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Review

Dry heating of whey proteins

Elise Schong, Marie-Hélène Famelart*

STLO, UMR 1253, INRA, Agrocampus Ouest, 35000 Rennes, France

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ABSTRACT

Whey protein products are of widespread use as food ingredients because of their high nutritional, biological and functional properties. Whey proteins are important structural components in many foods as used in their native form, for example for their heat-induced gelation abilities. Furthermore, they also offer reliable functionalities when modified by heating processes as denatured or aggregated proteins. Heat treatment of whey proteins in a liquid state has received much attention in recent years. While dry heating of whey proteins, say heating whey proteins in the dry state, is frequently cited in the literature as a potential and efficient means to improve the functional properties of proteins, it has received very little attention. We report first on the dry heating of whey products as applied to promote glycation of whey proteins with a low denaturation, and second, to promote their denaturation and aggregation and on their consequences on the functional properties of whey proteins.

1. Introduction

Dry heating of whey proteins or heating a whey protein powder has received very little attention, while dry heating of hen egg white is very commonplace in the egg industry. It was first applied on egg white at 55–65 °C for 3–5 days for its pasteurisation, because it allows reaching higher temperatures for egg white than in a liquid state without destabilization. But, since Kato, Ibrahim, Watanabe, Honma, and Kobayashi (1989) demonstrate that it improves the functional properties of egg white, the food-processing industry widely uses the dry heating of hen egg white at 65–85 °C for 7–14 d (Nau, Guérin-Dubiard, Baron, & Thapon, 2010). It is mostly applied in rooms at a regulated temperature and relative humidity (RH) to avoid an excessive decrease in the powder moisture.

The temperature and time of the dry heating are essential parameters, as the content in saccharides, the pH and the water activity (a_w) of the powder. While heating in solution is applied at relative high temperature for short time (60–95 °C less than one h), dry heating uses generally lower temperatures (50–80 °C) for longer time (h to days). However, some dry heating studies use higher temperatures (100–130 °C) for shorter time (O'Mahony, Drapala, Mulcahy, & Mulvihill, 2017). In research studies, pH and composition of the reactants are adjusted in the liquid state, the mixture is generally freeze-dried and the powder is usually adjusted at a known initial RH or a_w, by storage in selected saturated salts, for example. The power is then dry heated in an oven, in tightly sealed glass tubes. In that process, only the initial a_w is controlled and can evolve, due to the potential accumulation of water by the Maillard reaction. In some studies, the whole equipment controlling the a_w is introduced in the oven and the aw is controlled all along the process. We will report once on dry heating applied on mixtures of whey protein isolate and saccharide powders (Hiller & Lorenzen, 2010). Moreover, it has been said that dry heating produces a limited protein denaturation (Augustin & Udabage, 2007; Morgan et al., 1999) at a temperature lower than the glass transition temperature (Tg) range (~75 to 120 °C for whey protein isolate (WPI) or βlactoglobulin (βlg) at a_w from 0.64 to 0.23, respectively (Zhou & Labuza, 2007)) and this is why an increasing number of studies are devoted to the dry heating as a mean to increase the functional properties of milk proteins. According to Zhou and Labuza (2007), denaturation temperature (Td) at low water contents of WPI or βlg are from 96 to 180 °C at a_w 0.85 to 0.11, respectively, a much higher value than in the liquid state.

As the dry heating of whey proteins is an efficient way to produce glycated proteins, and as Maillard type-glycated proteins could carry biological and techno-functional benefits, we report on that technology as studied on whey proteins in scientific papers. To our knowledge, there are no recent reviews that deal with the dry heating of whey proteins and their consequences on functional properties of proteins.

We report first on studies on dry heating applied for glycation reaction. Moreover, we report on studies of dry heating as a process that induces aggregation of whey proteins, either as detrimental or desired. Although the processes of glycation and aggregation are intimately related, because glycation is generally the first step of both, the former studies are conducted with added reducing sugar with the aim to limit

* Corresponding author.
E-mail address: marie-helene.famelart@inra.fr (M.-H. Famelart).

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the structural modifications of whey proteins, such as their aggregation and the production of brown colour, while the latter are conducted in conditions promoting denaturation and aggregation of proteins, generally without adding sugar and at higher temperature and time of dry heating. We have divided these parts in a section presenting the conditions applied during the dry heating and a section on consequences of dry heating on the functional properties of proteins. To help the reader, the section on the conditions applied during glycation is also divided in treatments at temperatures lower and higher than 50 °C. Regardless of the a_w or RH value of the experiment, temperatures lower than 50 °C are lower than the Tg of the WPI powders, and protein mobility and reactions rates are significantly reduced and vice versa (Zhou & Labuza, 2007).

2. Dry heating in conditions promoting the glycation of whey proteins

2.1. Generalities

Heating proteins in the presence or with traces of a reducing sugar often leads to Maillard reactions (Augustin & Udabage, 2007). These reactions constitute a very complex network of reactions with diverse pathways. At the beginning, a reducing sugar such as lactose condenses with a compound possessing a free amino group, like the ε-group of lysine or the α-amino group of terminal amino acids, to form N-substitute glycosylamine. Then, glycosylamine undergoes the Amadori rearrangement to form ketosamines known as early glycation products. Many further ways are then possible, leading either to reductones and dehydroreductones, which are powerful antioxidants or to the Strecker degradation or to the Schiff's base/furfural pathway with formation of water and brown nitrogenous polymers and copolymers called melanoidins that constituted advanced glycation end-product or AGE (Martins, Jongen, & van Boekel, 2000). As one of the products of the reaction is water, a high content of water inhibits the reaction, and the reaction occurs most rapidly at intermediate value of a_w, $0.5 < a_w < 0.8$, say for dried and intermediate-moisture products (Ames, 1990).

An increasing number of studies reports on increased functional properties of glycated proteins. Some recent reviews (Liu, Ru, & Ding, 2012; O'Mahony et al., 2017) report on glycation of dairy proteins, by solid state or liquid heating processes, but none on dry heating whey proteins for other aims than protein glycation.

2.2. Conditions of dry heating and changes induced in the physicochemical properties of proteins

2.2.1. Glycation at low or medium temperatures ($T \leq 50$ °C)

According to Martins et al. (2000), an increasing reactivity between sugar and the nucleophilic amino groups is obtained at high temperature and in an alkaline environment, as the amino groups are deprotonated and so, more nucleophilic. Maillard reactions take place in solution or in solid state, provided a little moisture is present, typically 60–80% RH (Kato, 2002). The number of condensed sugars, the size of the polymers, the nature of the intermolecular protein bonds and the properties of the protein polymer-sugar conjugates depend on the nature of the sugar (Chobert, Gaudin, Dalgalarrondo, & Haertle, 2006). Many temperatures, adjusted pH, sugars, protein mixture and time of dry heating have been tested, as shown in Table 1 and we will describe in more details some of the physicochemical changes induced by these dry heating experiments in the following.

Heat treatment of βlg B in the dry state at 50 °C in the presence of 100 mol lactose/mol βlg leads to a family of conjugates with different numbers of bound lactose. The mean number of bound lactose is dramatically higher in the dry treatment than in the liquid treatment, even with higher lactose to βlg ratios or longer heating times (French et al., 2002; Morgan et al., 1998; Morgan et al., 1999; Morgan et al., 1999;

Table 1
Conditions of glycation at low or medium temperature (≤ 50 °C).

Temperature (°C)	Time	pH adjustment before the dry heating	Protein powder	Saccharide	Ratio saccharide/protein	RH (%)	References
50	2–48 h	7.0 & 7.2	βlg	Lactose	50 & 100 (mol/mol)	65	Morgan et al., 1998; Morgan et al., 1999; Morgan et al., 1999; Morgan, Léonil, Mollé, & Bouhallab, 1999
50	1–96 h	7.2	βlg	Lactose	100 (mol/mol)	65	French, Harper, Kleinholz, Jones, & Green-Church, 2002
50	51 & 96 h	7	βlg or αlac	Lactose & glucose	10 & 100 (mol/mol)	65	Medrano, Abirached, Panizzolo, Moyna, & Añón, 2009
50	0–10 d	7.5	βlg	Lactose & lactulose	1:1 (w/w)	65	Matsuda, Kato, & Nakamura, 1991
40 & 50	6 d	7	βlg	Galactose & tagatose	1:1 (w/w)	44	Corzo-Martínez, Moreno, Olano, & Villamiel, 2008
40	1–7 d	7.8	βlg	Xylobiose	1:1 (w/w)	30–40	Yajima, Onodera, Takeda, Kato, & Shiomi, 2007
40	23 d	7	βlg	Prebiotic galactooligosaccharide (GOS)	1:1 & 1:3 (w/w)	44	Luz Sanz, Corzo-Martínez, Rastall, Olano, & Moreno, 2007
50	3 d	8.0	βlg & αlac	Maltopentaose	0.3:1 & 0.5:1 (w/w)	65	Enomoto et al., 2007 & 2009
50	12–48 h	9.0	αlac	Allose, fructose & glucose	13:1 (mol/mol)	55	Sun, Hayakawa, Puangmanee, & Izumori, 2006
30–75	18 h-36 d	6–8	WPI, WPC & milk powder	Lactose	0.02:1–0.6:1 (w/w)	30–80	Boland, Hill, Higgs, Haggarty, & Campanella, 1999