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Editors

Pathways to Environmental Sustainability

Methodologies and Experiences

Springer

Chapter 6
Hypercritical Separation Technology (HYST): A Sustainable Technology for Agricultural By-products Valorization

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Abstract Agricultural activities produce worldwide about 3 billion tonnes of by-products and residues per year, that represent an important source of food, feed and bioenergy. The technologies currently available for these resources exploitation are not economically advantageous and not environmental friendly. Hypercritical Separation Technology (HYST) is an innovative technology based only on physical process, for the disaggregation of biomass. By this technology, a flour for human consumption with high vitamin and minerals content can be obtained from cereal bran. The HYST system has proved to be efficient to produce also feed with high nutritional value and improved digestibility. In the bioenergy sector, this technology could play a crucial role, for a sustainable and cheap production of second generation biomethane. Future projects to explore the potentialities of this technology will involve new agricultural residues, such as grape pomace, source of antioxidants and rice bran, source of proteins, regarding the food application, and the production of chemicals from fermentative process of lignocelluloses biomass for green chemistry applications.

Keywords Waste biomass · Functional foods · Biofuels · Sustainable technology · Green chemistry

6.1 Introduction

The agricultural sector produces a large amount of by-products and wastes, representing an increasing interest as industrial crops both due to economic reasons and environmental concerns. Agricultural activities produce worldwide about 3 billion tonnes of by-products and residues per year, that could represent an important

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R. Salomone, G. Saija (eds.), *Pathways to Environmental Sustainability*,
DOI 10.1007/978-3-319-03826-1_6,

source of food, feed and raw materials for the production of second generation biofuels and green chemistry products. In Italy 20 million tonnes of agricultural residue every year rot in the fields (ENEA 2006). In particular the world milling industry transforms every year about 350 million tonnes of wheat, producing about 80 million tonnes of by-products (about 25 %), with no real value, end up totally in feed, carrying starch, protein, over 70 % of the vitamin B6 contained in the grain, more than 50 % of the B5 more than 33 % of vitamins B1 and most of Fe, Zn, Mg, K, that remain caught in a web of indigestible fiber. These nutrients are an important source of food, even more important if directed to support programs for food in developing countries. Other by-products, such as grape residue from the processing of the grapes retain proteins and lipids of good nutritional value, as well as phenolic compounds that are extremely interesting for their beneficial effects on human health (Ruberto et al. 2007).

Currently, the food industry shows a growing interest in the production of functional foods, which are generally obtained by adding "bioactive" ingredients. The availability of technologies capable of producing functional foods directly from biomass containing these bioactive compounds by removal of indigestible substances and antinutritional factors, could be a turning point for this area.

Even more, the EU directive Waste Framework Directive 2008/98/EC (EU 2008), as regards food waste, gives priority to the reduction of waste at source, followed by reuse, recycling and recovery, with the elimination as a last choice.

The extraction of nutrients from residues of the food industry with the use of technology currently available is not, however, a process economically advantageous, because of low yields in the face of production processes extremely expensive. More than 20 million tonnes of straw and prunings, in codigestion with animal wastes, can potentially meet about 10 % of national demand for natural gas, which we are importing almost entirely from overseas. The Directive 2009/28/EC (EU 2009) on the promotion of energy from renewable sources establishes a 10 % target of energy needs in the transport sector to be covered by renewable fuels by 2020. In 2012 Italy will reach its 4.5 % share, which will almost entirely be covered by biofuels produced outside Italy.

The limiting factor for an effective utilization of lignocellulose in the processes of conversion into biofuels is the difficulty of hydrolysis of cellulose and hemicellulose, strongly linked with the matrix of non degradable lignin. Efficient technologies of pretreatment, with low operating costs and available at industrial level are therefore indispensable to facilitate the enzymatic hydrolysis and to provide an adequate production of second generation biofuels.

6.2 Technology

The Hyst technology (Hypercritical Separation Technology—Patent Application WO 2011/061595 A1), invented by Eng. Umberto Manola, consists of a set of machines diagrammed to process primarily biomass, but also inorganic substances with a water content $< 15\%$, exclusively through a physical process.

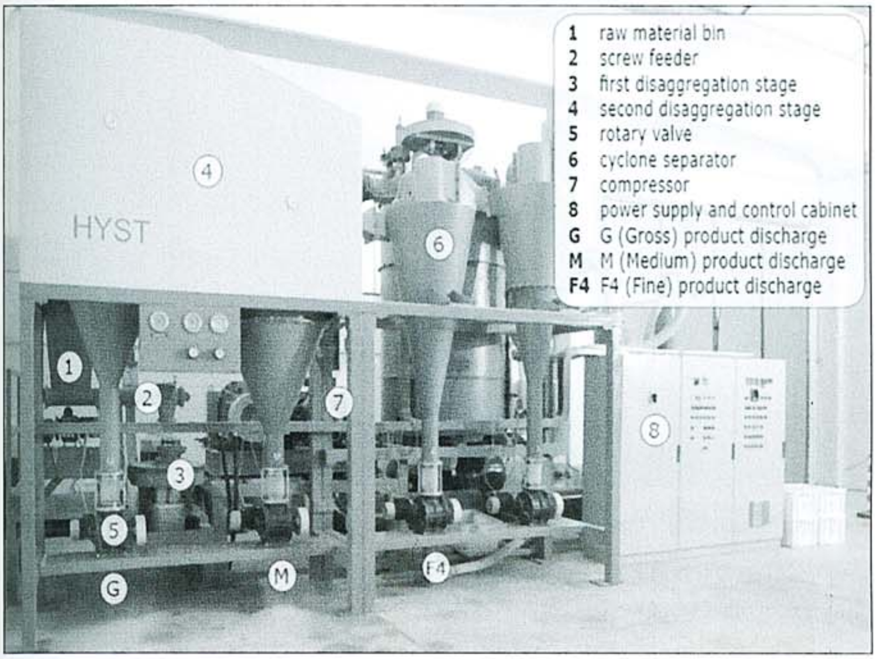

Fig. 6.1 HYST plant for the processing of agricultural residues

The system causes the disaggregation of the plant structure through reciprocal collisions between the particles within a current of air, without the aid of grinding rolls. In this way the raw material remains at room temperature, thus preserving its nutritional and organoleptic properties. The product of the disaggregation is then separated into several fractions of different physical and chemical characteristics, which can be used individually or mixed.

The system (Fig. 6.1), which constitute self-sufficient units, is modular; by varying the unit number is then possible to adjust the production capacity to the availability of biomass and/or the demands of the market.

The HYST plant has a modest energy demand, about 20 kWh for biomass ton treated, in comparison to the 500–1000 kWh of the other systems of treatment, with no need of chemical substances or water, with zero emissions and low operating costs.

Thanks to this technology from 100 kg of biomass is possible to extract 20 kg of lignin and cellulose and 25 of digestible fiber for zootechny. The remaining can be treated to produce 27 l of ethanol.

6.3 Applications

Encouraging preliminary studies have been carried out on the application of HYST process in several strategic sectors, hereafter are described some of the most relevant.

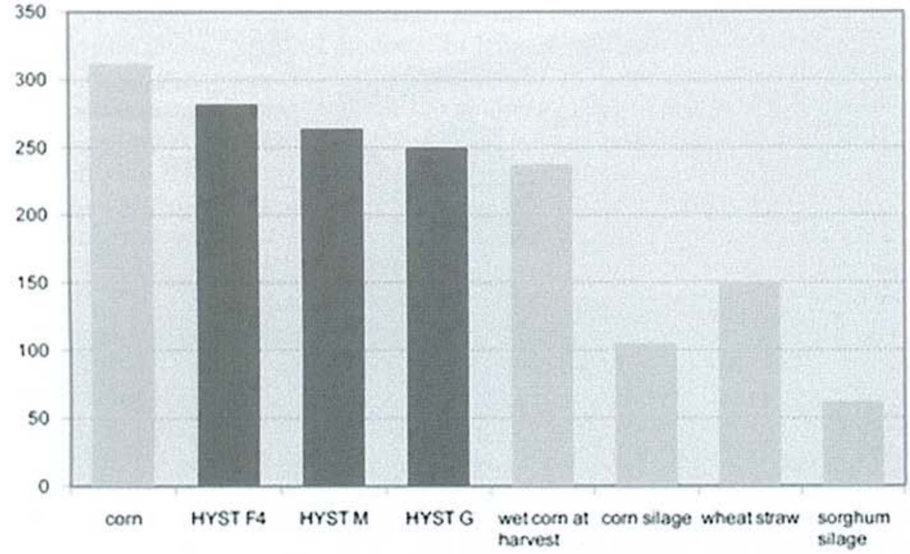

Fig. 6.2 Biomethane production (m^3/t w.b.) of HYST matrices from cereal straw compared with production of other biomass

6.3.1 Green Energy

The Italian transposition of the European Directive 2009/28/EC (EU 2009) for the renewable energies has established an increase of five times of the national biogas production. From the other side the ethical debate on the subtraction of land for the no-food production is always present. To achieve EU goals it will therefore be necessary to use second-generation biofuels (i.e. produced from agricultural by-products and residues), currently absent from the market because production technology still needs to be fully developed.

The HYST technology applied on straw flour has resulted in an energy density, in terms of methane production per ton of raw material, increased up to three times compared to corn silage (which is the reference biocrop; Fig. 6.2).

The HYST biomethane would be better valorized not in the electricity sector but in the automotive sector, where it could cover about 9 % of energy needs in the Italian transport sector (based on data processed by Unione Petrolifera databook 2012); complying with *double counting* rules (*Double counting*: introduced with the Directive 2009/28/EC (EU 2009), conventionally doubles the energy content of second-generation fuels, precisely in order to encourage industry efforts in this area) near the 10 % renewable energy share target for 2020 by means of only Italian unused raw materials. The excellent results and extremely low energy consumption of HYST pretreatment allows significantly lower biomethane production costs compared to those of biofuels currently on the market. HYST biomethane can even

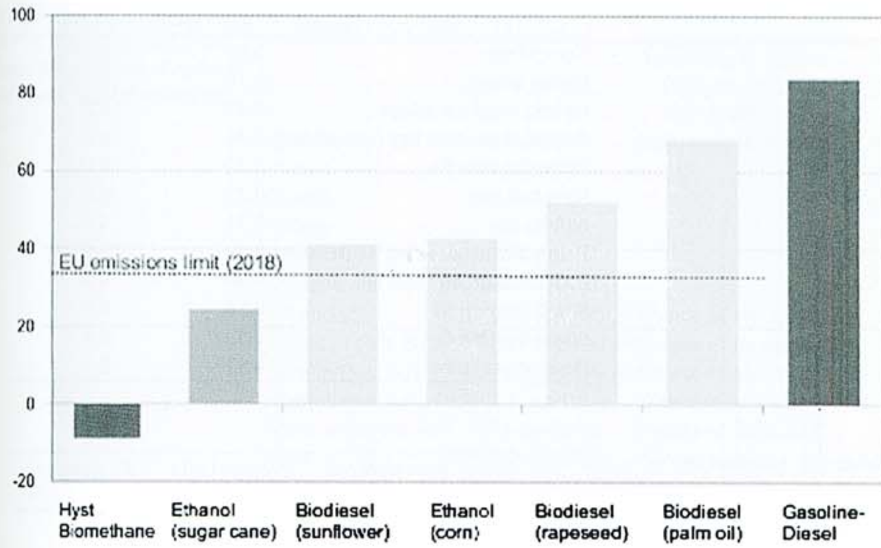

Fig. 6.3 GHG emissions [gCO_2eq/MJ] grams of CO_2 equivalent per unit of energy (MJ) released by the combustion of fuel

compete with costs of traditional fuels, 0.54 € per liter of gasoline equivalent, versus 0.67 € for first generation biomethane.

Furthermore HYST biomethane produced from residues of agricultural activities in codigestion with animal waste will not only easily meet European obligations but it will even absorb CO_2 from the atmosphere (−9 gCO_2eq/MJ; Fig. 6.3).

These results are possible because the HYST system can process agricultural residues with minimal energy consumption, along with significant environmental benefits deriving from improved management of animal wastes.

6.3.2 *Animal Feeding*

The use of agricultural and agroindustrial by-products in animal feed is an ancient practice, as it is the best way to enhance products considered as waste. Cereal straw, corn stalks or wheat bran are characterized by nutritional value (measured in UFL, forage unit for milk production) lower than citrus or beet pulps. They are, however, fundamental in the feeding of dairy cattle, beef and pigs.

The digestibility of a dry matter for animal feeding is inversely proportional to the lignin content in the matrix (Kamalak et al. 2004). To release the nutrients from lignin to increase their availability, the residues in the past were processed with chemicals or with mechanical treatments. HYST technology can operate the same disaggregation only with a physical process.

Table 6.1 The effects of processing on wheat straw

	UFL/Kg d.m.	Protein (%)
Corn silage	0.93	8.5
Barley silage	0.78	10.5
Hybrid sorghum silage	0.77	10.5
Polyphite meadow hay (second cut)	0.74	11.4
Straw fraction F4	0.72	10.1
Ryegrass hay	0.72	9.1
Alfalfa hay	0.71	17
Polyphite meadow hay (first cut)	0.70	10.9
Fodder sorghum	0.88	10
Straw fraction M	0.58	7.5
Straw fraction G	0.58	6.4
Base wheat straw	0.57	7.3

Table 6.2 Increase in nutritional value resulting from HYST treatment of three fibrous foods

	Raw material (UFL)	Average UFL increase (%)	UFL increase fraction F4 (%)
Wheat straw	0.57	6.7	25
Corn straw	0.48	6.5	33
Wheat bran	0.89	4.1	20

The laboratories of the Department of Animal Sciences of the University of Milan have studied cereal and corn straw, and wheat bran treated with HYST technology to assess the changes in nutritional value by the method of Menke and Steingass (1988). The separation process allows to obtain three fractions in order of decreasing granulometry: Gross, Medium, Fine (G, M, F4). On these samples nutritional value and digestibility analysis have been carried out. The chemical analysis showed a reduction of lignin and of the fiber fractions, with a significant increase of nutrients, especially proteins and starch, higher in the finest fractions (Dell'Omo et al. 2011).

The biological analysis showed that after lignin removal the digestibility increased substantially, in particular the F4 fraction from bran was 69.4 % in comparison of 59.8 % of the non treated bran, and the F4 fraction from straw digestibility increased from 44.9 to 56.7 %.

As shown in Table 6.1, the fraction F4 of wheat straw (15 % of total processed material) has a high concentration of nutrients: Consequently, an increase of nutritional value measured in UFL of 25 %. This was more evident in corn straw, where the increment was of 33 % (Table 6.2; Dell'Omo et al. 2011). These data are extremely interesting both for Developing Countries, where these by-products are the only feed available, and for the developed countries to reduce production costs and to optimize the resources.

6.3.3 *Human Nutrition*

Today, the by-products of milling industries (bran, wheat flour middlings) are exclusively destined for animal feed. However, the HYST treatment of such by-prod-

Table 6.3 Characteristics of HYST flour produced from bran. (Department of Animal Sciences, Milan University, 2011)

Chemical composition (% d.m.)		
		According to Regulation (EC) No. 1924/2006 (EU 2006)
Protein	21–24%	High protein content
Starch	48–55%	
Lipids	3.3–3.5%	
Fibers	4.8–15%	
Minerals	3.5–4%	
Vitamin and mineral content (% d.m.)		
Vitamin E	1.39 mg/100 g	Source of vitamin E
Thiamin (Vit. B1)	0.93 mg/100 g	Source of thiamin
Niacin (Vit. B3)	18.3 mg/100 g	Source of niacin
Pantothenic Acid (B5)	2.1 mg/100 g	Source of pantothenic acid
Folic acid (Vit. B9)	77 µg/100 g	Source of folic acid
Iron	9.2 mg/100 g	Source of iron
Zinc	3.08 mg/100 g	Source of zinc
Magnesium	271 mg/100 g	Source of magnesium

ucts produces protein flours meeting high nutritional requirements and thus eligible to be used in deficiency situation caused by malnutrition and/or undernutrition.

The innovative features of HYST technology allow to optimize the use of raw materials, creating new natural food with a high nutritional profile without introducing any toxic or chemical compound. Processing with the HYST system by-products of the milling industry, now used only for the production of feed, a flour can be obtained in which vitamins and minerals are more abundant than in the common cereal flours with a product yield of 15–20 %.

The analytical results show that the flour obtained from soft wheat bran by the HYST technology has an high protein content (up to 24 %), when the conventional wheat flour has a maximum average content of 14 %. According to Regulation CE 1924/06 (EU 2006) HYST flour can be labeled as having high protein content and source of all the micronutrients. In fact, 100 grams of HYST flour provide the recommended daily dose of vitamin B3, which is essential for metabolic functions, and over 60 % of the daily dose of vitamin B1 (Table 6.3), which is recognized by the European Food Safety Authority as a promoter of brain function in children.

These results are particularly interesting if compared to the artificially fortified flours, as for example a flour added according to USDA standards, as shown in Fig. 6.4. With its exceptional vitamins and minerals content and it completely natural origin, the HYST flour can be normally consumed as common food, but can also fit the functional food market requirements, and, most importantly, open new perspectives in solving the food scarcity problem.

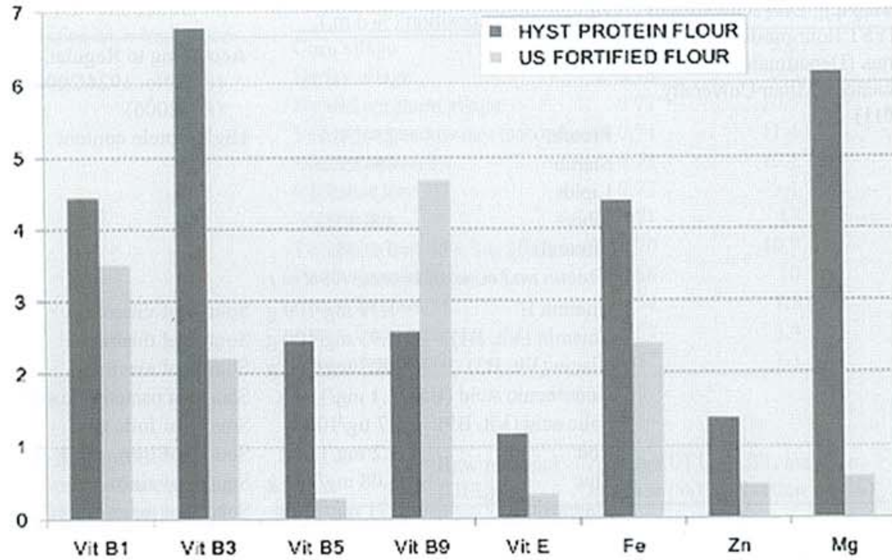

Fig. 6.4 Micronutrient content of HYST flour: comparison with artificially fortified foods (values parameterized to the significant content according to EU legislation)

6.4 Future Perspectives

Future research goals will be to optimize the HYST process on the studied agricultural by-products and applications, but also to explore the potentialities of other interesting residues.

6.4.1 Human Nutrition

The preliminary studies for the nutritional and functional characterization have been carried out on products obtained from the processing HYST bran from wheat residues. Future researches will be focused on other agricultural by-products of interest, considering also the possible experimentation on specific population groups.

Wheat semolina is a typical product of Italian agriculture, and its bran could be the first analyzed for the easy availability and large market.

Rice husks contains high amounts of beneficial antioxidants including tocopherols, tocotrienols, and oryzanols. Current rice milling technology produces rice bran from different layers of the kernel caryopsis. Under current practices, these layers are combined and then steam-extruded to form a stabilized rice husks pellet that is storage-safe prior to oil extraction (Lloyd et al. 2000). Recently, FAO reported that the annual production of rice husk in the world amounts to 4.3 million tonnes.

The main components of the husks are oils, proteins and carbohydrates. It is then used for the extraction of oils, and as an ingredient in food for humans and feed for animals. The extraction of oils from rice husks, which currently is conducted almost exclusively in Asia and in the United States, involves the use of n-hexane, which can be emitted into the atmosphere and has a negative impact on the environment. The extracted oil, subsequently, before being used requires further extraction steps. Other enzymatic processes provide the simultaneous extraction of proteins and fats from rice husk (Hanmoungjai et al. 2002).

Furthermore, proteins extracted from rice, are considered extremely interesting as functional ingredients (Tang et al. 2003). Thanks to the high content of lysine, the protein derived from rice husk are hypoallergenic (Helm and Burks 1996), and this can be used as an ingredient in food formulations for children with allergies (Burks and Helm 1994). The amino acid profile of rice proteins can be considered better than that of casein and soy as it corresponds to amino acid needs of children aged 2–5 years (Wang et al. 1999).

The main goal of the compositional study of the HYST processed rice husk products could be the development of a flour enriched in amino acids and antioxidants to be used alone or mixed with other traditional flours for specific population groups (e.g. malnourished children for its amino acid profile).

There is also an increasing interest in the exploitation of residues generated by the wine industry (Arvanitoyannis et al. 2006). In particular, the grape pomace may constitute an alternative for the extraction of natural antioxidant compounds, which are considered to be entirely safe compared to synthetic antioxidants. The skins are a rich source of molecules of great interest, including oil, hydrocolloids and dietary fiber. Furthermore, the grape pomace is characterized by a high content of polyphenolic compounds, which are not extracted during the process of wine production (Kammerer et al. 2004). The waste products obtained after the production of wine, constitute a very economical source for the extraction of matrices with a high content of antioxidants (Alonso et al. 2002; Negro et al. 2003; Gonzalez-Paramas et al. 2004). The identification of cheap technologies for the processing of skins could be a significant boost to their exploitation.

The application of the HYST process on this kind of residues would have the aim of obtaining fine fractions high in dietary fiber and polyphenolic compounds, to be used as such or as functional ingredients to be added to flour or other food, after the selection of the more suitable grape pomace (in terms of cultivar and kind of production).

6.4.2 Green Chemistry

The chemical industry is showing a growing interest in the possibility of obtaining chemicals from renewable raw materials (biochemicals) in alternative to the existing products, derived mostly from fossil fuels. The "green chemistry" has many advantages: almost inexhaustible availability of renewable resources, lower environmental impact, biodegradability of products, reduction of CO_2 emissions, lower energy consumption and lower raw material.

In particular the conversion of lignocellulosic biomass into oligo-and monosaccharides for the production of fuels and chemicals by microorganisms, is an extremely attractive option for the petrochemical industry for the production of a new generation of chemical molecules base. Researchers from the U.S. Department of Energy (DOE) have identified numerous building blocks which may be obtainable from biomass (Werpy et al. 2004).

Among the building blocks of renewable origin listed by US DOE there are several organic acids (succinic, maleic, aspartic, furanic, itaconic, levulinic, glucanic) that can be used for the production of bioplastics, biolubricants and biosolvents.

HYST process could be applied in the pretreatment step for the production of succinic and lactic acids from lignocellulosic biomass to facilitate the difficult hydrolysis phase. The results will be economically evaluated in order to compare the production costs to those produced by fermentative process of cereals, as the succinic acid or of petrochemical origin as lactic acid.

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