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Impact of thermal treatment versus cold atmospheric plasma processing on the techno-functional protein properties from *Pisum sativum* 'Salamanca'

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ABSTRACT

This study aimed at evaluating the potential of cold atmospheric pressure plasma (CAPP) treatment for the functionalization of dry bulky and powdery food materials. CAPP treatment was capable of modifying protein and techno-functional properties of different flour fractions from grain pea (*Pisum sativum* 'Salamanca'). Experiments using a pea protein isolate indicated that the reason for the increase in water and fat binding capacities in protein rich pea flour to 113% and 116%, respectively, is based on plasma-induced modifications of the proteins as their solubility was increased to 191%. This is also supported by detected changes in tryptophan fluorescence spectra. With increasing treatment times the fluorescence emission intensity increased at 328 nm and decreased at 355 nm indicating structural and/or compositional changes of the proteins. The results indicate that the application of CAPP can be exploited as a means to modulate functionality of dry bulk materials in the food sector.

1. Introduction

Food engineering may also be described as the attempt to preserve, transform, create or destroy structures that have been imparted by nature or processing (Aguilera and Stanley, 1999). To fulfill the consumer demands, during the last century the food industry developed a multitude of products now available in the supermarket. Thereby, major advances in food engineering came from transfer and adaptation of knowledge from related fields such as chemical and mechanical engineering (Aguilera, 2005). In the past, the focus was largely at the processing or macroscopic level through the adaptation of unit operations and design of process equipment to transform and preserve foods. Further improvements on the quality of existing foods and the creation of new products to satisfy expanding consumer demands during this century will be based largely on interventions at the microscopic level, as the majority of elements that critically participate in transport properties, physical and rheological behavior, textural and sensorial traits of foods are below the 100 μm range (Aguilera, 2000). Among others, those microstructural elements substantially contributing to techno-functionality, food identity and quality are mainly fibers, small particulate material in powders, starch granules and protein assemblies (McClements, 2007). Particularly the tools and basic knowledge of food material science favors the change in scale of intervention and further shift the focus of the food industry from processes to products (Aguilera, 2005; Cussler and Wei, 2003).

Many food processing operations aim at modifying raw materials or intermediates in order to provide products with desirable traits and functional properties. For producing high quality consumables, intermediates and end products in powder or bulk form, efficient and high-performance processes are at least as important as the use of high-grade raw materials (Cuq et al., 2011). Surface modification using cold atmospheric pressure plasma (CAPP) is an effective and economical technique for many materials and of growing interests in food engineering, as it is quite difficult to design granular and powder products fulfilling both needs, adequate bulk properties followed by a special treatment to modify the surface properties (Chu et al., 2002; Förch et al., 2004; Höcker, 2002; Schröder et al., 2001). The surface-effects, such as plasma sputtering and etching, induced by applying CAPP to foodstuffs, may offer an innovative approach to enhance the surface and techno-functional properties selectively while the bulk attributes of the materials remain unchanged (Fricke et al., 2012, 2011; Schröder et al., 2001). Plasma gas is composed of highly excited atomic, molecular, ionic, and radical species and consists of a large number of reactive species such as electrons, positive and negative ions, free radicals, gas atoms, molecules in the ground

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or excited state, quanta of electromagnetic and UV radiation (photons) as well as visible light (Laroussi & Leipold, 2004). Plasma, the fourth state of matter, could be generated in a large range of temperature and pressure by means of coupling mechanical, thermal, nuclear radiant energy or carriers of an electric current to a gaseous medium (Conrads & Schmidt, 2000). Density and temperature of the electrons are altered depending on type of energy supply and amount of energy transferred to the working gas. High temperature plasma thereby implies that all species are in a thermal equilibrium state. Low temperature plasma is subdivided into thermal plasma (quasi-equilibrium plasma) being in local thermal equilibrium state and non-thermal plasma (non-equilibrium plasma) also called cold plasma (Schlüter et al., 2013). Low pressure glow discharge plasmas are of great interest in fundamental research but must be contained in costly air tight enclosures making them expensive and time consuming. Therefore, innovative plasma sources operating at atmospheric pressure by retaining the properties of low pressure media were developed (Kogelschatz, 2002,1999). Economic and operational advantages have led to the development of a variety of atmospheric plasma sources for several scientific and industrial applications. Thus, CAPPs have received a great deal of attention in the last two decades. CAPP may be obtained by a diversity of electrical discharges such as corona discharge, micro hollow cathode discharge, atmospheric pressure plasma jet, gliding arc discharge, dielectric barrier discharge or by radiofrequency (rf) and microwave. Due to its remarkable potential for being environment friendly and energy saving, its flexibility and capability for creating new products and its clear ecological advantages, enormous potential is attributed to the CAPP technology in a large number of diverse and unrelated fields in scientific and industrial areas.

It was shown, that the high-density of ionized and excited species in the plasma can change the surface properties of normally inert materials such as ceramics or glass (Jiang, 2005; Meyer-Plath et al., 2003; Taubert et al., 2013). In particular, modification of the surface energetics of the materials can improve the techno-functional bulk properties, as the flowability, compactibility, clumping, particle sphericity as well as the adhesion strength, surface and coating properties and could therefore contribute to improved handling, application and storage characteristics (Fitzpatrick and Ahrné, 2005; Spillmann et al., 2007; Watano et al., 2000). In recent years, the main objective of the plasma based research work is to ensure high microbial product safety and enzymatic stability by the application of CAPP under retaining the initial product quality (Fernández et al., 2013; Fröhling et al., 2012a; Hertwig et al.; Pankaj et al., 2013; Surowsky et al., 2013). Thus, CAPP also qualifies as a new discipline in food processing and has been considered as an emerging nonthermal technology for the improvement of food safety since it is capable of effectively inactivating a wide range of microorganisms including spores and viruses (Baier et al., 2014; Birmingham, 2004; Surowsky et al., 2014; Terrier et al., 2009). For this purpose, CAPP has been applied for the decontamination of raw agricultural products, egg surface and real food systems and is proved to have specific potential for treatment of foods (Schlüter et al., 2013). Furthermore, it was observed that, similar to the plasma application in material science, CAPP is capable of modifying wet and dry surfaces of agricultural and food stuff (Grzegorzewski et al., 2010; Khanal et al., 2014; Misra et al., 2015). Up to now, this unique feature is only used in the non-food sector. The technology transfer from those research fields and industrial branches to food science and technology may offer an innovative approach for the targeted modification and functionalization of powdery and bulky food surfaces.

Within the context of the protein crop strategy, emphasis is currently being placed on the sustainability, low cost and nutritional properties of plant-based proteins as an alternative to the established animal-based proteins that are currently in the market. Legumes, as peas, beans and lentils, historically been utilized mainly as whole seeds, constitute a promising alternative to the critically considered use of soy. However, in recent years, interest has grown in the utilization of legumes in other forms (e.g. like flour, concentrate, isolate) rather than the whole seeds (Doxastakis, 2000; Saio, 1993). Depending on the production process of alternative legume flour fractions their techno-functional properties are limited (Sun and Arntfield, 2010). For this purpose, a considerable amount of work has been accomplished in order to modify legume-based raw materials, intermediates and products while preserving their nutritional value.

Main objective of this study was to investigate the possible use of the CAPP technology for the modification of techno-functional properties and protein solubility of protein-rich, starch-rich, and fiber-rich fractions as well as of a protein isolate from grain pea (*Pisum sativum* 'Salamanca') and to contrast the obtained effects with those induced by a comparable thermal treatment.

2. Material and methods

2.1. Pea flour fractions

Grain peas (*P. sativum* 'Salamanca', Norddeutsche Pflanzenzucht, Hans Georg Lembke GmbH, Hohenlieth, Germany) with a crude protein content of 20% (Kjeldahl (§64 LFBG), $N = 6.25$) served as test material. Dry seeds were hulled using a shelling machine (F. H. SCHULE Mühlenbau GmbH, Reinbeck, Germany), finely ground and classified (CONDUX CSM 80 classifier mill, Erich Netsch GmbH, Hanau, Germany) into a protein-rich (PPF, crude protein content 48.3%, Kjeldahl (§64 LFBG), $N = 6.25$) and a starch-rich (PSF, crude protein content 15.3%) pea flour fraction characterized by a maximum particle size of 500 μm (MEZ, Prag, Czech Republic). Pea testa flour (PTF, crude protein content 2.8%, Kjeldahl (§64 LFBG), $N = 6.25$) was prepared using a centrifugal mill (Ultra Centrifugal Mill ZM 200, Retsch, Haan, Germany). Pea protein isolate (PPI) was recovered from PPF by extraction with distilled water (1:8 w/v) adjusted to pH 1.5 (concentrated hydrochloric acid) under stirring (300 rpm) at room temperature for 30 min. Extract was centrifuged (Megafuge 2.0 R, Heraeus Sepatech GmbH Dusseldorf, Germany) at 4000 g and 4 °C for 60 min. The clear supernatant was collected and proteins were precipitated by adjusting the pH to 4.5 (1 M sodium hydroxide solution). Following freeze drying (Christ Alpha 1–4 Gefriertrocknungsanlage, Christ Gefriertrocknungsanlagen Osterode, Germany) and grinding (Ultra Centrifugal Mill ZM 200, Retsch, Haan, Germany) of the precipitate, the PPI (crude protein content 81.2%, Kjeldahl (§64 LFBG), $N = 6.25$) was stored at −20 °C until CAPP treatment.

2.2. Cold atmospheric pressure plasma (CAPP) treatment

For semi-direct CAPP treatments of dry bulk materials, a surface dielectric-barrier air-discharge (SDBD) system similar to that described by Oehmigen et al. (2010) was used. The SDBD plasma source consists of an array of 7 concentric ring-shaped electrodes (85 mm outer diameter) embedded in a 1.5 mm thick epoxy-glass bulk material mounted into the upper shell of a petri dish (90 mm diameter). Plasma treatments were performed in a cylindrical reaction chamber (15 cm height and 10 cm inner diameter), which surrounds the sample holder mounted on a height adjustable rotary shaker (JD 20, JVM Antriebe, Jöst, Dülmen, Gernamy). The SDBD plasma source was screwed in the cover of the reaction chamber assuring a constant installation position during the entire tests. Further details regarding the plasma source set-up can be found elsewhere (Bußler et al., 2015). In order to

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