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1     **Oat straw pyrolysis with ammonium chloride doping: Analysis of evolved gases,**  
2                     **kinetic triplet, and thermodynamic parameters**

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7     **Abstract**

8             The purpose of this work was to determine the effect of the addition of  $\text{NH}_4\text{Cl}$  to  
9     oat straw on the evolved gases, kinetic triplet, and thermodynamic parameters of the  
10     pyrolysis process at 873 K. A complementary approach allowed to assess the effects of  
11     the pyrolysis of chlorine- and nitrogen-enriched biomass. The thermal analysis of  
12     biomass was performed for four heating rates (5, 10, 20, and 30 K/min). The doping of  
13      $\text{NH}_4\text{Cl}$  in the straw favoured i) carbonisation of the chars, ii) formation of C–N bonds,  
14     iii) reduction of evolved  $\text{CH}_4$  and  $\text{CO}_2$ , and iv) an increase in the mean values of the  
15     effective activation energy and all thermodynamic parameters. A group of reactions that  
16     best fit the experimental data of the pyrolysis process was selected. It was necessary to  
17     use unspecified mechanisms to describe the reaction model, particularly for samples  
18     enriched with  $\text{NH}_4\text{Cl}$ .

19     **Keywords:** Biomass; thermogravimetric analysis; activation energy; reaction model

## 20 1. Introduction

21 The production structure of the agricultural industry in Poland is based on  
22 cereals, which account for almost 70% of all crops. Cautious estimates indicate that the  
23 oversupply of cereal straw amounts to approximately 12.5 million tonnes per year  
24 (Gradziuk et al., 2020). To avoid straw storage and waste, it is recommended to use  
25 straw for energy purposes or to produce valuable materials. However, of the key  
26 problems with the use of different types of straw for thermal processes is the presence  
27 of chlorine, which comes from crop fertilisation. Compound fertilisers, including  
28  $\text{NH}_4\text{Cl}$ , are commonly used in fields for wheat cultivation (Ishikawa et al., 2015).  
29 Applying ammonium chloride fertilisers is beneficial because it improves tolerance to  
30 wheat drought (Kastury et al., 2018).

31 The pyrolysis process is a promising thermal technology that can convert  
32 agricultural biomass into biochar, oil, and gas products. Pyrolysis of biomass fertilized  
33 with ammonium chloride enables the production of nitrogen-rich chars. Such chars can  
34 be successfully applied in  $\text{CO}_2$  capture, catalytic processes and as an adsorbent for  
35 removing harmful aqueous pollutants, including heavy metals and organic chemicals  
36 (Kasera et al., 2022; Leng et al., 2020). Furthermore, the pyrolysis of agricultural  
37 biomass is part of the effort to decarbonise Poland, with the aim of achieving zero net  
38 carbon dioxide emissions by 2050. Extensive research on the pyrolysis process of  
39 chlorine-containing feedstocks has been conducted on wheat straw (Du et al., 2014),  
40 coconut and cashew nut shells (Tsamba et al., 2006), corn stover residues (Johansen et  
41 al., 2011), wood doped with KCl (Wang et al., 2017), NaCl-loaded cellulose (Rahim et  
42 al., 2015), cellulose nanofibril doped with  $\text{NH}_4\text{Cl}$  (Pajarito et al., 2019), and biomass  
43 co-pyrolysed with polyvinyl chloride (Ephraim et al., 2018). However, when the above

44 studies were analysed, a gap in knowledge regarding the reaction kinetics and  
45 thermodynamic process parameters for chlorine-containing biomass and biomass doped  
46 with inorganic chlorine was noticed. Therefore, for this type of biomass pyrolysis,  
47 complete knowledge should be provided by determining the kinetic triplet, i.e., the  
48 effective activation energy ( $E_\alpha$ ), pre-exponential factor ( $A$ ), and kinetic model  $f(\alpha)$ , as  
49 well as thermodynamic parameters, i.e., enthalpy change ( $\Delta H$ ), Gibbs free energy  
50 change ( $\Delta G$ ), and entropy change ( $\Delta S$ ). Thermogravimetric analysis (TGA) is used  
51 successfully to study biomass thermal characteristics, the kinetic triplet, and  
52 thermodynamic parameters such as function temperature, time, and degree of  
53 conversion ( $\alpha$ ) (Rammohan et al., 2022; Shen et al., 2023; Zhang et al., 2022). The  
54 effective activation energy of the pyrolysis process depends on the type of biomass, the  
55 applied iso-conversion method,  $\alpha$ , the addition of a catalyst, and the doped raw material  
56 (Li et al., 2019; Quan et al., 2016; Rammohan et al., 2022). Although the  $E_\alpha$  values of  
57 the biomass model compounds, i.e., hemicellulose, cellulose, and lignin, are known, it is  
58 difficult to determine the maximum or mean  $E_\alpha$  value for other types of biomass (Wang  
59 W. et al., 2022). Moreover, the maximum value of  $E_\alpha$  may be different for different  
60 values of  $\alpha$ , e.g. 0.65 (Dessi et al., 2021) or 0.9 (Shen et al., 2023). Biomass pyrolysis is  
61 a multi-stage process involving various simultaneous reactions. Therefore, despite  
62 numerous investigations (Li et al., 2019; Quan et al., 2016; Rammohan et al., 2022;  
63 Shen et al., 2023; Zhang et al., 2022), assigning a specific reaction mechanism remains  
64 problematic in the wide range of  $0.1 \geq \alpha \geq 0.9$ .

65         This study fills the research gap related to the kinetic and thermodynamic  
66 analysis of pyrolysis of chlorine-enriched biomass.  $\text{NH}_4\text{Cl}$  was selected as the source of  
67 chlorine added to the biomass. This chloride decomposes at temperatures ranging from

68 290 to 350 °C, depending on the heating rate. This allows to study the impact of NH<sub>4</sub>Cl  
69 addition on oat straw pyrolysis at 600 °C. The chlorine released can react with the gas  
70 phase and char. Nitrogen and hydrogen in NH<sub>4</sub>Cl are elements originally present in the  
71 organic matter of oat straw. The kinetic triplet ( $E_{\alpha}$ ,  $A$ , and  $f(\alpha)$ ), as well as  
72 thermodynamic parameters ( $\Delta H$ ,  $\Delta G$ , and  $\Delta S$ ), were estimated for the pyrolysis process  
73 with  $\alpha$  from 0.1 to 0.9 in steps of 0.05 for oat straw, oat straw with 4% addition of  
74 NH<sub>4</sub>Cl, and oat straw with 6% addition of NH<sub>4</sub>Cl. The results of this study will make a  
75 significant contribution to advancing the current knowledge in the field. In addition, the  
76 use of energy from agricultural waste can facilitate the decarbonisation process and the  
77 shift away from fossil fuels.

## 78 **2. Materials and methods**

### 79 **2.1. Materials characterization and experimental procedure**

80 The basic material for the investigation was oat straw (OS) collected from a farm  
81 located in the Świętokrzyskie Province (Poland). Then, two samples were prepared by  
82 doping the base material (OS) with ammonium chloride (NH<sub>4</sub>Cl) at 4 and 6 mass%. The  
83 pure ammonium chloride (a white crystalline powder) used for the analysis was  
84 manufactured by Chempur (Poland). Ammonium chloride is completely sublimated  
85 when heated to 602 K in an inert atmosphere, which has been previously verified  
86 (Jerzak et al., 2023). Therefore, it is justified to study the pyrolysis process at 873 K.

#### 87 **2.1.1. Proximate and ultimate analyses**

88 The proximate and ultimate analyses of the OS are shown in Table 1. First, the  
89 moisture content of the OS was determined using the oven-drying method according to  
90 ISO 18134-2:2017-03. The OS had a moisture content of 6.03%, which allowed it to be  
91 ground in a ball mill without the need for drying. An intersieve fraction of 100–200  $\mu\text{m}$

92 OS was used for further studies. Other standard methods used for proximate and  
93 ultimate analysis were ISO 18123:2016-01 for volatile matter, ISO 18122:2016-01 for  
94 ash content, and ISO 16948:2015-07 for carbon (C), hydrogen (H), nitrogen (N)  
95 content, and ISO 16994:2016-10 for chlorine (Cl) content. The chlorine content in OS  
96 was determined to be 0.27% (air-dried basis). Straws from various types of cereals can  
97 contain 0.06 to 0.79% Cl (Strömberg and Björkman, 1997). As shown in Table 2, the  
98 prepared feedstocks contained 0.27, 2.70, and 4.40% chlorine.

#### 99 2.1.2. Fibre analysis

100 The acid detergent fibre (ADF) and acid detergent lignin (ADL) contents were  
101 determined, as well as the neutral detergent fibre (NDF) content using the ISO  
102 13906:2009 and ISO 16472:2007 standards, respectively.

#### 103 2.1.3. FTIR spectral analysis

104 A compact and modular Fourier transform infrared (FTIR) spectrometer (Bruker  
105 Alpha II) was used to identify the functional groups of the organic compounds in the  
106 investigated feedstocks and chars. The infrared absorption frequency was in the 400–  
107 4000  $\text{cm}^{-1}$  range.

#### 108 2.1.4. Thermogravimetric-mass spectrometry analyses

109 Thermogravimetric analysis (TGA) was performed using an STA 449 F3 Jupiter  
110 Thermal Analyser (Netzsch, Germany). Approximately 5 mg of well-mixed sample was  
111 heated non-isothermally from room temperature to 873 K at heating rates of 5, 10, 20,  
112 and 30 K/min. Argon was used as a carrier gas with a flow rate of 40 mL/min. Evolved  
113 pyrolysis gases formed by decomposition of sample were detected with the 403  
114 Aëolos® Quadro - quadrupole mass spectrometer manufactured by Netzsch. The  
115 acquisition interval of the mass spectrometry signal (MS) was 1 s.

### 116 2.1.5. Pyrolysis at laboratory scale

117 Pyrolysis was also carried out in a fixed-bed reactor to investigate the impact of  
118 doping ammonium chloride into OS on char composition. FTIR and ultimate char  
119 analyses were performed. The residence time of the sample in the fixed-bed reactor at a  
120 temperature of 873 K was 3 min. Additional details about the experimental pyrolysis  
121 process are described in work (Jerzak et al., 2023).

## 122 2.2. Kinetic triplet analysis

123 On the basis of thermogravimetric analysis, it is possible to predict the  
124 relationship between temperature ( $T$ ),  $\alpha$ , and rate of the pyrolysis process. For this  
125 purpose, the kinetic triplet ( $E_\alpha$ ,  $A$ , and  $f(\alpha)$ ) was determined, which is helpful for the  
126 evaluation, design, and scale-up of the pyrolysis process (Mumbach et al., 2022).

### 127 2.2.1. Activation energy

128 The effective activation energy of a complex thermal decomposition reaction  
129 can be estimated with commonly used model-free methods (EL-Sayed, 2022; Zhang,  
130 2021). The course of a chemical reaction depends on its ability to overcome the  $E_\alpha$ . The  
131 higher the  $E_\alpha$  required, the more challenging the reaction will be to initiate and  
132 maintain.

133 At the beginning, the degree of conversion from TGA analysis is expressed as  
134 follows:

$$135 \alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (1)$$

136 where  $m_0$ ,  $m_t$ , and  $m_f$  denote the initial mass of feedstock, the mass of feedstock at  
137 time  $t$ , and final mass of the sample at the end of the reaction, respectively.

138 According to the International Confederation for Thermal Analysis and Calorimetry  
139 (EL-Sayed, 2022), methods that use multiple heating rate programmes are

140 recommended for estimating reliable kinetic parameters. The mass loss of a solid owing  
 141 to a single-step reaction as a function of the temperature and  $\alpha$  is given by Eq. (2).

$$142 \quad \frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

143 where  $t$  is the reaction time,  $k(T)$  is the reaction rate constant, and  $f(\alpha)$  is the reaction  
 144 model.

145 The temperature dependence of the reaction rate constant  $k(T)$  is represented by the  
 146 Arrhenius equation.

$$147 \quad k(T) = Ae^{-E_a/RT} \quad (3)$$

148 where  $R$  is universal gas constant, J/mol · K.

149 For non-isothermal conditions, a constant heating rate ( $\beta$ ) mode is defined as

$$150 \quad \beta = \frac{dT}{dt} \quad (4)$$

151 After considering Eqs. (3) and (4), Eq. (2) becomes

$$152 \quad \frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = Ae^{-E_a/RT} f(\alpha) \quad (5)$$

153 Integrating both sides of Eq. (5) gives

$$154 \quad g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-E_a/RT} dT \quad (6)$$

155 where  $g(\alpha)$  is integral conversion function (reaction model).

156 Isoconversional methods are widely used to calculate the effective activation  
 157 energies when the  $E_\alpha$  is a function of the temperature at a constant  $\alpha$ . These methods do  
 158 not need a reaction model to estimate  $E_\alpha$ . Three isoconversional methods—Friedman  
 159 (FR), Eq. (7), Flynn–Wall–Ozawa (FWO), Eq. (8), and Kissinger–Akahira–Sunose  
 160 (KAS), Eq. (9) —were used to estimate the effective activation energies during the  
 161 pyrolysis of feedstocks. The subscript  $i$  represents the  $i$ -th  $\beta$ .

$$162 \quad \ln \left( \frac{d\alpha}{dt} \right)_{T_{\alpha,i}} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (7)$$

$$163 \quad \ln \beta_i = \ln \left( \frac{A_\alpha E_\alpha}{Rg(\alpha)} \right) - 5.331 - 1.052 \frac{E_\alpha}{RT_{\alpha,i}} \quad (8)$$

$$164 \quad \ln \left( \frac{\beta_i}{T_{\alpha,i}^2} \right) = \ln \left( \frac{A_\alpha R}{E_\alpha \cdot Rg(\alpha)} \right) - \frac{E_\alpha}{RT_{\alpha,i}} \quad (9)$$

165 The differential Friedman method can be applied for linear and non-linear heating  
 166 program, and it is therefore commonly used. On the other hand, FWO and KAS are  
 167 integral methods in which a constant  $E_\alpha$  is assumed in very narrow intervals of the  $\alpha$ . As  
 168 a result, the change of  $E_\alpha$  with  $\alpha$  induces an integration error in the FWO and KAS  
 169 methods. By using small  $\alpha$  segments the integration error is overcome. Comparison of  
 170  $E_\alpha$  determined with the use of integral methods with the Friedman method allows to  
 171 confirm the validity of the adopted size of the alpha segment. If the thermal analysis of  
 172 pyrolysis is preceded by a sample heating and holding programme at 105 °C (to remove  
 173 moisture), the kinetic parameters can already be determined for  $\alpha = 0.05$  (Guo et al.,  
 174 2022). For samples containing moisture, the kinetic analysis starts with  $\alpha > 0.05$  (Hu et  
 175 al., 2022; Varma et al., 2021). In this study,  $\alpha$  values from 0.1 to 0.9 were analysed in  
 176 steps of 0.05. For constant  $\alpha$  values, plots of  $\ln(d\alpha/T_\alpha^2)$ ,  $\ln(\beta)$ , and  $\ln(\beta/T_\alpha^2)$  versus  
 177  $1000/T_\alpha$  were straight lines whose slopes were  $E_\alpha/RT_\alpha$  for the FR, FWO, and KAS  
 178 methods respectively.

### 179 2.2.2. Pre-exponential factor

180 The pre-exponential factor supported by  $E_\alpha$  enables a better understanding of the  
 181 pyrolysis process. According to the Arrhenius Eq. (3), the reaction proceeds faster if the  
 182 value of  $A_\alpha$  is high and  $E_\alpha$  does not change. The  $A_\alpha$  values for all kinetic methods were  
 183 calculated using Eq. (7).

### 184 2.2.3. Reaction model

185 The master plot method (Eq. 10) provided by the Criado approach (Criado et al.,  
 186 1989) was used to evaluate the ideal kinetic models of the  $f(\alpha)$  and  $g(\alpha)$  patterns  
 187 observed for solid-state reactions.

$$188 \quad Z(\alpha) = \frac{f(\alpha) \cdot g(\alpha)}{f(0.5) \cdot g(0.5)} = \left(\frac{T_\alpha}{T_{0.5}}\right)^2 \cdot \frac{(d\alpha/dt)_\alpha}{(d\alpha/dt)_{0.5}} \quad (10)$$

189 The  $E_\alpha$  and  $A_\alpha$  are not included in this method. Furthermore, the reaction mechanism  
 190 determined by the Criado method is not limited by  $\beta$ . The temperature at a certain value  
 191 of  $\alpha$  is denoted as  $T_\alpha$ , where  $T_{0.5}$  specifies the temperature at  $\alpha = 0.5$ . The change in  $\alpha$  as  
 192 a function of time ( $d\alpha/dt$ ) was taken from the TGA analyses. A complete list of  
 193 kinetic reaction models included in the evaluation is provided (see supplementary  
 194 materials). In addition to commonly used reaction mechanisms, list of kinetic reaction  
 195 models contains reaction orders other than unity (Trache et al., 2017) and kinetic  
 196 equations with an unjustified mechanism (Zhang et al., 1999).

### 197 **2.3. Thermodynamic parameters**

198 Thermodynamic parameters such as enthalpy change ( $\Delta H$ ), change in the Gibbs  
 199 free energy ( $\Delta G$ ), and entropy change ( $\Delta S$ ) were calculated using Eqs. (12)–(14),  
 200 respectively.

$$201 \quad \Delta H = E_\alpha - R \cdot T_\alpha \quad (12)$$

$$202 \quad \Delta G = E_\alpha + R \cdot T_m \cdot \ln\left(\frac{\kappa_B \cdot T_m}{h \cdot A_\alpha}\right) \quad (13)$$

$$203 \quad \Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (14)$$

204 where  $\kappa_B$  is Boltzmann constant, equal to  $1.381 \cdot 10^{-23}$  J/K,  $T_m$  is the temperature  
 205 corresponding to the highest peak from the derivative thermogravimetric curves (DTG)  
 206 curves, and  $h$  is Plank constant, equal to  $6.626 \cdot 10^{-34}$  J · s.

207 The determination of thermodynamic parameters makes a valuable contribution to the  
208 analysis of reaction pathways of pyrolysis processes. The  $\Delta H$  value represents the  
209 energy exchange between the reactant and activated complex during the pyrolysis  
210 process. The direction of heat transfer can be determined from the value of the  $\Delta H$ . If  
211  $\Delta H$  is positive, heat must be supplied to the pyrolysis process. Similarly, the change in  
212 Gibbs free energy represents the increase in total energy of the system with the addition  
213 of reagents and the formation of the activated complex (Maia and de Morais, 2016).

#### 214 **2.4. Statistical analysis**

215 Data collected from proximate, ultimate and fibre experiments were analysed  
216 using descriptive statistics. Values were expressed as mean  $\pm$  standard deviation of the  
217 observations. The fit of the lines to the TGA experimental results, the coefficient of  
218 determination, and the standard deviation were determined in the Grapher ® 20.2.321  
219 software. The statistical analysis of energy activation was performed at significance  
220 level of 0.05 using MS Excel.

### 221 **3. Results and discussion**

#### 222 **3.1. Fourier transform infrared analysis**

223 First, the composition of the feedstocks and chars studied was assessed using  
224 FTIR analysis. The spectrum of  $\text{NH}_4\text{Cl}$  includes seven vibration modes of the  $\text{NH}_4^+$   
225 group and one stretching vibration of N–Cl at  $690\text{ cm}^{-1}$  (Kumar Trivedi, 2015). The  
226 three peaks located close to each other at  $3114\text{ cm}^{-1}$ ,  $3014\text{ cm}^{-1}$ , and  $2803\text{ cm}^{-1}$  indicated  
227 asymmetric stretching, combined bands of  $\nu_2 + \nu_4$ , and the out-of-plane bends,  
228 respectively (Wagner and Hornig, 1950). Among the remaining peaks, two were the  
229 most intense, at  $1750\text{ cm}^{-1}$  and  $1385\text{ cm}^{-1}$ , which were assigned to the  $\nu_2 + \nu_4$   
230 combination and out-of-plane bends, respectively. All samples showed a low intensity

231 peak at  $1996\text{ cm}^{-1}$  corresponding to the  $\nu_2 + \nu_6$  N–H bond combination (Wagner and  
232 Hornig, 1950). As expected, the FTIR spectra for OS, OS+4NH<sub>4</sub>Cl, and OS+6NH<sub>4</sub>Cl  
233 were similar. The low content of NH<sub>4</sub>Cl in the OS+4NH<sub>4</sub>Cl and OS+6NH<sub>4</sub>Cl samples  
234 could be the reason for the absence of distinctive NH<sub>4</sub>Cl bands. In the OS, OS+4NH<sub>4</sub>Cl,  
235 and OS+6NH<sub>4</sub>Cl samples, the spectra coming from vibrations of O–H ( $3330\text{ cm}^{-1}$ ), C–H  
236 ( $2918$  and  $2851\text{ cm}^{-1}$ ), C=O ( $1641\text{ cm}^{-1}$ ), C–H ( $1510\text{ cm}^{-1}$ ), and C–O ( $1249\text{ cm}^{-1}$ ) were  
237 visible (Chemistry Database, 2020), whereas they were not visible after pyrolysis. The  
238 intensity of the C–O peaks ( $1029\text{ cm}^{-1}$ ) was significantly weaker, and the characteristic  
239 absorbance bands of cellulose and hemicellulose i.e., C–O ( $1029\text{ cm}^{-1}$ ) and C–H ( $653$   
240 and  $559\text{ cm}^{-1}$ ) (Chen et al., 2022), were significantly weaker in chars than in feedstocks.  
241 The flattening of the char spectra proves decomposition of the organic matrix,  
242 particularly some oxygen-containing structures through a deoxygenation and  
243 dehydration reaction. Samples doped with NH<sub>4</sub>Cl caused the disappearance of C–H  
244 bonds at  $1371\text{ cm}^{-1}$  in the spectra and the promotion of C–N bonds at  $1157\text{ cm}^{-1}$  in the  
245 surface char. This conclusion is in line with the ultimate analysis of the chars shown in  
246 Table 2, which confirmed the promotion of carbonisation and nitrogen capture upon the  
247 addition of NH<sub>4</sub>Cl to the OS.

### 248 **3.2. Thermogravimetric and mass spectrometry analysis**

249 The calculated results from Eq. (1) and DTG for the three investigated samples  
250 at  $\beta$  values of 5, 10, 20, and 30 K/min are included (see supplementary materials).  
251 Analysing the curves representing the degree of conversion, the pyrolysis process can  
252 be divided into three stages, starting with moisture evaporation and slow decomposition  
253 of the sample ( $0 < \alpha < 0.1$ ), the main pyrolysis process ( $0.1 < \alpha < 0.9$ ), and finally slow  
254 decomposition. The doping of OS with NH<sub>4</sub>Cl did not affect the char yield at 873 K.

255 However, as reported by Wang et al., (2017), the doping of biomass with KCl increased  
256 the yield of char. The effect of  $\beta$  on the temperature at the maximum conversion ( $T_m$ ) of  
257 the samples is observed. The lowest value of 593 K was obtained with the OS sample at  
258 a  $\beta$  of 5 K/min, and an increase in  $\beta$  shifted  $T_m$  towards higher temperatures. In the  
259 remaining investigated samples (OS+4NH<sub>4</sub>Cl and OS+6NH<sub>4</sub>Cl), such a tendency was  
260 observed for the 5, 10 and 20 K/min samples. Despite repeating the analysis three times  
261 for the  $\beta$  of 30 K/min,  $T_m$  was always lower for that heating rate than for the 20 K/min  
262 heating rate. Furthermore, analysis of the DTG curves revealed peaks corresponding to  
263 the decomposition of doped NH<sub>4</sub>Cl into OS. The peaks are most visible at  $\beta = 5$  K/min,  
264 and they are located at 465 K for OS+4NH<sub>4</sub>Cl and 468K for OS+6NH<sub>4</sub>Cl.

265         The thermal treatment of biomass results in the release of pyrolysis gases.  
266 Evolved gas species were identified by scanning positive ions on the basis of their  
267 mass-to-charge ratio ( $m/z$ ). Specific ion fragments were scanned, and their  $m/z$  values  
268 were 2, 15, 16, 17, 18, 28, 30, 36, 44, 46, 50, 70, and 72. However, interference from  
269 the ionic currents of other gas fragments prevented clearly determining  $m/z = 2, 16, 17,$   
270  $28, 36, 70, 72$ . HCl was expected to evolve from the pyrolysis gas of the biomass in the  
271 temperature range of 673–873 K, as reported by Cheng et al. (2021). In this case, signal  
272 interference was strong at  $m/z = 36$ , and thus no evidence of HCl release was observed.  
273 Note that the sample contained a significant amount of potassium, which, according to  
274 the latest reports (Wang B. et al., 2022), favours the retention of HCl in the char.  
275 Doping the biomass with chlorides or PVC usually increases the release of HCl.  
276 However, the methoxy groups bonded to the lignin structure can be cleaved by HCl,  
277 producing CH<sub>3</sub>Cl (Czégény et al., 2015). For this reason, doping OS with NH<sub>4</sub>Cl can  
278 favour the production of CH<sub>3</sub>Cl. Figs. 1(a–s) present the evolved gas species of CH<sub>4</sub>,

279 H<sub>2</sub>O, NO, CH<sub>2</sub>O, CO<sub>2</sub>, NO<sub>2</sub>, and CH<sub>3</sub>Cl for the studied samples. To ensure the  
280 readability of Figs. 1(a–s), the gas ion currents are shown only for three  $\beta$  values. For  
281  $m/z = 18$  (H<sub>2</sub>O and NH<sub>4</sub><sup>+</sup>) and 30 (NO and CH<sub>2</sub>O), two possible types of gases were  
282 assigned. The curves in Figs. 1(d–f) and Figs. 1(g–i) may reflect the release of one or  
283 more of these gases. Interestingly, although the samples doped with NH<sub>4</sub>Cl exhibited  
284 increased inorganic nitrogen content, nitrogen was not released into the pyrolysis gases.  
285 This is evidenced by the results shown in Figs. 1(g–i) and Figs. 1(m–o). NO and NO<sub>2</sub>  
286 are primarily produced by reaction precursors, e.g., HCN and NH<sub>3</sub>, but also through OH  
287 radicals formed as a result of breaking C–OH bonds (Cheng et al., 2021). Generally, a  
288 higher  $\beta$  promoted the release all gaseous species. Consequently, the area under the  
289 peaks also increased with increasing  $\beta$ . The maximum values of the ionic currents for  
290 all gases occurred in the temperature range of 573–673 K. Moreover, an increase in  $\beta$   
291 shifted the maximum peak towards higher temperatures. Analysing the evolved gases  
292 shown in Figs. 1(d–f), it was noticed that the addition of NH<sub>4</sub>Cl resulted in the  
293 formation of a second peak of lower intensity. The first peak dependent on  $\beta$  was  
294 attributed to NH<sub>4</sub><sup>+</sup> ions, probably from NH<sub>4</sub>Cl decomposition, and the second one  
295 reflects water. At  $\beta = 30$  K/min, doping the OS with NH<sub>4</sub>Cl evidently inhibited the  
296 evolution of CH<sub>4</sub>, H<sub>2</sub>O, NO, CH<sub>2</sub>O, CO<sub>2</sub>, and NO<sub>2</sub>. However, for  $\beta$  of 5 and 10 K/min,  
297 this tendency was not observed. Decarbonylation and decarboxylation reactions were  
298 inhibited for OS samples enriched in NH<sub>4</sub>Cl, which was manifested by the less intense  
299 CO<sub>2</sub> peaks observed in Figs. 1(j–l). As can be seen from Figs. 1(p–s), the doping of  
300 NH<sub>4</sub>Cl to OS favoured the release of only CH<sub>3</sub>Cl.

### 301 3.3. Kinetic triplet determination

#### 302 3.3.1. Activation energy

303 The activation energy values were determined by applying the FR, FWO, and  
304 KAS methods at  $\alpha$  values of 0.1–0.9. Calculations were performed assuming that it was  
305 a first-order reaction. The fitting line and the coefficients of determination ( $R^2$ ) are  
306 given for each studied  $\alpha$  value (see supplementary materials). The  $R^2$  values of the  
307 points to the straight line were slightly weaker at the low  $\alpha$  values of the OS+4NH<sub>4</sub>Cl  
308 and OS+6NH<sub>4</sub>Cl samples. Regarding the  $R^2$  values, the FR method had the highest  
309 agreement with the pyrolysis of OS, OS + 4NH<sub>4</sub>Cl, and OS+6NH<sub>4</sub>Cl. The value  $R^2 >$   
310 0.96 indicates the credibility of the results obtained. The comparison of the changes in  
311  $E_\alpha$  and  $A_\alpha$  for the studied samples as a function of  $\alpha$  is shown in Figs. 2(a–f). The error  
312 bars in Figs. 2(a), (c) and (e) are estimates of the 95% confidence levels on the mean  
313 value of  $E_\alpha$ , and range from 0.3 kJ/mol to 152.8 kJ/mol depending on the type of  
314 sample and  $\alpha$ . As the reaction progresses (at  $\alpha = 0.1$ –0.8), the  $E_\alpha$  of the OS sample  
315 changes almost linearly from approximately 148 to 192, from 161 to 184, and from 152  
316 to 174 kJ/mol as determined using the FR, FWO, and KAS methods, respectively. The  
317 OS pyrolysis process at  $\alpha > 0.8$  allows for the removal of a small amount of heavy  
318 volatile fraction. Therefore, at  $\alpha = 0.9$ ,  $E_\alpha$  rapidly increased to 323, 308, and 297 kJ/mol  
319 using the FR, FWO, and KAS methods, respectively. With a high  $\alpha$ , an evident upward  
320 trend in the activation energy estimated for wheat straw pyrolysis was reported (Luo et  
321 al., 2020). The high  $E_\alpha$  values can be explained by the energy requirement for lignin  
322 decomposition, which is much greater than that for the degradation of hemicellulose and  
323 cellulose. Throughout the considered range of  $\alpha$ , the mean  $E_\alpha$  values for the OS sample  
324 were 182 (FR), 181(FWO), and 171 kJ/mol (KAS), values that were slightly higher than  
325 that reported by Szufa et al. (2020), which was 145 kJ/mol (mean value for  $0.1 < \alpha <$   
326 0.8). OS doping with NH<sub>4</sub>Cl (OS+4NH<sub>4</sub>Cl and OS+6NH<sub>4</sub>Cl samples) significantly

327 increased  $E_\alpha$  at  $\alpha$  values of 0.15–0.75. In this range,  $E_\alpha$  changed parabolically and  
328 successively for OS+4NH<sub>4</sub>Cl and OS+6NH<sub>4</sub>Cl, with maximum values of 253 kJ/mol  
329 (FR) and 257 kJ/mol (FWO). A lower energy barrier was revealed in the final stage of  
330 pyrolysis ( $\alpha = 0.9$ ) of the OS+4NH<sub>4</sub>Cl and OS+6NH<sub>4</sub>Cl samples than of the OS sample.  
331 However, considering the entire range of  $\alpha$ , it was demonstrated that the addition of  
332 NH<sub>4</sub>Cl to OS increased the mean  $E_\alpha$ . A positive correlation of the increase in the mass  
333 of NH<sub>4</sub>Cl in the sample from 4% to 6% with the average  $E_\alpha$  was observed only for the  
334 KAS method. For the FR and FWO methods, the mean  $E_\alpha$  decreased from 214 to 211  
335 and from 219 to 218 kJ/mol, respectively.

### 336 3.3.2. Pre-exponential factor

337 The estimation of  $A_\alpha$  was performed for all  $\beta$  values included in this study.  
338 However, the differences in  $A_\alpha$  indicated that  $\beta$  had only a slight influence. Therefore,  
339 Figs. 2(b), (d), and (f) show  $A_\alpha$  values for the heating rate of 10 K/min. The values of  
340  $A_\alpha$  are related to  $E_\alpha$  according to Eq. (7). As a result, a positive correlation was found  
341 between the increase/decrease in the  $E_\alpha$  and the value of  $A_\alpha$ . The doping of NH<sub>4</sub>Cl to  
342 OS increased  $A_\alpha$  but only at values of  $\alpha$  from 0.15 to 0.5. The range of the values of  $A_\alpha$   
343 (in first-order reactions) reported in the literature for biomass pyrolysis ranged from  $10^5$   
344 to  $10^{29}$  1/s (Karuppasamy Vikraman et al., 2021; Sangaré et al., 2022; Stančin et al.,  
345 2021). In most cases, a low value of  $A_\alpha$  ( $<10^9$  1/s) favours surface reactions,  
346 whereas  $A_\alpha \geq 10^9$  1/s indicates a simple complex reaction (a looser junctional complex)  
347 (Karuppasamy Vikraman et al., 2021). The difference between  $A_\alpha$  values at the  
348 beginning and end of pyrolysis in OS+6NH<sub>4</sub>Cl samples was of the same order ( $10^6$ ) for  
349 all method. The  $A_\alpha$  fluctuations were especially noticeable for samples doped with  
350 NH<sub>4</sub>Cl. A high value of  $A_\alpha$  suggests a complex chemical reaction (Hu et al., 2022).

## 351 3.3.3. Reaction models

352 Generally, it is difficult to predict a single reaction model for the entire biomass  
 353 pyrolysis process as it is not a single-step process (Karuppasamy Vikraman et al., 2021;  
 354 Rammohan et al., 2022; Shen et al., 2023; Singh et al., 2021; Zhong et al., 2023). The  
 355 possible mechanism of the pyrolysis reactions for OS, OS+4NH<sub>4</sub>Cl, and OS+6NH<sub>4</sub>Cl  
 356 was predicted for  $\beta$  values of 5, 10, 20, and 30 K/min in the range of  $0.1 < \alpha < 0.9$  using  
 357 Eq. (10). Figures 3(a–c) show the overlap of the theoretical curve with the experimental  
 358 data, which made it possible to determine the reaction mechanism. The theoretical  
 359 curves describe reaction-order models (F), nucleation models, and, more specifically,  
 360 power law (P) and Avrami–Erofeev (A), geometrical models (R), diffusional models  
 361 (D), and other kinetic equations with unjustified mechanisms (G) (see supplementary  
 362 materials). The unjustified mechanism has not yet been used to describe the pyrolysis  
 363 process (Casal and Marbán, 2020; Vlaev et al., 2008). However, as shown in Figs. 3(a–  
 364 c), it was necessary to use mechanism G to overlap some experimental data with  
 365 different  $\alpha$  values. To ensure the readability of Figs. 3(a–c), the lines of the theoretical  
 366 models start at the first fitting to the experimental data. The consistency between the  
 367 fitted curves (th.) and the experimental data (exp.) was evaluated through the residual  
 368 sum of squares (RSS) (Mumbach et al., 2022), and the results are shown (see  
 369 supplementary materials).

$$370 \text{ RSS} = \sum \left[ \left( \frac{d\alpha}{dt} \right)_{exp.} - \left( \frac{d\alpha}{dt} \right)_{th.} \right]^2 \quad (15)$$

371 The reaction models for each  $\beta$  and  $\alpha$  value that best fit the OS, OS+4NH<sub>4</sub>Cl,  
 372 and OS+6NH<sub>4</sub>Cl pyrolysis are shown in Table 3. With  $\alpha = 0.5$ , no fit of the theoretical  
 373 curves was performed because it was the reference point and thus  $Z(\alpha) = 1$ . The  
 374 reaction model of the OS pyrolysis was a combination of unjustified reaction order and

375 diffusion mechanism. At the initial stage of OS pyrolysis, models G3/2 ( $\alpha = 0.1$ ),  
376 F3/4( $\alpha = 0.15$ ), and D6 ( $\alpha = 0.2$ ) best reflected the experimental data for 5, 10, 20, and  
377 30 K/min. The pyrolysis reaction probably had increasing resistance to diffusion, as  
378 evidenced by the D6 model (de Jesus Gariboti et al., 2022). When  $\alpha$  increased to 0.45,  
379 the lowest reaction order (not exceeding 0.5) was observed for the entire OS pyrolysis  
380 process. In this case, F1/5 best matched the 11 experimental results. As  $\alpha$  increased  
381 further from 0.55 to 0.8, the reaction order increased to unity, and the presence of the  
382 D4 and D5 models was noted. The reaction order increased significantly to F4, F3, F3,  
383 and F2 for  $\beta$  values of 5, 10, 20, and 30 K/min, respectively, at  $\alpha = 0.85$ . Further  
384 continuation of the pyrolysis process required much higher reaction orders than F5.  
385 Chemical reaction orders that exceeded F5 at the final stage of biomass decomposition  
386 were confirmed by Rammohan et al. (2022). The reaction order may even be higher  
387 than 7 if lignin is decomposing (Zhong et al., 2023). However, for OS for the entire  
388 range of  $\alpha$  values, the reaction order was reported to be 3.4 (Szufa et al., 2020). This  
389 result is close to the reaction orders obtained in this work but only for  $\alpha$  values above  
390 0.8.  $\text{NH}_4\text{Cl}$  doped into OS samples as shown in Figs. 3(b) and (c) clearly changed the  
391 mechanisms controlling the pyrolysis process. The first difference was the reaction  
392 mechanism at  $\alpha = 0.1$ . The pyrolysis of OS+6 $\text{NH}_4\text{Cl}$  was governed by F2, F3, and F4  
393 (second-, third-, and even fourth-order reactions), whereas for OS it was the G3/2  
394 mechanism. Then, at  $\alpha$  values higher than 0.5, models G1 and G3/2 were identified that  
395 were not present for the OS sample. Fitting the experimental data of the OS+6 $\text{NH}_4\text{Cl}$   
396 sample required the use of more G models than that of the OS+4 $\text{NH}_4\text{Cl}$  sample. Another  
397 effect of the addition of  $\text{NH}_4\text{Cl}$  to the OS sample was the reduction of the reaction order  
398 at the final stage of pyrolysis. Compared to the OS sample (reaction order  $> F5$ ), the

399 reaction orders in the OS+6NH<sub>4</sub>Cl sample were reduced to F3 (for 5 and 10 K/min) and  
400 F2 (for 20 and 30 K/min).

### 401 **3.4. Thermodynamic parameters estimation**

402 Figures 4(a–i) show the enthalpy, Gibbs free energy, and entropy changes  
403 calculated using Eqs. (12)–(14), respectively. In the calculations of thermodynamic  
404 parameters, the  $E_{\alpha}$  and  $A_{\alpha}$  values estimated using the FR, FWO, and KAS methods  
405 were used. The influence of  $\beta$  on the thermodynamic parameters was insignificant, and  
406 thus Figs. 4(a–i) present the results only for 10 K/min. The  $\Delta H$  value reflects the energy  
407 consumed in the reaction. The positive  $\Delta H$  values confirm the endothermic  
408 characteristic of OS, OS+4NH<sub>4</sub>Cl, and OS+6NH<sub>4</sub>Cl pyrolysis, in which the samples  
409 absorbed heat to break bonds. In the case of the OS sample, the absorption heat caused  
410 the decomposition and degradation of the cellulose, hemicellulose, and lignin fibres.  
411 Furthermore, the OS+4NH<sub>4</sub>Cl and OS+6NH<sub>4</sub>Cl samples showed higher  $\Delta H$  values  
412 owing to heat adsorption related to NH<sub>4</sub>Cl decomposition. The conditions of the active  
413 complex formation depend on the difference between  $E_{\alpha}$  and  $\Delta H$ . When the difference  
414 between  $E_{\alpha}$  and  $\Delta H$  is lower, it means that the energy required to initiate the pyrolysis  
415 reaction (activation energy) is close to the amount of energy released during the reaction  
416 (enthalpy change). This indicates that the pyrolysis conditions are more favorable and  
417 efficient for energy production. Doping with NH<sub>4</sub>Cl slightly worsened the pyrolysis  
418 conditions, as indicated by the increase in the maximum difference between  $E_{\alpha}$  and  $\Delta H$   
419 (at  $\alpha = 0.9$ ) from 5.3 for OS to 5.6 for OS+6NH<sub>4</sub>Cl. Similar values of 5–6 kJ/mol for  
420 biomass pyrolysis have been reported in several papers (Hu et al., 2022; Sangaré et al.,  
421 2022; Varma et al., 2021). The  $\Delta G$  value refers to the total increase in energy of the  
422 system for the formation of the activated complex.  $\Delta G$  also provides information about

423 the preferred method for achieving reaction equilibrium. The mean  $\Delta G$  values decreased  
424 slightly after OS doping with  $\text{NH}_4\text{Cl}$  for all three models. A values greater than 0  
425 confirms that the pyrolysis process was non-spontaneous and required an energy supply.  
426 The last thermodynamic state function of the system is entropy, which represents the  
427 degree of disorder of the system. Figures 4(c), (f), and (i) show negative  $\Delta S$  values for  
428 OS with  $\alpha$  values ranging from 0.1 to 0.8 (FR and FWO) and from 0.1 to 0.85 (KAS).  
429 Negative  $\Delta S$  values indicate that the reactions were close to their thermodynamic  
430 equilibrium and that the products had a lower degree of disorder than the reactants. The  
431 lowest  $\Delta S$  values for  $\alpha = 0.1$  (for OS+6 $\text{NH}_4\text{Cl}$ ) suggest that the initial stage of pyrolysis  
432 occurs more easily if sufficient heat is provided. Interestingly, OS+4 $\text{NH}_4\text{Cl}$  sample had  
433 the lowest  $\Delta S$  value (based on the FR method) at an  $\alpha$  value of 0.65. Thus, doping of  
434  $\text{NH}_4\text{Cl}$  to OS favoured an increase in mean  $\Delta S$ .

#### 435 **4. Conclusions**

436 In this study, the effect  $\text{NH}_4\text{Cl}$  doping of oat straw on the pyrolysis process was  
437 investigated up to 873 K using complementary research methods. It was demonstrated  
438 that doping oat straw with  $\text{NH}_4\text{Cl}$  influenced the process. Decarbonylation and  
439 decarboxylation reactions occurred slowly based on analysis of the evolved gases.  
440 The mean activation energy increased throughout the pyrolysis process by 29.3, 37.0,  
441 and 37.3 kJ/mol for the FR, FWO, and KAS methods, respectively. Moreover, there  
442 were difficulties in fitting the experimental results to theoretical curves. Therefore, more  
443 frequent use of undefined reaction mechanisms (G1 and G3/2) was necessary.

#### 444 **Appendix A. Supplementary data**

445 E-supplementary data for this work can be found in e-version of this paper online.

#### 446 **Declaration of Competing Interest**

447 The authors declare that they have no known competing financial interests or personal  
448 relationships that could have appeared to influence the work reported in this paper.

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634 **Credit authorship contribution statement**

635 **Wojciech Jerzak:** Conceptualization, Methodology, Investigation, Writing - Original

636 Draft, Review & Editing, Resources, Visualization;

637 **Marcin Gajek:** Data curation, Formal analysis, Investigation, Writing - original draft;

638 **Aneta Magdziarz:** Investigation, Writing - Review & Editing, Supervision, Project

639 administration, Funding acquisition.

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