85	96
4	78 (1 st stage) / 35 (2 nd stage)	8: 1	1.1	25	79	87	89
5	78 (1 st stage) / 25 (2 nd stage)	6: 1	1.1	25	63	72	82
6	35	10: 1	1.1	25	83	88	95
7	35	12: 1	1.1	25	82	87	97
8	35	8: 1	1.1	25 / Recycled glycerol (from Exp. 2)	80	87	94
9	35	6: 1	1.1	35 / Recycled glycerol (from Exp. 1)	79	82	88

954

955 **Table 3.** Continued. ^a

Experiment	T/°C	Ethanol to oil molar ratio	[KOH] (wt %) ^b	Mass fraction of glycerol (wt %) ^c	Ester content (wt %) 1 st stage (30 min)	Ester content (wt %) 2 nd stage (50 min)	Ethanolysis & Separation Yield (wt %)
<i>IMSO_b (Brown seeds)</i>							
10	35	6:1	1.1	25 / Recycled glycerol (from Exp. 1)	78	84	90
11	35	8:1	1.1	25 / Recycled glycerol (from Exp. 2)	82	87	95
12	35	8:1	1.6	25 / Recycled glycerol (from Exp. 2)	85	88	87
13^d	35	8:1	1.1	25 / Recycled glycerol (from Exp. 4)	82	88	100

956 ^a Stirring speed set to 250 rpm during the first stage and the first 5 min of the second stage. ^b 1.1 wt % = 1.0 + x wt %, with x calculated given the
957 IMSO acid value. ^c On basis of the initial oil mass; addition always conducted at 35°C, except for exp. 5 for which temperature was reduced to
958 25°C; ^d Larger scale test (×3).

959

960 **Table 4.** Characterization of produced IMSOEEs with regards to their organic and inorganic components before and after dry-purification ^a.
 961 Efficiency of the dry-purification method for the focused contaminants is also given in brackets. ^b

Treatment stage of the FAEE product	Esters (wt %)	Free glycerin (wt %)	MGs (wt %)	DGs (wt %)	TGs (wt %)	Total glycerin (wt %)	Water (mg/kg)	
Unpurified IMSOEEs of departure	88.5	0.06	2.58	0.75	0.27	0.86	343	
IMSOEEs after dry-purification	95.8 (+8)	0.01 (-83)	2.46 (-5)	0.53 (-29)	0.22 (-19)	0.72 (-16)	647 (+87)	
Specifications of EN-14214 ^c	96.5	0.02	0.80	0.20	0.20	0.25	500	
Chemical element contents (mg/kg) ^d								
	Ca	Fe	K	Mg	Na	P	S	Sn
Unpurified IMSOEEs of departure	< 0.001	< 0.003	104.9	< 0.001	< 0.073	< 0.006	< 0.038	28.00
IMSOEEs after dry-purification	< 0.001	< 0.003	< 0.031 (-100)	< 0.001	< 0.073	< 0.006	< 0.038	25.53 (-9)
Specifications of EN-14214 ^c	5 ^e	- ^f	5 ^g	5 ^e	5 ^g	10	10	- ^f
Percent mass composition of the identified FAEEs								
	C16:0	C18:0	C18:1 (oleate)	C18:1 (cis-vaccenate)	C18:2	C18:3	C20:1	C22:1
Unpurified IMSOEEs of departure	3.16	2.01	31.87	2.41	25.47	13.73	4.13	572
IMSOEEs after dry-purification	3.41	2.14	33.82	2.56	27.03	14.57	6.02	6.26

964 ^a Standard deviations (wt %): 0.08 on esters, 0.003 on free glycerin, 0.05 on MGs, DGs, and TGs. ^b Method efficiency assessed as a function of removal
 965 percentage of each contaminant (η_c) calculated by $\eta_c = 100 \times (x_f - x_0) / x_0$, where x_0 and x_f are the contents of each contaminant before and after treatment. ^c All
 966 indications are limits, except for the ester content giving the maximum value. ^d Detection limits (mg/kg) of the analytical method used (ICP-AES): 0.001 for Ca

967 and Mg; 0.003 for Fe; 0.031 for K; 0.073 for Na; 0.006 for P; 0.038 for S; 0.023 for Sn; Maximum standard deviation (mg/kg): 0.001 for Ca, Mg, Fe, P, and Sn;
968 0.05 for Na; 0.01 for K and S; regarding contaminant content below or equal to the observed ICP-AES detection limit, this latter value was used to evaluate the
969 treatment efficiency. It should be mentioned that some other metals have not been detected (Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Hg, Li, Mn, Mo, Ni, Pb, Sb, Sr,
970 Ti, V, and Zn). ^e For (Ca + Mg). ^f No specification exists regarding this species. ^g For (Na + K).
971

972 **Table 5.** Operating conditions of ethyl biodiesel (IMSOEEs) conversion along with key results of biolubricant (IMSO2E1HEs) synthesis (a) and
 973 purification (b).

974

(a) Biolubricant synthesis

T/°C	MR (2E1H to IMSOEEs)	[KOH]/(wt %) ^a	Reaction time/min
70	2	2	65
	P/bar = 0.50	P/bar = 0.10	P/bar = 0.05
IMSOEE conversion (wt %) ^b	47.5	91.2	93.3
Biolubricant synthesis yield (wt %)	46.7	81.0	90.8
IMSOEE mass fraction (wt %)	26.4	4.4	3.4
IMSO2E1HE mass fraction (wt %)	34.8	63.8	71.2

975

976

(b) Biolubricant purification (bubble-washing & vacuum distillation) ^c

Treatment stage of the IMSO2E1HE product	K (mg/kg)	IMSOEEs (wt %)	IMSO2E1HEs (wt %)	2E1H (wt %)	Ethanol (wt %)			
Unpurified IMSO2E1HEs of departure	7600 ^d	4.42	63.79	27.26	0.01			
IMSO2E1HEs after purification	0.29	5.44	88.17	Not detected	Not detected			
Percent mass composition of the identified IMSO2E1HEs (IMSOEEs)								
	C16:0	C18:0	C18:1 (oleate)	C18:1 (cis-vaccenate)	C18:2	C18:3	C20:1	C22:1
Unpurified IMSO2E1HEs of departure	2.36 (0.15)	1.48 (0.10)	22.76 (1.60)	1.76 (0.13)	18.21 (1.29)	9.64 (0.67)	3.87 (0.20)	3.70 (0.26)
IMSO2E1HEs after purification	3.35 (0.19)	2.11 (0.19)	32.17 (2.01)	2.49 (0.15)	24.77 (1.67)	12.57 (0.79)	5.63 (0.27)	5.25 (0.34)

977 ^a On basis of the initial IMSOEE mass; the residual catalyst content (from IMSO conversion into IMSOEEs by KOH catalyzed ethanolysis) was not counted. ^b IMSOEE conversion
 978 (wt %) = $(\bar{x}_{IMSOEEs}^0 - \bar{x}_{IMSOEEs}^t) / \bar{x}_{IMSOEEs}^0 \times 100$ where $\bar{x}_{IMSOEEs}^0$ and $\bar{x}_{IMSOEEs}^t$ are mass fractions in IMSOEEs at respectively time 0 and time *t* of the reaction. ^c Sample purified:
 979 IMSO2E1HEs obtained at P/bar = 0.10. See **Table A1** (Appendix A) for details regarding the analysis methods selected. For K quantification by ICP-AES, detection limit and maximum
 980 standard deviation: 0.031 and 0.01 mg/kg, respectively. Like esters, the two alcohols were quantified by GC-FID (**Table A1**, Appendix A). ^d Value estimated on the basis of the amount
 981 of catalyst used for the biolubricant synthesis.

982 **Table 6.** Some specific functional properties of the produced biofuel (IMSOEEs) and biolubricant (IMSO2E1HEs) – Comparison with
 983 corresponding standard quality specifications. ^a

Property	IMSOEEs biofuel	Biodiesel specifications		IMSO2E1HEs biolubricant	RO2E1HEs biolubricant (Ineos, 2018)	Standard deviations ^b
		min	max			
Acid value (mg KOH/g)	0.34	-	0.50	12.2	0.5	± 0.02
Color (Gardner)	10.4	-	-	4.7	1.0	± 0.2
Density (kg/m ³)	882 ^(15°C)	860 ^(15°C)	900 ^(15°C)	875 ^(20°C)	870 ^(20°C)	± 3·10 ⁻⁵
Viscosity (mm ² /s) at 40°C	5.0	3.5	5.0	8.6	9.0	± 0.1
at 100°C		-	-	2.8	3.0	± 0.1
Flash point (°C)	425	101	-	-	200	± 12
Cloud point (°C)	-5	-12	-3	-	-	± 1
Pour point (°C)	-9	-16	-5	-	-69	± 2
Cold filter plugging point (°C)	-11	-	-	-	-	-

984 ^a Biofuel and biolubricant are obtained after dry-purification; see **Table A1** in Appendix A for details regarding the methods leading to the above
 985 given property values. Biolubricant properties are compared for two classes of esters obtained from the same alcohol i.e. 2E1H (2-ethyl-1-hexanol)
 986 with two different oils IMSO (Indian mustard seed oil) and RO (rapeseed oil). ^b These standard deviations are common to determination of both
 987 biofuel and biolubricant specific functional properties.

988

APPENDICES

989

990

991 **Appendix A – Biodiesel & Biolubricant**

992

993 **Table A1.** Analysis equipment and operating conditions regarding to the production, purification and characterization of biodiesel and biolubricant

994 carried out in this work.

995

Objective	Experimental technique	Equipment	Operating conditions
Biodiesel & Biolubricant production			
Monitoring of the transesterification with ethanol or 2-ethyl-1-hexanol	Off-line GC-FID with preliminary GC-MS	Agilent Technologies (USA)	<p>•<i>Preliminary sample neutralization & Ester quantification:</i> Please refer to Nitièma-Yefanova et al. (2016) (Appendix B, S.I.). •<i>Ester quantification:</i> Please refer to Mohammad et al. (2017) except for the oven temperature program: 60°C (2 min), 60-200°C (10°C/min), 200-240°C (5°C/min), 240°C (7 min for IMSOEEs, 16 min for IMSO2E1HEs). <i>After centrifugation of the sampling tubes</i>, 0.1 mL of the organic phase was poured in vials prefilled with 1 mL of stock solution, i.e. a mixture of well-known composition in the internal standard selected for FAEE quantification (MHD) with n-heptane. The <i>response factors of all FAEEs</i> relatively to MHD were assigned to the value obtained for ethyl oleate (major component of IMSOEEs, Table 1). Regarding biolubricant quantification, the <i>response factors of all IMSO2E1HEs</i> were assigned to 1 (commercial standard of 2-ethyl-1-hexyl oleate unavailable) while 1-pentanol was selected as internal standard to determine the residual 2-ethyl-1-hexanol and potential traces of ethanol. Note that MHD was used instead of methyl nonadecanoate recommended in the European standard EN-14103 of May 2011 (EN-14103, 2011) because of overlapping with the ethyl linoleate GC peak (Nitièma-Yefanova et al., 2016 (Appendix B, S.I.)).</p>

996

997 **Table A1.** Continued.

Objective	Experimental technique	Equipment	Operating conditions or Standard
Biodiesel characterization – (a) Dry-purification			
Glyceride (TGs, DGs, MGs), free glycerin and FAEE contents	GC-FID	INEOS Enterprises (France)	EN-14105 (EN-14105, 2011), except for FAEEs: EN-14103 (EN-14103, 2011)
Water content	Coulometric Karl Fischer titration	INEOS Enterprises (France)	ISO-12937 (EN-ISO-12937, 2000)
Potassium and other elements (Ca, Fe, Mg, Na, P, S, Sn) contents	ICP-AES	ARCOS by SPECTRO; Scott-type double-pass spray chamber combined with cross-flow nebulizer (Germany)	Please, refer to Nitièma-Yefanova et al., 2015 (Pohl et al., 2010 ; Caumette et al., 2010)
Biodiesel characterization – (b) Fuel properties			
Acid value	Volumetric titration	INEOS Enterprises (France)	EN-14104 (EN-14104, 2003)
Color	Colorimetry	INEOS Enterprises (France)	ASTM-D1544 (ASTM D1544-04, 2010)
Density (15°C)	Oscillating U-tube	INEOS Enterprises (France)	ISO-12185 (EN-ISO-12185, 1996)
Viscosity (40°C)	Capillarity viscometer	INEOS Enterprises (France)	ISO-3104 (EN-ISO-3104, 1996)
Flash point	Estimation	-	Vapor-liquid equilibria estimation based on composition in FAEEs (from GC-FID), their molecular structure, and their vapor pressures as pure components (Carareto et al., 2012)
Cloud point	Estimation	-	Correlation based on number of carbon atoms and composition in FAEEs (from GC-FID) (Bolonio et al., 2015)
Cold filter plugging point (°C)	Estimation	-	Correlation based on number of carbon atoms and composition in FAEEs (from GC-FID) (Bolonio et al., 2015)
Pour point	Estimation	-	Correlation based on number of carbon atoms and composition in FAEEs (from GC-FID) (Bolonio et al., 2015)

998

999 **Table A1.** Continued.
 1000

Objective	Experimental technique	Equipment	Operating conditions
Biolubricant characterization – (a) Purification by bubble-washing & vacuum fractional distillation			
Monitoring of the bubble-washing	Flame-AES	Sherwood Scientific Model 410 (UK)	Air-butane flame in on emission wavelength of 769.9 nm to measure K content in washing solution; calibration with pure water and standard solutions of K.
Validation of vacuum distillation	GC-FID	Agilent Technologies (USA)	See above “Biodiesel & Biolubricant production” •Ester identification, •Ester quantification, and •HP-INNOWAX column, Table A1.
Biolubricant characterization – (b) Specific functional properties			
Acid value	Volumetric titration	INEOS Enterprises (France)	ISO-6618 (ISO-6618, 1997)
Color	Colorimetry	INEOS Enterprises (France)	ASTM-D1544 (ASTM D1544-04, 2010)
Density (20°C)	Oscillating U-tube	INEOS Enterprises (France)	ISO-12185 (EN-ISO-12185, 1996)
Viscosity (40 and 100°C)	Capillarity viscometer	INEOS Enterprises (France)	ISO-3104 (EN-ISO-3104, 1996)

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1002

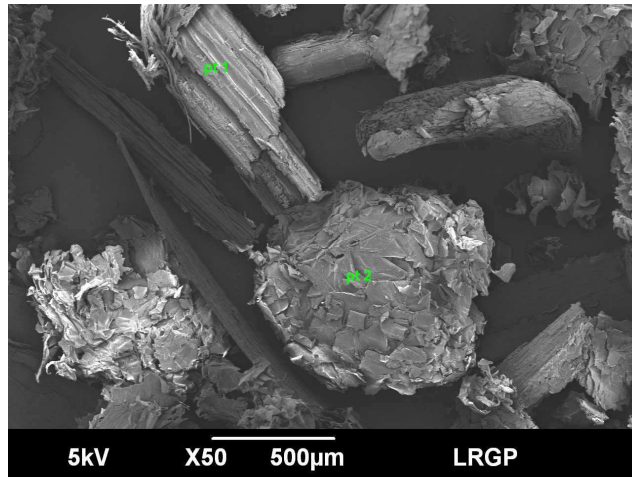
1003 **Appendix B – Fine Indian mustard stems (FIMS) details as adsorbent**

1004

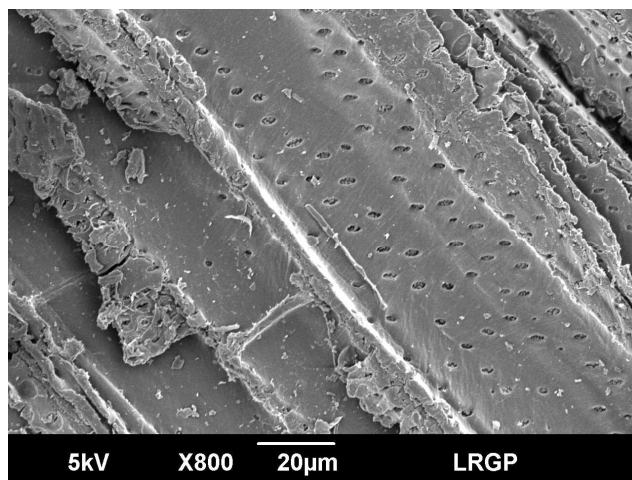
1005 **Details** of the equipment and operating conditions selected to carry out FIMS
1006 characterization are listed in **Table B1 (Rapp et al., 2018)**.

1007 The average particle size $D [3,2]$ (Sauter mean diameter) measured by laser diffraction
1008 is $254 \mu\text{m}$ (the smallest particles being larger than $10 \mu\text{m}$ diameter). Morphological analysis by
1009 scanning electron microscopy (SEM) reveals a heterogeneous structure (**Figure B1**) with a
1010 heterogeneous mass composition in the main elemental components *i.e.* C, O, Ca and K, as
1011 observed when coupling SEM with microanalysis by energy dispersive X-ray spectroscopy
1012 (EDS) (**Figure B2**). Existence of macropores as noticed in **Figure B1b** is confirmed by
1013 Brunauer-Emmet-Teller (BET) method (**Figure B3**) showing a quite flat adsorption profile,
1014 specific to macroporous material of diameter larger than 50 nm , with low specific area (< 1
1015 m^2/g) and very small pore volume ($\approx 0.07 \text{ cm}^3/\text{g}$).

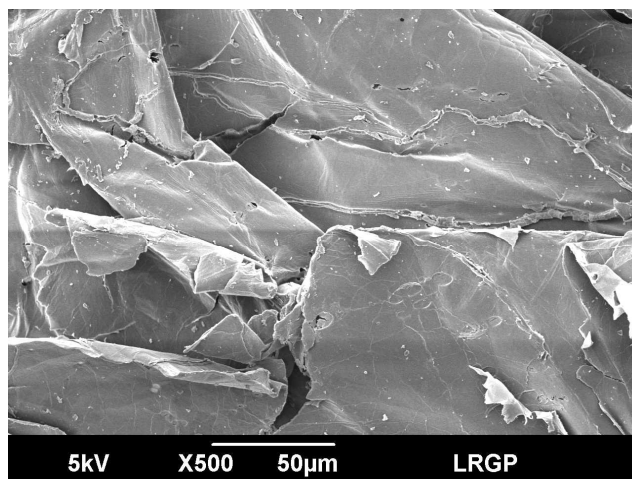
1016



(a)



(b)



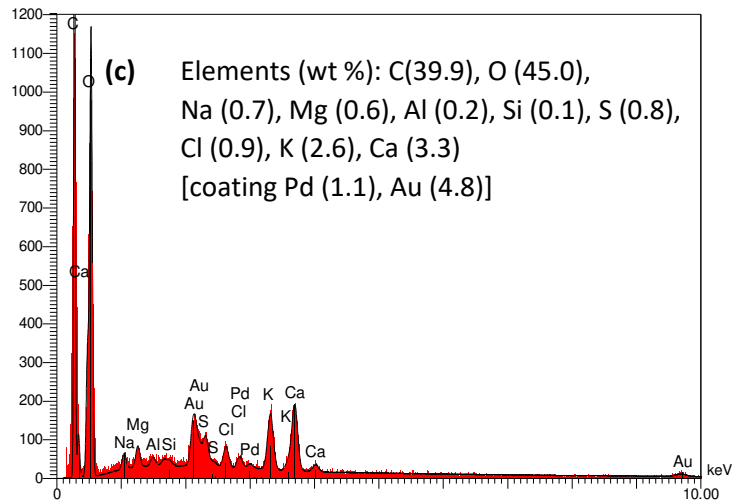
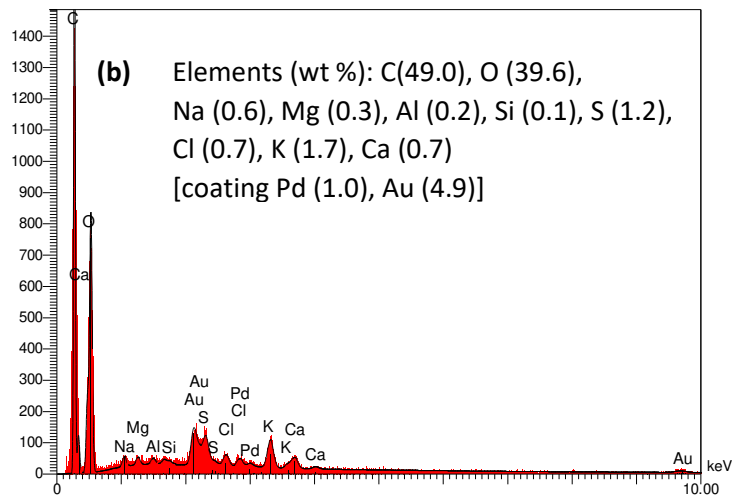
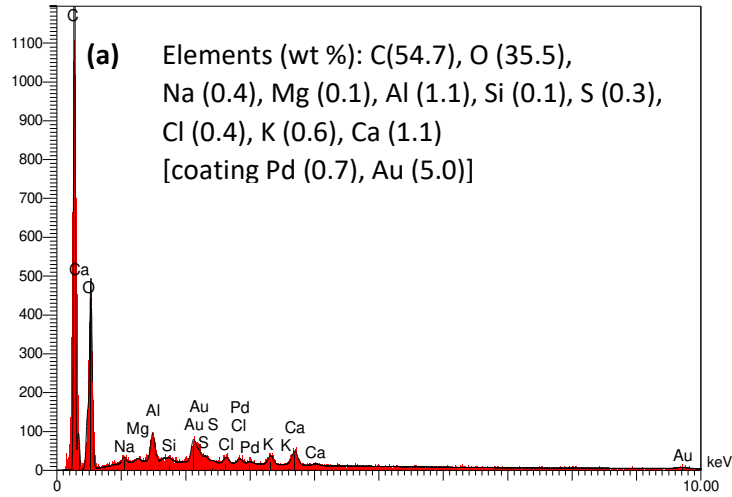
(c)

1017

1018 **Figure B1.** SEM analyses of FIMS (secondary electrons with gold-palladium coating).

1019 (a) whole sample; (b) bark (pt1); (c) core (pt2).

1020



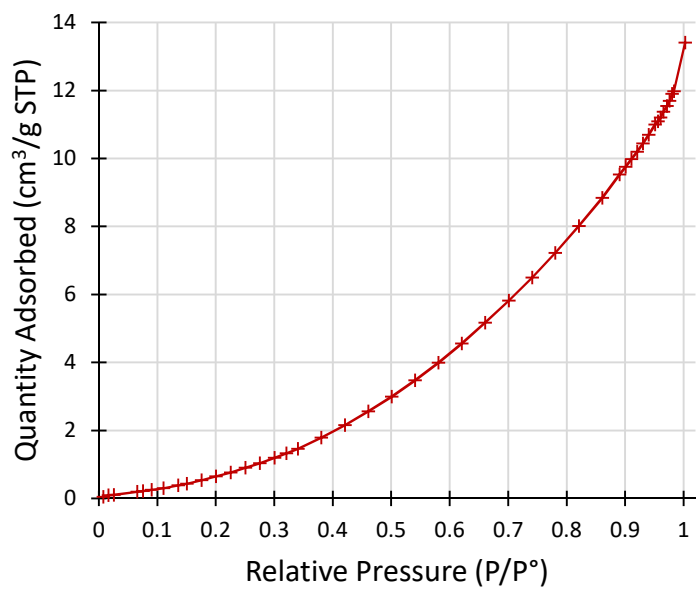
1021

1022 **Figure B2.** EDS analyses of FIMS (secondary electrons with gold-palladium coating).

1023 (a) whole sample; (b) bark; (c) core.

1024

1025



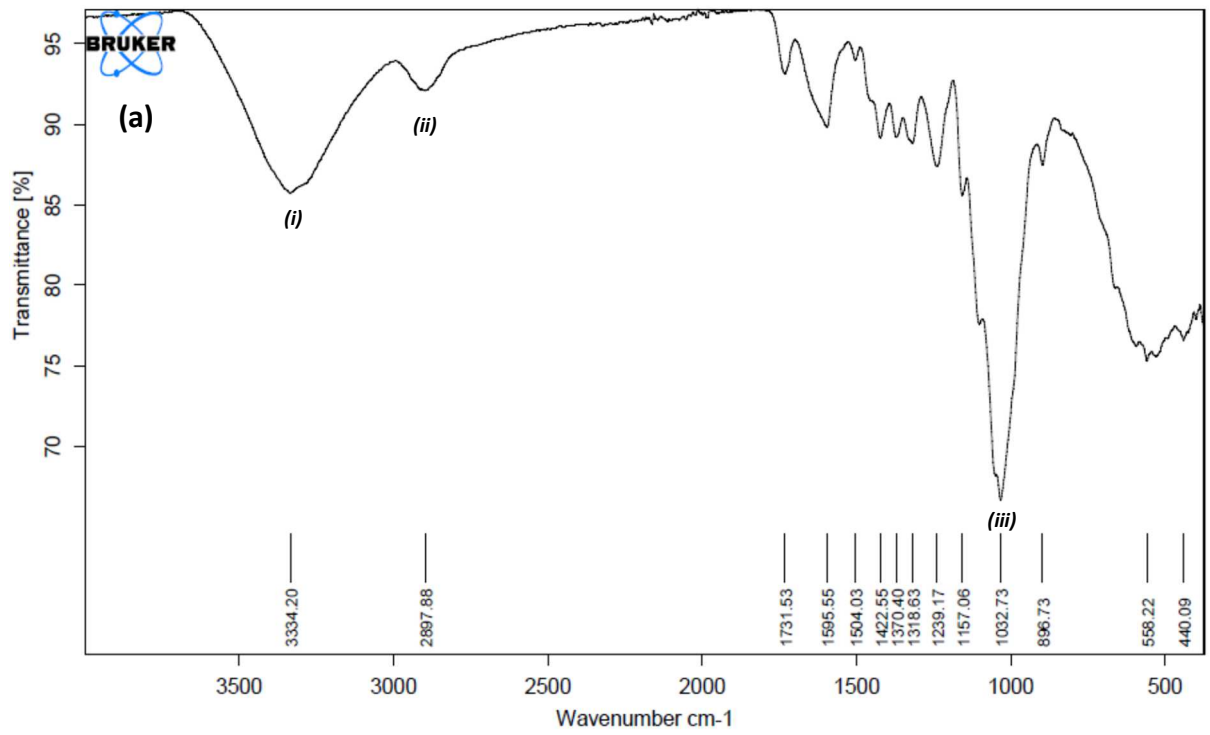
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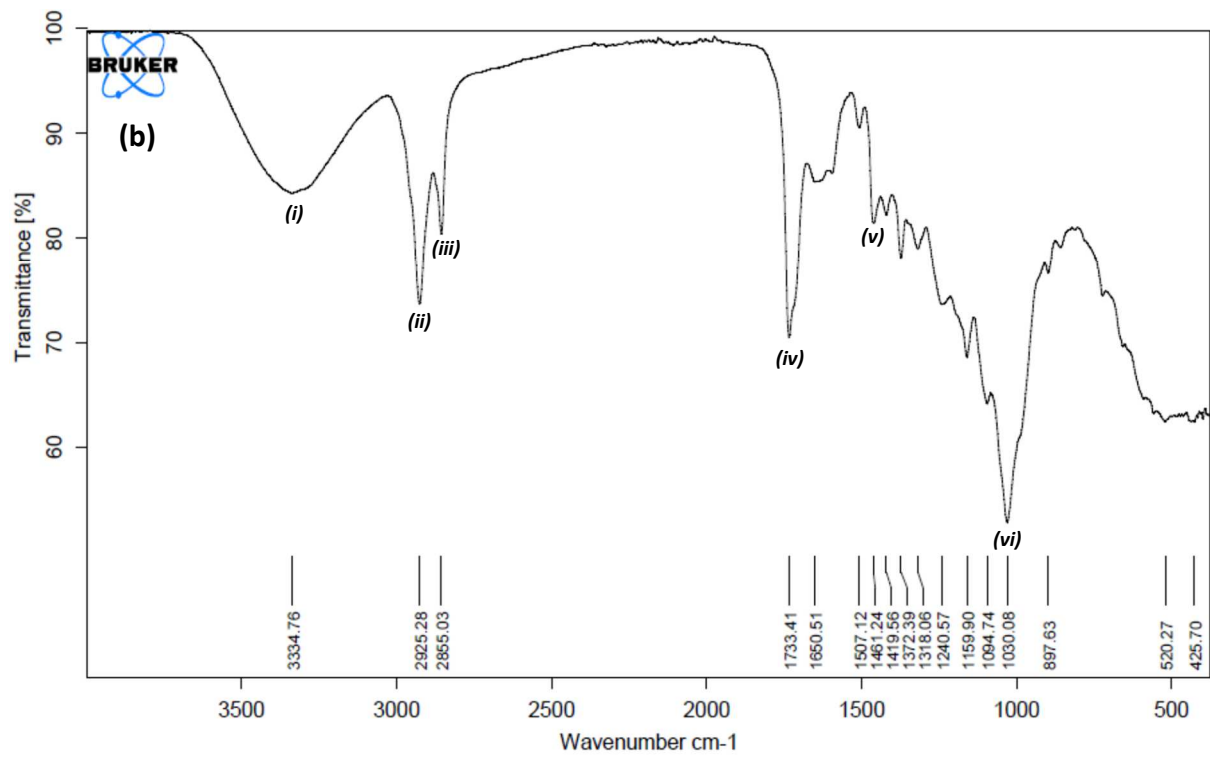
Figure B3. N₂ adsorption isotherm of FIMS.

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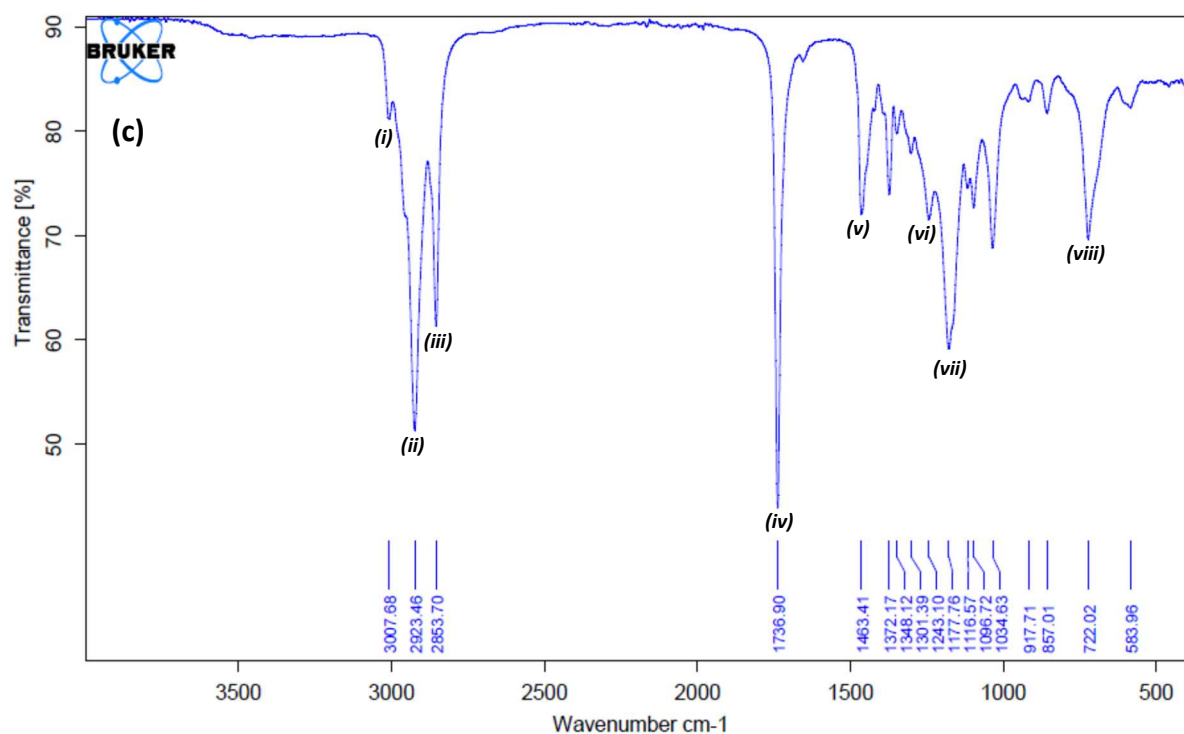
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1036 **Figure B4.** FTIR spectra of FIMS before (a) and after (b) use as adsorbent for biodiesel (c)
 1037 dry-purification.

1038 (a) (i) free hydroxyl O-H stretching at the range of 3500 to 3300 cm^{-1} , (ii) alkyl C-H stretching
 1039 at 2898 cm^{-1} , (iii) etheric C-O stretching at 1033 cm^{-1} . (b) (i) free hydroxyl O-H stretching at
 1040 the range of 3500 to 3300 cm^{-1} , (ii) symmetric vibration of methyl CH_3 at 2925 cm^{-1} , (iii)
 1041 asymmetric stretching vibrations of methylene CH_2 at 2855 cm^{-1} , (iv) stretching of carbonyl
 1042 $\text{C}=\text{O}$ bond in an ester at 1733 cm^{-1} , (v) bending of CH_3 and CH_2 at 1461 cm^{-1} , (vi) etheric C-O
 1043 stretching at 1033 cm^{-1} . (c) (i) and (iii) methylene symmetric and asymmetric stretching
 1044 vibrations at 3008 and 2854 cm^{-1} respectively, (ii) prominent band attributed to symmetric
 1045 vibration of CH_3 at 2923 cm^{-1} , (iv) intense band assigned to the stretching of $\text{C}=\text{O}$ bond of an
 1046 ester at 1737 cm^{-1} , (v) bending of the CH_3 and CH_2 groups at 1463 cm^{-1} , (vi) antisymmetric
 1047 axial stretching vibrations of $\text{C}-\text{C}(=\text{O})-\text{O}$ bonds of the ester at 1243 cm^{-1} , (vii) asymmetric axial
 1048 stretching vibrations of $\text{O}-\text{C}-\text{C}$ bonds at 1178 cm^{-1} , (viii) out of plane deformation of the olefinic
 1049 groups $\text{C}=\text{CH}$ specific to the unsaturated derivatives in the range 900-700 cm^{-1} (Mazivila et
 1050 al., 2015; Feng et al., 2018).

1051

1052 **Table B1.** Analysis equipment and operating conditions selected for FIMS adsorbent characterization.

1053

Objective	Experimental technique	Equipment	Operating conditions
Average particle size (Sauter mean diameter) D[3,2]	Laser diffraction	Malvern Master sizer 2000 (UK)	Size range: 0.02 to 2000 μm
Morphology	SEM	JEOL microscope; model JSM-6490 LV (Japan)	Please, refer to Nitièma-Yefanova et al., 2015
Elemental chemical composition	SEM-EDS	JEOL microscope; model JSM-6490 LV (Japan) + SAMX-IDFIX system (microanalysis) (France)	Please, refer to Nitièma-Yefanova et al., 2015
Surface area and porosity	N ₂ adsorption isotherms + BET method	Sorptomatic 1990, ThermoQuest CE Instruments (Italy)	Please, refer to Nitièma-Yefanova et al., 2015
Chemical structure (bonds/rings)	FTIR	Bruker Alpha-P spectrophotometer, equipped with an Attenuated Total Reflectance (ATR) crystal accessory (Switzerland)	For each spectrum: 128 scans applied at a resolution of 4 cm^{-1} with the wavenumber ranging from 4000 to 375 cm^{-1}

1054