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Review

The use of sub-critical water hydrolysis for the recovery of peptides and free amino acids from food processing wastes. Review of sources and main parameters

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ABSTRACT

Food industry processing wastes are produced in enormous amounts every year, such wastes are usually disposed with the corresponding economical cost it implies, in the best scenario they can be used for pet food or composting. However new promising technologies and tools have been developed in the last years aimed at recovering valuable compounds from this type of materials. In particular, sub-critical water hydrolysis (SWH) has been revealed as an interesting way for recovering high added-value molecules, and its applications have been broadly referred in the bibliography. Special interest has been focused on recovering protein hydrolysates in form of peptides or amino acids, from both animal and vegetable wastes, by means of SWH. These recovered biomolecules have a capital importance in fields such as biotechnology research, nutraceuticals, and above all in food industry, where such products can be applied with very different objectives.

Present work reviews the current state of art of using sub-critical water hydrolysis for protein recovering from food industry wastes. Key parameters as reaction time, temperature, amino acid degradation and kinetic constants have been discussed. Besides, the characteristics of the raw material and the type of products that can be obtained depending on the substrate have been reviewed. Finally, the application of these hydrolysates based on their functional properties and antioxidant activity is described.

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1. Introduction

The world population has grown to more than seven billion in the last five years, to satisfy the growing food demand generated, developed countries have resorted to intensive livestock farming, intensive agriculture, industrial fishing, fish farming and other techniques which allow an increase in production and a decrease in cost. Furthermore, this increase in production has required an advancement in other areas such as the generation of new and better pest controls, improvements in animal feed and even the development of better transgenic techniques.

If only agricultural activity and food production is taken into account, large amounts of wastes are produced daily. A comprehensive classification of wastes and by-products generated, and the target compounds that can be recovered from them has been published recently (Mullen et al., 2015), the main sources of waste being agriculture, fish processing and farming exploitation. For example, when edible oil is extracted from seeds (soybean, rapeseed, cottonseed, sunflower and others), the by-products obtained are cakes and meals with a high protein content. These food wastes have been traditionally used as low added-value raw materials for the production of livestock feed, fertilizers or ethanol (Kolesárová et al., 2011). In the case of fish or shrimp processing, the amount of waste can be as high as 60% of the animal weight. After the fish fillets are obtained, the remaining 50–60% of the whole fish is discarded as by-product or waste (Torres et al., 2007); in the case of shrimps, about 30% the living weight of this crustacean is discarded as waste (Quitain et al., 2001). Livestock produces large amounts of highly polluting effluents that are rich in high quality protein such as blood or offal (Rendueles et al., 1997). Other kinds of protein-rich by-products generated on a large scale are hog hair, which constitutes up to 1% of total hog weight (Esteban et al., 2010); and the feathers produced during poultry processing (Zhu et al., 2010).

In the last decades, the application of sub-critical water properties to extract desirable compounds from plants, algae and animal by-products, has been revealed as a powerful tool. This is because it is cheap, doesn't require the use of reagents and it is also not a contaminant.

Sub-critical water (SW) is that which is maintained in liquid state at temperatures higher than boiling point because of the high pressure applied in the process. Water is considered to be sub-critical in the range from 100 °C at 0.10 MPa to 374 °C at 22 MPa (King, 2000). Physical-chemical properties of the water under these conditions change drastically. At ambient temperatures water shows a high capacity to dissolve and extract ionic and polar compounds. Nevertheless, when the temperature and pressure are set within the subcritical range, non-polar compounds can also be extracted (Go et al., 2014; Guo et al., 2014). This can be explained by alterations in its electrochemical properties, for example the dielectric constant decreases from 78 Fm^{-1} at 25 °C and 0.1 MPa to 14.07 Fm^{-1} at 350 °C and 20 MPa (Uematsu and Frank, 1980), which allows water to interact with non-polar substances, thus decreasing their binding force and dissolving them. Furthermore, the ionic product of water increases at high temperatures when compared to water at ambient temperature (from 10^{-14} to 10^{-12} in sub-critical conditions). This increment in the concentration of H^+ and OH^- in the aqueous medium raises the reactivity of water and, consequently, its activity as an acid- or base-like catalyst for hydrolysis reactions. When sub-critical water is applied under appropriate combination of temperature, pressure and reaction time, the organic matter can be hydrolyzed and subsequently the compounds contained inside can be released and extracted. One of the most hydrolyzed biopolymers by means of sub-critical water technology are proteins; which are released from the matrix and

broken down into valuable peptides and free amino acids that can be easily recovered by conventional techniques such as ultra-filtration or spray-drying. From an environmental point of view, recovering valuable compounds (such as peptides and amino acids) from food wastes leads to creation of more sustainable and environmental friendly processes as long as the amount of waste is reduced. Furthermore, the protein recovery helps to increase the harnessing of natural resources used as raw material in the food industry.

Other technique that has been studied in depth for the treatment of food wastes is the enzymatic hydrolysis (Guérard et al., 2001; Karam and Nicell, 1997). The main advantage of the enzymatic reaction is that it is possible to predict which peptides will be obtained, which allows the process to be standardized. Besides, the amount of salt employed to keep the pH constant is relatively low and no amino acid degradation take place. Furthermore, the production of free amino acids is low unless several enzymes are used in combination.

Other alternative methods for protein hydrolysis that could be considered are those based on chemical hydrolysis. Such methods employ high temperature along with highly concentrated acids or alkalis. However, chemical hydrolysis generates a high salt content in the final product after the neutralization step; moreover, controlling the peptide size of the final product is difficult, unless the final goal is to produce free amino acids, in which case a total hydrolysis can be achieved (Alvarez et al., 2012b). Besides, certain amino acids are completely destroyed in the process (Fountoulakis and Lahm, 1998). Finally, SWH does not require reagents and no salt is added to the final product; but it leads to amino acid degradation and the sequence of the peptides obtained cannot be predicted.

When comparing these techniques for protein hydrolysis from an economical point of view, the reagent price has to be considered, as well as the energy employed and the cost of equipment. Enzymes are by far the most expensive of all reagents employed for protein hydrolysis; besides, the pH and reaction temperature has to be carefully controlled. When chemical hydrolysis is carried out, the cost of reagent is very low, since commonly used reagents such as hydrochloric acid or sodium hydroxide are employed. The equipment required is practically the same as that employed in enzymatic reactions. Finally SWH does not require reagents, since compressed air can be used; but the process is carried out at high temperatures and high pressures, meaning that specific equipment has to be designed and the energy cost is the highest of the three methods. Energy consumption can be minimised by using well isolated reactors, coupling efficient heat exchangers and optimising the pressure, temperature and residence time of the process.

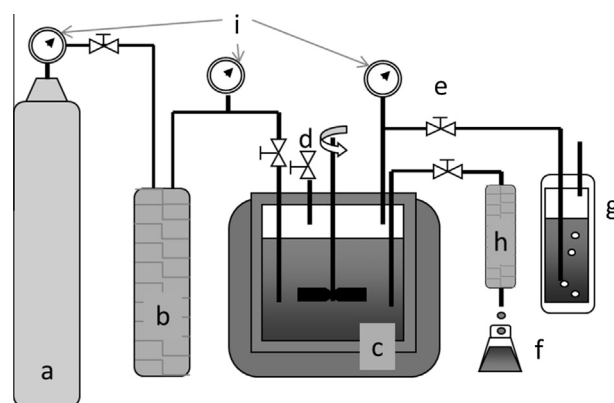


Fig. 1. Scheme of a common SWH reactor. a: Gas reservoir; b: heat exchanger, c: stirred reactor; d: safety valve; e: vent for exceeding gas; f: sample; g: exhaust bubbling; h: heat exchanger; and i: pressure gauges.

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