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Adji Diop, Imed Ben Talouba, Laurent Balland, Nordine Mouhab

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1 Thermal characterization of a biodiesel nitration: 2 bio-additive's synthesis by calorimetric methods

3 DIOP Adj, BEN TALOUBA Imed ^{*1}, BALLAND Laurent, MOUHAB Nordine

4 Laboratoire de Sécurité des Procédés Chimiques (LSPC-EA4704), Normandie Univ, UNIROUEN, 76000
5 Rouen, France

6 Abstract

7 The aim of this study was to synthesize a substitute to the 2-Ethyl Hexyl Nitrate (EHN) by
8 nitrating a biodiesel. EHN is commonly used to improve the auto-ignition properties of diesel
9 fuels. The biodiesel was obtained by trans-esterification of canola oil. The nitration reaction
10 was carried out in a reaction calorimetry RC1 with semi-batch mode to study its exothermic
11 behavior. Mixed sulfuric/nitric acid was used as nitrating agent. The impact of the synthesis
12 temperature on the thermal behavior and on the reaction medium composition was
13 investigated. The final product was analyzed by using several analytical techniques such as
14 iodine number, infrared spectrometry, GC-MS and mass spectrometry. This analytical study
15 combined with the results of thermal stability study in DSC, allowed to highlight that
16 chemical transformations play an important role on the thermal reaction behavior and on the
17 Maximum Temperature of the Synthesis Reaction (*MTSR*). In addition to the mixed acid
18 decomposition, the synthesis at high temperature involves the production of nitrated products:
19 methyl-8-nitro oleate, methyl-10-nitrate stearate, methyl-10-nitrate-9-nitrostearate. Also, the
20 Cooperative Fuel Research (CFR) engine was used to analyze the cetane number of diesel
21 fuel mixed with our additive according to the ASTM D613 standard. The results showed an
22 increase in cetane number of 3.2 points.

23
24 Keywords: methyl oleate, cetane number, reaction calorimeter, DSC, *MTSR*

25 1 Introduction

26 The industrialization and motorization in recent years come along with a high demand for
27 petroleum products and an increase in air pollution [1]. It has been established by the
28 Interprofessional Center for Technical Studies of Atmospheric Pollution (CITEPA), in
29 France, that the automotive sector (mainly diesel engines) plays a leading role in air pollution
30 (CO_2 , CO, NO_x , SO_2).

31 To reduce the pollution related to diesel engines, several solutions have been tested including
32 the setting up of catalytic oxidation pots, particles filters [2] and the use of additives, mainly
33 cetane number improvers [3].

34 Cetane improver additives are commonly used to increase engine performances. According to
35 Beatrice *et al* 1996 [4], an increase in the cetane number reduces NO_x and particle emissions.
36 There are a lot of cetane number improvers [5] [6] but the 2-EthylHexyl Nitrate (ENH) is the
37 main additive used for diesel. The EHN is an energy molecule obtained by nitration of iso-
38 octanol (fossil fuels) with mixed nitric/sulfuric acid (1:1.5 w/w).

*imed.bentalouba@univ-rouen.fr

39 Several studies showed that the iso-octanol nitration is a strongly exothermic reaction which
40 takes place in a heterogeneous liquid-liquid mixture [7] [8]. EHN additive is thermally
41 unstable and sensitive to heat. Its thermal instability is mainly due to energetic functional
42 groups like nitro (C–NO₂) and nitrate (C–O–NO₂). Those functional groups are composed of
43 easily broken C–N covalent bonds. In fact, according to Yang et al 2014 [9], several
44 industrial accidents in China are due to the loss of control during the EHN synthesis. The
45 thermal behavior of this reaction need to be carefully investigated to assess the associated
46 risks [10].

47 With the scarcity of fossil fuels, it is important to reduce the dependency on petroleum
48 products. The goal of the work described in this article is to synthesize a substitute to the
49 EHN by nitrating a trans-esterified vegetable oil (biodiesel). Many studies on the use of
50 biodiesel as biofuels [11][12] or as bio-additive [13] have been realized over the years. The
51 biodiesel's particularity is that it contains less carbon, less sulfide, less water and more
52 oxygen atoms than fossil diesel. Therefore, it is less dangerous for humans [14] and its
53 amount of oxygen atoms improves combustion [15].

54 In this article, the biodiesel obtained from canola oil was used. According to Abdullah et al
55 2010 [16], the presence of double bonds favors the nitration reaction. And the canola oil has a
56 lot of double bounds compared to the other vegetable oils. The classic mixed sulfuric/nitric
57 acid [17] (1.5:1 w/w) was used as the nitrating agent.

58 First, a study about the identification and the characterization of the chemical compounds that
59 results from nitration by various analytical techniques (infrared spectrometer, GCMS, electro
60 spray ionization mass spectrometer, and iodine index measurement) was conducted. Then, a
61 complete study on the thermal stability of the reaction mixture (reagents and products) was
62 realized. This study uses the thermal information given by a reaction calorimeter RC1 and a
63 DSC type microcalorimeter. The quality of the synthesized bio-additive was determined by
64 measuring its cetane number according to the ASTM standard D 613.

65 **2 Materials and products**

66 **2.1 Products**

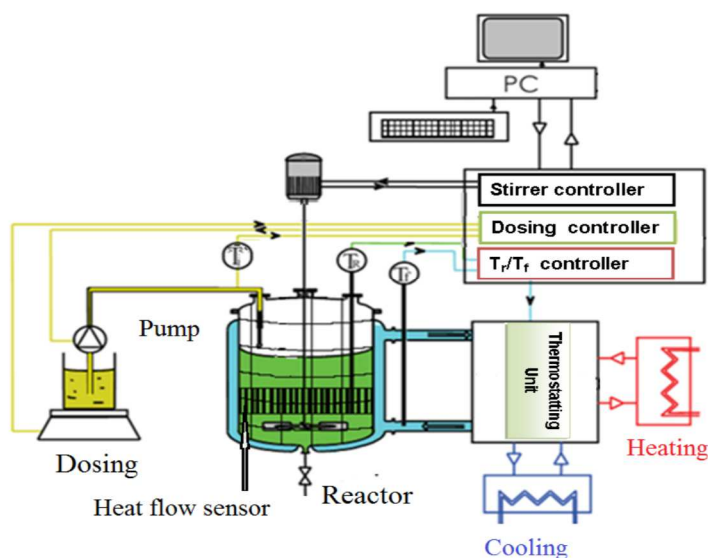
67 The biodiesel (Diester®) used was obtained by trans-esterification of canola oil and was
68 provided by Saipol company (Grand-Quevilly-France). Nitric (65%w/w), sulfuric (95% w/w)
69 acids used as nitrating agent and solvents (potassium iodide 1% volumetric, sodium
70 thiosulfate (Na₂S₂O₃) 0.1M, bicarbonate solution for analysis (>99.7%) and Wijs reactive 0.1
71 mol·L⁻¹) are provided by Fisher Chemical. The methyl nonadecanoate (> 98%) for GC
72 analysis was supplied by Sigma Aldrich.

73 **2.2 Materials**

- 74 ▪ Calorimetric reactor RC1-RTCal

75 The nitration was carried out in a calorimetric reactor RC1-RTCal (Mettler®) operating in
76 semi-batch mode. It is equipped with an AP00-0.5-RTCal reactor vessel with 0.5L capacity.
77 Mixing system is made of an impeller with one baffle. The experimental device is presented

78 in Fig. 1. The reactor has a temperature control system (between -20°C and $+165^{\circ}\text{C}$) and an
79 *RTCal* measurement technology based on thermal flow sensors located on the reactor wall.
80 The temperature regulation includes a thermostatic group which takes care of the various
81 regulation modes thanks to a fluid (Rodorsil 47 V20). This device provides real-time
82 monitoring of the heat released by the nitration reaction which is highly exothermic.



83

84

Fig. 1. Reaction calorimeter RC1-RTCal (Mettler®)

85

- Differential Scanning Calorimeter DSC Q20

86 The reactive and products stability study was based on thermograms analysis obtained with
87 the DSC Q20. The DSC was provided by TA Instruments with purge using extra pure
88 nitrogen ($50 \text{ mL}\cdot\text{min}^{-1}$). It can work in isothermal and non-isothermal conditions. DSC
89 measures temperature with accuracy of $\pm 0.05 \text{ K}$. Its specific sensitivity is $1\text{mW}\cdot\text{kg}^{-1}$ [18].The
90 device detects temperature changes between the sample and the reference to measure heat
91 flow over time and temperature. Gold-plated high pressure crucibles (M20 crucibles from
92 Swiss Institute for the Promotion of Safety and Security) were used for measurement [19].

93

- Chemical analysis materials

94 The FTIR IR Affinity-1S from Shimadzu (400 to 4000 cm^{-1}), GC-MS from Agilent
95 technology 7890A GC/5975C VL MSD, and the mass spectrometry with electro spray
96 ionization from Waters LCT Premier were used to identify and quantify chemical species.

97 GC-MS analyses were performed in a GC6850 gas chromatography coupled with a 5975C
98 MSD Quad Instrument with electrons impact ionization at 70 eV . A HP5-MS 5% Phenyl
99 Methyl Siloxane capillary column (Agilent 19091S-433E) with a 0.25 mm i.d., 30 m nominal
100 length and $0.25 \mu\text{m}$ phase film diameter was used. The carrier gas was helium at a flow rate of
101 $15 \text{ mL}\cdot\text{min}^{-1}$.

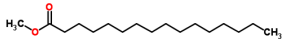
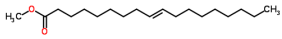
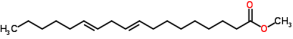
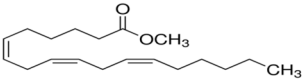
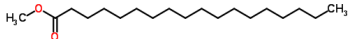
102 3 Synthesis and chemical analysis

103 3.1 Experiment

104 Considering the chemical instability of the mixed acid (nitrating agent), it was prepared just
105 before the synthesis reaction (nitration). 86.4 g of sulfuric acid was introduced with a flow
106 rate of $4\text{g}\cdot\text{min}^{-1}$ into the reaction calorimeter filled with 57.6 g of nitric acid. The mixture was
107 stirred at 200 rpm and kept at 5°C during the addition. At the end, the mixture, composed of
108 HNO_3 27 %, H_2SO_4 58%, H_2O 15% (w/w), was kept in the fridge at the same temperature.

109 To carry out the synthesis reaction, 144g of mixed acid was dosed with a flow rate of $4\text{g}\cdot\text{min}^{-1}$
110 into the reactor initially filled with 150 g of biodiesel composed of 92% of methyl oleate
111 (determined by GC-MS Table 1). These operating conditions are chosen after preliminary
112 study on the effect of parameters such as a flow rate, stirring speed on thermal behavior in
113 order to ensure the safe operation of the reactor. The synthesis reaction was carried out at 600
114 rpm stirring speed, in the isothermal mode. This experiment was realized at seven different
115 temperatures (10-15-20-25-30-40 and 50°C). The Mettler RC1 operating software allows to
116 record the thermal signal (power profile) and to monitor the reaction progress. The final
117 product was then transferred to a separating funnel and separated in two phases. Only the
118 organic phase (which contains the nitrated products) was analyzed. Before the analysis, the
119 organic phase was, first, washed with a bicarbonate solution at 2% w/w, and then with
120 distilled water until a neutral pH was obtained.

121 [Table 1: Fatty Acid Methyl Esters \(FAME\) from canola composition](#)

Compounds	% w/w
Methyl palmitate	
	2.2
Methyl oleate	92.0
	
Methyl linoleate	2.5
	
Methyl linolenate	2.8
	
Methyl stearate	0.5
	

123 3.2 Nitration Product analysis

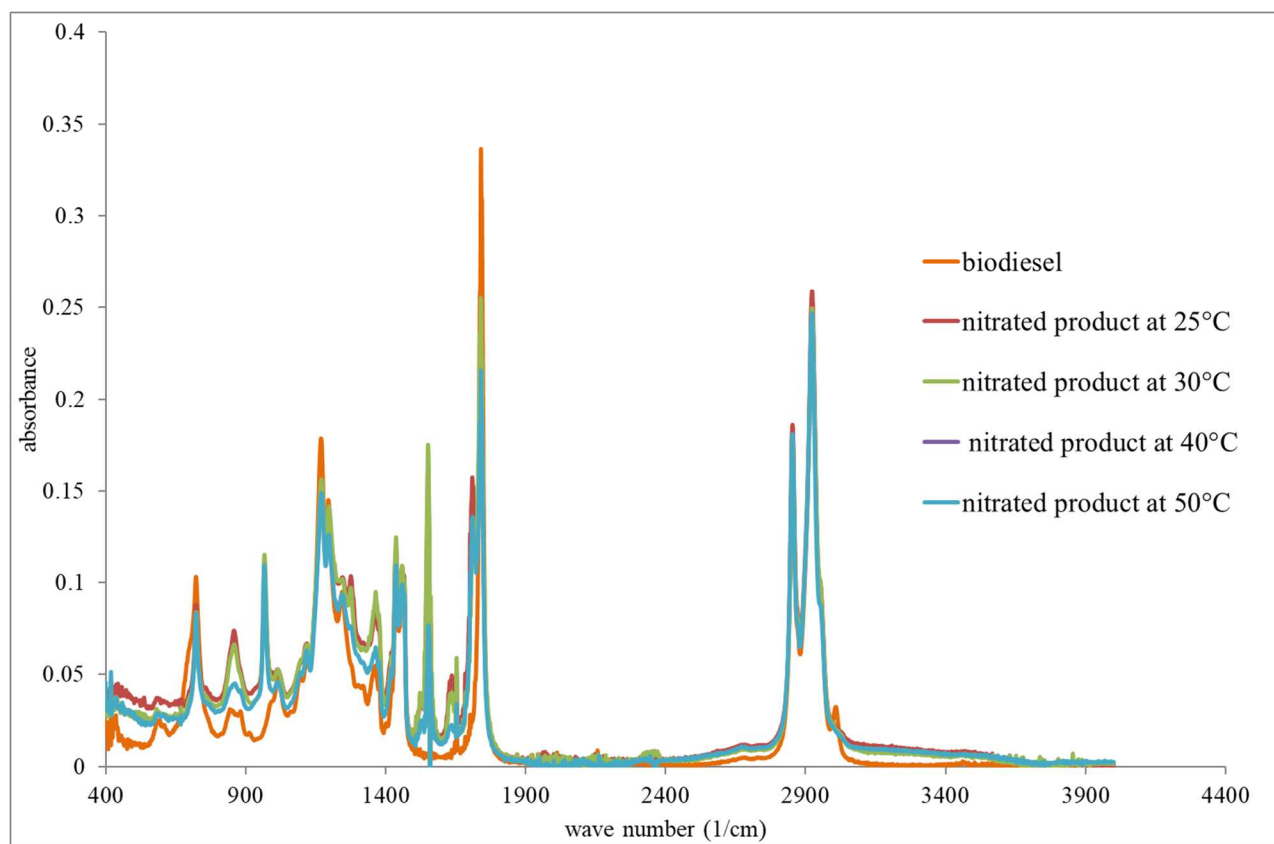
124 Infrared analysis and electro-spray ionization mass spectrometry were used to identify and
125 quantify the different chemical compounds produced during the biodiesel nitration.

126 3.2.1 Infrared analysis

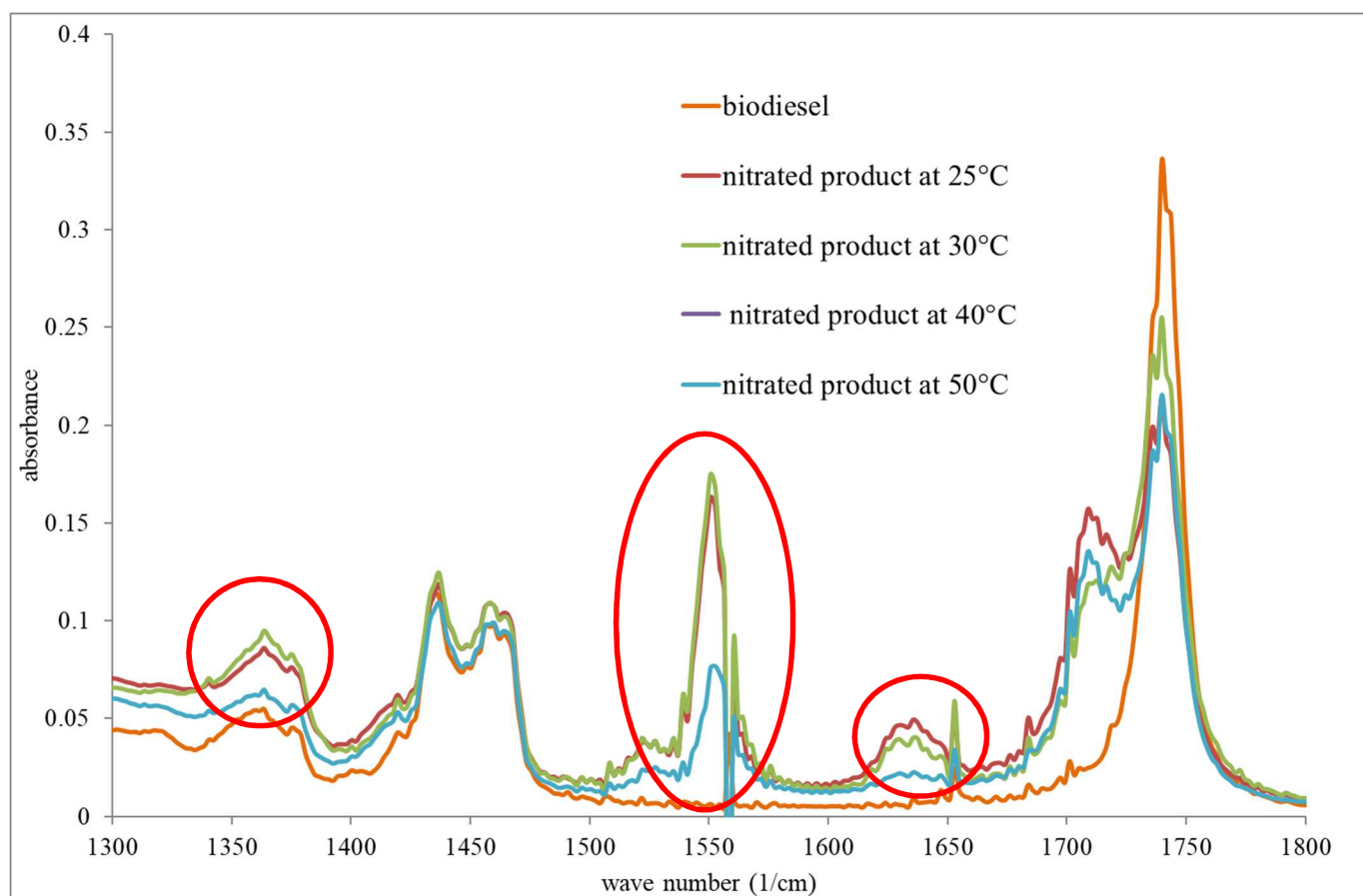
127 Fig. 2 shows the FTIR spectra of biodiesel and nitrated products at different temperatures.
128 These spectra were obtained after defining the baseline corresponding to the air spectrum with
129 50 scans. An absorbance difference is noted between 800 and 1700 cm^{-1} . It allows to identify
130 new functional groups present in the nitrated product (Table 2). The value of the nitrated
131 products absorbance depends on the synthesis temperature.

132 The characteristic ester frequency C=O bonds at 1750 cm^{-1} , alkane frequency C-H bonds
133 between 2900-3000 cm^{-1} and alkene frequency C=C stretch at 1650 cm^{-1} with weak intensity,
134 obviously appear in all spectra. The spectrum of the nitrated product shows the presence of
135 three new peaks at 1363, 1550 and at 1635 cm^{-1} . They respectively indicate the stretching of
136 symmetric NO_2 , that of assymmetric NO_2 and the absorption of ONO_2 (fig.3).

137 The absorption spectrum at 1363 cm^{-1} (fig.3) indicating a symmetric vibration of R- NO_2 for
138 nitrated products, can also be observed in biodiesel but is less intense. This peak in the
139 biodiesel spectrum corresponds to the vibration of CH_2 groups which is supposed to appear at
140 1370 cm^{-1} .



142 Fig. 2. IR spectra of biodiesel and nitrated products at different temperatures



143

144

Fig. 3. Zoom on the IR spectra

145

Table 2: Determination of new functional groups after the reaction

Groups	Theoretical wave number cm^{-1}	Experimental wave number cm^{-1}
RNO ₂ (Asymmetric)	1560-1548	1550
RNO ₂ (Symmetric)	1397-1310	1363
RONO ₂	1640-1620	1635

146

147 To complete this IR analysis which only identifies the functional groups, electro spray
 148 ionization mass spectrometry was used to identify the synthesized molecules.

149 3.2.2 Electro spray ionization mass spectrometry

150 The electro spray ionization mass spectrometry allows to avoid the degradation of the nitrated
 151 products during the heating in the chromatography column. The samples (biodiesel and nitro
 152 product) were diluted with acetonitrile to a concentration of 20 $\mu\text{g/mL}$, before being
 153 introduced into a capillary tube with a flow rate of 15 $\mu\text{L}\cdot\text{min}^{-1}$. Peaks of the spectrum in Fig.
 154 4a correspond to methyl oleate, methyl linolenate and the methyl linoleate. These molecules
 155 are in a ionic adduct form $[\text{M} + \text{Na}]^+$ at $m/z = 319$, $m/z = 315$ and $m/z = 317$.

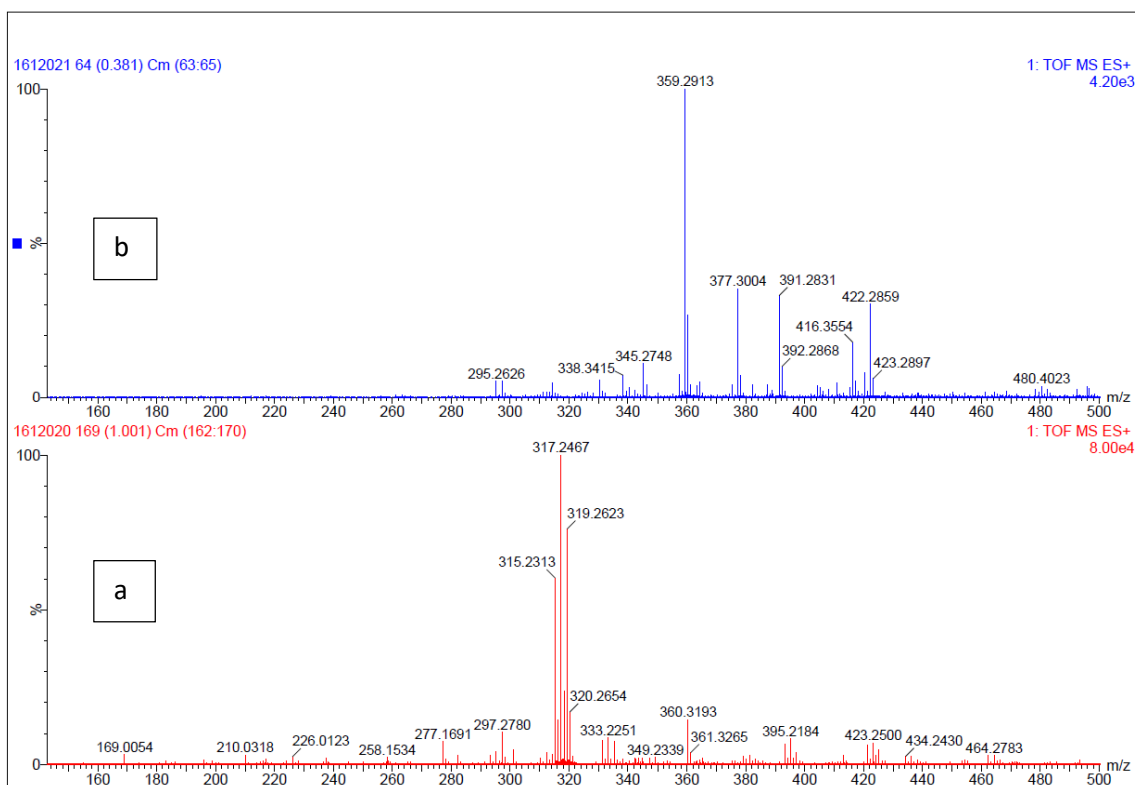


Fig. 4. Biodiesel and nitrated biodiesel mass spectrum

For the nitrated biodiesel (Fig. 4b), intense peaks at m/z 359, 377 and 422 are observed. These peaks correspond to $[M+NH_4]^+$ ion. Table 3 shows the different identified compounds.

Table 3: Molecules after the nitration reaction

Empirical formula	Molar mass	Structural formula
$C_{19}H_{35}NO_4$ A (Methyl-8-nitro oleate)	$341\text{g}\cdot\text{mol}^{-1}$	
$C_{19}H_{37}NO_5$ B (Methyl-10-nitrate stearate)	$359\text{g}\cdot\text{mol}^{-1}$	
$C_{19}H_{36}N_2O_7$ C (Methyl-10-nitrate-9-nitrostearate)	$404\text{g}\cdot\text{mol}^{-1}$	

156

157

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159

160

161

162 This study reveals that the nitration reaction can be performed on the carbon atoms carrying
163 the double bond as well as those in the beta position. This result contradicts Abdullah *et al*
164 (2010) [16] work which indicates that during the nitration process the NO₂ or NO₃ groups are
165 attached only on the unsaturated carbon atoms.

166 Three compounds were identified A (Methyl-8-nitro oleate), B (Methyl-10-nitrate
167 stearate) and C (Methyl-10-nitrate-9-nitrostearate).

168 3.3 Study of the reaction selectivity

169 GC-MS and iodine index measurement were used to determine the molar proportion of each
170 compound A, B and C.

171 3.3.1 Measurement of the conversion rate

172 The nitration reaction's conversion rate was determined by using a GC-MS with addition of
173 an internal standard (methyl nonadecanoate) according to the 2011 EN14103 standard. Each
174 solution was dissolved in 10 mL of toluene (GC purity $\geq 99.5\%$). 2 μ L of the sample was
175 injected in the column previously heated at 60°C. This column was heated to 200°C with a
176 10°C/min heating rate then at 5 °C·min⁻¹ to 240°C. Finally, the column was maintained at this
177 temperature during 7 min. The runtime was 30 min. Splitless mode was used.

178 Results are presented in Table 4

179 *Table 4: Total conversion of the nitration reaction*

Temperature (°C)	Conversion rate (%)
25	94.6
30	92.7
40	97.0
50	89.2

180

181 Table 4 shows that the reaction conversion rate (the production of all molecules A, B and C)
182 varies with temperature and is maximal at 40 °C. The selectivity of B and C was determined
183 by using the iodine index method.

184 3.3.2 Determination of the molecules selectivity

185 The iodine number of oils and fats measures their unsaturation degree. The Wijs method [20],
186 commonly used, requires 30 min absorption time. Sodium thiosulfate solution 0.1M was used
187 as a titration reactant. The measurement of the biodiesel iodine index before and after the
188 nitration reaction allowed to calculate the conversion of unsaturations (the loss of the double
189 bonds). This value was used to determine the proportion of molecules B and C according to
190 the equation 3-1.

191
$$X = \frac{\text{iodine index}_{t_0} - \text{iodine index}_{t_f}}{\text{iodine index}_{t_0}}$$
 3-1

192 The proportion of A was obtained by making a difference between the conversion rate of the
 193 reaction (Table 4) and the unsaturations conversion rate. Results are gathered in Table 5
 194 which shows that at high synthesis temperature, the selectivity of B and C decreases.

195 *Table 5: Determination of the molecule's selectivity*

Temperature °C	Total conversion rate (%)	Selectivity of B and C (%)	Selectivity of A (%)
25	94.6	95.2	4.8
30	92.7	68.0	32.0
40	97.0	42.9	57.1
50	89.2	41.6	58.4

196
 197 The results obtained in this study show that the reaction mechanism of biodiesel nitration
 198 (aliphatic chain) is more complex than that of the aromatic compounds. Indeed, three
 199 molecules with different selectivity had been identified (Table 5).

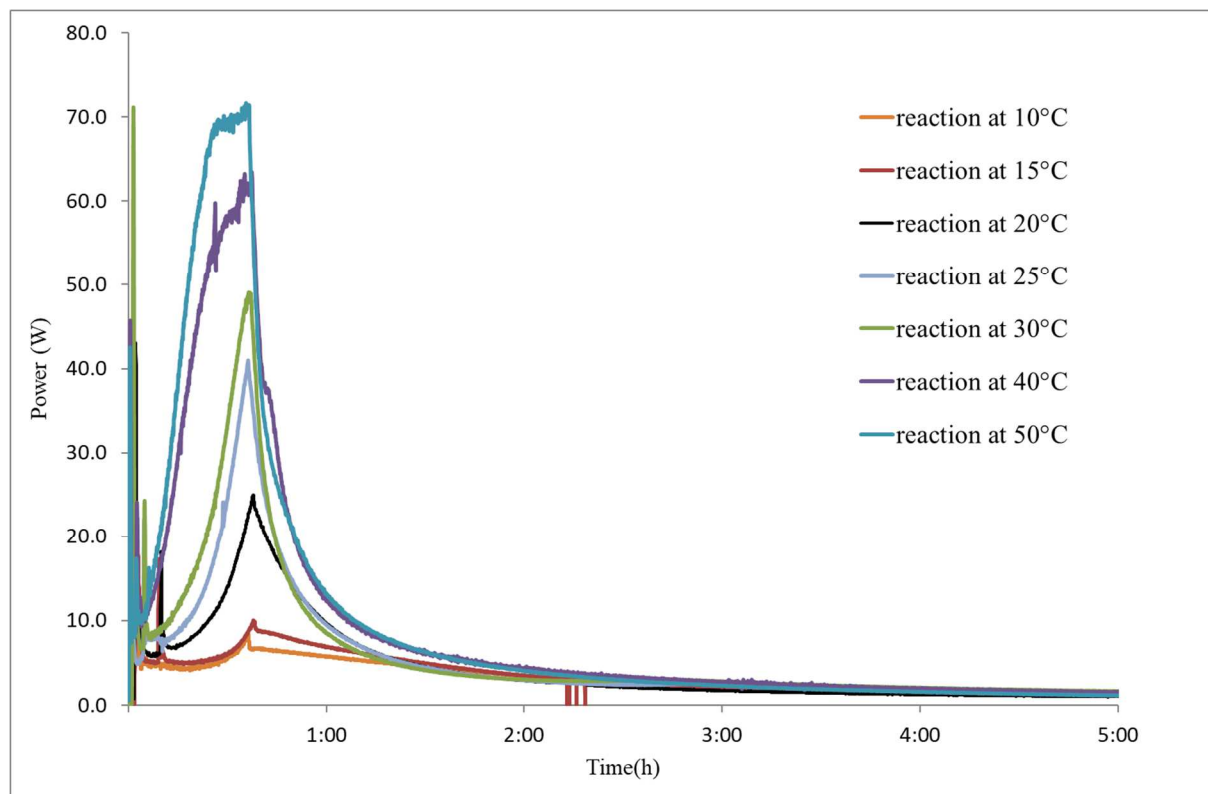
200 During the synthesis at low temperature (below 20°C), the final product is a stable micro
 201 emulsion preventing phase separation. This stability may be due to the hydrophilic behavior
 202 of the saturated nitrated products (B and C) at low temperatures.

203 4 Calorimetric study

204 4.1 Determination of the reaction heat

205 The integration of the experimental power profiles (equation 4-1) obtained according to the
 206 conditions presented in section 3, shows that the heat released by the reaction varies with the
 207 temperature (Table 6). This change in the thermal behavior has also been observed by Chen et
 208 *al* 2012 [21] in their work about the nitration of iso-octanol but no interpretation has been
 209 given. Power profiles (q_r) are shown in Fig.5. Sudden variation of the thermal power with
 210 time at the beginning of the reaction corresponds to the nitration of the small amount of the
 211 products as Methyl linolenate and Methyl linoleate. Such thermal behavior may present a risk
 212 of thermal runaway.

213
$$Q_R^{\text{Exp}} = \int_{t_0}^t q_r dt$$
 4-1



215

216

Fig.5. Power profiles at different temperatures

217

Table 6: Heat released by the synthesis reaction at different temperatures

Temperature °C	Heat (kJ)	Conversion rate (%)
25	112.5	94.6
30	106.3	92.8
40	161.9	97.0
50	171.9	89.2

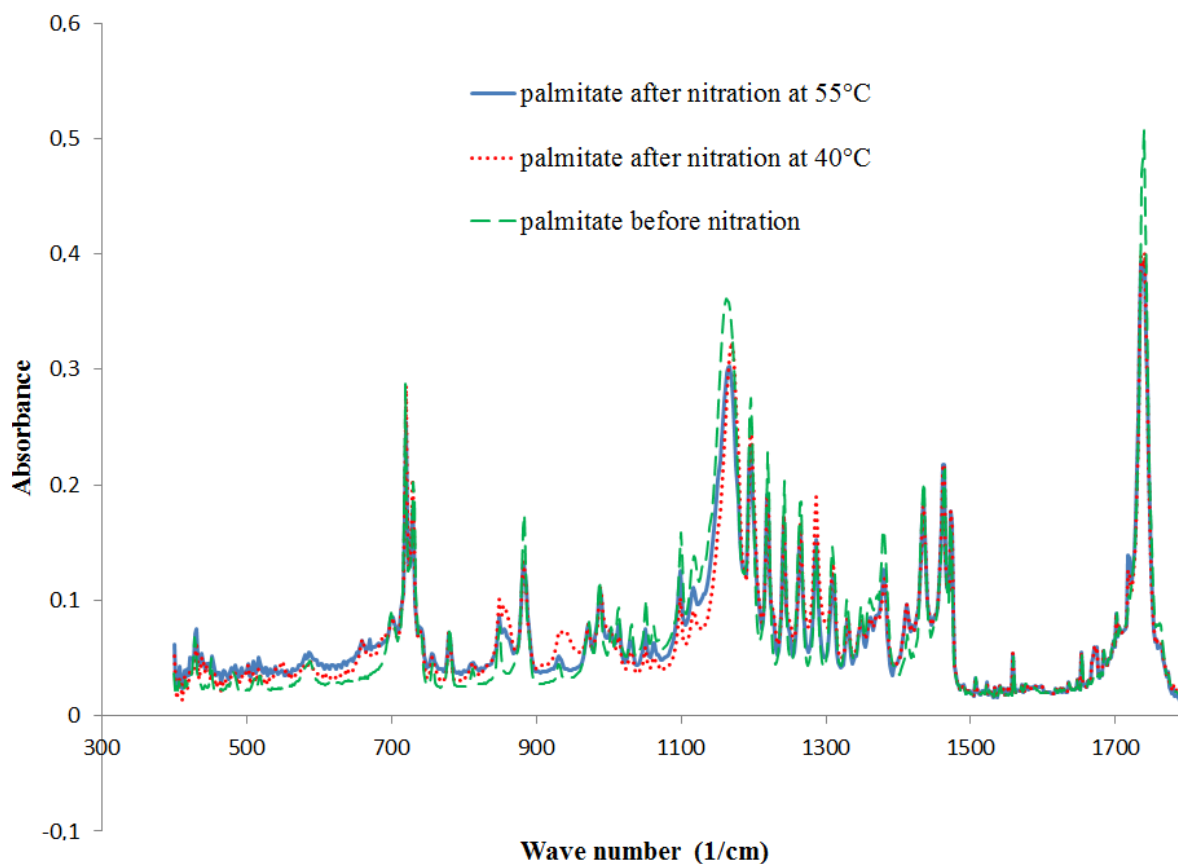
218 The total heat released by the reaction (table 6) represents all the thermal effects linked to the
 219 products synthesis, to the mixing phenomena and to the possible decomposition in case of
 220 unstable compound. In section 3.3.2, a modification of the reaction mechanism according to
 221 the synthesis temperature was noticed. In addition to other phenomena mentioned above, the
 222 modification of the reaction mechanism is likely to contribute to the change in the total heat
 223 released by the reaction.

224 Heat related to the mixing phenomena and the decomposition of unstable compounds are
 225 presented in sections 4.2 and 4.3.

226 4.2 Heat of mixing measurement

227 To measure the heat of mixing, the power profile obtained without nitration reaction have to
 228 be integrated. The operating conditions were kept identical to those in the synthesis reaction
 229 (section 3.1) except for the biodiesel reactant. In fact, to avoid the nitration reaction, the
 230 biodiesel was replaced by a molecule close to its main molecule (methyl oleate): methyl
 231 palmitate.

232 The absence of the reaction was confirmed by the palmitate infrared spectrum after the
233 reaction (fig.6: no nitro group was detected). The non-reactivity of the methyl palmitate is due
234 to the absence of unsaturated carbons.

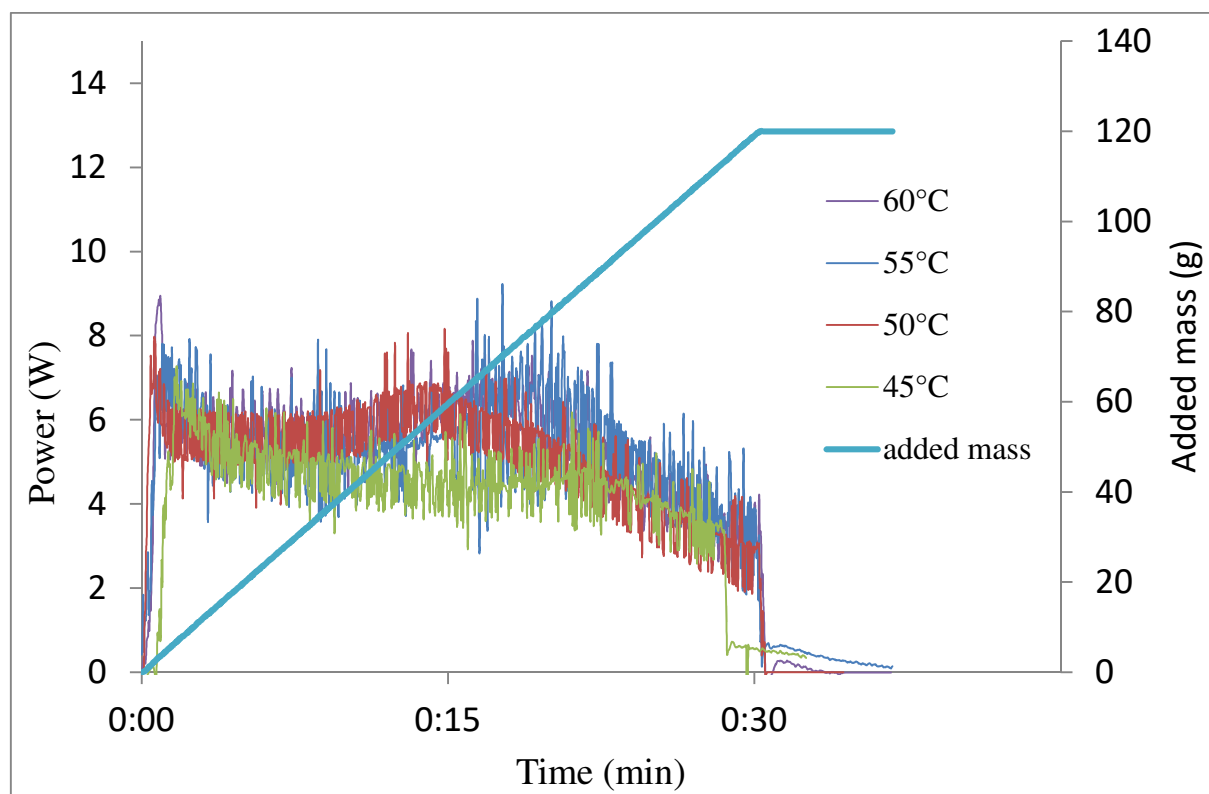


235

236

Fig. 6: Methyl palmitate IR spectrum before and after the reaction

237 The heat of mixing below 40°C could not be measured because the melting point of methyl
238 palmitate is higher than 35°C.



239

240

Fig.7. Power profiles obtained with the palmitate

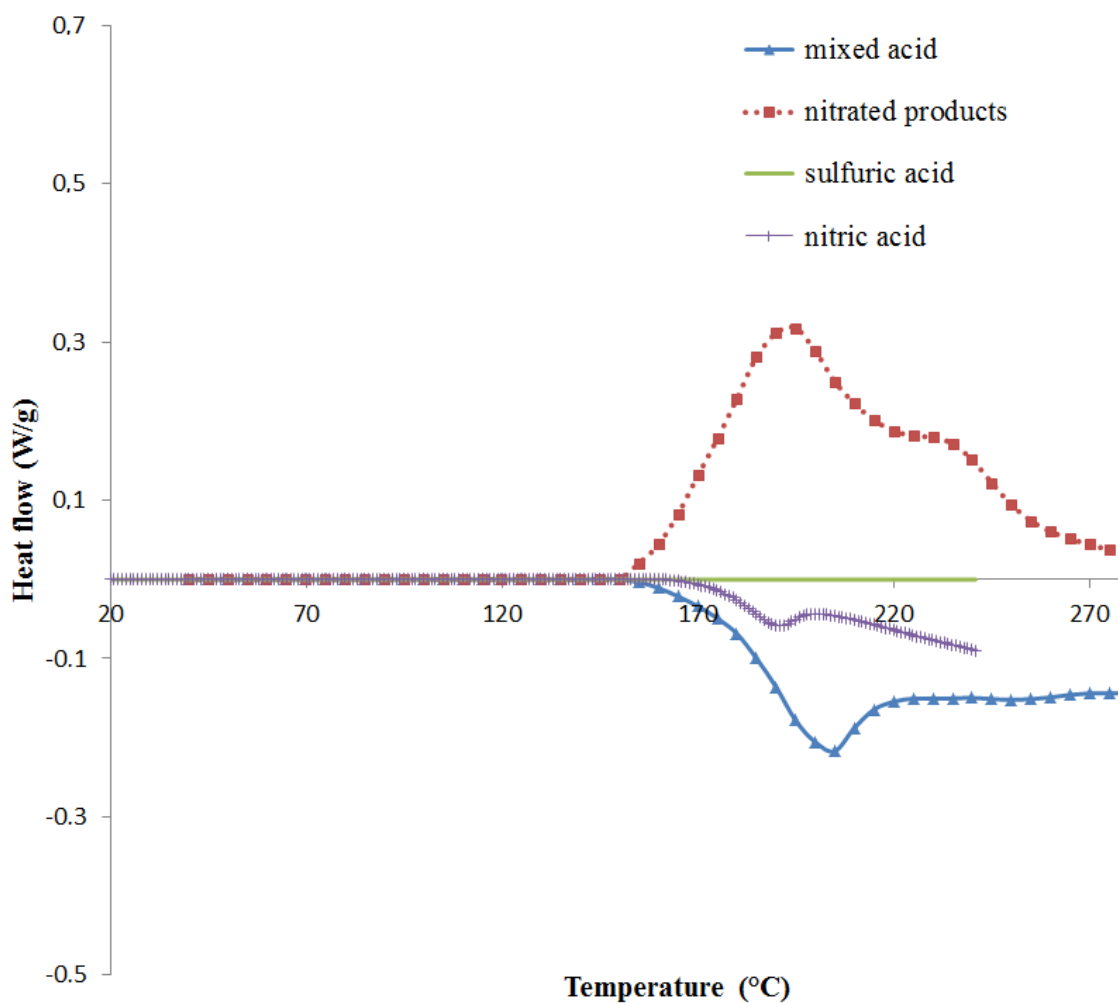
241 Fig.7. shows that the power profiles are identical regardless of the temperature. The average
 242 heat is about 8J. All power profiles return to the baseline at the end of the addition,
 243 demonstrating the absence of any chemical transformations.

244 4.3 Measurement of the decomposition heat

245 The measurement of the heat released during the decomposition was done in two steps. Pure
 246 products: nitrated products, nitric acid, sulfuric acid and mixed acid (sulfo-nitric acid) were
 247 analyzed first (fig.8), then samples of mixed acid with different percentages (w/w) of nitrated
 248 products (fig.9). These analyses were realized using a DSC in a non-isothermal mode with
 249 Gold-plated high-pressure crucibles and a heating rate of $2^{\circ}\text{C}\cdot\text{min}^{-1}$. According to Liu et al
 250 [22], the advantage of DSC test under non-isothermal condition is its swiftness and high
 251 efficiency in a short time.

252 For pure products (fig.8) no signal of decomposition is observed in our range of synthesis
 253 temperature ($<50^{\circ}\text{C}$). The only thermal effects are detected beyond synthesis temperatures.
 254 Nitric acid and mixed acid's DSC curves show an endothermic effect at $T_{onset} = 181.3^{\circ}\text{C}$
 255 which is attributed to the decomposition of the nitric acid [23]. This temperature was
 256 determined by the tangent method from zero curvature. Regarding to the nitrated product, it
 257 exhibits an exothermic peak at $T_{onset} = 150.9^{\circ}\text{C}$ which correspond to its decomposition. Its
 258 thermal instability was mentioned in other works [9] [24] [21]. The T_{onset} of our additive
 259 decomposition is closed to that of fossil nitrated product (EHN) [8].

260

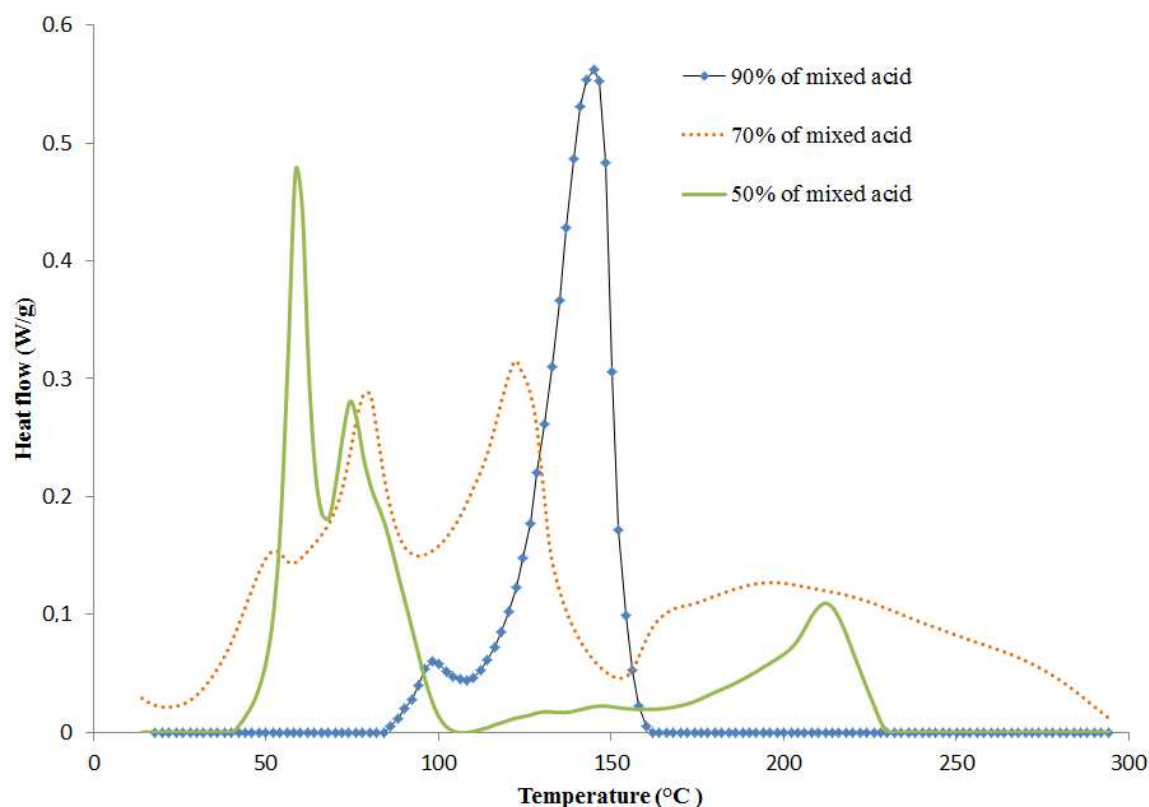


262

263

Fig. 8. Pure sulfo-nitric acid and pure nitrated product decomposition

264 Fig.9 shows the DSC curves of sulfo-nitric acid mixed with nitrated products. The initial
 265 decomposition temperatures T_{onset} are 48.83°C, 70.39°C and 77.96°C respectively for 50 %,
 266 70% and 90% of mixed acid. Obviously, when the quantity of nitrated products added into the
 267 mixed acid increased, lower onset temperatures are observed. It is also noted that the specific
 268 enthalpy decreases with the amount of nitrated products (table 7). This enthalpy (ΔH) reported
 269 to the total sample mass was determined by integrating the area under the exothermic curve.



270

271

Fig.9. Study of the decomposition mixed sulfo-nitric and nitrated products

272 This study allows to demonstrate that the decomposition of the sulfo-nitric mixed acid and
 273 nitrated products also contributes to the modification of the total heat released during the
 274 synthesis reaction (Fig.5).

275

Table 7: Results of DSC analysis

Component of sample (w/w)	T_{onset} (°C)	ΔH (J/g)
90% of mixed acid and 10% nitrated products	77.96	502.0
70% of mixed acid 30% nitrated products	70.39	474.1
50% of mixed acid 50% nitrated products	48.83	332.1

276

277 4.4 Study of the safety parameters

278 In the light of the strong exothermicity of the nitration reaction and the mixed acid
 279 decomposition in the presence of the nitrated products, the determination of the Maximum
 280 Temperature of the Synthesis Reaction (*MTSR*) is more than necessary to avoid the possible
 281 risk of thermal runaway.

282 The Maximum Temperature of Synthesis Reaction (*MSTR*) is the temperature reached by the
 283 reaction mixture if the energy potential of the main reactions is released under adiabatic
 284 conditions [25].

285 This decomposition releases an excess of energy causing a thermal runaway. To evaluate this
 286 temperature, it is necessary to determine the ΔT_{ad} (the temperature variation in adiabatic
 287 mode) according to equation 4-2.

$$288 \quad \Delta T_{ad} = \frac{Q_R^{exp}}{C_p M_r X'_r} \quad 4-2$$

289 with C_p the heat capacity of reaction mixture obtained with reaction calorimeter, M_r the mass
 290 of the reaction mixture and X'_r the full conversion of the biodiesel.

291 The calculation of the $MTSR$ was done in semi-batch mode according to equation 4-3 [26]
 292 [25]. The results are given in Table 8. They show a considerable increase in $MTSR$ from an
 293 isothermal of 40 °C. This can be explained by the fact that the value of the adiabatic
 294 temperature increase ΔT_{ad} used for the calculation of $MTSR$, considers the enthalpy of the
 295 nitration reaction in addition to the decomposition enthalpy.

$$296 \quad MTSR = T_P + \Delta T_{ad} \cdot X_{ac, max} \quad 4-3$$

297 with $X_{ac, max}$ the maximum accumulation of the unreacted reactant and T_P the synthesis
 298 temperature.

299 In our case, the nitric acid is in stoichiometric excess over biodiesel. Thus $X_{ac, max}$ is obtained
 300 at the end of the addition.

301 Table 8: Safety parameters of nitration reaction

Temperature (°C)	Conversion (%)	C_p (J·g ⁻¹ ·°C ⁻¹)	ΔT_{ad} (°C)	$X_{ac, max}$ (%)	$MTSR$ (°C)
25	94.6	2.1	194.4	30.3	83.8
30	92.8	2.0	194.8	36.5	101.2
40	97.0	2.2	262.8	49.5	171.1
50	89.2	2.1	313.6	50.5	208.5

302 If we compare results in table 7 with those in table 8, it appears that the lowest $MTSR$
 303 (83.8°C) is higher than the maximum T_{onset} obtained in decomposition study (77.96°C). In
 304 case of loss of temperature control, this means that the decomposition reaction would be
 305 triggered before completion of the synthesis reaction, which would further lead to very severe
 306 consequences. According to Stoessel's criticality index used for the risk assessment of a
 307 chemical reaction [27], this implies that the runaway is too fast for a safety barrier to be
 308 efficient. These results correspond to a Stoessel's criticality class of 5 if the nitration reaction
 309 conducted in these operated conditions.

310 5 Measurement of the bio-additive cetane number (index)

311 The cetane number is the measurement of the diesel fuel ignition performance. It is obtained
312 by making some comparison with reference fuels in a standardized test. Higher cetane number
313 indicates that the ignition properties of the fuel are better [28]. This index is obtained
314 according to ASTM D 613. The equipment used was a Cooperative Fuel Research (CFR)
315 engine. A standard diesel of cetane number 50 was used to prepare two samples of 1% and
316 5% concentration in bio-additive. For each mixture, the cetane number was measured at two
317 synthesis temperatures 25 and 40 °C. The results of the cetane number analysis are listed in
318 Table 9. They show that the bio-additive synthesized in this study allows to increase the
319 cetane number of the reference diesel. A 5% addition of the bio-additive to the reference
320 diesel improves the cetane number by 3 points.

321 Table 9: Cetane number with the CFR engine

Synthesis temperature (°C)	CN fuel		
	CN fuel	CN fuel +1% additive	+ 5% additive
25	50.0	50.9	52.9
40	50.0	50.9	53.2

322 Canoira *et al* 2012 [13] obtained a 5 points increase in the fuel cetane number by mixing their
323 nitrated biodiesel to fossil diesel in a concentration of 1000 mg.L⁻¹. With our bio-additive a
324 5% addition (concentration of 49g.L⁻¹) to the reference diesel improves the cetane number by
325 3 points. It seems clear that our bio-additive is much less efficient than Canoira *et al* one. It
326 may be due to the fact that Canoira *et al* used a biodiesel containing 33.0 %, 54.20% and 16%
327 of methyl linoleate while ours contains only 2.5%. According to Abdullah *et al* 2010 [16],
328 during the nitration process of biodiesel, NO₃ or NO₂ groups are grafted to the double bonds
329 of carbon atoms. Based on this statement, biodiesel containing more double bonds, once
330 nitrated, tend to be more energetic than others. That could explain the big different between
331 these 2 results.

332 However, the difference between our additive and the EHN is not so high. Indeed a 2.5% and
333 a 5% addition of EHN on BN20 (diesel with 20% of methyl ester) leads respectively to an
334 increase in cetane number of 2.5 and 6.5 points [29].

335 6 Conclusion

336 The results of chemical analysis of the nitrated products showed the presence of 3 different
337 compounds (methyl-8-nitro oleate, methyl-10-nitrate stearate and methyl-10-nitrate-9-
338 nitrostearate), whose selectivity varies according to the synthesis temperature. Some of these
339 compounds, particularly the methyl-8-nitro oleate and the methyl-10-nitrate-9-nitrostearate,
340 were also identified by Canoira *et al.* [13] and Malins *et al.* [30].

341 The heat released by the chemical transformation obtained with the reaction calorimeter RC1-
342 *RTCal* varies with the synthesis temperature. This difference in the thermal behavior is due to
343 the complexity of the reaction mechanism as well as the instability of the nitrated products
344 and sulfo-nitric acid mixture. The study of the thermal stability shows that the T_{onset} of the
345 decomposition is around 40°C. Thus, at high synthesis temperature (beyond the T_{onset}), the
346 heat measured by the RC1 corresponds to the sum of the heat released by the nitration
347 reaction and that of the mixture decomposition. This thermal and chemical behavior shows
348 the complexity of the aliphatic compound nitration compared to the aromatic compounds one.

349 The modification of thermal behavior according to the synthesis temperature increases the
350 risk of thermal runaway. The Maximum Temperature of the Synthesis Reaction (*MTSR*)
351 obtained is higher than the sulfo-nitric acid temperature of decomposition, which leads to
352 important risks of thermal runaway. To avoid thermal runaway while having a high conversion
353 rate, the synthesis temperature, the flow rate of sulfo-nitric acid as well as the temperature
354 control of the cooling fluid are the main parameters on which we can lean on.

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