UPGRADING AND VALORISATION OF FOOD WASTES BY SUPERCRITICAL CARBON DIOXIDE EXTRACTION

Erika Vági*[1],Ildikó Kmecz[1], Béla Simándi[1], Libe de Las Fuentes[2]
[1]Department of Chemical Engineering, Budapest University of Technology and Economics,
Muegyetem rkp. 3. H-1521, Budapest, Hungary,
fax: 00-36-1-4633197, *erikavagi@yahoo.co.uk
[2]Gaiker, Parque Tecnológico, Zamudio, Spain

Agro-food industry produces generally less hazardous waste than other industrial sectors and due to its natural origin this waste is mostly biodegradable. These could be the reasons why this sector has not been subjected to strict environmental regulations. But the lack of knowledge regarding pollution load of the wastes generated and/or the use of non-adequate technologies, together with bad housekeeping practices, has derived important environmental problems that need to be solved. This is especially crucial in countries or regions where due to the use of old technology, bad practices or to the high concentration of this type of industries, the wastewater and solid waste generated cause important environmental problems.

AWARENET stands for Agro-Food Wastes Minimisation and Reduction Network and is supported by EU Growth Programme. This network started in January 2001 and it is the first one on agro-food wastes prevention, minimisation and valorisation, focusing on the main 5 food industrial sectors: meat, fish, dairy, fruit and vegetables and wine production. The innovation of AWARENET is that it has integrated the vision of the agro-food industrial waste problem from three different and critical points of view: regulatory issues, technology and market, with the final objective to propose a global R&D European strategy for agro-food industrial wastes. Currently the consortium counts 32 members from 14 different European countries, including Newly Associated States.

Since AWARENET has been working for three years now a short summary of its achievements seems appropriate. During its first year, the network activities have focused on defining the main European issues on agro-food industrial wastes, such as:

- Compilation/assessment of agro-food wastes legislation related issues at European and national level
- Elaboration of an inventory of agro-food wastes in Europe for the five industrial sectors approached
- Identification of main production processes and their critical points in terms of waste generation within these sectors
- Preliminary identification of marketable products from agro-food wastes

In the second year of AWARENET a deeper analysis of the main food production processes for the evaluation of minimisation strategies and waste valorisation technologies has been completed. The processes have been selected both for their economic and waste volume generation (waste = non utilised raw matter to yield the main product) importance. Specific sectorial expert groups have been arranged to evaluate each production process and identify critical points giving rise to solid and liquid wastes. Best practices to avoid waste

generation and minimisation strategies have been identified for each process. In parallel, market issues have also been preliminarily approached, considering marketable products coming from each waste or by-product and comparing current waste disposal costs (landfilling) with the return coming from different valorisation procedures.

One of the main tasks of AWARENET is to identify and define valuable tools that will help food producers in Europe in prevention and minimisation of the generation of wastewater and solid wastes, and the subsequent reduction of the costs for their treatment and disposal. Accordingly, AWARENET members have evaluated existing prevention, minimisation and treatment technologies for liquid and solid wastes, together with preliminary waste valorisation alternatives, in a deep study of 19 food production processes significant in Europe, considering:

- milk processing, yoghurt and cheese manufacturing (dairy sector)
- fish filleting, smoking, curing, salting and canning and molluscs and crustaceans processing (fish sector)
- beef, pork and poultry processing (meat sector)
- white and red wine production (wine sector)
- starch (wheat, corn, potato), sugar (sugar beet) vegetable oils, fruit and vegetable juice and processed and preserved vegetables and fruits production (fruit and vegetable sector)

A flow diagram summarises all the information gathered for each process, linking it with inventory of wastes, market and regulatory issues covered by other tasks within the network.

The network has been involved in the evaluation of market issues related to technologies for agro-food waste management and minimisation and the identification of marketable products coming from this wastes. Furthermore, best available prevention, minimisation and valorisation technologies have been identified. Last but not least, updating of European and national legislation on food wastes, management and valorisation technologies and new products coming from these wastes is being performed. Finally a handbook compiling all the network conclusions has been publicly released. It aims to be a useful tool and reference manual for food producers in Europe so as to prevent, minimise and promote valorisation of their food wastes and considering not only the legislation in force and the real amount of wastes generated but also the current market demands in Europe.
The handbook and all the other information and agro-food waste related documents are publicly available at our interest group at http://ew.eea.eu.int.

Recently one of the most important environmentally concern in the agro-food sector is the high amount of accumulated wastes with high organic content, which implies high treatment cost. However, these wastes most often contain high valued, biological active compounds (antioxidants, proteins, oils, vitamins and natural colorants) that would be reasonable to recover and apply in different fields of pharmaceutical-, cosmetic- and food industries. For the minimisation and valorisation of these wastes environmentally accepted and economically reasonable process is needed. The supercritical carbon-dioxide extraction is a suitable method to recover the valuable compounds and products from agro-food by-products or wastes. Agro-food by-products appear as a good raw material for many active substances, and $scCO_2$ can be considered a clean technology suitable for upgrading processes.

Supercritical extraction can be applied alone or in combination with conventional extraction. This is the case for example of the extraction of astaxanthin from the shells and heads of crustaceans using ethanol as co-solvent.

In this work some case studies of extraction of food wastes and by-products are summarized (**Table 1**), which have been carried out in our laboratory. These by-products contain high amount of useful and market related compounds.

Table 1. : Extraction of agro-food wastes (yield, g/100 g dry material)

Raw material	Solvent			Active compounds
	Carbon dioxide	*n*-Hexane	Ethanol	
Tomato pomace	3.87	3.39	57.92	lycopene, tocopherols
Sea buckthorn pomace	13.19	15.15	33.64	β-carotene, tocopherols
Olive pomace	12.22	12.10		tocopherols, squalene
Corn germ residue	11.42	12.29	19.88	tocopherols, phytosterols
Wheat germ	8.92			tocopherols
Hibiscus	15.47	16.31	20.74	tocopherols, phytosterols

Clean, solvent residual-free products can be obtained with $scCO_2$ extraction, meanwhile similar amounts of extracts can be determined by traditional solvent extraction with *n*-hexane due to the similar solvent properties of $scCO_2$ and *n*-hexane. With ethanol higher amounts of products can be achieved as polar compounds are soluble, though it might result the dilution of active compounds. The vegetable oils are well soluble in almost all applied solvents and the fatty-acid compositions are similar. Lipophyll compounds (carotenoids, tocopherols, steroids) can be extracted in high concentrations with $scCO_2$ and *n*-hexane solvent extractions.

Examining one case study the possibilities of extraction from agro-food industrial wastes will be shown. Corn germ oil is produced by mechanical pressing, therefore significant amount of residue is available that contains around 20% of soluble oil after first pressing and ~ 10% after the second one. The corn germ oil possesses health-preventative properties due to the compositions of fatty acids and tocopherols. The sitosterols found in corn germ oil lower blood cholesterol, therefore suitable for dietary functional food.

As the mechanical pressing contain two steps, the solvent extraction of two residues from the first pressing step (Sample 1) and from the second pressing step (Sample 2) were examined. Traditional solvent extractions with four solvents (ethanol, isopropanol, ethyl-acetate and *n*-hexane) and high pressure extraction with $scCO_2$ were compared with the aim of preparing high quality corn germ oils with comparable quality to mechanical pressed oil. The $scCO_2$ extraction was carried out at 450 bar and at different temperatures; therefore the quantitative and qualitative comparisons were possible. The yields of extraction with the five applied solvents can be seen in **Figure 1**. It can be concluded that the yields increased with

the solvent power of the solvents and twice amount of oil can be extracted from Sample 1 than that of Sample 2. The compositions of fatty acids were similar, major constituents were linoleic acid (54.9–56.8%), oleic acid (27.7-29.8%), palmitic acid (10.5-14.3%). The composition of tocopherols showed differences depending on the applied solvents and / or the applied temperatures. In higher amount the γ-tocopherol was identified, while α-, δ-, β-tocopherols were found in smaller amounts. The highest tocopherol concentrations were achieved by solvent extraction with isopropanol and ethyl acetate solvents, while increasing the temperature of SFE higher amount of tocopherol was recovered. The extracts obtained by apolar solvents contained the highest amounts of β-sitosterols. The oil extracted at 450 bar and 80°C contained higher amount of β-sitosterol than the mechanically pressed oil.

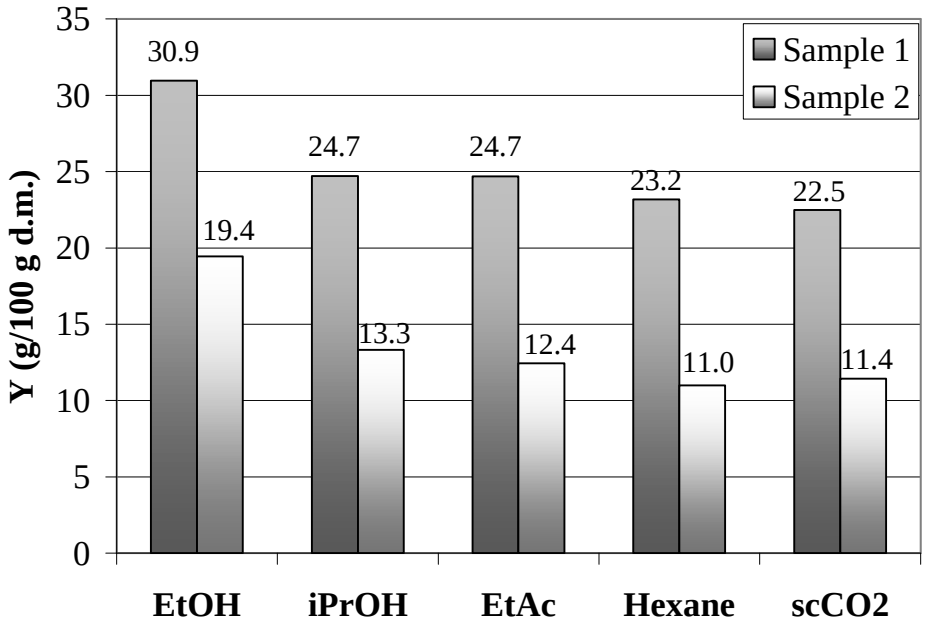

Figure 1.: Extraction of corn germ residue from first pressing (Sample 1) and from second pressing steps (Sample 2)

Throughout this case study (extraction of corn germ residue) it can be stated that the products obtained by scCO2 extraction possess high biological values; therefore the usage is reasonable for well-defined purposes (food-, cosmetic- and/or pharmaceutical industries). Natural oils, waxes, colours, aromas and flavours can be extracted either from raw material or from agro-food wastes, by-products with the aim of produce high quaility products.