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Thermal degradation of α -pinene and β -pinene: An experimental study

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17 **Abstract**

18 Thermal degradation plays a very important role in the understanding of pyrolysis and
19 oxidation. Parameters of ignition, flammability and flame propagation depend on it. In this
20 context, the aim of this study is to study experimentally thermal degradation of two terpene-
21 derived biofuels: α -pinene and β -pinene. Thermogravimetric analyses are performed for four
22 heating rates (3, 5, 10, 20 K/min) under two atmospheres: air and nitrogen. Kinetic parameters
23 are extracted using three different methods. Activation energies for these two biodiesels are
24 given for the first time. In addition, GC-MS analyses are performed to study gaseous
25 emissions of these two compounds. Results show that α -pinene is slightly more reactive than
26 β -pinene. Comparisons with literature show that activation energies of these two biofuels are
27 close to diesel and sunflower biofuel ones. Obtained results will be useful for numerical
28 simulations of biodiesel combustion, as an alternative to fossil fuels.

29 **Keywords:** α -pinene; β -pinene; TGA; GC-MS; activation energy.

30

31 **1 Introduction**

32 In an international context of reduction of pollutants emissions and use of fossil fuels,
33 biofuels are of major interest because the need of transportation is still increasing [1].
34 Terpenes-derived fuels are seen as a promising alternative to fossil fuels to reduce global
35 greenhouse gases emissions [2, 3]. They can be used either as ground transportation fuels or
36 as jet fuels. Among the alternative fuels for internal combustion engines, they belong to the
37 biodiesel family [4]. Moreover, they can also be used as additives or as jet fuel [5]. Recently,
38 studies were performed to study combustion kinetics of several terpenoid jet fuel compounds.
39 In their article, Oßwald et al. [6] investigated experimentally the combustion kinetics of
40 farnesane, p-menthane and p-cymene with an atmospheric high temperature flow reactor
41 coupled with molecular beam mass spectrometric detection.

42 Other terpenoid compounds, namely α - and β -pinene, are of interest for additives or
43 surrogates of transportation fuels. These two monoterpenes are isomers of jet fuel JP-10
44 ($C_{10}H_{16}$) and present a high-energy density and a low freezing point [5]. Moreover, high-
45 energy renewable fuels can be synthesized via α -pinene [6].

46 The use of α - or β -pinene as biodiesel is of interest because these two compounds are
47 naturally present in many vegetal species, and naturally emitted (biogenic Volatile Organic
48 Compounds) by many species, especially in summer [7] because their emissions increase with
49 temperature. They can also be obtained by oil extracted from pine wood [5], via sugar by
50 *Escherichia coli* bacteria [8] or via roots of *Paeonia lactiflora* species [9]. Another interest for
51 pinene dimer is that there already **exists** experimental data on the combustion characteristics
52 of α -pinene/air mixtures [10].

53 **The thermal degradation and the combustion of biodiesel have been studied in several**
54 **works [11-19].** Most of them consist in numerical study on combustion kinetics or
55 experimental study on combustion characteristics. **Based on the qualitative and**
56 **quantitative assessment of reaction products, a reaction scheme for the pyrolysis of β -**
57 **pinene was suggested by Zheng et al. [14].** With some generalizations of the reaction
58 **scheme, a kinetic model of the competitive parallel and consecutive first-order reactions**
59 **shown good agreement with the experimental data.** Zhang et al. investigated the α -
60 **pinene ozonolysis under different environmental conditions in a smog chamber [15].**
61 **Second-order rate constant has been determined for several relative humidity values.**
62 **They have shown that increasing relative humidity from 20 % to 80 % leads to a rate**
63 **constant 1.6 times higher.** They have also demonstrated that the presence of diesel soot
64 **increases this rate constant.** The fly ash prohibits the reactions, whereas H₂SO₄-treated
65 **fly ash promotes the reactions.** Recently, in 2019, Bhanu Teja [16] investigated the
66 **emissions of biodiesels and mentioned that the preparation of biodiesels with additional**
67 **compounds can reduce CO and HC emissions.**

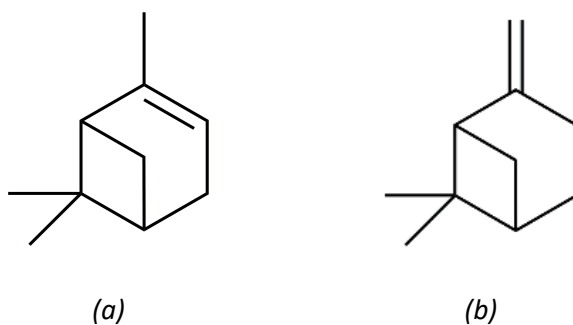
68 Nevertheless, there is no data in the literature on the thermal degradation of such compounds.
69 This work aims at giving experimental data on thermogravimetric analyses of α - and β -pinene
70 and on the gaseous mixtures emitted during the thermal degradation of these two compounds.
71 Different experiments were performed using adapted experimental setups for different
72 temperatures, heating rates and atmospheres (nitrogen and air). **The originality of this**
73 **experimental study is to obtain kinetic parameters of two terpenes: α -pinene and β -**
74 **pinene.** Such data do not exist yet in the literature and will be useful to evaluate the
75 **potential of these organic biofuels to replace conventional diesel fuels.**

76 Section 2 is dedicated to the presentation of the two experimental setups, of the two studied
77 terpenes and of the kinetic methods used. Results will be presented and discussed in section 3.

78 2 Materials and methods

79 2.1 Materials

80 The two studied fuels α - and β -pinene are liquid at ambient conditions and were bought pure
81 (98 %) from Sigma Aldrich. The chemical formula of these two isomers is $C_{10}H_{16}$ and their
82 skeletal formulas are presented in Figure 1.



83 **Figure 1.** Skeletal formulas of the two studied terpenes: α -pinene (a) and β -pinene (b).

84 Thermal degradations of these two terpenes is investigated using thermo-gravimetric analyses
85 and a gas-chromatograph coupled to a mass spectrometer (GC-MS) device. Experiments were
86 performed using the setups described in the next section.

87 2.2 Thermogravimetric analysis

88 Thermal analyses were performed using a thermogravimetric analyser (Mettler Toledo,
89 TGA/SDTA 851e). A picture of the used apparatus is presented in Figure 2. **The total flow**
90 **rate was 150 mL.min⁻¹, the reactive flow was 100 mL.min⁻¹ and the purge flow was 50**
91 **mL.min⁻¹.** The tests were carried out under nitrogen and air atmospheres with a flow rate of
92 100 mL.min⁻¹ (purge flow of 50 mL.min⁻¹) for the two compounds. Four heating rates were
93 studied for both compounds and atmospheres: 3, 5, 10 and 20 K.min⁻¹. Average initial mass of

94 sample placed in the crucible was 50 mg. Experiments were performed between 303 and 1273
95 K. **The uncertainty of these TGA experiments depends on several factors (apparatus,**
96 **vibrations, atmosphere pressure and temperature, ...). The uncertainty of the data has**
97 **been calculated based on the reproducibility of the results, it has been found during this**
98 **work to be 1.17 %.**



99

100 **Figure 2.** Picture of the used TGA device.

101

102 **2.3 Kinetic Analysis**

103 Following the mass loss as a function of temperature, it is possible to obtain different kinetic
104 parameters. Three methods were used in this article: **Kissinger-Akahira-Sunose (KAS)** [20],
105 **Flynn-Wall-Ozawa (FWO)** [21] and **Friedman** methods [22]. They are briefly described in
106 this section.

107 The general expression for the decomposition of a liquid sample is

$$108 \quad \frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (1)$$

109 where α is the conversion rate, representing the amount of sample thermally degraded at time
110 t , and $k(T)$ is the rate constant at temperature T .

111 Conversion rate α is calculated as follows:

112
$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

113 where m_0 , m_f and m_t are respectively initial mass, final mass and mass at time t given by TGA
114 device.

115 Constant rate generally obeys the Arrhenius equation:

116
$$k(T) = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad (3)$$

117 with A the pre-exponential factor (min^{-1}), E_a the activation energy ($\text{kJ} \cdot \text{mol}^{-1}$), R the universal
118 gas constant ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) and T the temperature (K).

119 Combining equations (1) and (3), we obtain the general equation to calculate kinetic
120 parameters:

121
$$\frac{d\alpha}{dt} = f(\alpha) \cdot A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad (4)$$

122 with $f(\alpha)$ the conversion function.

123 Kinetic parameters E_a and A are then obtained with the following equations for the three
124 studied methods.

125 **Kissinger-Akahira-Sunose (KAS)** method is based on the following equation [20]:

126
$$\ln \frac{\beta}{T^2} = \ln \left(\frac{A \cdot R}{E_a} \right) - \frac{E_a}{R \cdot T} \quad (5)$$

127 with β being the heating rate.

128 **Flynn-Wall-Ozawa (FWO)** method is based on the following equation [21]:

129
$$\ln \beta = \ln \left(\frac{A \cdot E_a}{R} \right) - 5.331 - 1.052 \frac{E_a}{R \cdot T} \quad (6)$$

130 Finally, **Friedman** method is based on the following relation [22]:

131
$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A \cdot f(\alpha)) - \frac{E_a}{R \cdot T} \quad (7)$$

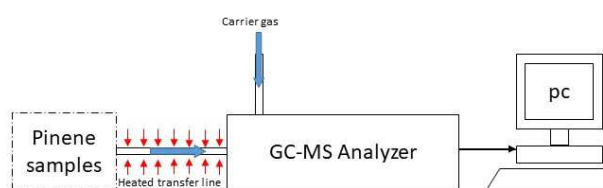
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133 2.4 Study of the emitted compounds

134 A second type of experiments was performed to study the emitted gaseous mixtures when α -
135 pinene and β -pinene are heated. Samples were heated from 309 to 573 K at 40 K/min, hold 10
136 min at 573 K and then injected in a gas chromatograph coupled to a mass spectrometer (GC-
137 MS) to identify the different chemical compounds emitted. Used GC-MS was an Agilent
138 Technologies device equipped with a 7890A GC system and a 5975C triple axis detector MS
139 system. Detector and injector temperatures were set at 773 K. Used column was from Agilent
140 Technologies, type HP-5MS, 30 m*250 μ m*0.25 μ m. Helium at 3 mL/min was used as
141 carrier gas. Column was heated from 303 to 323 K at 3 K/min and hold 10 minutes and 323
142 K, then heated from 323 to 773 K at 20 K/min and hold 1 minute at 773 K. Identification of
143 the compounds is made using the NIST library. A picture of the GC-MS apparatus and a
144 scheme describing the experiments are presented in Figure 3.



(a)



(b)

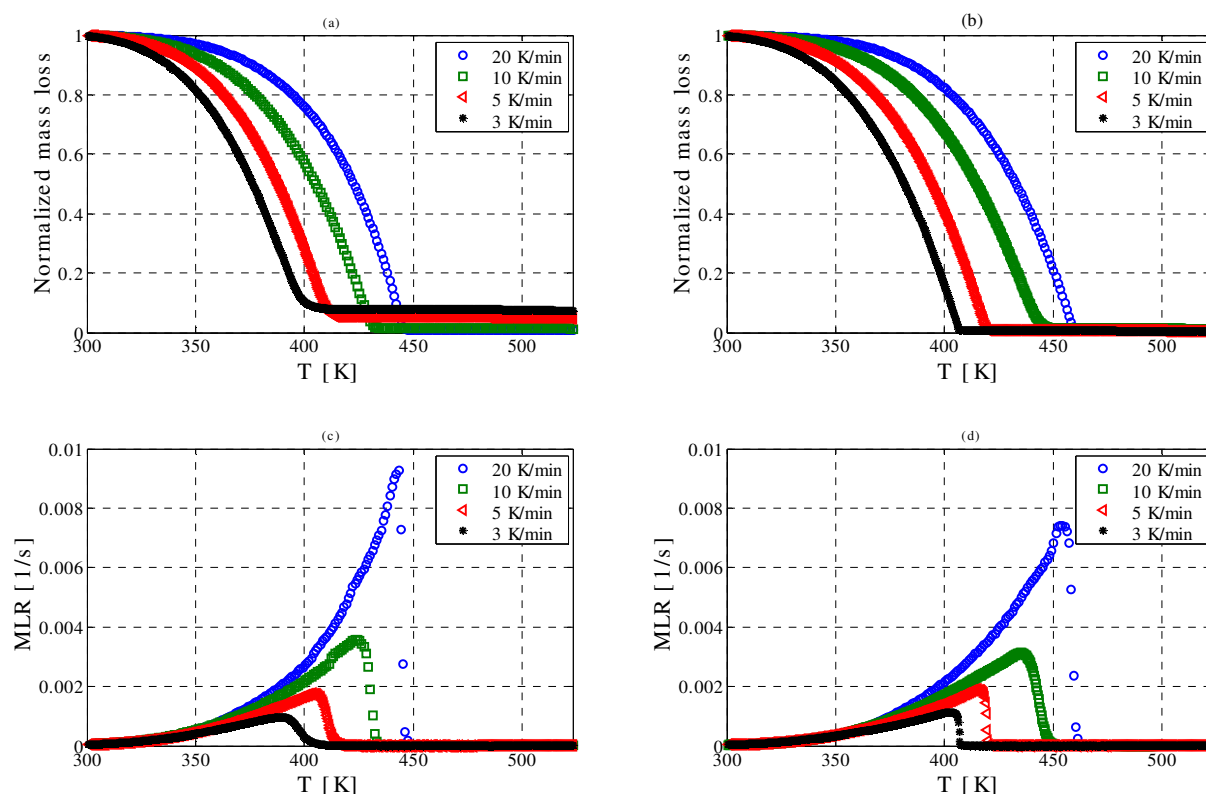
145 **Figure 3.** Picture of the GC-MS device (a) and scheme of the experimental setup (b).

146 **3 Results and discussions**

147 As stated in the previous section, thermo-gravimetric analyses were performed under air and
148 nitrogen atmospheres. Results are presented for these two atmospheres and the different
149 studied heating rates. GC/MS results are then presented.

150 **3.1 TGA results under air (oxidizing atmosphere)**

151 Thermogravimetric analyses results are presented for the two compounds in Figure 4. This
152 Figure presents the normalized mass loss (a) and mass loss rate (derivation of mass loss as a
153 function of time) (c) of α -pinene, and respectively the same results for β -pinene (b), (d). It is
154 clear reading this Figure that thermal decomposition behaviour is similar for the two pinene
155 dimers under air atmosphere. Mass loss is starting at 323 K for the 4 studied heating rates.



156
157 **Figure 4.** TGA results as functions of temperature under air: normalized mass loss of α -
158 pinene (a) and β -pinene (b), mass loss rate of α -pinene (c) and β -pinene (d).

159 One can note that the main difference between the two compounds under air is that α -pinene
160 is not totally decomposed for the two lowest heating rates: 3 and 5 K/min. On the contrary,
161 there is no residue with β -pinene for all heating rates. Maximal degradation temperatures are
162 increasing when heating rate is increasing for α -pinene, it goes from 402 K at 3 K/min to 443
163 K at 20 K/min and for β -pinene from 407 to 461 K respectively. Temperatures of maximum
164 heating rates are found to be of 389, 404, 424, 443 K for α -pinene and of 403, 415, 435, 453
165 K for β -pinene for heating rates of respectively 3, 5, 10 and 20 K/min.

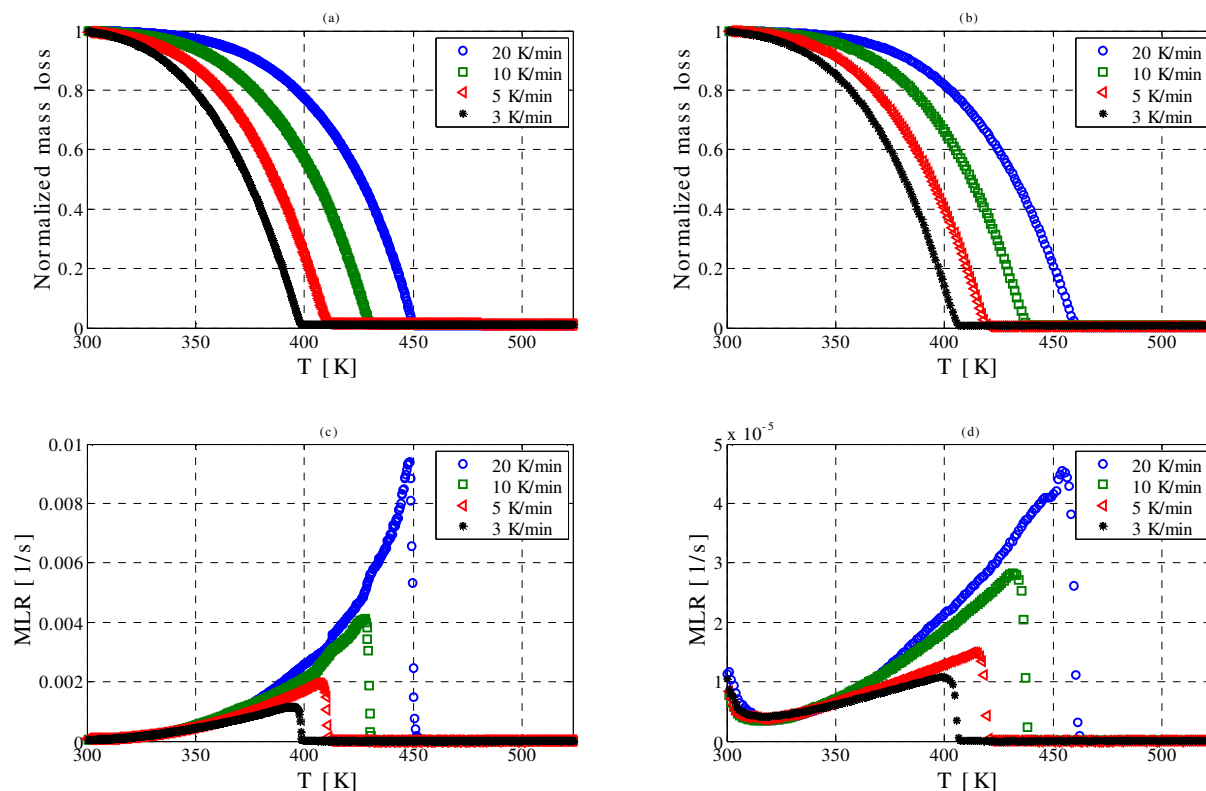
166 **α -Pinene is not completely degraded for low heating rates (residual mass ~7%). This**
167 **incomplete degradation can be explained by the molecular structure of α -pinene,**
168 **characterized by an internal double bond. With this structure, the molecule can react**
169 **with oxygen with low-velocity reactions to form complex structures that resist to low**
170 **heating rate. The residual mass is lower (~1%) for β -pinene because the external double**
171 **bond gives more stability to the molecule.**

172

173 3.2 TGA results under nitrogen (inert atmosphere)

174 Figure 5 presents the results of TG analyses (normalized mass loss and mass loss rate) for α -
175 and β -pinene for 4 heating rates under nitrogen atmosphere. We can see in this Figure that
176 both fuels have the same overall degradation behaviour, similarly, to results under air
177 atmosphere. However, residues at the end of degradation process are much lower than under
178 air for α -pinene (cf. section 3.3). This can be explained by the absence of the oxidizing
179 molecules O_2 , which form stable components with the degraded structure of α -pinene.

180



181
 182 **Figure 5.** TGA results as functions of temperature under nitrogen: normalized mass loss of α -
 183 **pinene (a) and β -pinene (b), mass loss rate of α -pinene (c) and β -pinene (d).**

184 We can see in Figure 5 that maximal degradation temperatures are shifted to higher values
 185 when heating rate is increasing. These maximal temperatures are found to be of 399, 411,
 186 430, 451 K for α -pinene and of 406, 420, 439, 462 for β -pinene at respectively 3, 5, 10 and 20
 187 K/min. For α -pinene, temperatures of maximum MLR are shifted from 393 to 448 K between
 188 3 and 20 K/min and respectively from 399 to 454 K for β -pinene. These lower values for α -
 189 pinene show that this compound is more sensitive to evaporation and degradation and that β -
 190 pinene exhibits better stability and more resistance to degradation than α -pinene.

191

192 3.3 Comparison between the two atmospheres

193 To compare the behaviour of the two studied fuels between air and nitrogen atmospheres,
194 Table 1 presents the percentage of residues in the crucible at the end of TG experiments for
195 both atmospheres and fuels. The decomposition of α -pinene under air atmosphere presents
196 more residue than under nitrogen, as already explained. It is also noticeable in this Table that
197 **the fraction of residual mass decreases when heating rate increases in the case of α -**
198 **pinene in air atmosphere. In the other cases, the residual mass is too low (~1%) to be**
199 **compared.**

200

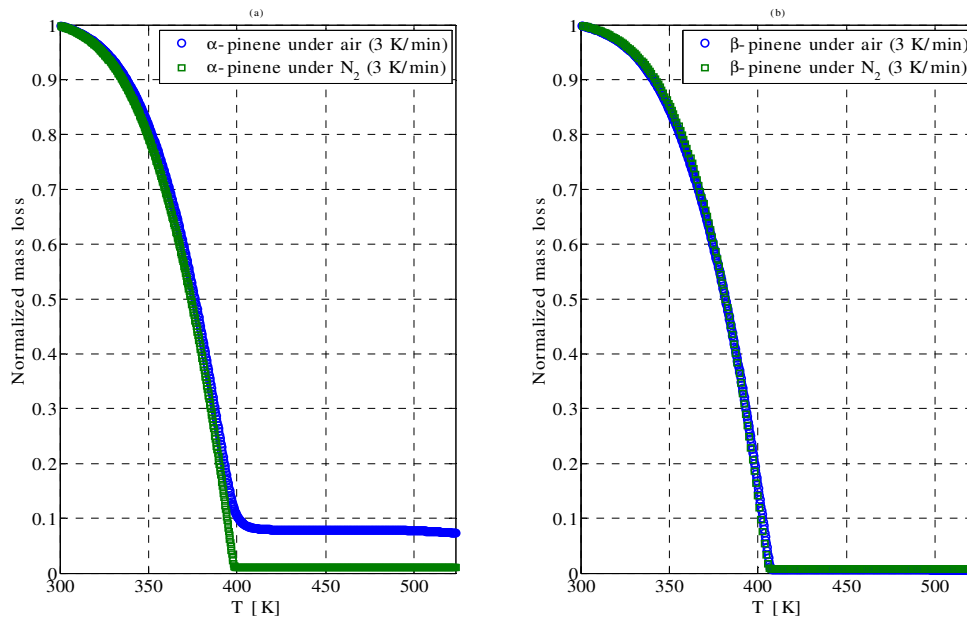
201 **Table 1.** Percentages of residual mass after TG experiments for two fuels under air and N₂
202 atmospheres.

| Heating rate [K/min] | % residual mass (%) | | | |
|-------------------------|----------------------|-----------------|---------------------------------|-----------------|
| | Under air atmosphere | | Under N ₂ atmosphere | |
| | α -pinene | β -pinene | α -pinene | β -pinene |
| 3 | 7.86 | 0.6 | 1 | 0.7 |
| 5 | 5.22 | 0.7 | 1.3 | 0.5 |
| 10 | 1.51 | 1.3 | 1.2 | 0.6 |
| 20 | 0.8 | 0.8 | 0.7 | 0.2 |

203

204 Figure 6 compares degradation behaviour of α - and β -pinene under air and nitrogen
205 atmospheres at 3 K/min. We can notice that the change of atmosphere has few **impacts** on the
206 maximal degradation temperature. For β -pinene, almost no difference between the two

207 atmospheres is noticed. For α -pinene, the main differences are the presence of residues under
208 air atmosphere.



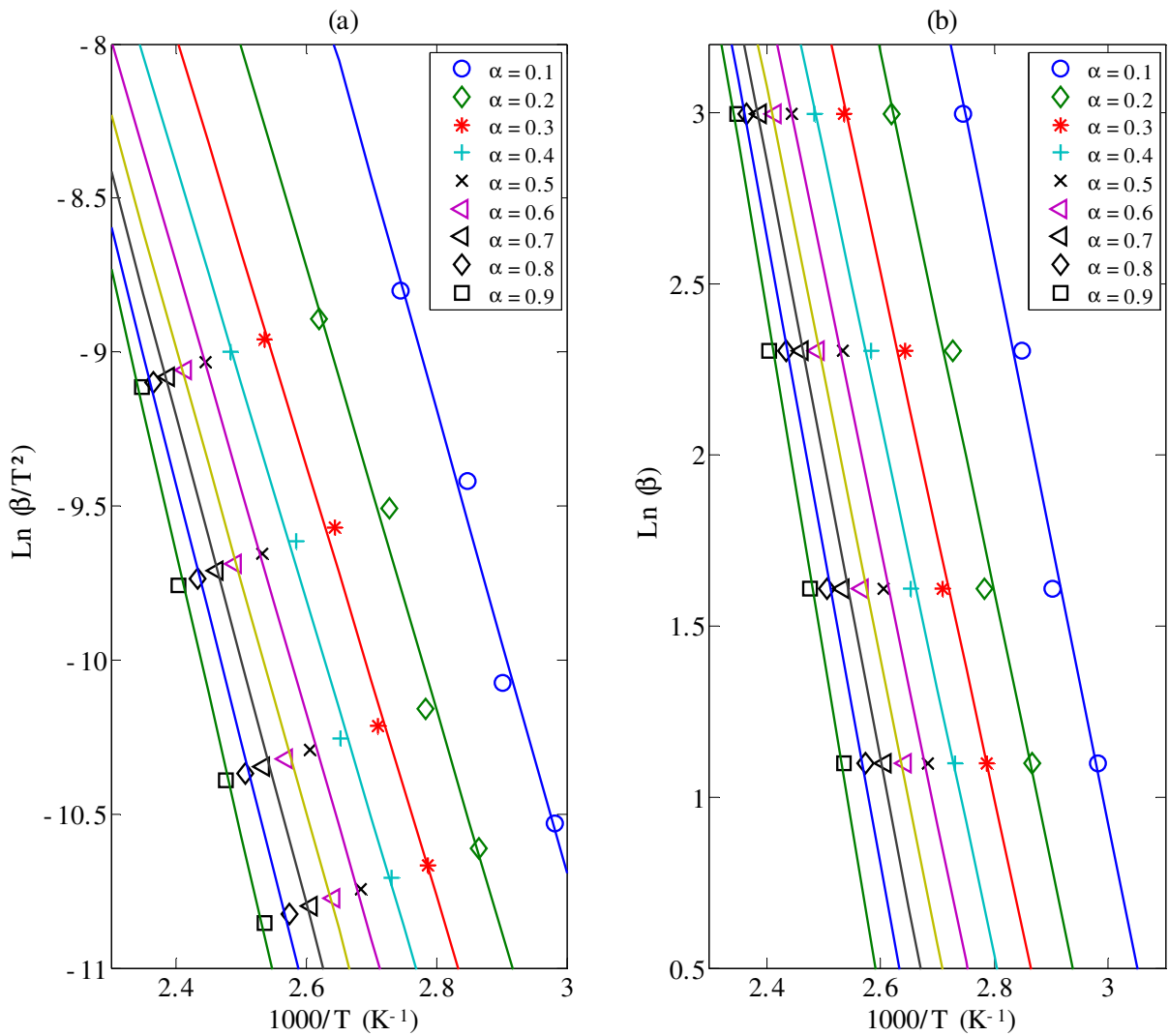
209

210 **Figure 6.** Mass loss at 3 K/min as a function of temperature under air and nitrogen
211 atmospheres: (a) α -pinene and (b) β -pinene.

212

213 3.4 Kinetic parameters

214 According to equations (7) and (8), kinetic parameters are determined by plotting $\ln(\beta/T^2)$ vs
215 $(1000/T)$ and $\ln(\beta)$ vs $(1000/T)$ for respectively **KAS** and **FWO** methods. Figure 7 presents
216 these plots for α -pinene under air atmosphere along with the linear interpolations. Kinetic
217 parameters result for both fuels and atmospheres are presented in Table 2.



218

219 **Figure 7.** KAS (a) and FWO (b) plots for α -pinene TGA experiments under air atmosphere.

220 One can see in Figure 7 that linear interpolations are good. All the correlation coefficients are
 221 higher than 0.9. It can be noticed in Table 2 that activation energies given by **FWO** methods
 222 are higher than **KAS** ones for all fuels and conditions. **Friedman** method gives activation
 223 energies values between **KAS** and **FWO** methods. The order of magnitude is the same for the
 224 three methods for activation energies, but pre-exponential factors values highly depend on the
 225 method. Effect of the atmosphere is clear for α -pinene: activation energies values are on
 226 average 20 % lower under nitrogen than under air. It is less clear for β -pinene where values
 227 are close. This result was expected (cf. Figure 6) and is due to the presence of residues for α -
 228 pinene. Even if results are on the same order of magnitude for the two fuels, it is clear that β -

229 pinene presents lower activation energies: values are on average 15 % lower for β -pinene
 230 under air atmosphere and 5 % lower under nitrogen atmosphere.

231

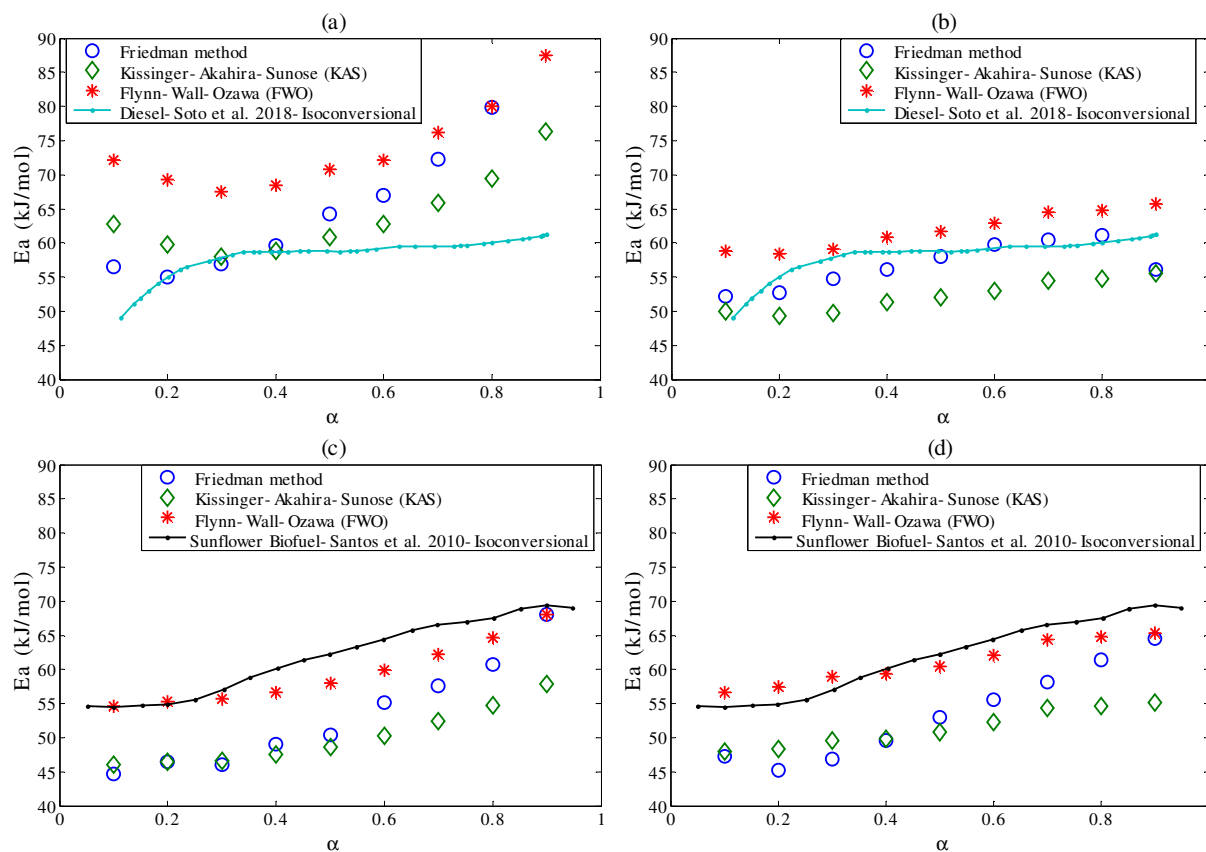
232 **Table 2.** Kinetic parameters for α - and β -pinene for three different methods and two
 233 atmospheres.

| Kinetic parameters | α -pinene | | | | β -pinene | | | |
|--------------------|------------------|-----------------------|----------------------|-----------------------|-----------------|-----------------------|----------------------|------------------------|
| | Under air | | Under N ₂ | | Under air | | Under N ₂ | |
| | Ea (kJ/mol) | A(min ⁻¹) | Ea (kJ/mol) | A(min ⁻¹) | Ea (kJ/mol) | A(min ⁻¹) | Ea (kJ/mol) | A (min ⁻¹) |
| KAS | 60.84 | 5.12 10 ⁴ | 48.64 | 8.46 10 ² | 52.00 | 1.80 10 ³ | 50.85 | 1.24 10 ³ |
| FWO | 70.83 | 1.91 10 ¹¹ | 58.06 | 4.90 10 ⁹ | 61.69 | 9.45 10 ⁹ | 60.51 | 6.85 10 ⁹ |
| Friedman | 64.30 | - | 50.45 | - | 57.98 | - | 53.00 | - |

234

235 Activation energies as functions of conversion rate are given in Figure 8 for the three methods
 236 for α - and β -pinene under both atmospheres. For sake of comparison, values of diesel by Soto
 237 et al. [23] under air and sunflower biofuel by Santos et al. [24] under nitrogen are also
 238 presented in this Figure. As already noticed, we can see that **FWO** method gives the highest
 239 values for activation energies and **KAS** method the lowest ones. **Friedman method** values
 240 are between these two methods, but the three methods give values with the same order of
 241 magnitude. The comparison with the diesel values of Soto et al. [23] under air show that α -
 242 pinene values are slightly higher but follow the same trend for **Friedman** method. It is
 243 noticeable that β -pinene values for isoconversional method are very close to diesel values
 244 obtained with the same method. Diesel values are higher for a conversion lower than 0.5 and
 245 lower for a conversion rate larger than 0.5, but relative gap between the two fuels does not
 246 exceed some percents.

247 Under nitrogen, we compared our values with the ones obtained for sunflower biofuels with
 248 isoconversional method by Santos et al. [24]. It is interesting to notice that sunflower biofuel
 249 and α -pinene have almost similar activation energies values for conversion rates of 0.1, 0.2,
 250 0.3 and 0.9. For β -pinene **FWO** values, values are also very close and even equal for a
 251 conversion rate of 0.4.



252
 253 **Figure 8.** Activation energy as a function of conversion rate for α -pinene under air (a) and
 254 nitrogen (c) and for β -pinene under air (b) and nitrogen (d). Dots: present measurements.

255 Straight lines: comparison with literature other fuels.

256
 257 **3.5 Gaseous emissions: GC-MS results**

258 Composition of gaseous mixture emitted by heated α - and β -pinene is presented in Table 3.
 259 We can see in this Table that, in addition to undegraded α -pinene (just evaporated), main

260 compounds emitted by α -pinene are camphene and carene. These two compounds are isomers
 261 of α -pinene (chemical formula $C_{10}H_{16}$). This obtention of heavy compounds means that
 262 heating temperature was not high enough to obtain to obtain higher pyrolysis gases. We
 263 obtain similar results for β -pinene: main emitted compounds are α -pinene and carene. At this
 264 heating temperature, β -pinene does not degrade but is rearranged in α -pinene. We can notice
 265 that for the two studied fuels, carene is a major emitted compound. As previously noted, we
 266 can say that α -pinene is slightly more reactive β -pinene, since a large part of this last
 267 compound is converted into α -pinene when heated.

268

269 **Table 3.** Major compounds emitted by heated α - and β -pinene under air atmosphere.

| α -Pinene | mass % | β -Pinene | mass % |
|------------------|--------|------------------|--------|
| α -Pinene | 87 | β -Pinene | 85.2 |
| Camphene | 6.78 | α -Pinene | 8.05 |
| (+)-4-Carene | 2.45 | 3-Carene | 5.54 |
| Cyclohexene | 1.92 | Benzene | 0.36 |
| Dimethyl ether | 0.42 | Dimethyl ether | 0.25 |
| | | 1,4-Pentadiene | 0.14 |
| | | Toluene | 0.12 |

270

271 4 Conclusion

272 **The analysis of the thermal degradation of two biofuels was performed in this work.**

273 **Kinetic parameters were extracted for the first time for α - and β -pinene from**

274 **experimental data using different methods, essentially derived from previous works of**

275 **Ozawa and Kissinger on the interpretation of thermogravimetric curves related to**
276 **various heating rates.**

277 **The mass loss curves inform about the behavior of the two biofuels studied in each**
278 **considered atmosphere (air and nitrogen). The experiments in the case of α -pinene**
279 **under air shows the formation of some residues, the amount of the residues increases**
280 **according to the fact that the heating rate is reduced, which clearly shows the presence**
281 **of reactions between α -pinene and air atmosphere forming components resistant to**
282 **temperature.**

283 **GC-MS analysis during α -pinene mass loss shows the emission of camphene and carene.**
284 **In the case of β -pinene, the results show isomerization reactions to give α -pinene and**
285 **carene. This result indicates a different behavior of the two compounds under air**
286 **atmosphere. In the second part, concerning nitrogen atmosphere, the residual mass is**
287 **almost the same for both fuels.**

288 **Thanks to the present study, a database on the chemical kinetics parameters of the two**
289 **pinene isomers is available. This database is based on kinetic analysis theory and**
290 **experiments. The activation energies of the two isomers are determined and compared**
291 **to the activation energy values of the diesel standard fuel and sunflower biofuel. These**
292 **activation energy values are very closed, especially for the calculation results from**
293 **Friedman method in the case of air atmosphere.**

294 **This comparison strongly encourages both terpenes to be considered as an alternative to**
295 **petroleum-based fuels. These results underline an opportunity to use them as future**
296 **biofuels in engines, with operating conditions similar to the ones of diesel engines. The**
297 **kinetic analysis carried out in this paper contributes to the science of organic biofuels.**

298 **Present results can be considered as important data in chemical kinetics to characterize**
299 **pyrolysis and combustion reactions.**

300

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