



Towards a more sustainable circular bioeconomy. Innovative approaches to rice residue valorization: The RiceRes case study

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ABSTRACT

The paper reports an overview of the RiceRes project aiming at the multivalorization of all the wastes of the rice value chain, namely straw, husk and bran in order to improve resources eco-efficiency.

A wide range of bio-products and bio-materials with different added value has been produced starting from these wastes in the framework of the RiceRes project. Among them, insulating materials for green building have been obtained from rice straw mixed with waste wool, biofillers from husk for polymer composites, mono- and di-glyceride mixtures and high-added value molecules for the food industry from bran.

1. Introduction

In recent years, interest in the concept of a circular economy (CE) that maximizes efficient use of resources and minimizes waste has expanded rapidly. Still, a report by the enterprise Circular Economy shows that the global economy is only 9% circular, which leaves ample room for future growth and innovative new approaches (de Wit et al., 2019). For such wastes to be efficiently valorized, biorefineries must be capable of producing not only high-volume, low-added value, but also low-volume, high-added value bio-products. Here we describe how biomass waste from rice production can be strategically valorized, and how biorefineries offering a portfolio of bio-products and renewable energy may target specific markets and reach new consumers.

For every ton of rice produced, about 1.35 tons of straw are produced (Blengini and Busto, 2009) along with 0.20 tons of rice husk and 0.07 tons of rice bran (Tuck et al., 2012) (Fig. 1).

The hollow stem of the rice plant is called "straw" and is considered a biomass waste by-product of rice production. Straw is composed of cellulose, lignin, waxes, minerals and silicates. In the past, it was used for stuffing animals, and as litter in stables. Today, other more resistant and better performing materials have replaced rice straw for these

purposes, thus reducing it to a biomass waste.

These wastes must be handled carefully due to potentially serious environmental and health implications, which include greenhouse gas emissions and release of particulate matter known to cause respiratory irritation and obstruct visibility on roads (Junpen et al., 2018; Sanchis et al., 2014). Open field burning of rice straw (RS) releases as much as 13 tons of CO₂ per hectare along with other harmful gases and particulate matter. If RS is instead tilled back into the paddy, anoxic conditions after flooding lead to high emissions of methane which contributes to field emissions carrying 68% of the total global warming potential of rice production (Blengini and Busto, 2009; Gadde et al., 2009).

We thus proposed an alternative solution for valorization of RS that allows the creation of bio-composites utilizing waste wool, as a non-chemical binding agent. During processing, rice husk and rice bran are removed from the grain. While some energy can be recovered from incinerating the husk, much more value can be gained by using this material to produce an array of bio-products. A variety of biofillers were produced as a result of rice biomass valorization by using different components of rice husk (RH) and different treatments as well. The fillers obtained from RH were then compounded with thermoplastic

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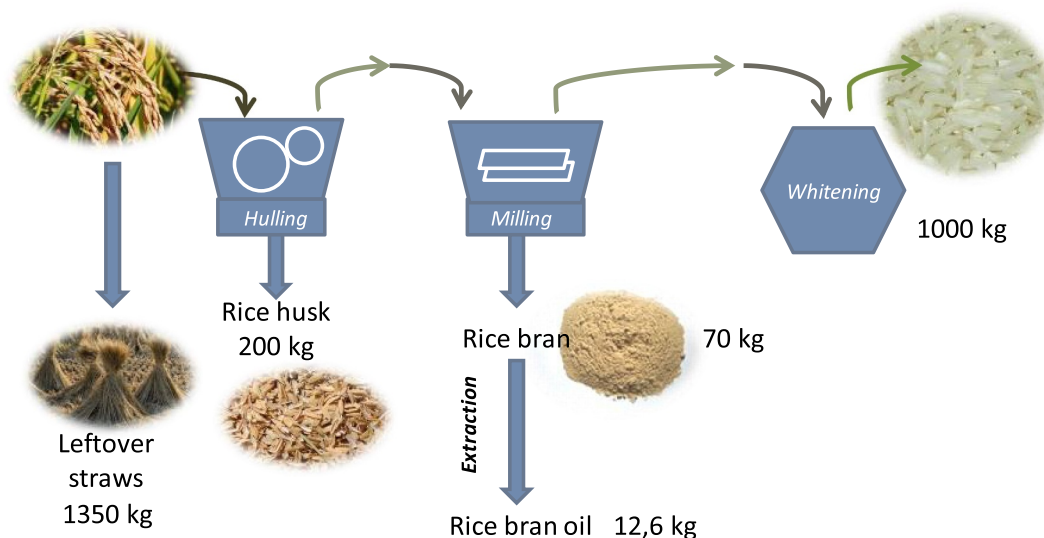


Fig. 1. Wastes produced along the rice value chain.

biopolymers to produce novel polymer biocomposites with enhanced performance (Bertini et al., 2012; Canetti et al., 2016).

Rice bran (RB), which is produced in large amounts during white rice processing, has been mostly exploited in animal feed and in various human health applications (Friedman, 2013). RB contains about 20% oil, that on a global scale would give around 6 million tons of Rice Bran Oil (RBO) per year, but few countries take advantage of RB as a potential source of food grade vegetable oil, in particular India, exploiting about 66% of RB produced (Gopala Krishna, 2013). As with most cereals, there are endogenous microbial lipases in rice which start to degrade oil within hours of extraction. This leads to a highly acidic product that is not suitable for human or animal consumption. Moreover, high variability of free fatty acid (FFA) content (ranging from 40 to 80%) hampers its valorization to high-value chemicals through traditional methods of esterification and transesterification (Zaccheria et al., 2015). However, by exploiting high FFA content, our project proposed two novel value-adding processes. On one hand, RBO can be transformed into monoglycerides, which are routinely used as additives in food and cosmetic formulations. On the other hand, RBO can be also converted into high purity FFA that may be used as feedstock for the production of FFA-derived chemicals (Biermann et al., 2011). Moreover, the oil also contains valuable sterols that can be used as precursors of nutraceutical compounds. Oil extraction leaves a residue rich in sugars and protein that can be extracted and valorized as well.

A multidisciplinary approach was adopted in order to exploit the oil, phytosterols, carbohydrates and protein fraction in the bran, whereas husk and straw were used in the formulation of different building materials. This plan required a panoply of different expertise including vegetable oils chemistry, organic synthesis, heterogeneous and enzymatic catalysis, natural products chemistry, composite formulation, and mechanical properties evaluation of the materials produced. The RiceRes project introduces not only novel uses for extracted chemicals, but also environmentally friendly methods for performing these extractions.

Moreover, the valorization process of rice straw proposed has the added benefit of exploiting two other biomass waste products: wool wastes from sheep breeding and technical hemp. The primary role of EU sheep farming is meat and milk production and animals selected for these purposes usually produce coarse, low-quality wool which is usually disposed of. Annual shearing, which is necessary for the well-being of the animal, produces 1.5–3 kg of coarse wool per animal (that is >200 thousand tons in EU of which 18–20 thousand tons in Italy).

In addition, technical hemp is the by-product of hemp plants

cultivation for seeds and oil production; the plant which has reached ripening produces seeds, useful for nutraceutical purposes, but at the same time increases its lignin content, thus resulting in highly lignified and low-quality hemp fibers (technical hemp).

Here we report the results of “RiceRes: From waste to resource: an integrated valorization of the rice productive chain residues”, a project funded by the Cariplo Foundation (Italy) with the aim to upgrade all the residues and wastes of the rice productive chain by transforming them into a portfolio of bio-products with different added value. The project was planned therefore not only to boost the concept of circular- and bio-economy, but also to support rice farmers in Northern Italy by adding profit to the rice production chain.

2. Materials and methods

All experimental procedures are reported in the Supporting information.

3. Results and discussion

3.1. Valorization of rice straw

Waste wool and straw were thoroughly mixed and treated with a sodium hydroxide solution. The alkaline treatment swells the wool fibers and partially destroys their morphological structure, causing the release of keratin (the wool protein) in the form of a viscous adhesive matrix. The resulting blend of partially destroyed fiber, hydrolysed proteins and rice straw is then molded in the desired shape. With respect to RS, soda treatment has the effect of swelling cellulose, thus increasing hydrophilicity and water adsorption. Alkaline treatment of both the materials allows formation of a bio-composite in which the wool acts as a protein matrix responsible for cohesion between the fibers while RS constitutes the reinforcing fiber (Bianchetto Songia et al., 2012). The resulting composite material is dried in a stove inside a mold.

These reinforced panels are also self-supporting, and the value of thermal conductivity is $(\lambda) \approx 0.043 \text{ W/m K}$, which is slightly higher than that of polystyrene $(\lambda) \approx 0.03 \text{ W/m K}$.

The rice straw lends itself well as a building material as it has a high thermal insulation and sound absorbing power, is a renewable, eco-compatible and biodegradable resource, has a high breathability, and can be used in anti-seismic structures. A fundamental aspect to be considered is that the adhesion between the fibers is obtained without

the use of any artificial or synthetic binder. Furthermore, the alkaline treatment transforms the cysteine amino-acid present in wool proteins in huge amount into lanthionine which is no longer digestible by moths; thus, tarmicidal treatment is not required, unlike with wool mats currently used for insulation purposes. In addition, the panels exhibit excellent fire-retardant and sound-absorbing behavior. Flame retardant tests have been carried out according to the EN ISO 15025:2003 standard. The result evidenced that the material has flame retardant properties and does not ignite even after 180 s flame contact (class 1). Acoustic performances have been measured according to the EN ISO 10534-2:2001. Bio-composites show good acoustic performances in particular for high frequencies.

As far as the strength of these composites is concerned, a breaking load of 211.8 N/cm² and an elongation break of 1% were measured for the panel containing 25% of total fibers weight. Furthermore, at the end of their life they can be shredded and allowed to naturally biodegrade.

This type of bio-composite has many advantages. As shown by previous studies (Kim et al., 2014) wool composites show good fire resistance, a critical property of building materials. Composites from natural materials also have the advantage of reduced health risks associated with handling (laying and removing) and with the entire life cycle. Additionally, it has been demonstrated that thermal conductivity of a pure wool insulation or a wool-hemp blend of similar density does not differ significantly (Ye et al., 2006).

Furthermore, wool is able to absorb VOCs (Volatile Organic Compounds) such as formaldehyde (Aluigi et al., 2009). This may contribute to lower the Sick Building Syndrome due to low concentration of formaldehyde and other VOCs released from furniture and paintings in new and restored buildings.

Since the amount of waste wool would not be sufficient to meet all of the demand for building insulation, the ability to extend its utility with combined use of widely available agricultural residues without sacrificing quality is a welcome development. This also addresses the need to dispose plant biomass in an economic and environmentally sound way. The incorporation of rice straw into such composites is a feasible disposal method.

The aforementioned hemp-wool-straw composites are also a potential solution to improving the nutrient cycle within rice cultivation. As mentioned, the used insulation materials can be ground into small pieces and left to decompose naturally after use. If this ground material was then incorporated into the soil, it might then serve as amendment fertilizer. Wool has been shown to act as a slow release fertilizer and to increase the protein and nutrient content of various crops. In fact, wool waste may provide nitrogen, phosphorous, potassium, and sulfur for multiple growing seasons from a single application (Zheljazzkov et al., 2008). As the flow of rice straw off the field would presumably be more frequent than the flow of discarded composites onto the field, this delayed decomposition could prove to be advantageous.

3.2. Valorization of rice husk

The variety of methods available for preparation of husk biofillers (Fig. 2) and their incorporation into composites is a unique and important aspect of RiceRes project.

In fact, ball-milled rice husk was successfully used for preparing polymer-matrix composites for food packaging (Bertini et al. unpublished results). Lignin was mixed with thermoplastic biopolymers, i.e. polylactic acid and poly(3-hydroxybutyrate), attaining innovative polymer matrix biocomposites (Bertini et al., 2012; Canetti et al., 2016). Bio-silica from rice husk is industrially used in the manufacturing of fuel-saving tires (Eksambekar, 2013).

Here we describe the use of rice husk ash (RHA) mixed with polypropylene and show the results relating to the characterization of polypropylene-RHA composites prepared by melt compounding. The mixing temperature was opportunely set at 190 °C to promote the best working of the maleic anhydride grafted polypropylene. Pure processed

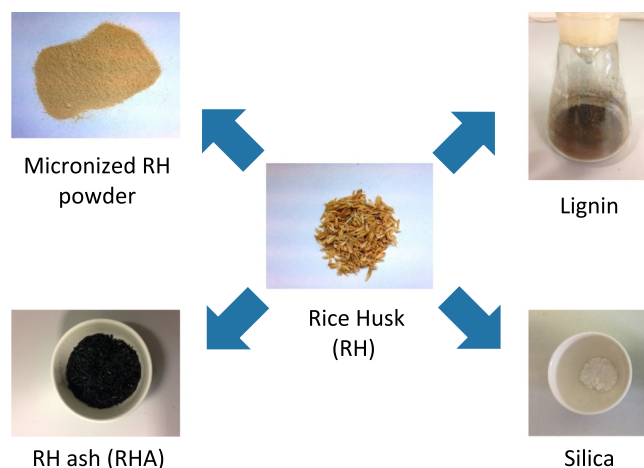


Fig. 2. Biofillers obtained from rice husk.

polypropylene matrix (gPP) shows lower average molecular weight (M_w) than the virgin unprocessed matrix (about 10%), indicating that the adopted mixing conditions induce slight thermo-mechanical degradation of the polymer chains due to the stress exerted during the melt processing. Otherwise, all the composites show M_w and molecular weight distribution (M_w/M_n) values similar to those of the unprocessed polypropylene. The presence of RHA seems to preserve the thermo-mechanical degradation of polymer matrix during melt processing.

As it is well known, the addition of fillers may influence the crystallization and melting behavior of the polymer matrix, thus affecting the ultimate properties of the materials. The effect of RHA on the thermal properties of gPP-based composites was first investigated by differential scanning calorimetry (DSC) scans carried out in dynamic conditions. The values of crystallization temperature (T_c), melting temperature (T_m) and melting enthalpy (ΔH_m) are reported in Table 1.

The gPP-RHA composites show higher T_c compared to gPP polymer matrix; moreover, by increasing the RHA loading, the corresponding T_c continues to enhance suggesting a nucleating effect of the filler. Moreover, all composites present a similar melting endotherm with T_m at around 163 °C, which is the characteristic melting point of isotactic polypropylene.

The crystallization behavior was studied under isothermal conditions at different temperatures in the range 126–135 °C. A progressive increase of the rate of crystallization is observed with an increasing amount of filler in the gPP-RHA composites. The half-time of crystallization ($t_{0.5}$) defined as the time required to reach 50% of the complete crystallization, was calculated and the results obtained at 130 °C are reported in Table 1. All gPP-RHA composites exhibit smaller $t_{0.5}$ than the polymer matrix and a progressive reduction of the semi-crystallization time is observed with the increase of biofiller content. The significant enhancement in the polypropylene crystallization rate can be ascribed to the nucleant role played by the RHA biofiller. The isothermal crystallization kinetics was described by the Avrami equation, which permits to evaluate the overall crystallization rate constant (K_n) and the Avrami index (n). An Avrami index around 3, indicating a three-dimensional growth of crystalline units, developed by heterogeneous nucleation, is calculated for all composite compositions in the entire crystallization temperature range. The crystallization rate parameter is influenced by the presence of biofiller, and K_n value increases with enhancing the RHA content in the composite. A similar effect ascribed to the interactions between biofiller and thermoplastic polymer matrix was previously reported for lignin- and keratin-based composites (Bertini et al., 2013; Canetti and Bertini, 2007).

The effect of the RHA on the thermal stability and degradation of the composites was studied by means of thermogravimetric analysis (TGA) carried out under both inert and oxidative atmosphere. Table 1

Table 1
Thermal properties for gPP and gPP-RHA composites.

Sample	T_c^a (°C)	T_m^a (°C)	ΔH_m^a (J/g)	$t_{0.5}^b$ (min)	$T_{5\%}^c$ (°C)	T_{max}^c (°C)	$T_{5\%}^d$ (°C)	T_{max}^d (°C)
gPP	110	162	101	11.4	407	464	272	365
gPP-RHA5	112	163	92	4.4	418	468	278	368
gPP-RHA10	115	163	89	2.7	425	470	280	373
gPP-RHA20	117	163	80	1.8	427	472	287	387

^a Obtained by DSC in dynamic scan at 20 °C/min.

^b Obtained by isothermal crystallization at 130 °C.

^c Determined by TGA under nitrogen atmosphere.

^d Determined by TGA under air atmosphere.

summarizes the TGA experimental data including the temperature at which the initial 5% mass loss occurs ($T_{5\%}$) and the temperature of maximum rate of mass loss (T_{max}). In general, the composites showed an enhancement of the thermal stability, being the degradation process shifted to higher temperatures. The $T_{5\%}$ and T_{max} value of the gPP-RHA composites enhance progressively with the increase of the RHA content and a T_{max} improvement of 22 °C is obtained for the composite with 20% RHA compared to reference gPP sample under oxidative atmosphere. The RHA present in the composite is able to produce a char yield that is responsible to the increase of the composite temperature degradation. The increase is more pronounced for the runs carried out under air atmosphere; in fact, the char is a carbon-based residue that undergoes slow oxidative degradation. The char acts as a barrier to heat and mass transfer, hindering the diffusion of the oxygen from the gas phase to the polymer matrix and, at the same time, the out-diffusion of the volatile decomposition products. The capability to form char during the thermal degradation is a basic aspect of intumescent flame retardant systems and some bio-based compounds coming from renewable resources (lignin, starch, cellulose) were evaluated as char formers in intumescent formulations (Réti et al., 2008).

Finally, the combustion properties of RHA-based composites were evaluated by means of pyrolysis combustion flow calorimetry (PCFC), a small-scale technique developed in recent years, based on the principle of oxygen consumption. The addition of RHA into the polymer matrix is of benefit to reducing the combustion parameters obtained by PCFC, i.e. total heat released (THR), heat release capacity (HRC), and peak heat release rate (PHRR), for all investigated composites (Table 2).

According to each individual component and their relative proportion, the theoretical value of the combustion parameters for the composites can be calculated assuming that there is no effect of interaction between the components on the combustion behavior of material. The experimental combustion parameters for the composites were always lower than the theoretical ones, thus pointing out the positive interaction between RHA and polymer matrix on these combustion parameters. In addition, the presence of the biofiller affects the temperature at PHRR (T_p) that enhances with increasing the RHA content (Table 2). These data are in complete agreement with T_{max} values obtained by the TGA experiments (see Table 1).

Table 2
Combustion parameters for gPP and gPP-RHA composites.

Sample	THR (kJ/g)		HRC (J/g K)		PHRR (W/g)		T_p (°C)
	Exp ^a	Theor ^b	Exp ^a	Theor ^b	Exp ^a	Theor ^b	
gPP	44.0 ± 0.8	–	1176 ± 17	–	1167 ± 15	–	486 ± 1
gPP-RHA5	40.8 ± 0.8	41.9	1109 ± 15	1129	1103 ± 14	1109	487 ± 1
gPP-RHA10	37.9 ± 0.4	39.7	1027 ± 11	1070	1019 ± 9	1050	488 ± 1
gPP-RHA20	33.2 ± 1.2	35.4	886 ± 42	952	881 ± 41	934	490 ± 1

^a Experimental value.

^b Theoretical value calculated according to each individual component and their relative proportion.

3.3. Valorization of rice bran oil

As previously mentioned, the amount of free fatty acids in RBO can be very high due to the presence of an endogenous lipase in bran. This makes it unsuitable not only as raw material for oleochemistry but also as a power generator's feedstock.

However, within the RiceRes project, a method was developed to convert RBO with a FFA content up to 84% into a mono- and diglyceride mixture, widely used as emulsifiers in food with the E471 code (Fig. 3).

This mixture was obtained carrying out a one-step esterification + transesterification reaction over an amorphous solid acid. Yields are higher than those obtained by enzymatic transesterification of oil (triglyceride, TG) with glycerol, and competitive with the esterification of FFA using homogeneous acids such as methansulfonic acid, that generates significant amounts of wastewaters as a by-product. Esterification with higher amount of glycerol, a low value by-product of the biodiesel industry, gave an oil with low acidity suitable to feed power generators (Zaccheria et al., 2015).

On the other hand, a significant number of high-value products (e.g. surfactants, lubricants, coatings) require FFA in their manufacturing (Biermann et al., 2011). We have thus investigated the use of RBO as a valuable feedstock for the production of FFA-derived chemicals. To this aim, RBO was submitted to a preparative lipase-catalyzed hydrolysis to obtain pure FFA. Upon an enzymatic screening, the lipase from *Candida rugosa* (CRL) was selected as the biocatalyst and it was immobilized on a solid support for ease of handling, stability and re-usability. The poor yield (5%) achieved in the covalent immobilization of CRL on Eupergit® C, an epoxy-acrylic carrier, versus the yield resulting from hydrophobic adsorption of the enzyme on Octyl-Sepharose® CL-4B (45%), was balanced by the higher stability of the former biocatalyst under the reaction conditions that required a co-solvent to solubilize RBO. Specifically, the biotransformations were run either in a homogeneous (*tert*-butanol/water) (Torres-Salas et al., 2014), or in a biphasic system (phosphate buffer/iso-octane) at room temperature. Under both conditions, CRL hydrolyzed RBO into FFA in a high conversion (85–96%). Upon process scale-up (10 g scale) and product purification by flash chromatography, good FFA yields (65–70%) were obtained. FFA so obtained can be used as starting material for the esterification reaction with RB sterols into potentially active biomolecules. The high acidity of

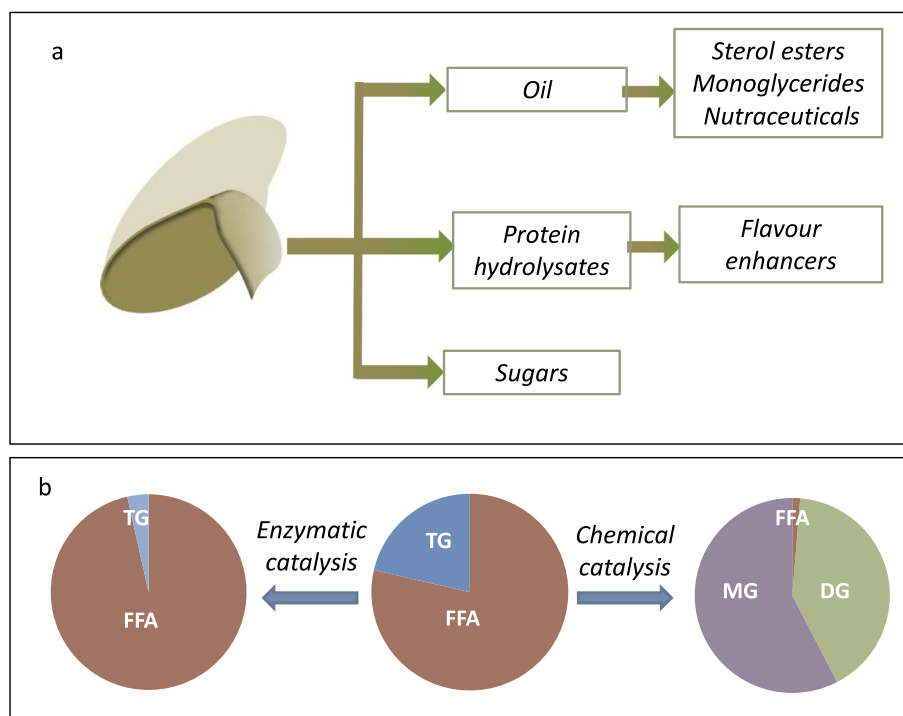


Fig. 3. (a) Valorization of rice bran; (b) transformation of acidic oil under different catalytic treatments.

RBO, so far considered as a bottleneck in the exploitation of RBO, has been here turned into an advantage, that is making available FFA mixtures as valuable synthetic precursors.

Furthermore, the oil also contains γ -orizanol, a mixture of ferulic acid esters of phytosterols. These sterols can be easily obtained from γ -orizanol and esterified with fatty acids, such as stearic or oleic acid to obtain more lipophilic compounds that have shown to have health benefits by lowering plasma low-density lipoprotein (LDL) cholesterol.

The reaction can be easily carried out in the presence of solid acids such as a mixed $\text{SiO}_2\text{-ZrO}_2$ or $\text{SiO}_2\text{-Al}_2\text{O}_3$ oxides. The ester of stearic acid with 5- α -cholestanol can be obtained in 92% yield by reacting a stoichiometric amount of the reagents at 180 °C for 12 h over a $\text{SiO}_2\text{-ZrO}_2$ catalyst using a gentle flow of N_2 to remove the water formed during the esterification. The reaction does not involve the use of a solvent and produces no waste as the catalyst can be separated and re-used.

It is worth underlining the impact of this transformation in the context of green chemistry. Among the different metrics that have been proposed so far, Reaction Mass Efficiency (RME) was used to assess the “greenness” of the esterification reaction carried out by using a $\text{SiO}_2\text{-ZrO}_2$ catalyst in a solvent-free system. RME is, in fact, a simple, objective, and easily derived metric that better captures the materials used during a chemical transformation (Constable et al., 2002). This parameter is defined as “the percentage of the mass of the reactants that remain in the product” and takes into account atom economy, yield and stoichiometry of reactants. In other words, the higher is the RME, the lower is the environmental impact of a transformation. The RME calculated for the new synthesis with $\text{SiO}_2\text{-ZrO}_2$ was 89.4%. This value is slightly higher than that associated to the synthesis patented by Higgins III (1999) which accounts for an RME of 85.2% and involves the use of fatty acid in excess and catalytic amounts of NaHSO_4 . It should be noted that the RME for a typical synthesis of an oleic acid ester (Vogel et al., 1989) is 41.5%, thus showing a poor utilization of the reactants (that is, the mass of the reactants that remain in the product is almost half of that found in the first two syntheses).

Preliminary tests on the esterification of rice bran FFA with hydrolyzed γ -oryzanol gave a 84% yield in 12 h.

Finally, new multifunctional conjugates were designed and synthesized by linking the steroidal framework of natural occurring γ -oryzanol and γ -oryzanol-derived phytosterols to a wide range of bioactive natural compounds such as fatty acids, phenolic acids, amino acids, lipoic acid, retinoic acid, curcumin, and resveratrol to verify if this conjugation strategy might enhance some γ -oryzanol bioactivities. The antioxidant activity, the in vitro antiproliferative activity on three different human cancer cellular lines and the potential hypocholesterolemic effect were studied. It was found, in particular, that 2 out of 15 derivatives displayed an improved antioxidant activity with respect to that of γ -oryzanol, while 3 out of 15 were found to inhibit tumor cell proliferation (Lesma et al., 2018).

3.4. Valorization of rice bran proteins

Rice bran (RB) also contains a significant amount of protein (RBP), about 10–15%, that has been recognized to be nutritionally superior to other proteins for human consumption, especially due to its reported hypoallergenicity (Sharif et al., 2014). However, numerous factors, such as RB structural complexity, poor solubility, strong aggregation as well as difficulty of separation from other components of vegetable material are severe limiting factors in the use of RBP as food ingredients. To date, suitable RBP processing technologies to prepare RB isolates, concentrates, and hydrolysates at an industrial scale are still lacking (Orio et al., 2017; Liu et al., 2019).

With the aim of setting-up reliable and efficient methods for exploitation of RB proteins as well as of RB carbohydrates, representing in turn up to ca. 50% of this waste (Sharif et al., 2014; Sutanto et al., 2017), defatted rice bran (DRB) was submitted to extraction by chemical and/or enzymatic methods. Specifically, treatment of RB with hot water (85 °C for 24 h) allowed the solubilization of about 30% of the starting material. Nuclear magnetic resonance (NMR) and mass spectrometry (MS) analysis indicated that the aqueous extract, after precipitation of complex-carbohydrates with 2-propanol, is essentially composed only by saccharose (ca. 10% the whole starting material) and ca. 13% of proteins. The protein content could be increased up to ca. 30% (starting from 17%) by treatment with commercially available

carbohydrases (Viscozyme®) that catalyze the hydrolysis of the glycosidic bonds of rice bran polysaccharides, thus enhancing the extractability of the entrapped protein components. The protein-enriched residue (RBP) was submitted to enzymatic proteolysis followed by ultrafiltration and the taste-enhancing properties of the resulting RBP hydrolysates were characterized.

As an alternative approach to carbohydrase-aided protein extraction, DRB was treated with a 1:1 mixture of α -amylase and amyloglucosidase in order to release starch-bound proteins by hydrolysis of starch contained in commercial samples of RB. The obtained extract (ca. 40% w/w) was found to be very rich in glucose, as clearly indicated by the ^1H NMR spectrum, but very poor in proteins (only 5.6%). On the other hand, such a treatment improved the extractability of unbound proteins. In fact, re-solubilization of the de-starched solid residue with hot water led to an extract containing ca. 31% of proteins. Composition of water-soluble polysaccharides of this extract was investigated by submitting it to chemical hydrolysis with 2 M trifluoroacetic acid. Thin layer chromatography (TLC) and NMR analysis of the hydrolyzed sample revealed the presence of four monosaccharides: arabinose, glucose, xylose and galactose in order of abundance.

3.4.1. Sensory characteristics of RBP hydrolysates

Two proteases (Flavourzyme® and/or Alcalase®) were used to produce hydrolysates which were separated by membrane ultrafiltration. Two of the fractions with peptide sizes <5 kDa, i.e. F and AF, prepared by using both Flavourzyme® and a combination of Alcalase® and Flavourzyme®, were submitted to sensory analysis by trained panelists that described umami and sweet as the only taste attributes for both samples (see Fig. 4). It is known that vegetable protein hydrolysates (HVP) may contain unfavorable flavour components, in particular bitter-tasting amino acids/peptides, that limit their utilization as food ingredients. The complete absence of bitterness in the taste profiles of both Flavourzyme®-treated (F) and Alcalase®/Flavourzyme®-treated (AF) RBP (Fig. 4), make RB an economical and easily accessible raw material for the preparation of value-added products including HVP (Hydrolysed Vegetable Proteins) with flavour enhancing properties (Bagnasco et al., 2013).

3.5. Further research

Creating a sustainable biorefinery will depend heavily on balancing the material flows (Venkata Mohan et al., 2016). With the creation of different bio-products, we also create different use phases and product lifespans. Therefore, it is important to consider where the various fractions of initial biomass are ending up, and when. It has been discussed that products actually should not be made to last the maximum time possible as this would stop the natural flow of materials, inhibit innovation, and likely involve intense chemical modification of substances. Thus, it is worth noting that the various products created in this project are designed to function well, but also to eventually degrade in a predictable way. This ensures that biological nutrient flow continues, and that circularity is preserved. However, some materials will obviously take longer to enter back into the production cycle than others. For example, while a food product will likely be consumed within a year of production, a composite used for green building will likely take a decade or several decades to complete its use phase. Meanwhile, the flow of rice residues should be relatively consistent each year. Therefore, a successful rice biorefinery should utilize straw in several different ways, always with the option of incineration for energy being available as a final resort. As energy recovery from lignocellulosic materials has shown to be more efficient with the aid of biological fermentation (Kumar et al., 2009), the possibility of including a biogas digester should also be considered.

Within the CE scheme, smaller loops should be established over wider loops when possible. For example, re-using waste within a factory would be favorable to moving the waste to a different location to be

utilized. While rice bran and rice husk are generated only after the rice has been removed from the farm, rice straw is left over on the field. Therefore, when farms are already treating straw in a way that allows it to be used as fertilizer, moving the straw to a separate biorefinery would not be favorable. This presents one of the main risks to sustainability in the RiceRes project as well as many CE projects in general. Because of the economic drive of such projects, it can become more profitable to make less environmentally sustainable choices. This is where policy and regulation become exceedingly important in the implementation of the CE. For the farmer who has the space and capability to process some or all of the straw generated by his own crop, the increased profit from selling the straw to a biorefinery could lead to a reliance on mineral fertilizer sources. This would mean increased impact from transporting straw off-site, producing mineral fertilizers, and transporting those fertilizers on-site. Each of these activities would of course make the final product one with a higher overall environmental impact.

4. Conclusions

A biorefinery based on residues and waste from the rice production chain (bran, husk, straw) represents an opportunity both to minimize waste production and to upgrade those components, which are associated with a disposal cost.

Overall the importance of the RiceRes project is represented by the network it engaged which, thanks to a combination of complementary levels of expertise, consistent interaction and effective communication, was able to lay the groundwork for the creation of a biorefinery model that brings innovation to the rice production chain according to the principles of the Circular Economy.

Credit author statement

Emily Overturf: Writing - Original Draft Preparation, creation and/or presentation of the published work, specifically writing the initial draft

Nicoletta Ravasio: Supervision Oversight and leadership responsibility for the research activity planning and execution, including mentorship external to the core team

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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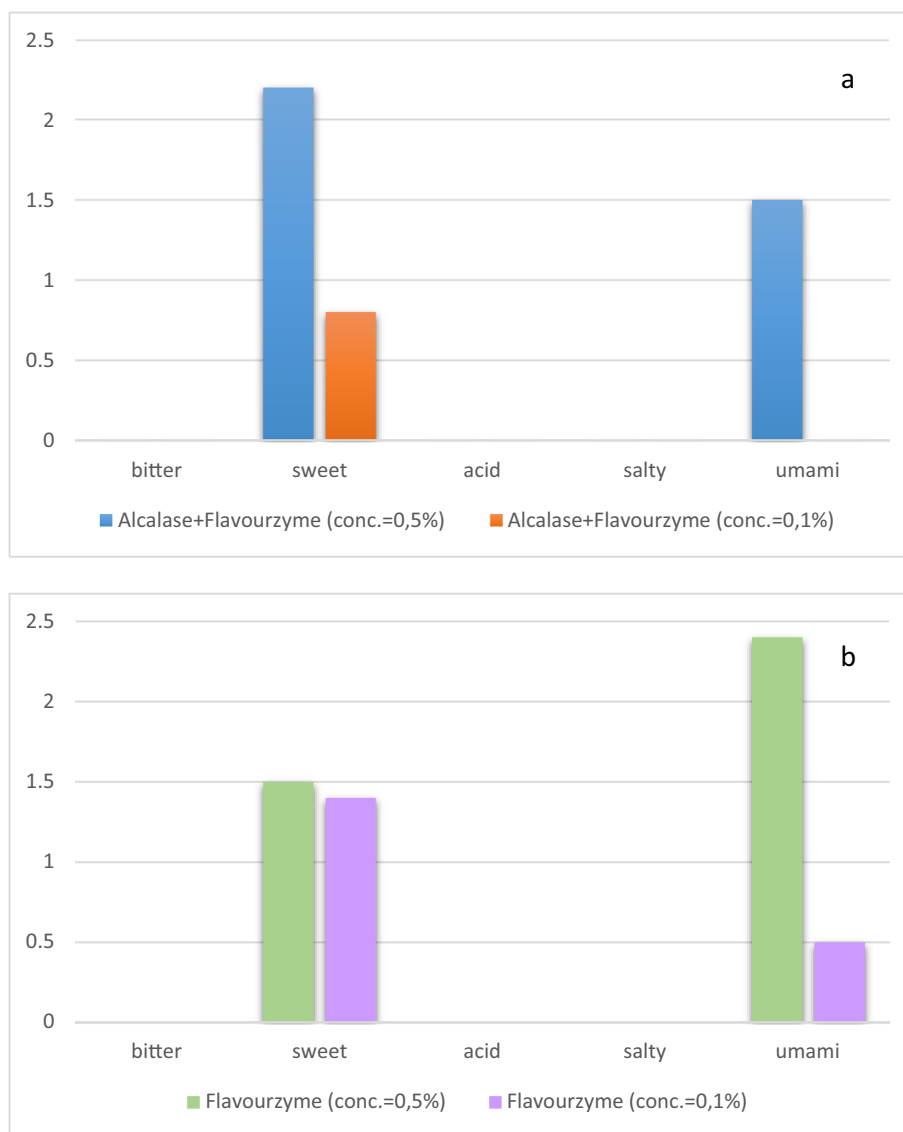


Fig. 4. Sensory characteristics of RBP hydrolysates obtained by Alcalase+Flavourzyme (a) or Flavourzyme (b) treatment. Sample concentration: 0.1% (0.1 g/100 mL) or 0.5% (0.5 g/100 mL).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biteb.2020.100427>.

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