ADVANCED TECHNOLOGIES IN SUNFLOWER OIL EXTRACTION

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SUMMARY - This paper reviews the main technological advances which have been realised in sunflower oil extraction on the laboratory, pilot and industrial scale over the last decade, with particular reference to the conceptual innovations, rather than technical improvements. Attention is focused on the new extraction strategies involving the use of water and super-critical carbon dioxide.

INTRODUCTION

The technology for the production of edible sunflower seed oil on an industrial scale is fairly standardized and the basic process has remained relatively unchanged since the advent of continuous solvent extraction some 45-50 years ago. The classical process involves five steps: seed drying and storage, seed pre-treatment, oil extraction, oil processing, defatted meal processing.

Although sunflower oil extraction is normally recognized as a highly mature technology not requiring significant further development, a conspicuous amount of research is in progress. This research is mainly aimed to the searching of new solvents, safer than hexane and offering a higher quality final products, above all from a toxicological point of view.

This paper reviews the main technological advances which have been realised in sunflower oil extraction on the laboratory, pilot and industrial scale over the last decade.

NEW SOLVENT EXTRACTORS

While some older plants still employ only mechanical extraction and other mills without expellers use direct solvent extraction, pre-press/solvent extraction is largely the preferred method on an industrial scale. This technology involves a preliminary oil squeezing by continuous screw presses, followed by a solvent extraction of the pressed, partially defatted cake. The most widely-used solvent in modern industrial plants is commercial hexane and extraction is currently performed using continuous counter-current processes based on percolation or immersion. The miscella, after filtration, is distilled and combined with expeller oil before being sent for rectification.

The pre-pressing of seeds in conventional sunflower technology highly complicates the plant requirements from an engineering point of view, and negatively affects the quality of both the oil and cake, because of the considerable heating (up to 150 C) induced by the high pressures involved.

To overcome these problems, Turkay et al. (1985) proposed a new extractor system which eliminates the seed pre-pressing step and uses a moving bed of seeds continuously washed with fresh hexane sprayed from mobile nozzles. In this innovative extraction system, originally designed for sugar beet extraction, the temperature of the solvent and seed are kept a few degrees below the boiling point of the solvent so that high oil solubility and diffusion rates are obtained. High temperatures also favourably affect the solvent flow through the seed bed. In order to extract the oil with low residence time and high extraction yields, fresh solvent without any recirculation is used. This diffuser represent an interesting attempt to develop a continuous single-stage cross-current oilseed extraction technology. The experiments performed on a pilot scale by Turkay and co-workers have shown that the optimum extraction conditions are: 50-53 C solvent temperature, 40-45 C extractor temperature, 90 min extraction time and 0.9-1.0 mm particle size. The resulting miscella in this system is more diluted than that obtained from conventional multicell extractors, thus raising the evaporation costs.

Another new solvent extractor which eliminates the pre-pressing step has been recently proposed by Coenen et al. (1989). This extraction method, developped by Krupp Industries Ltd, is a multistep counter-current extraction process using an in-line rotor/stator-homogenizer, where very efficient diffusion takes place. The necessary grinding of the sunflower seeds for extraction occurs within the extractor, thus eliminating the conventional operations of grinding and conditioning as well. Laboratory trials with a four-stage counter-current extraction process, have shown an oil recovery of 98.9 % and a residual oil content in the defatted meal of 0.72 %, vs approximately 2 % for conventional processes.

NEW ORGANIC SOLVENTS

Although various organic solvents have been used commercially and others have been proposed on the basis of encouraging laboratory results, hexane is currently the solvent of choice for oilseed processing, including sunflower seed. Occasional shortages of hexane, several catastrophic explosions and fires, and above all toxicological and environmental concerns have, however, motivated the search for new solvents. A comprehensive review of alternative organic solvents for oilseed extraction has been published by Johnson et al. (1983), while more recently Rittner (1992) reviewed the potential of ethyl alcohol in the extraction of vegetable oils.

Mention has been made in the literature of over 70 organic solvents, including alkanes, cycloparafins, aromatic and halogenated hydrocarbons, alcohols, aldehydes, ketones, esters, ethers, amines, and various solvent mixtures. From these studies current interest has focused on ethanol, isopropanol and methylene chloride.

AQUEOUS EXTRACTION

Oil extraction is an energy-intensive industry and much of the energy consumed is needed for solvent evaporation. Solvents which allow non-evaporative methods of recovery result in a considerable reduction in operating costs and this justifies the interest of research and industry in the extraction of seed oil by water.

Water is immiscible with oil and therefore represents a poor solvent for these kinds of natural substances. Nevertheless, many researchers have used water systems for the physical separation of oil from oilseeds. The advantages and disadvantages of aqueous processing vs hexane extraction are listed in table 1.

The physical recovery of oil from seeds by means of water requires that a majority of the oil cells in the raw material be ruptured during the grinding step, in order to free the oil globules and to allow them to coalesce and emulsify with water. Insufficient grinding results in low oil recovery and a corresponding high oil residues in meal, while excessive grinding yields mayonnaise-like emulsions that are difficult to break.

The water used in oil extraction may be acidic, basic or contain salts or chemicals, depending on the undesirable substances to be removed (e.g. chlorogenic acid) and the type of final protein product desired (defatted meal, protein concentrate or isolate). An acidic pH (close to the isoelectric point of sunflower globulins) is used when normal meals or protein concentrates are desired, whereas a basic pH is required to produce protein isolates. As an additional benefit with sunflower seed, water extraction greatly reduces the chlorogenic acid content of defatted meals, thereby improving their nutritional value and functional properties.

The aqueous extraction of oil has been applied in the laboratory/pilot scale processing of various oilseeds. Regarding sunflower seeds, a highly innovative technology involving oil extraction by water has been developed at the Stazione Sperimentale per le Industrie degli Oli e dei Grassi of the Italian Ministry for Industry and Trade (Lanzani et al., 1983, 1988; Mariani el al., 1987; Lanzani, 1990). The process was realized at industrial level mainly for research purposes, including the selection of the best working conditions and the evaluation of the energy and running costs. The plant, having a working capacity of 1.4 tons of raw material per hour, has been developed in cohöperation with the Nuova-Maip Pieralisi Industry Ltd and is suitable for the production of both feed and food-grade defatted meals. The process for the production of oil and feed-grade meal includes a preliminary seed flaking step, followed by heat conditioning (90 C for 20 min), grinding, the addition of 80 % of acidified hot water (pH 4.1-4.3), and gramolation for about 30 min at 45-50 C. The aim of heat conditioning is to inactivate the lipases and lipoxidases, responsible for oil acidification and oxidation during processing and storage. After gramolation, the heterogeneous 3-phase system is split by means of a decanter and the oil and aqueous phases clarified by centrifugation. The extraction water is usually recycled before refilling, while the solids are pressed and dried.

The results obtained during 30 days running at an industrial level indicate an oil yield of 92%. The quality of the oil appears good, having an acidity number ranging from 0.2 to 0.6, a negligible peroxide number and a content in waxes and other compounds precipitable by winterization lower than 0.1 %. The organoleptic properties of the oil obtained by the wet process seem to be less acceptable than those of conventionally-extracted oil; this is mainly ascribable to the higly marked almond flavour.

Food-grade defatted meals show a straw yellow colour and have an improved nutritional quality. Aqueous extraction, in fact, removes a large quantity of chlorogenic acid, without significantly reducing the albumin content. Feed and food-grade defatted meals can be stored for long periods of time, because of their low moisture content and the complete denaturation of the deleterious enzymes.

Economic evaluation shows that oil produced by the wet process is slightly more expensive than that obtained via conventional hexane extraction. This greater cost is however counterbalanced by the better quality of the final products, especially from a toxicological point of view, and by the versatility of the process, which is particularly adaptable to small production units.

EXTRACTION WITH SUPERCRITICAL FLUIDS

Among the alternative solvents proposed for oil extraction, liquified and especially supercritical gases have recently attracted the most attention, as is testified by the large number of scientific papers published on this topic and by the symposia and congresses on supercritical fluids (SCF) organized in the last ten years.

When a gas such as carbon dioxide is compressed and mantained below its critical temperature (31.1 C for carbon dioxide), it becomes a liquid. If, during compression, the liquified gas is heated and allowed to exceed its critical temperature, it will revert to a gas and no amount of additional pressure will reliquify it. The gas is now supercritical and shows a solvent power comparable to that of conventional liquids.

The solvent power of a SCF is related to its density, which in turn depends on its pressure and temperature. As a general rule the solvent power of a SCF increases with pressure at a given temperature, while increases or decreases when temperature rises at constant pressure. Any increase in the solvent power of SCF increases not only the solubility of a given solute but also the number of compounds solubilized. This means, therefore, that at low solvent powers SCF are highly selective, while at high solvent powers they exhibit low selectivity. In order to produce a SCF extract which is higly selected and as close as possible to a steam distillate, the SCF must be used at a very low solvent power working in the supercritical area near the critical point.

On the contrary, if a total extract from a natural product is desired, the SCF must be used at high solvent powers, operating at high pressures, where high densities are obtained.

From the above discussion it is clear that the SCF are "geometrically variable" solvents whose efficiency, in terms of selectivity and extractability, can be further modified by the use of suitable entrainers or co-solvents. Polar entrainers such as methanol or ethanol lead to increase selectivity and solvent power against the molecules interacting with the co-solvent, while non-polar entrainers such as hydrocarbons increase the solvent power for the extraction of heavy compounds like triglycerides.

Although the use of SCF can be traced back to the 1930s, only recently it has become a reality in the petroleum, coal and food industries, where they are rapidly increasing in importance as their advantages become known. Carbon dioxide is certainly the most important compound used on the laboratory, pilot and industrial scale for the extraction of natural products as a supercritical fluid. Besides carbon dioxide, however, nitrous oxide, ammonia, carbon disulfide, sulfur dioxide, and certain organic compounds such as ethane, propane, butane and ethylene, as well as the halogenated hydrocarbons (chlorotrifluoromethane) have been used.

In this process, the carbon dioxide is compressed well above its supercritical pressures (73.8 atm) to between 500-1,000 atm, conditioned at the desired temperature (usually 40-80 C) and then passed through the extractor containing the flaked oilseed. The extracted oil is recovered from its solution by lowering the pressure in either one or two stages.

Although supercritical carbon dioxide (SC-CO2) has been used in the extraction of many different materials, only recently has its use in vegetable oil extractions been explored on laboratory/pilot scale. This research has mainly involved the extraction of oil from soybean, corn germ and cottonseed (Friedrich et al., 1982; Mangold, 1983; Friedrich and Pryde, 1984; Christianson et al., 1984; List et al., 1984a,b; Snyder et al., 1984; List and Friedrich, 1985, 1989; Eldridge et al., 1986; Wilp and Eggers, 1991), while only two papers are available in the literature regarding oil extraction from sunflower seed using SC-CO2 (Stahl et al., 1980; Dakovich et al., 1989).

Although no commercial seed oil extraction plants using SC-CO2 are known to be in operation, the interest of industry in this innovative technology is great, due to the numerous advantages which it presents in comparison to the conventional hexane extraction (table 2). Moreover, the prospects for the commercial application of this process could be increased: a) by adding to our knowledge, as yet incomplete, the thermodynamic properties of the oil/SC-CO2 mixtures; b) by developing a suitable engineering hardware technology for continuous operation; c) by increasing our knowledge of the optimal processing conditions for each specific raw material, as well as the chemical and functional properties of the final products. Some engineering solutions for the continuous high pressure extraction of oilseed have been proposed by Eggers et al. (1985), while as far the behaviour of the specific oilseeds treated with

Tab. 1 - Some of the advantages and disadvantages of aqueous extraction vs conventional hexane processing

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ADVANTAGES
- Plentiful supply at low cost
- Nonflammable, nonexplosive, nontoxic, nonpolluting
- Removal of antinutritional factors, such as chlorogenic acid
- Production of higher quality defatted edible meals
- Drying of the raw material before extraction is not required

DISADVANTAGES
- Lower solvent power
- Whey fractions are easily contaminated by bacteria
- The oil fraction usually needs to be demulsify
- Residual oil content (about 4 %) in meals and in protein concentrates or isolates could cause storage problems
- Protein products (meal, concentrates, isolates) need to be dried using energy-intensive equipment

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Tab. 2 - Some of the advantages and disadvantages of supercritical CO2 processing vs conventional hexane extraction.

ADVANTAGES
- Plentiful supply at low cost
- Nonflammable, nonexplosive, nontoxic and nonpolluting
- Lack of reactivity
- Solvent power and selectivity can be modified
- Low viscosity and high diffusivity reduce the extraction time
- Extracts can be easily fractionated
- Energy saving
- Production of high quality oils with low free fatty acids
- Solvent easily removable from oil and meal products

DISADVANTAGES
- High operating pressures involve expensive processing equipments (high investment costs)
- Lack of engineering hardware technolgy for continuous operation
- Batch processing results in low working capacities

SCF, a 4-year research project focusing on sunflower seeds and carried out under the auspices of the EEC (Project SONCA/ECLAIR), is currently underway at the Instituto Industrie Agrarie of the University of Pisa. This project includes: a) an evaluation of the role of the various process parameters and substrate characteristics on product yields and properties; b) the chemical and functional characterization of extracted oil and defatted meal; c) a technical appraisal of SCF extraction in the sunflower oil production, also in comparison with conventional technologies based on the use of organic solvents.

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