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## ► To cite this version:

C. Lefèvre, P. Bohuon, L. Akissoé, L. Ollier, B. Matignon, et al.. Modeling the gelatinization-melting transition of the starch-water system in pulses (lentil, bean and chickpea). *Carbohydrate Polymers*, 2021, 264, pp.117983. 10.1016/j.carbpol.2021.117983 . hal-03892043

**HAL Id: hal-03892043**

**<https://institut-agro-montpellier.hal.science/hal-03892043>**

Submitted on 24 Apr 2023

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1  
2 **Modeling the gelatinization-melting transition of the**  
3 **starch-water system in pulses (lentil, bean and**  
4 **chickpea)**

5  
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16  
17  
18 **Keywords**

19 Starch, Gelatinization, Melting, DSC, Modeling, Pulses

## 20 **Abstract**

21 Cooking-induced conversion of starch, the major carbohydrate in pulses, is crucial for the  
22 digestibility of the seed. The gelatinization-melting transition of lentil, bean and chickpea  
23 starches was studied using Differential Scanning Calorimetry at different temperatures ( $T$   
24 values ranged from 20 to 160 °C) and water contents ( $X$  from 0.2 to 3 kg kg<sup>-1</sup> db).  
25 Gelatinization and melting endotherms were successfully modeled as two desummed Gaussian  
26 functions. This modeling enabled to generate the degree of starch conversion for any  $T$  and  $X$   
27 conditions, a valuable indicator that could be used in predictive cooking models. As previously  
28 reported for melting, the temperature of gelatinization was found to depend on moisture in a  
29 way that can be modeled using the Flory-Huggins equation. The results suggest that starch  
30 undergoes melting transition irrespective of water content. The similar starch conversion  
31 diagram for the three pulses suggest that starches have similar thermal behavior.

32

33

## 34 **Highlights**

- 35 ➤ Overlapping gelatinization and melting peaks from DSC thermogram are desummed.
- 36 ➤ Heat flow is successfully modeled as two Gaussian functions depending on  $T$  and  $X$ .
- 37 ➤ Starch undergoes melting transition regardless of its water content.
- 38 ➤  $T_G$ , like  $T_M$ , is a function of water content modeled using the Flory-Huggins equation.
- 39 ➤ The starch conversion diagram is similar in lentil, bean and chickpea.

40

## 41 Abbreviations

DSC	Differential Scanning Calorimetry
FWHM	Full Width at Half Maximum
G	First endotherm of gelatinization
M	Melting endotherm
R	Gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )
RMSE	Root-mean-square error
T	Temperature ( $^{\circ}\text{C}$ )
$T_i$	Temperature at maximum peak $i$ ( $^{\circ}\text{C}$ )
X	Water content of starch flour ( $\text{kg kg}^{-1}$ dry basis)

### Greek symbols

$\beta_i$	Dimensionless area of peak $i$
$\beta_{G,\infty}$	Dimensionless area of peak G in excess water
$\Delta h_{i,0}$	Change in molar enthalpy of gelatinization ( $i = \text{G}$ ) or melting ( $i = \text{M}$ ) per repeating unit ( $\text{J mol}^{-1}$ )
$\Delta T_i$	Parameter related to the width of peak $i$ ( $^{\circ}\text{C}$ )
$\Delta T_{i,0}$	Parameter related to the width of peak $i$ when water content is zero ( $^{\circ}\text{C}$ )
$\Delta T_{i,\infty}$	Parameter related to the width of peak $i$ in excess water ( $^{\circ}\text{C}$ )
$\zeta_G$	Correlation parameter used to calculate $\beta_G$
$v_g$	Molar volume of repeating unit ( $\text{m}^3 \text{mol}^{-1}$ )

$v_w$	Molar volume of water ( $\text{m}^3 \text{mol}^{-1}$ )
$\tau$	Degree of starch conversion
$\varphi$	Heat flow (W)
$\bar{\varphi}$	Normalized dimensionless heat flow
$\phi$	Volume fraction of water in starch-water mixture ( $\text{m}^3 \text{m}^{-3}$ )
$\chi_i$	Flory interaction parameter for $i$ transition ( $i = \text{M or G}$ )

42

43

## 44 1. Introduction

45 Pulses are the edible seeds from plant family *Leguminosae* (also called *Fabaceae*). Hundreds  
46 of varieties are grown worldwide, especially in India (Hoover, Hughes, Chung & Liu, 2010).  
47 The FAO declared 2016 the International Year of Pulses (IYP) to promote pulses because of  
48 their potential to make food production systems more sustainable. Indeed, pulse crops provide  
49 a sustainable source of nitrogen (Crews & Peoples, 2004) which enhances soil fertility. They  
50 reduce water use and increase agricultural productivity (Gan et al., 2015). In many developing  
51 countries, pulses are already part of human and animal consumption, particularly because of  
52 their high protein content, 15-30 % db (Hoover et al., 2010). In addition, pulses contain 40-  
53 70 % db of carbohydrates, including starch (20-50 % db) and dietary fibers (15-30 % db)  
54 (Hoover et al., 2010; Tosh & Yada, 2010; Hall, Hillen & Garden Robison, 2017). Health  
55 organizations now recommend pulses in all human diets for nutritional and environmental  
56 reasons (Margier et al., 2018). However, their consumption can cause digestive problems due  
57 to the presence of anti-nutritional factors and limited knowledge about cooking procedures  
58 (Coffigniez et al., 2018a; Coffigniez et al., 2018b; Coffigniez et al., 2019). In humans, the  
59 digestive enzymes have difficulty hydrolyzing native starch, the main component of pulse  
60 seeds, because of its crystalline and granular structure. In raw pulses, the resistant starch  
61 content is high (Hoover et al., 2010). Therefore, heat treatment is required to increase the  
62 proportion of rapidly digestible starch and improve digestibility. Giraldo Toro et al. (2015)  
63 observed a strong correlation between the gelatinization rate and the digestibility of plantain  
64 starch flour. They postulated that the cooking process does not influence the final digestibility  
65 of plantain starch if the gelatinization rate is sufficient. Therefore, starch digestibility entirely  
66 depends on temperature and water content. We realized that the nutritional quality of cooked  
67 pulses could be monitored by modeling the degree of starch conversion (Briffaz, Bohuon,  
68 Méot, Dornier & Mestres, 2014). Phase diagrams of starch-water systems have already been

69 investigated for different food products, for example, rice (Briffaz, Mestres, Matencio, Pons  
70 & Dornier, 2013) and plantain (Giraldo Toro et al., 2015), but not pulses. Differential  
71 Scanning Calorimetry (DSC) is widely used to investigate phase transitions of starch by  
72 measuring the heat flow associated with the gelatinization and melting of starch granules  
73 when heated. The shape of the DSC thermogram depends on the starch water content. At  
74 low water content, a biphasic endotherm is observed (Donovan, 1979). The two roughly  
75 overlapping peaks were related to the order-disorder transition and the hydration of starch  
76 crystallites, respectively (Donovan, 1979): G for gelatinization and M for melting (Donovan  
77 & Mapes, 1980). In excess water, some authors associated the single apparent peak with the G  
78 endotherm (Donovan, 1979), while others consider that the DSC signal could hide a small  
79 peak M, which overlaps the dominant peak G (Blanshard, 1987; Tananuwong & Reid, 2004),  
80 suggesting that starch undergoes both order-disorder transition and melting in excess water.  
81 The aim of this study was to investigate gelatinization and melting transitions of starch-water  
82 system using DSC to model a starch conversion diagram specific to pulses. This tool could be  
83 applied to develop a predictive cooking model to improve the nutritional value of pulses. We  
84 used a desummation procedure in an attempt to dissociate the gelatinization and melting  
85 events. Three pulse varieties (lentil, bean and chickpea) were analyzed to compare the thermal  
86 behavior of pulses with different physiochemical and morphological characteristics. These  
87 three varieties are the most commonly eaten in France (Margier et al., 2018).

88

## 89 2. Materials and methods

### 90 2.1 *Material*

91 Green lentils (*L. culinaris*, var. Anicia), navy beans (*P. vulgaris*, var. Linex) and chickpeas  
92 (*C. arietinum*, var. Elvar) were provided by Cibèle (Saint-Georges-Sur-Arnon, France), Cavac  
93 (La Roche-sur-Yon, France) and Moulin Marion (Saint-Jean-sur-Veyle, France), respectively.

94 The lentils were harvested in 2017 and the beans and chickpeas in 2018. All seeds were stored  
95 in a vacuum pack at 7 °C until use.

## 96 2.2 *Starch extraction*

97 Starch was first extracted from the pulses using dry fractionation. The lentil hulls were  
98 removed from the seeds with dry abrasion using a DMS 500 huller (Electra, Poudenas,  
99 France). Dehulled lentils were sieved through a 2 mm mesh screen to separate the hull  
100 residues. Dry fractionation of chickpeas and beans was performed by Improve SAS (Dury,  
101 France). The seeds were crushed at 700 rpm using a SM 300 cutting mill (Retsch GmbH,  
102 Haan, Germany), equipped with a 8 mm sieve. The hulls were removed from the kernels  
103 using a MZM 1-40 zigzag air classifier (Hosokawa Micron, Evry, France). The dehulled  
104 pulses were ground into flour at different speeds (18 000 rpm for lentils and 20 000 rpm for  
105 beans and chickpeas), using a high speed impact mill UPZ equipped with a pill mill  
106 (Hosokawa Alpine, Augsburg, Germany). Starch and protein fractions from the resulting  
107 flours were separated using an ATP air classifier (Hosokawa Alpine, Augsburg, Germany) at  
108 6 500 rpm for lentils, 8 000 rpm for beans and 10 000 rpm for chickpeas. The coarse fraction  
109 from lentils was ground and air classified once again to improve the fine fraction yield,  
110 according to Tyler, Youngs & Sosulki (1981). The resulting coarse fractions from all pulses  
111 were rich in starch but additional starch purification was performed using wet separation.  
112 Coarse fractions were suspended in water and centrifuged at 5 000 rpm. The pellet was  
113 recovered, wet purified a second time and then dried at 45°C. All starch samples were stored  
114 at 14 °C.

## 115 2.3 *Water and total starch content*

116 Water content of the starch sample was calculated on a wet basis by drying 5 g of each pulse  
117 starch sample for 2 h at 132 °C ( $\pm 2$  °C) according to the standard method NF EN ISO 712

118 (2010). Total starch content was estimated using the enzymatic procedure according to Holm,  
119 Björck, Drews & Asp (1986).

#### 120 2.4 *Differential scanning calorimetry*

121 Thermal transitions associated with starch gelatinization and melting were determined using a  
122 DSC 8500 instrument (Perkin Elmer, Norwalk, USA) calibrated with indium as standard.  
123 Starch flour was weighed in stainless steel pans and deionized water was added using a  
124 micropipette. The amount of water was adjusted to obtain a water content  $X$  ranging from 0.2  
125 to 3 kg kg<sup>-1</sup> db (kg water/kg dry starch), to study starch samples from low to excess moisture  
126 conditions. The total weight of each sample was approximately 40 mg. The pans were  
127 hermetically sealed and allowed to stabilize at 14 °C between 5h and 24h before analysis,  
128 depending on the water content of the sample. The pans were then heated from 20 °C to  
129 160 °C at a rate of 10 °C/min, with an empty sealed pan as reference. First, 14 different water  
130 contents were performed for lentil, as presented in Table 1. Since some resulting heat flows  
131 were similar, the number of moisture conditions has been reduced to 10 and 13 for bean and  
132 chickpea, respectively. For lentil and chickpea, at  $X = 0.2$  kg kg<sup>-1</sup> db the temperature at the  
133 end of starch conversion exceeded 160 °C. To prevent damage to the pan due to the  
134 increasing pressure inside, the maximum temperature of heating could not exceed 160°C  
135 under the experimental conditions of the study. Therefore, the corresponding DSC  
136 thermograms were not analyzed. All measurements were duplicated. In total, 28, 20 and 26  
137 samples were measured for lentil, bean and chickpea flour, respectively. A blank thermogram  
138 (empty pans in reference and sample ovens) was recorded daily. The heat flow (mW) of  
139 sample pans minus the variation of heat flow of the blank during heating was recorded using  
140 the Pyris Thermal Analysis Software (Perkin Elmer, Norwalk, USA).

141

142 Table 1. Experimental conditions of the database by pulse type: water content ( $X$ ) of starch  
 143 samples analyzed with DSC from 20 °C to 160 °C.

$X$ (kg kg <sup>-1</sup> db)	Lentil	Bean	Chickpea
0.2	nd	×	nd
0.3	×	–	×
0.4	×	×	×
0.5	×	×	×
0.6	×	×	×
0.8	×	×	×
1.0	×	×	×
1.2	×	–	–
1.5	×	×	×
1.6	×	–	×
1.8	×	×	×
2.0	×	×	×
2.5	×	–	×
3.0	×	×	×

144 ×: measured in duplicate  
 145 nd: incomplete signal detected by DSC at  $T \leq 160$  °C  
 146 –: not tested

147 2.5 *Starch conversion diagram modeling*

148 DSC thermograms plot heat flow ( $\phi$ ) as a function of temperature ( $T$ ). In excess water, a  
 149 single endotherm is observed at low temperature and commonly assigned to the gelatinization  
 150 process (G) (Donovan, 1979). With decreasing water content, a second endotherm appears at  
 151 higher temperature. It was described as the melting (M) of starch granules (Donovan, 1979).  
 152 The two roughly overlapping peaks were desummed as a function of  $T$  and  $X$ . The degree of  
 153 starch conversion was calculated using the model and represented as a diagram.

154 2.5.1 *Modeling the DSC peaks*

155 DSC thermogram data ( $\phi$  versus  $T$ ) were analyzed using a desummation procedure with two  
 156 Gaussian functions illustrated in Fig. 1. First, a baseline was subtracted from the heat flow to

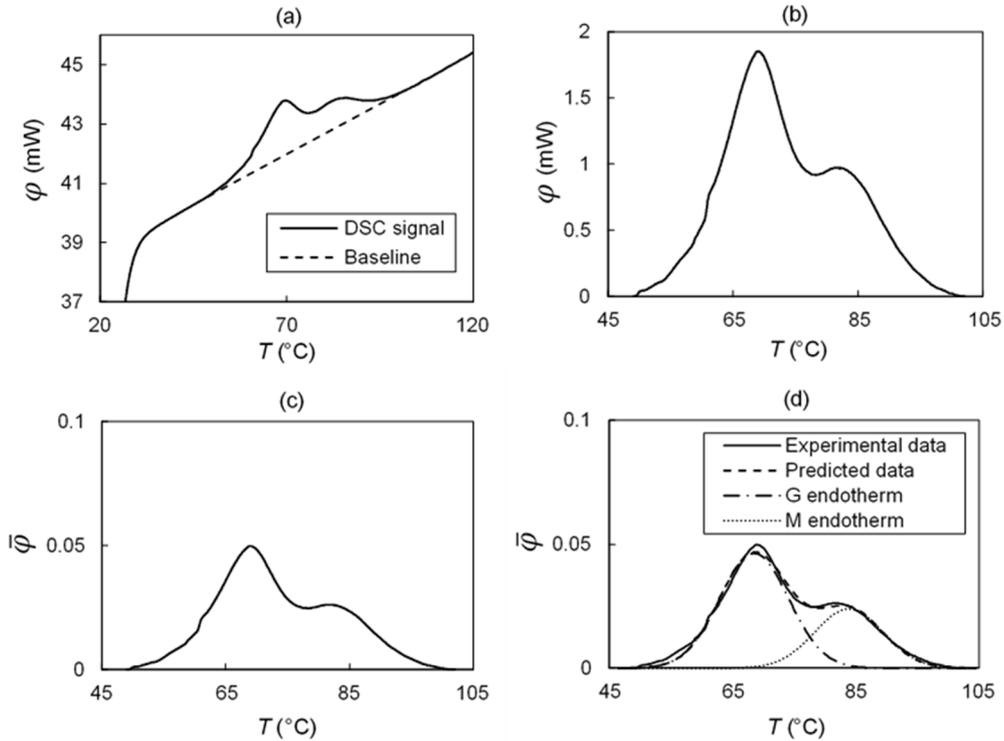
157 simplify the process of curve fitting. The resulting heat flow was non-dimensionalized and  
 158 multiplied by 1000, to avoid low parameter values by increasing the scale. Lastly, each  
 159 dimensionless value for heat flow ( $\bar{\varphi}$ ) was fitted in relation to the sum of two peaks ( $i = G$  or  
 160 M) as follows:

$$161 \quad \bar{\varphi} = \sum_{i=G,M} \frac{\beta_i}{\Delta T_i \sqrt{2\pi}} \exp\left(-\frac{1}{2} \left(\frac{T-T_i}{\Delta T_i}\right)^2\right) \quad (1)$$

162 where  $T_i$  (°C) is the temperature at maximum peak  $i$ ;  $\Delta T_i$  (°C) controls the width of the peak  $i$   
 163 and is related to the full width at half maximum (FWHM) of the peak  $i$  according to  
 164  $2\sqrt{2\ln(2)} \times \Delta T_i = \text{FWHM}$ ;  $\beta_i$  is the dimensionless area of peak  $i$ . Therefore:

$$165 \quad \int_{-\infty}^{\infty} \bar{\varphi} = \beta_G + \beta_M = 1 \quad (2)$$

166 Parameters from Eq. (1) depend on the water content  $X$  in the starch-water mixture.



167  
 168 Figure 1. Graphical explanation of the desummation procedure: (a) a baseline (--) was defined  
 169 for each DSC thermogram (solid line); (b) heat flow obtained after subtraction of the baseline;

170 (c) heat flow obtained after non-dimensionalization and multiplication by 1000; (d) the  
 171 dimensionless heat flow (solid line) was modeled as a bi-Gaussian function (--) showing  
 172 desummed G (-.-) and M (···) endotherms.

### 173 2.5.2 Peak temperatures

174 The Flory–Huggins equation (Flory, 1953) was used to describe the relation between  $T_i$  ( $i = G$   
 175 or M) and the volume fraction of the water ( $\phi$ ) in the starch-water mixture:

$$176 \frac{1}{T_i} - \frac{1}{T_{i,0}} = -\frac{R}{\Delta h_{i,0}} \frac{v_g}{v_w} (\phi - \chi_i \phi^2) \quad (3)$$

177 Where  $\Delta h_{i,0}$  (J mol<sup>-1</sup>) is the change in the molar enthalpy of gelatinization ( $i = G$ ) or melting  
 178 ( $i = M$ ) per repeating unit (anhydroglucose);  $v_g / v_w$  is the ratio of the molar volume of the  
 179 repeating unit ( $v_g = 105.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ ) to the molar volume of the water  
 180 ( $v_w = 18.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ ) and, therefore,  $v_g / v_w = 5.8$ ;  $R$  is the gas constant  
 181 (8.31 J mol<sup>-1</sup> K<sup>-1</sup>);  $T_{i,0}$  (K) is the gelatinization ( $i = G$ ) or melting ( $i = M$ ) temperature of the  
 182 pure polymer and  $\chi_i$  is the Flory interaction parameter. To calculate  $\phi$ , the density of water  
 183 was taken to be 1 000 kg m<sup>-3</sup> and the density of starch was attributed an average value of  
 184 1 500 kg m<sup>-3</sup> (Cruz-Orea et al., 2002). Therefore,  $\phi$  (m<sup>3</sup> m<sup>-3</sup>) was expressed as a function of  
 185 water content  $X$ :

$$186 \frac{1}{\phi} = 1 + \frac{1}{1.5X} \quad (4)$$

### 187 2.5.3 Peak widths

188 The width-related parameter  $\Delta T_i$  represents the fact that, within one sample at fixed water  
 189 content, starch granules have slightly various sizes and compositions. This leads to individual  
 190 variations in the gelatinization or melting temperature and so broad peaks on DSC  
 191 thermogram (Carlstedt, Wojtasz, Fyhr & Kocherbitov, 2015).  $\Delta T_i$  decreases as a function of  
 192 water content. An empirical relation was used to describe  $\Delta T_i$  as a function of  $X$ :

$$193 \quad \frac{\Delta T_i - \Delta T_{i,\infty}}{\Delta T_{i,0} - \Delta T_{i,\infty}} = \exp\left(-\frac{X}{\gamma_i}\right) \quad (5)$$

194 where  $\Delta T_{i,0}$  (°C) and  $\Delta T_{i,\infty}$  (°C) are the values for  $\Delta T_i$ , with zero and excess water contents,  
 195 respectively;  $\gamma_i$  is the rate parameter of decrease for the two correlations. For melting,  $\gamma_M$   
 196 was not significantly different from 1. Its value was thus fixed at 1 to simplify the expression  
 197 of  $\Delta T_M$  with only 2 water-dependent variables.

#### 198 2.5.4 Amplitude of the peak area

199 With increasing water content,  $\beta_G$  increases and  $\beta_M$  decreases as shown by Eq. (2). A simple  
 200 empirical equation was used to describe  $\beta_i$  as a function of  $X$ :

$$201 \quad \beta_G = \beta_{G,\infty} \exp\left(-\frac{\zeta_G}{X}\right) \quad (6a)$$

202 where  $\beta_{G,\infty}$  is the dimensionless area of peak G in excess water and  $\zeta_G$  is a parameter for the  
 203 correlations.  $\beta_M$  was calculated with Eq. (2) and (6a):

$$204 \quad \beta_M = 1 - \beta_{G,\infty} \exp\left(-\frac{\zeta_G}{X}\right) \quad (6b)$$

#### 205 2.5.5 Degree of starch conversion

206 The degree of starch conversion  $\tau$  was defined for any temperature  $T$  and water content  $X$  as  
 207 the ratio between the enthalpy change calculated from the beginning of peak G to  $T$ , and the  
 208 whole enthalpy change from the beginning of peak G to the end of peak M (Eq. (7a)). The  
 209 integral of the sum of Gaussian functions is the sum of error functions (Eq. (7b)).

$$210 \quad \tau = \int_0^T \bar{\varphi}(T, X) / \int_0^{\infty} \bar{\varphi}(T, X) \quad (7a)$$

$$211 \quad \tau = \sum_{i=G,M} \beta_i \times \frac{1}{2} \left( 1 + \operatorname{erf} \left( \frac{T - T_i}{\Delta T_i \sqrt{2}} \right) \right) \quad (7b)$$

212 Finally, isovalues lines of degree of starch conversion  $\tau$  were represented as a temperature  $T$   
 213 versus water content  $X$  diagram.

#### 214 2.5.6 Parameters identification for modeling the starch conversion diagram

215 Two different procedures, referred to as sequential and overall identification methods, were  
 216 used and compared to identify the parameters. The sequential procedure consisted of two  
 217 steps. The first step involved identifying the 6 so-called primary parameters ( $T_i$ ,  $\Delta T_i$  and  $\beta_i$ )  
 218 in the DSC peak desummation model, by fitting dimensionless heat flow thermograms to  
 219 Eq. (1) for each water content  $X$ . The second step involved identifying the 13 so-called  
 220 secondary parameters ( $T_{i,0}$ ,  $\Delta h_i$ ,  $\chi_i$ ,  $\Delta T_{i,\infty}$ ,  $\Delta T_{i,0}$ ,  $\gamma_G$ ,  $\beta_{G,\infty}$  and  $\zeta_G$ ) used to described the  
 221 primary parameters as functions of  $X$ . They were identified by fitting primary parameters to  
 222 Eq. (3), (5) and (6a), respectively. The aim of the overall procedure was to identify the 13  
 223 secondary parameters at the same fitting session, by fitting all dimensionless heat flow  
 224 thermograms to the model combining Eq. (3), (5) and (6a) within Eq. (1). The curve fitting  
 225 toolbox (Matlab software, version R2019b, The MathWorks Inc., Natick, USA) with the  
 226 Levenberg-Marquardt algorithm was used to identify all parameters.

## 227 2.6 *Statistical methods*

228 The parameter values obtained from the two identification methods are given with a 95 %  
229 confidence level. The root-mean-square error (RMSE) was calculated between the  
230 dimensionless heat flow DSC thermograms (experimental data) and the dimensionless heat  
231 flows predicted by sequential and overall identification methods.

232

## 233 3. Results and Discussion

### 234 3.1 *Starch characterization*

235 The total starch content of starch flour was estimated at 95.2 % (*i.e.* kg starch/kg flour on a  
236 dry basis) for lentils, 96.8 % for beans and 92.1 % for chickpeas. Therefore, the thermal  
237 behavior of all starch flours was considered to be close to that of a pure starch-water mixture.  
238 The water content of starch flour was 12.2 % (*i.e.* kg water/kg flour) for lentils, 11.5 % for  
239 beans and 11.1 % for chickpeas.

### 240 3.2 *Modeling the starch conversion diagram*

#### 241 3.2.1 *Modeling the DSC peaks*

242 The experimental DSC thermograms show that the thermal behavior of the starch-water  
243 system is similar for the three pulses. The primary parameters identified using the  
244 desummation procedure (Eq. (1)) are presented in Fig. 2 with dots. At water contents below  
245 2 kg kg<sup>-1</sup> db, the presence of a biphasic endotherm meant it was easy to identify the so-called  
246 G and M peaks (Donovan & Mapes, 1980) and, therefore, the primary parameters. With  
247 increasing water content, the DSC signal has a single peak (which may be followed by a small  
248 shoulder that decreases in size), as reported for cereals, plantain and peas in the literature  
249 (Donovan, 1979; Cruz-Orea, Pitsi, Jamée & Thoen, 2002; Tananuwong & Reid, 2004; Briffaz

250 et al., 2013; Giraldo Toro et al., 2015). According to Eq. (1), there are two possible  
251 mathematical interpretations for this shape. The first assumes that  $T_M$  is higher than  $T_G$  and  
252  $\beta_G$  is close to 1. The second assumes that  $T_M$  and  $T_G$  are close and that  $\beta_G$  and  $\beta_M$  are also  
253 close. According to the second hypothesis, the melting transition makes a greater contribution  
254 to starch conversion than suggested in the first hypothesis. As the RMSE of the two non-  
255 linear regressions were closed (data not shown), we chose the first hypothesis to identify the  
256 primary parameters. Indeed, we do not yet fully understand the thermal transitions that appear  
257 on the DSC thermogram. Many theories proposed in the literature describe starch changes  
258 during gelatinization and melting. Donovan (1979) first suggested that swelling in the  
259 amorphous region of starch granules in the presence of water causes the disruption of  
260 crystalline parts by “stripping” starch chains on the surface. If there is sufficient water, all  
261 starch crystallites can be moisturized and melt cooperatively, resulting in a single peak on the  
262 heat flow thermogram. If water is limited, the remaining low-hydrated crystallites melt at a  
263 higher temperature, resulting in a biphasic endotherm. Evans & Haisman (1982) proposed that  
264 the two peaks were due to the different crystallite stability. The granules with less stable  
265 crystallites melt, which produces the first peak. This reduces the available water and, as a  
266 result, the more stable crystallites that remain melt at a higher temperature. With increasing  
267 water, the melting temperature decreases and, thus, the second peak shifts towards the first.  
268 Numerous other theories have been proposed and were reported by Ratnayake & Jackson  
269 (2007). In their study, they described starch gelatinization as a complex process that cannot be  
270 reduced to order-disorder transition because it induces structural and morphological changes  
271 in starch granules. They reported greater mobility of starch polymers and amylose molecules  
272 due to water absorption in the amorphous regions. This mobility leads to the formation of new  
273 intermolecular bonds, which occurs simultaneously to the so-called gelatinization process.  
274 They also highlighted that DSC measurements were unable to provide this type of information

275 with regard to polymer structure at low temperature. In the present study, starch was thus  
276 supposed to undergo gelatinization and melting according to one of the previous hypothesis.  
277 Since the aim of the study was modeling the degree of starch conversion, we did not perform  
278 further analysis of the starch morphology. To validate which hypothesis best describes the  
279 starch conversion under the conditions of the study, complementary techniques should be  
280 carry out, such as microscopy (Ratnayake & Jackson, 2007). For example, by combining the  
281 results from optical microscopy, X-ray scattering and DSC up to 100 °C, Carlstedt et al.  
282 (2015) showed that G and M endotherms could be interpreted as a eutectic transition and a  
283 liquidus line, respectively.

### 284 3.2.2 *Parameters identification from the sequential method*

285 The identification of primary parameters shows that the temperature of gelatinization (Fig. 2a)  
286 and melting (Fig. 2b), the width (Fig. 2c and 2d) and the relative area (Fig. 2e) of each peak  
287 depend on the starch water content. This phenomenon has been observed by many authors  
288 (Donovan, 1979; Evans & Haisman, 1982; Cruz-Orea et al., 2002; Tananuwong & Reid,  
289 2004; Briffaz et al., 2013). These trends are modeled with the 13 secondary parameters  
290 obtained from the sequential identification method and presented in Table 2.

291 For all studied pulses, the Flory-Huggins equation provides a satisfactory description of the  
292 relation between  $T_M$  and  $\phi$  (Fig. 2b). Overall, the corresponding secondary parameters  
293 obtained using the sequential identification method (Table 2) are in the same order as those  
294 found in previous studies. We found  $T_{M,0}$  values ranging from  $227.6 \pm 25.0$  °C to  
295  $307.8 \pm 37.5$  °C,  $\Delta h_{M,0}$  values from  $16.4 \pm 8.7$  kJ mol<sup>-1</sup> to  $23.8 \pm 4.4$  kJ mol<sup>-1</sup> and  $\chi_M$  values  
296 from  $0.62 \pm 0.05$  to  $0.65 \pm 0.3$  depending on pulse species. Previous studies, focusing mainly  
297 on cereals and potato starches, reported  $T_{M,0}$  values ranging from 167 °C to 258 °C,  $\Delta h_{M,0}$

298 values from 12.6 kJ mol<sup>-1</sup> to 54.4 kJ mol<sup>-1</sup> and  $\chi_M$  values from 0.48 to 0.51 (Donovan,  
 299 1979; Donovan & Mapes, 1980; Farhat & Blanshard, 1997; Cruz-Orea et al., 2002; Habeych,  
 300 Guo van Soest, van der Goot & Boom, 2009; van der Sman & Meinders, 2011).  
 301 Donovan (1979) reported that the maximum for the G endotherm was always observed at  
 302 66 °C for potato starches with  $\phi$  ranging from 0.28 to 0.81. Our results show that  $T_G$  can  
 303 indeed be considered constant around 66 °C when the water content is sufficient (*i.e.*  
 304  $X > 0.7$  kg kg<sup>-1</sup> db;  $\phi > 0.5$  m<sup>3</sup> m<sup>-3</sup>). An isothermal temperature of gelatinization has also  
 305 been reported by Carlstedt et al. (2015) for the same range of water content. However,  $T_G$   
 306 increases at a lower water content for all pulses (Fig. 2a). This observation is consistent with  
 307 the results presented by Evans & Haisman (1982). They reported a constant initial  
 308 temperature of gelatinization for water content above 0.6 kg kg<sup>-1</sup> db and a steep increase in  
 309 temperature with a decreasing water content. Thus, given the range of water contents under  
 310 study,  $T_G$  can be plotted as a function of  $\phi$  according to the Flory-Huggins equation with a  
 311 good fitting result (Fig. 2a). The secondary parameters obtained using the sequential  
 312 identification method (Table 2) differ from those previously reported for peak M.  $T_{G,0}$  is  
 313 lower than  $T_{M,0}$  and  $\Delta h_{G,0}$  is higher than  $\Delta h_{M,0}$ .  
 314 The width of G and M endotherms ( $\Delta T_G$  and  $\Delta T_M$ ) decreases with water content (Fig. 2c and  
 315 1d), as reported in previous studies (Donovan, 1979; Tananuwong & Reid, 2004). The  $\beta_G$   
 316 value shows that gelatinization becomes the predominant thermic event (*i.e.*  $\beta_G \geq 0.5$ ) when  
 317 the water content exceeds 1 kg kg<sup>-1</sup> db for all pulses (Fig. 2e). Blanshard (1987) suggested  
 318 that G and M endotherms merged at high water content, resulting in a single apparent peak.  
 319 Tananuwong & Reid (2004) confirmed this hypothesis using instrumental and mathematical

320 deconvolution procedures. Sequentially-determined  $\beta_{G,\infty}$  is associated with a high confidence  
321 interval (Table 2). Therefore, the melting in excess water (*i.e.*  $\beta_{G,\infty} < 1$ ) cannot be confirmed  
322 here by simply considering the results of the sequential method. However, the trailing  
323 shoulder after the peak G at  $X = 2 \text{ kg kg}^{-1} \text{ db}$  for all pulses seems to support this hypothesis.  
324 The same also applies to some extent at  $X = 3 \text{ kg kg}^{-1} \text{ db}$  for lentil and bean. This can be seen  
325 in Fig. 3a, 4a and 5a, which represent predicted dimensionless heat flows calculated with  
326 sequentially-determined secondary parameters in comparison with experimental  
327 dimensionless heat flows for lentil, bean and chickpea, respectively. The RMSE between  
328 experimental and predicted dimensionless heat flows were calculated for each sample tested  
329 (Fig. 3a, 4a and 5a).

### 330 3.2.3 *Parameter identification from overall method*

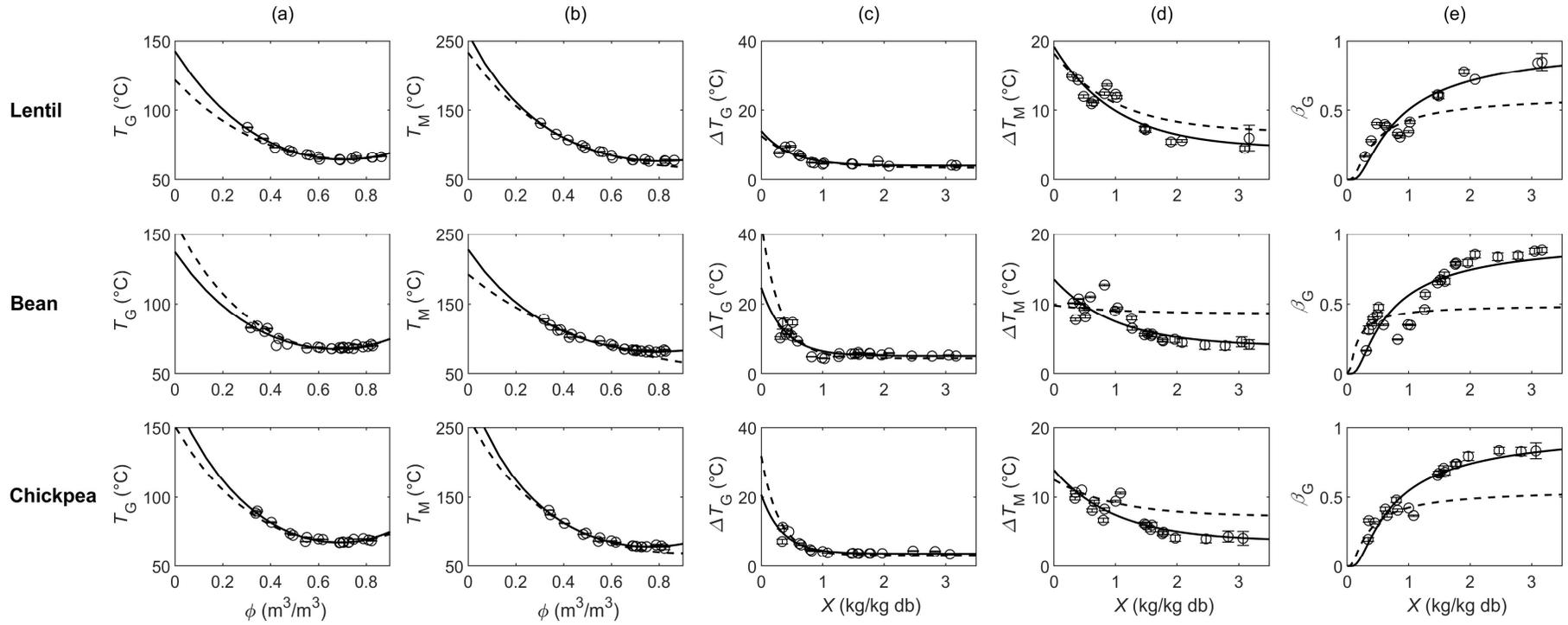
331 The 13 secondary parameters obtained using the overall identification method are presented in  
332 Table 2. Confidence intervals at 95 % are lower than those from the sequential method  
333 (Table 2), which leads to more precise modeling. The predicted dimensionless heat flows  
334 calculated with the secondary parameters obtained using the overall identification method are  
335 plotted in Fig. 3b, 4b and 5b with the associated RMSE between experimental and predicted  
336 dimensionless heat flows. These results are quite close to the predicted heat flows obtained  
337 using the sequential method (Fig. 3a, 4a and 5a) for lower water content ( $X < 2 \text{ kg kg}^{-1} \text{ db}$ ),  
338 with similar RMSE. The significant difference between the two methods is the position and  
339 contribution of peak M for water contents above  $2 \text{ kg kg}^{-1} \text{ db}$ . This is clearly shown by the  
340 value of  $\beta_{G,\infty}$ , which is significantly lower than that identified using the sequential method  
341 (Table 2) for all pulses. We found  $\beta_{G,\infty} = 0.61 \pm 0.01$  for lentil,  $0.49 \pm 0.01$  for bean and  
342  $0.66 \pm 0.02$  for chickpea with the overall identification method. This indicates that melting is

343 important for starch conversion in excess water, even if the DSC signal has a single peak. Our  
344 results are similar to the desummation curves presented by Tananuwong & Reid (2004) for  
345 potato, pea and normal and waxy corn starches, who postulated that the M endotherm is  
346 gradually incorporated into the predominant G endotherm. Their study shows a relative peak  
347 area of G and M endotherms which is also very similar to Fig. 2e. The desummation results  
348 obtained from the overall identification method confirms that G and M endotherms can be  
349 merged in one peak in excess water conditions.

350

351 For chickpea and bean, when all the water contents analyzed are considered together, the  
352 predictions for the dimensionless heat flows are slightly more precise with the overall method  
353 (0.34% and 0.45% errors on predicted values, respectively) compared to the sequential  
354 method (0.50% and 0.52% errors on predicted values, respectively). For lentil, the two  
355 methods are equally precise (0.28%), as expected when comparing Fig. 3a and 3b.

356



357

358 Figure 2. Primary parameters of the Gaussian functions modeled as a function of volume fraction of water  $\phi$  or as a function of water content  $X$   
 359 for lentil, bean and chickpea starches. Primary parameters (dots) were obtained using the desummation procedure and fitted to Eq. (3) (a,b), Eq.  
 360 (5) (c,d) and Eq. (6a) (e), respectively (solid lines). Results from the overall identification method (--) were later added for comparison, but were  
 361 not fitted directly from the primary parameters.

362

363 Table 2. Secondary parameters obtained using the sequential (S) and overall (O) identification method for lentil, bean and chickpea starches

Type of starch	$\frac{1}{T_i} - \frac{1}{T_{i,0}} = \frac{R}{\Delta h_{i,0}} \frac{v_g}{v_w} (\phi - \chi_i \phi^2)$	$\frac{\Delta T_i - \Delta T_{i,\infty}}{\Delta T_{i,0} - \Delta T_{i,\infty}} = \exp\left(-\frac{X}{\gamma_i}\right)$	$\beta_G = \beta_{G,\infty} \exp\left(-\frac{\zeta_G}{X}\right)$
----------------	---	--	--

364 (mean values  $\pm$  95 % confidence interval). The values were used to calculate the degree of starch conversion  $\tau = \sum_{i=G, M} \beta_i \times \frac{1}{2} \left( 1 + \operatorname{erf} \left( \frac{T - T_i}{\Delta T_i \sqrt{2}} \right) \right)$

		$T_{G,0}$ (°C)	$T_{M,0}$ (°C)	$\Delta h_{G,0}$ (kJ mol <sup>-1</sup> )	$\Delta h_{M,0}$ (kJ mol <sup>-1</sup> )	$\chi_G$	$\chi_M$	$\Delta T_{G,0}$ (°C)	$\Delta T_{M,0}$ (°C)	$\Delta T_{G,\infty}$ (°C)	$\Delta T_{M,\infty}$ (°C)	$\gamma_G$	$\beta_{G,\infty}$	$\zeta_G$
Lentil	S	142.5 ±9.6	260.1 ±19.5	30.5 ±3.8	19.8 ±2.0	0.71 ±0.02	0.62 ±0.03	13.99 ±6.17	19.14 ±2.42	3.99 ±0.97	4.51 ±1.45	0.47 ±0.33	1.00 ±0.16	0.69 ±0.21
	O	121.6 ±1.6	233.1 ±2.5	40.9 ±1.0	24.3 ±0.4	0.69 ±0.01	0.52 ±0.01	12.64 ±0.78	18.15 ±0.37	3.37 ±0.05	6.79 ±0.13	0.61 ±0.04	0.61 ±0.01	0.36 ±0.02
Bean	S	137.1 ±17.1	227.6 ±25.0	32.4 ±8.1	23.8 ±4.4	0.75 ±0.04	0.62 ±0.05	24.61 ±14.24	13.49 ±1.95	5.03 ±1.14	3.92 ±1.11	0.38 ±0.27	0.98 ±0.14	0.56 ±0.19
	O	158.5 ±4.3	192.1 ±1.8	26.3 ±0.9	36.8 ±0.9	0.74 ±0.01	0.36 ±0.01	43.21 ±4.49	9.79 ±0.28	4.37 ±0.06	8.62 ±0.12	0.31 ±0.01	0.49 ±0.01	0.13 ±0.02
Chickpea	S	170 ±14.4	307.8 ±37.2	24.3 ±3.3	16.4 ±8.7	0.73 ±0.02	0.65 ±0.03	20.64 ±11.53	13.89 ±1.92	3.63 ±0.77	3.63 ±1.06	0.34 ±0.20	1.01 ±0.12	0.61 ±0.16
	O	150.9 ±3.3	265.4 ±3.0	28.9 ±0.9	20.4 ±0.4	0.72 ±0.01	0.55 ±0.01	31.88 ±4.79	12.50 ±0.38	3.21 ±0.05	7.18 ±0.16	0.29 ±0.02	0.56 ±0.02	0.28 ±0.02

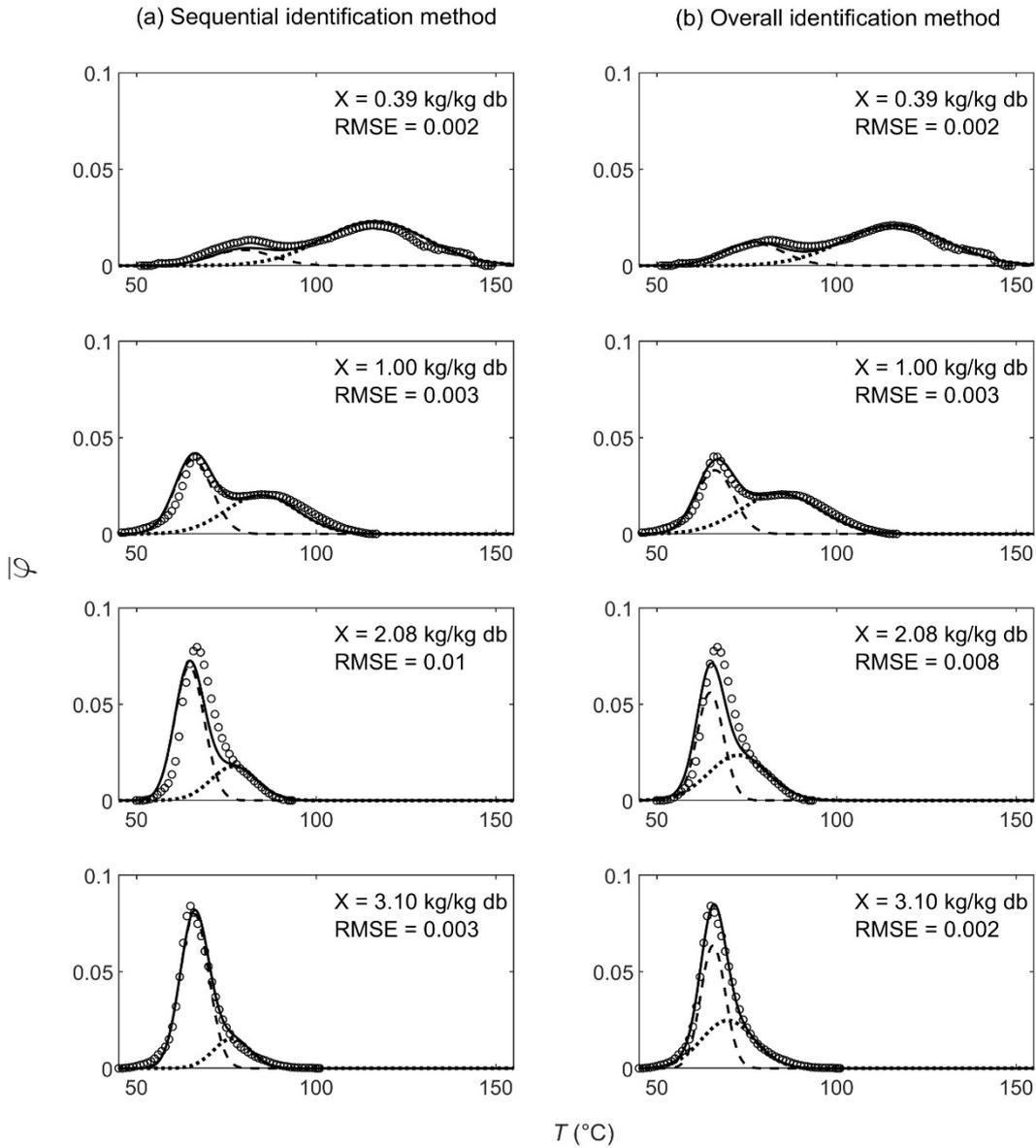
365  $\phi$  : volume fraction of water (m<sup>3</sup> m<sup>-3</sup>)

366  $X$  : water content (kg kg<sup>-1</sup> db)

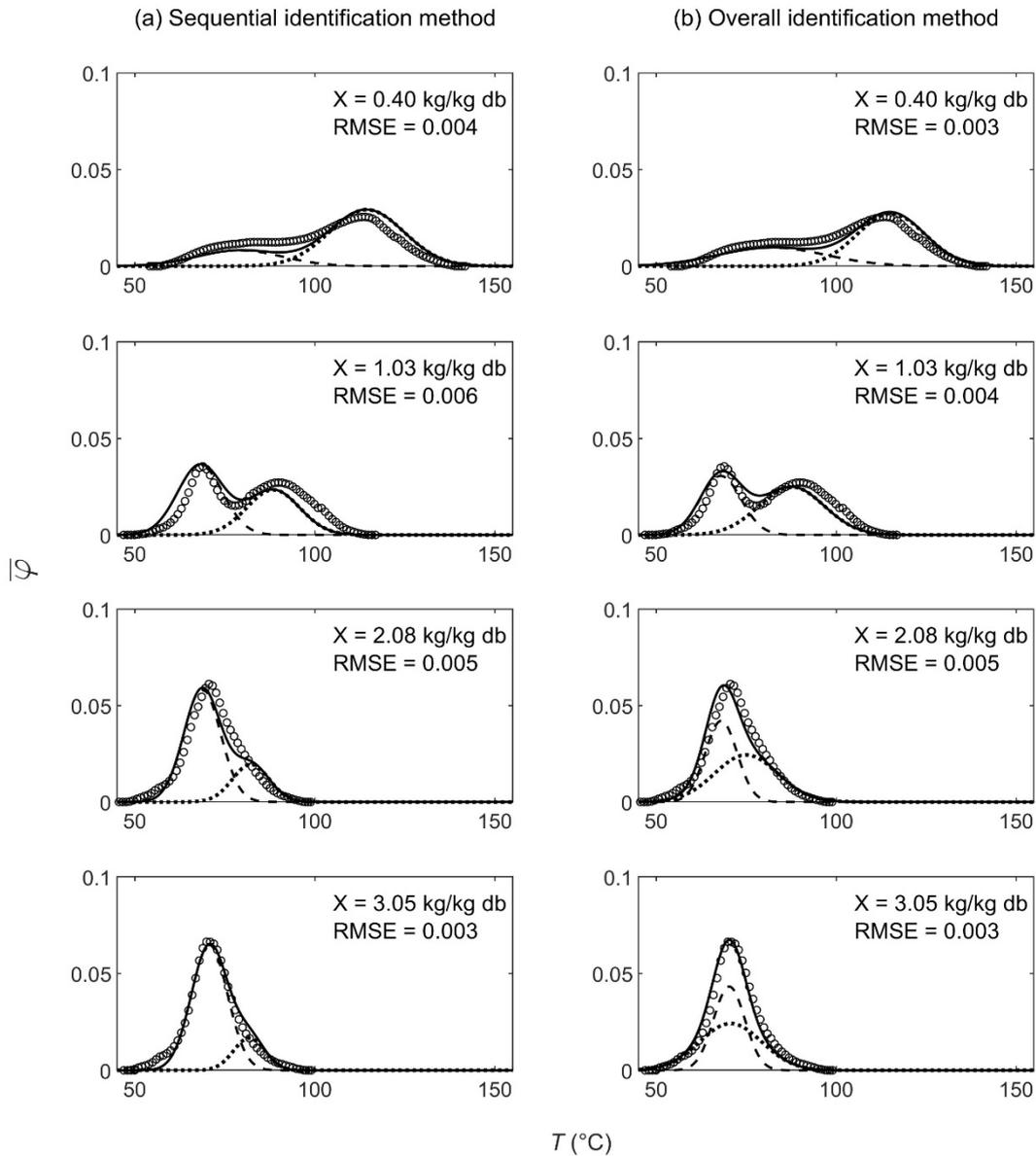
367  $\chi_M$  is fixed at 1.

368  $\beta_M = 1 - \beta_G$

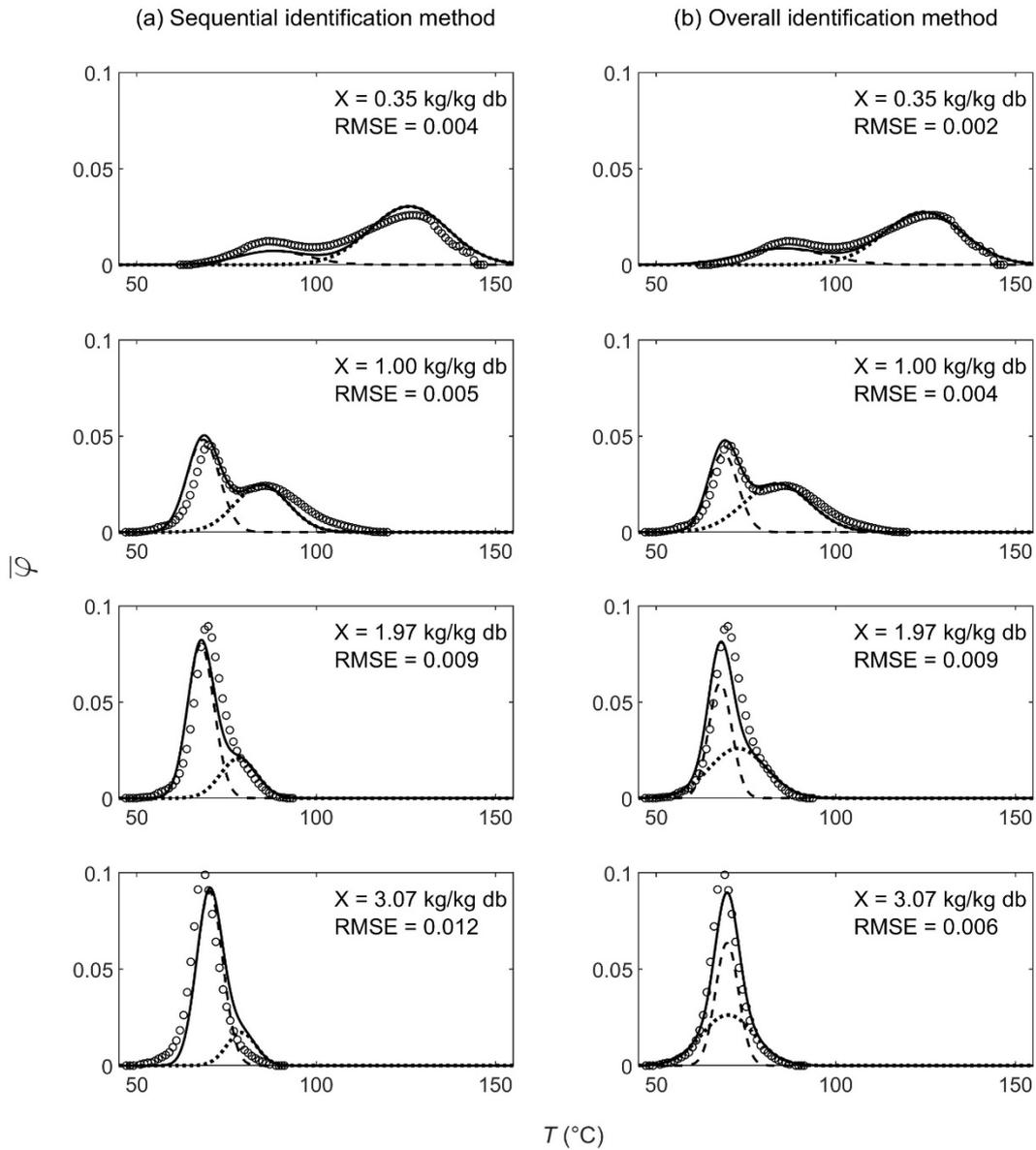
369



370  
 371 Figure 3. DSC thermograms of lentil starch at different water contents  $X$ : experimental (dots)  
 372 and predicted (solid lines) dimensionless heat flows, predicted G (--) and M (...) endotherms.  
 373 Predicted data were obtained using the sequential (a) and overall (b) identification method.  
 374 RMSE were calculated between experimental and predicted dimensionless heat flows for the  
 375 different water contents.  
 376



377  
 378 Figure 4. DSC thermograms of bean starch at different water contents  $X$ : experimental (dots)  
 379 and predicted (solid lines) dimensionless heat flows, predicted G (--) and M (...) endotherms.  
 380 Predicted data were obtained using the sequential (a) and overall (b) identification method.  
 381 RMSE were calculated between experimental and predicted dimensionless heat flows for the  
 382 different water contents.  
 383



384

385 Figure 5. DSC thermograms of chickpea starch at different water contents  $X$ : experimental  
 386 (dots) and predicted (solid lines) dimensionless heat flows, predicted G (--) and M (···)  
 387 endotherms. Predicted data were obtained using the sequential (a) and overall (b)  
 388 identification method. RMSE were calculated between experimental and predicted  
 389 dimensionless heat flows for the different water contents.

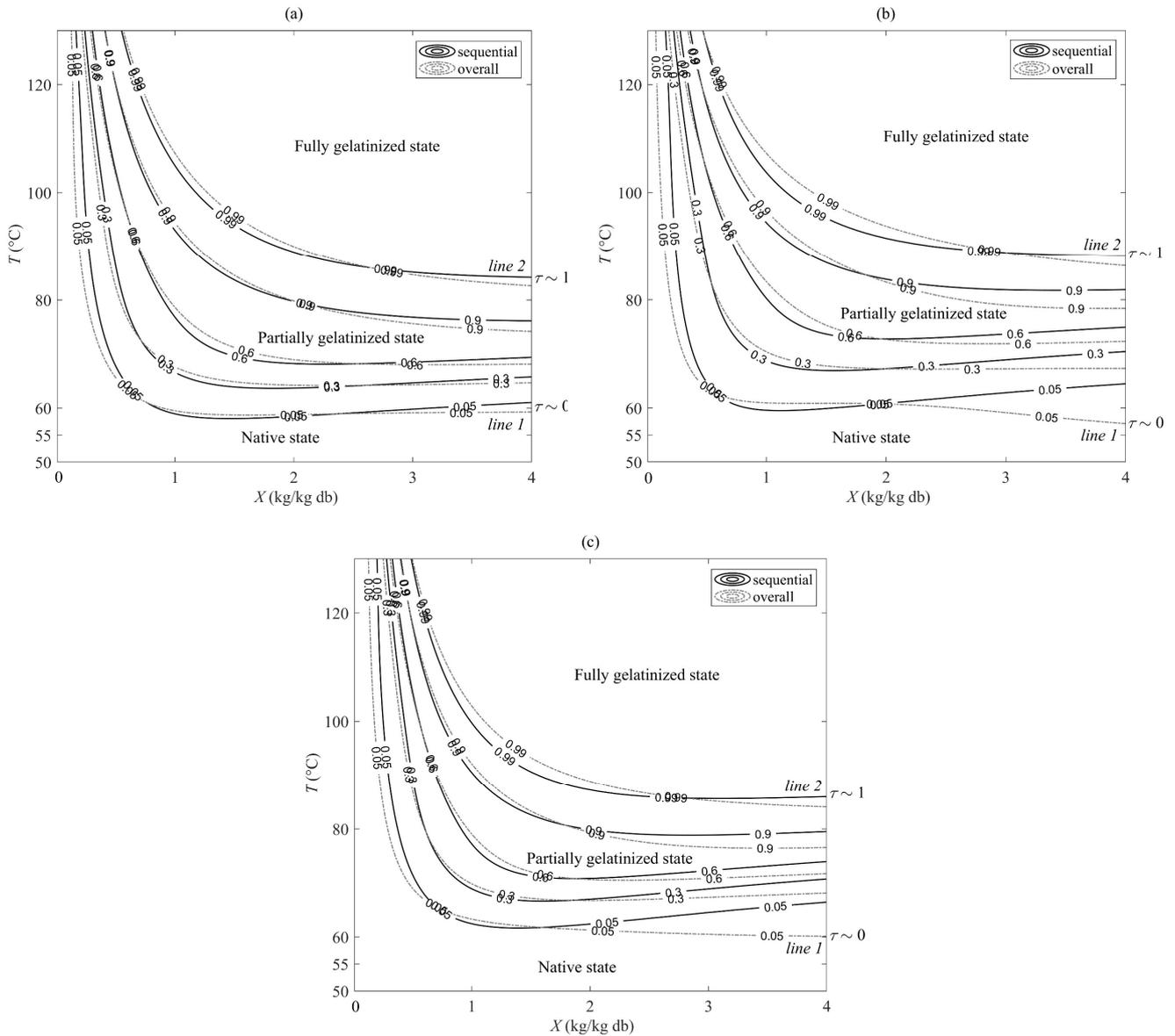
390

391 3.2.4 Starch conversion diagram

392 For lentil, the modeled diagrams of starch conversion obtained using the sequential and  
393 overall identification methods are similar (Fig. 6a). This is consistent with the similar results  
394 obtained from both methods, as discussed previously. For bean and chickpea (Fig. 6b and 6c),  
395 the two identification methods lead to different starch conversion diagrams when  $\tau$   
396 approaches 0. With the sequential method, the temperature at the beginning of gelatinization  
397 (*line 1* in Fig. 6) increases with water content when  $X > 1.5 \text{ kg kg}^{-1}$ . The overall method  
398 seems to reduce side effects in excess water, by giving a constant temperature at the  
399 beginning of gelatinization when  $X > 1.5 \text{ kg kg}^{-1}$ . For the three pulses, the starch conversion  
400 diagram obtained using the overall identification method thus appears to be more accurate.  
401 Moreover, isovalue lines of starch conversion degree defined three areas (native, partially  
402 gelatinized and fully gelatinized starch) which are consistent with the scanning electron  
403 microscopy images presented by Ratnayake & Jackson (2007) on various cereal and tuber  
404 starches.

405 Lentil, bean and chickpea have similar starch conversion diagrams as shown in Fig. 7,  
406 suggesting that starches have similar thermal behavior. Further analysis could be performed  
407 with other varieties in order to confirm this trend in all pulses.

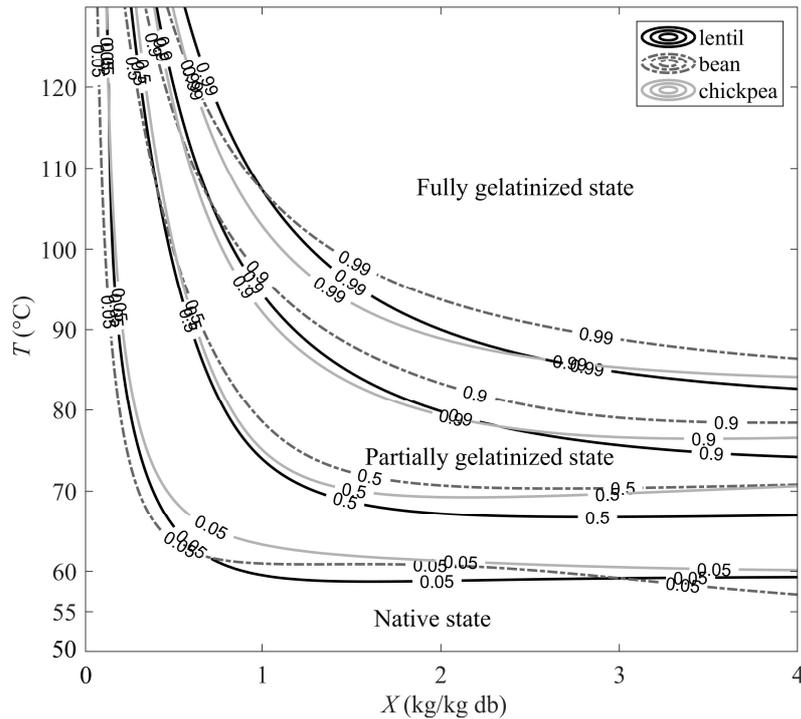
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409

410 Figure 6. Modeled starch conversion diagram of lentil (a), bean (b) and chickpea (c) starch–  
 411 water mixture (temperature  $T$  versus water content  $X$  and isovalue lines of degree of starch  
 412 conversion  $\tau$ ) obtained with the sequential (black line) or overall (grey line) identification  
 413 method. Three states can be distinguished: native state (below line 1:  $\tau \approx 0$ ), partially  
 414 gelatinized state (area between lines 1 and 2:  $0 < \tau < 1$ ) and fully gelatinized state (beyond  
 415 line 2:  $\tau \approx 1$ ).

416



417

418 Figure 7. Comparison of modeled starch conversion diagram of the three pulses' starch-water  
 419 mixtures (temperature  $T$  versus water content  $X$  and isovalue lines of degree of starch  
 420 conversion  $\mathcal{Z}$ ) obtained with the overall identification method.

421

#### 422 4. Conclusion

423 The method of desummation and modeling of DSC heat flow thermograms presented in this  
 424 study improves our understanding of the starch conversion process in various  $T$  and  $X$   
 425 conditions. The temperature of gelatinization can be modeled as a function of water content  
 426 according to the Flory-Huggins theory, as found previously for the temperature of melting.  
 427 The primary parameters suggest that starch undergoes melting transition regardless of water  
 428 content. As the water content increases, G and M endotherms overlap, producing a single  
 429 peak in the DSC heat flow thermogram. Both identification methods can predict the heat flow  
 430 of starch conversion precisely at various values for  $T$  and  $X$ . The overall identification method

431 generates a more precise degree of starch conversion, which can be integrated into a water  
432 transfer model to improve the cooking process for these pulses. In addition, the results suggest  
433 that the thermal behavior of lentil, bean and chickpea starches is similar despite their varietal  
434 differences. Thus, a common approach could be considered to optimize the nutritional value  
435 of all pulses.

436

## 437 5. Acknowledgements

438 We would like to thank Dr. V. Lullien and G. Maraval from INRAE (UMR IATE) for their  
439 technical help for the lentil starch extraction process. The research activities presented in this  
440 paper were supported by the Proveggas Project (22<sup>nd</sup> Unique Inter-ministerial Fund).

441

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