Enzymatic transformation of biomass: Valorization of rice bran oil and protein

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The valorization of rice bran, a by-product derived from the rice productive chain, has attracted the attention of the scientific community for the production of high added-value products, because of its great availability (around 700 million tons are produced per year). The composition of rice bran is 15-22% lipids, 34-52% carbohydrates, 7-11% fibers, 8-12% moisture and 10-16% highly nutritional proteins[1]. The fatty fraction of rice bran is rich in bioactive phytochemicals that have antioxidant and chemopreventive properties[2]. Also, the protein hydrolyzates of rice bran could be used as flavor enhancers; moreover, due to their highly nutritional value and according to some studies they have a therapeutic potential[2,3]. It is a challenge though to hydrolyze the rice bran and achieve the selective separation of its useful components. In this work, a combined process for the transformation of rice bran through enzymatic catalysis is studied.

1. Scope

The research here presented describes the preliminary results of the RiceRes Project (Fondazione Cariplo, call: Integrated Research on Industrial Biotechnologies, 2014-0558) whose aim is to upgrade all the residues and wastes of the rice productive chain by developing a rice-waste based biorefinery model.

Rice is the staple food for over half the world's population. As a consequence, rice milling gives rise to a massive amount of wastes, namely rice bran (ca. 70 kg/ton of rice) and rice husks (200 kg/ton of rice). Although rice bran is a rich source of highly nutritional proteins (10-16%), lipids (15-22%), carbohydrates (34-52%), and a number of micronutrients (*e.g.* vitamins, minerals, antioxidants, and phytosterols), it is currently underutilized[2].

Specific aim of this work is to exploit the protein and the oil fraction of rice bran by using a biotechnological approach to obtain high-added value products.

2. Results and discussion

Rice protein, ca. 7% by weight, is relatively low in comparison to that of other cereals. However, considering the worldwide annual production (over 700 million tons per year, *i.e.* 25% of total cereal products), the amount of potentially available protein is considerable[4]. This protein is not uniformly distributed in the grain but is mostly found in the bran fraction, which contains from 12 to 15% protein. Rice bran proteins (RBP) have excellent quality: they have a high nutritional value and optimal digestibility and are rich in essential amino acids; last but not least, they are gluten-free and hypoallergenic.

However, numerous factors such as structural complexity, poor solubility, strong aggregation as well as the difficulty of separation from the other components of the vegetable material make RBP hardly available, consequently limiting a possible industrial application.

To solubilize RBP and to enhance the extractability of the entrapped protein components, we developed a biocatalyzed process based on the use of proteases also in combination with carbohydrate-hydrolyzing enzymes. Proteases (such as Alcalase, Flavorzyme, etc.) allowed converting the protein fraction of rice bran into mixtures of more water-soluble peptides. On the other hand, carbohydrases, that catalyze the hydrolysis of the glycosidic linkages of rice bran polysaccharides, increased the solubility of the protein fraction.

A number of commercially available products namely Ceremix, Viscozyme, Ultraflow, Celluclast were used. These mixtures contain several carbohydrases such as cellulase, xylanase, hemicellulose, alpha-amylase, etc. The reactions were carried out in a glass reactor for 4 hours under the conditions of temperature and pH suggested by the suppliers for each biocatalyst. Results are reported in Figure 1.

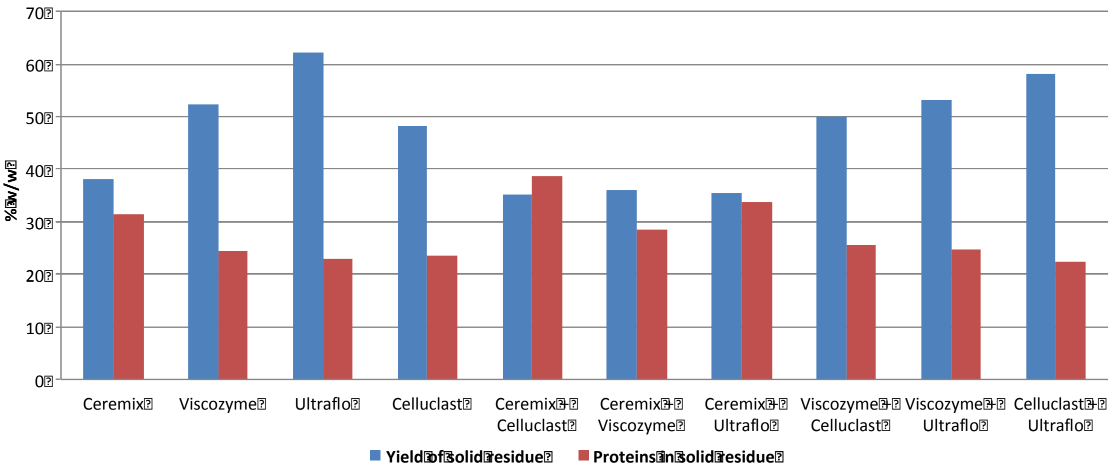

Figure 1. Yield of the solid residue and percentage of the proteins remained in the solid residue by using different enzyme combinations.

Rice bran oil (RBO) represents one of the most underutilized agricultural commodities in the world. Furthermore, its abundance of potentially health-promoting constituents makes RBO one of the most healthful vegetable oil. Nevertheless, immediately after the milling process, a rapid deterioration of the oil occurs as a consequence of endogenous lipase activity. Thus, RBO is characterized by a high free fatty acids (FFA) content that makes it unsuitable for human consumption. Only a limited amount of RBO (<10%) is currently processed into edible oil. For the same reason, RBO is also unsuitable for biodiesel production by transesterification. As a result, the utilization of rice bran is nowadays limited to animal feed.

A significant number of high-value products (*e.g.* surfactants, lubricants, coatings) require FFA in their manufacturing[5,6]. We have here investigated the use of RBO as a valuable feedstock for the production of chemicals. To this aim, RBO was submitted to a preparative lipase-catalyzed hydrolysis in *tert*-butanol/water at r.t. to obtain pure FFA. Upon purification by chromatography[7], FFA were obtained in a good yield (ca. 65%, 10 g scale).

3. Conclusions

It has been shown that by using an integrated biotechnological approach it is feasible to upgrade the by-products of the rice productive chain, such as rice bran, into novel bio-products (peptides as potential flavor enhancers, antioxidants, antimicrobial agents), or to transforming them through convenient bioprocesses.

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