Introduction

Poland is a large producer of hop, fruit, vegetables, herbs and other plant materials applied in numerous industry branches [1, 9÷11]. These materials are processed using different technologies, depending on the purpose of the final product. Especially interesting products may be obtained as a result of processing these materials or remains after processing using extractions with carbon dioxide in supercritical conditions. As a result of an extraction, the following may be obtained, depending on the type of material: oleoresins, oils, unsaturated oils, polyphenols and many other plant substances for application in the pharmaceutical, food or cosmetic industry. Selected solid post-extraction remains may also be used by the fodder industry. In the Institute of Fertilizers in Pulawy, Poland, a hop working process was implemented in 2000 on an industrial scale, using supercritical extraction. The experience obtained in this field, supplemented by results of studies conducted in the Institute’s research plant, was used to develop a plant extract technology using other materials. Based on this experience, assumptions and a process project were developed of a new, universal research-practical installation with a capacity of material processing equal to approx. 2000 t/y, for extracting plant materials. The installation was erected as part of the R PW project subsidized by PARP and it will be put into operation in mid-2011.

Materials

Hop processing

The 90-ties of the 20th century witnessed an intensive modernization of breweries in our country which led to significant technological changes in beer production. Hops used previously at a certain production stage were replaced first with granulated products, which are nowadays gradually substituted by hop extracts. Currently, beer is produced using granulated products as well as hop extracts. However, the use of extracts is gradually increasing and a further increase in interest in hop extract should be expected, especially from large beer manufacturers. The installations for hop processing constructed at the Institute of Fertilizers consist of two nodes: a drying node with hop granulation and a hop extraction node, and they currently constitute an integrated process line in which hop delivered by the manufacturer is dried, granulated, and then subjected to CO₂ extraction in supercritical conditions [2÷8]. The installation for hop processing was placed in Pulawy because eastern Poland is an important domestic facility of agricultural production, including hops (the Lubelszczyzna region holds approx. 82% of domestic hop production), and at the same time the Institute is placed here. Thus, this region is a natural material base for extract production. Despite a small participation of Poland in world hop production, Poland produces approx. 3,200 tons of hop yearly (for comparison, Germany produces approx. 30,000 tons) and hop production favorably shapes the structure of Polish agriculture. Moreover, this field of agricultural production creates many jobs, including employment in processing branches which cooperate with hop manufacturers.

Herbs

The total production of herbs in Poland is currently estimated at approx. 20,000 tons per year [9]. The total mass of materials obtained yearly from plantations, according to data from the last five years, equals approx. 17,000 tons. Herbal plantations in Poland take up an area over 30,000 hectares. Nearly 70 medical plant species are grown currently by almost 20,000 farms. Certain species of herbs contain oils, resins and other compounds which may be obtained using supercritical extraction and may be a subject of interest of the pharmaceutical, cosmetic and food industry. Modern herbal processing in Poland is based mainly on the production of plant drugs. Although according to certain assessments the production of herbal food and cosmetic products will have an increasingly larger economic significance, in Poland the biggest role in shaping herb cultivation will still be played by the production of plant drugs. It is expected that the largest amount of changes will occur on the market of plant drugs which will turn into a modern pharmaceutical market. It is estimated that the value of Polish herbal products will be shaped at a level of approx. 250 M€ and will have a high position among the countries of Eastern and Western Europe. The stable Polish market of products is dominated by traditional herbal products known for years. As opposed to other European plant drug markets, in Poland a large role is played by products used in diseases and digestive system disorders, as well as by those used for a general improvement of the body’s immunity. Also natural cosmetics containing specific plant substances arouse an increasingly bigger interest. A bigger demand for herbal cosmetics influences the increase of herbal companies’ interest in the production of different types of plant products for cosmetic purposes, especially active plant substances used for cosmetics with special effect. At the same time, the food product market has been offering new forms of food, including diet supplements, for many years now. Herbal products are more important functional elements of these products. Such a situation creates completely new possibilities for the herbal industry. An economically important agricultural production area is being created. Despite the constant broadening of the cultivable herb assortment, their harvest from natural state will still constitute one of the sources of raw materials for the herbal industry. It is estimated that approx. 100 species of medical plants in Poland are obtained from natural standings. The total mass of material obtained yearly amounts to 3÷5 thousand tons. The harvest of specific medical plant species falls within the range of several dozen kilograms to several hundred tons a year. It is believed that it is possible to obtain masses of herbal materials coming from natural standings at a level of 7 thousands tons per year, without a noticeable impact on the natural environment. Current domestic trends show that harvest from natural standings will decrease in the future in favor of materials coming mainly from cultivation. Poland is a country of large potential in herbal material production. Herbal cultivation in Poland has a long-standing tradition. There exist modern, specialized farms connected with herb cultivation; many of them cultivate certain herb species on an area over 20 ha. In the recent decades regions of herb cultivations were shaped which provides the possibility of obtaining large material portions of a relatively similar quality. Poland also has a significant number of own medical plant varieties. The herbal plants existing in Poland have a large processing
Waste from juice plants

Poland is an important juice manufacturer. The average production per year is as follows: strawberries - approx. 1.78 ths tons, raspberries - approx. 47 ths tons, blackcurrants - approx. 115 tons, redcurrants - 65 ths tons [10]. As a result of processing carried out in juice plants waste is created. This waste consists of seeds and pulp, including peels. In recent years the interest in EU and Poland has increased in new possibilities of using and managing juice pomace. Companies are created which deal with drying and extracting oil from oil plant and juice seeds. The most often used technique is cold-pressing; however, cold-pressing oil from berry fruit seeds is not efficient and usually leads to a polymerization of oil components. For this purpose, the most useful is supercritical extraction using carbon dioxide in a supercritical state (previously used in Poland only sporadically and on a small scale) which allows for an extraction of lipophilic elements from seeds in conditions that ensure a high hygienic quality of the post-extraction remain. As mentioned earlier, Poland is a leading world manufacturer of berry fruit, especially currants, strawberries and raspberries; thus, it is necessary to conduct development and industrial research of a large innovative potential, which will lead to a gradual solving of the problem of a complex management of pomace with a benefit to the environment, entrepreneurs and consumers who will be interested in consuming food that decreases the risk of occurrence of certain civilization diseases. Thus, the proper management of these three berry fruit seeds is of the large practical significance. Oils from the seeds of currants, raspberries and strawberries include approx. 50% linoleic acid and 30-35% of linolenic acid each. Oils from raspberries and strawberries contain only ω-linoleic acid (ALA), while oil from currants - ALA acid in the amount of 10÷19% and γ-linoleic acid (GLA) in the amount of 11÷24%. Next to evening primrose and borago, currants are the most important source of GLA acid. In a healthy, young human being’s body GLA acid, 18.3(n-6) is created in the liver from linoleic acid. The effectiveness of this process fades with age and it is necessary to introduce GLA acid with a diet or diet supplement. Seeds, especially those from currants and strawberries, contain also almost 20% of protein and approx. 50% of cellulose which constitute scarce diet elements. New technologies and techniques of separating berry fruit elements, insoluble in water, from juice allow for obtaining pomace of a high content of dry mass, often above 40% and over 30% of seed ratio. This leads to the decrease of waste and environmental threat; on the other hand – in accordance with the law on environment protection (JoL 2001, No. 62, item 627) and the act on waste (JoL 2001, No. 112, item 1206) - it is easier and cheaper to conduct further processing which involves recovering valuable materials for further use. Recovery is an activity which does not cause threats to the life, health of people nor for the environment; it leads to using waste in total or in part or to recovering substances and materials and their proper application. Especially friendly to the environment and consumers is the wasteful and solventless extraction of lipophilic elements of waste through an extraction with carbon dioxide in supercritical state, so-called SFE extraction (supercritical fluid extraction). This method is currently the best way to obtain oil extracts prone to oxidation, rich in ω- and γ-linolenic acids and tocopherol from plant materials. Scientific literature and electronic sources provide numerous pieces of information on the favorable use of bioactive elements, usually obtained through cold-pressing, from berry seeds cultivated in different countries. Oils refined from berry fruit seeds in the US and Germany are manufactured with the aim of producing sun and anti-ageing creams for skincare, and part of them is used as diet supplements. Knowledge about the supercritical extraction technology applied in domestic plant materials is insufficient. One 1/2 technical installation using this extraction technique in Poland obtained a high process efficiency and very promising composition and properties of oil extracts from blackcurrant; further experiments with the use of different seeds are underway. An important aim of studies and justification of their scope is the broadening of the market offer of standardized cosmetic oils from seeds of those fruits and the offering of pro-health food products – diet supplements and everyday food, enriched in products and extracts obtained from the post-extraction remains of currants, raspberries and strawberries. Individual studies have shown also that post-extraction remains of blackcurrant seeds from the SFE process on an experimental scale contain also, apart from a considerable content of nutrients, easily fermented cellulose fractions and are characterized by a potential pre-biotic effect. Initial studies also point to the occurrence of an effect of lowering lipid peroxidation indicators and increasing glycolytic activity of the bowel microflora. Therapeutic and pro-health properties of extracts from raspberries have been known for a long time, and they are ascribed to derivatives of ellagic acid and anthocyanins; in the last twenty years, studies have intensified on explaining the mechanisms of their pro-health activity. Post-extraction materials of strawberries and raspberries, obtained using the SFE technique, are less known; however, justified grounds exist for assuming that they contain hydrolyzed elagotannines whose properties and manner of isolating require further, complex studies.

Bases of supercritical extraction

Physical and transport properties of supercritical fluids

A liquid or gas are put into supercritical state (supercritical fluids, SF) if the temperature and pressure they are in exceed values of their critical parameters: temperature (Tc) and pressure (Pc). The created phase possesses intermediate values between liquid and gas. Fluids in supercritical state cannot be condensed by heightening the pressure. Through a change of temperature or pressure the physical and chemical properties of supercritical liquids may be changed, which is used in practice. Especially large changes of physical and chemical properties are observed near critical point. In this area even small pressure changes cause large fluctuations of the viscosity, diffusion and density indicator. Figure 1 presents a phase equilibrium diagram for carbon dioxide.
Characteristic points are marked on it: the so-called triple point and critical point. Moreover, areas of gas, liquid, and solid were marked, as well as the supercritical area. It should be noted that critical parameters for carbon dioxide are rather mild (Tc, Pc). Figure 2 presents images of carbon dioxide in different stages of phase changes. Figure 2.1 shows a two-phase system with a clearly marked border between liquid and steam. In Figure 2.2, as the container with carbon dioxide is heated, a slow blurring occurs of the border between liquid and steam. In Figure 2.3 one may observe the progress of this process, and in Figure 2.4 - a full transition to the supercritical state; only one phase will be shown clearly in the image.

Behavior of fluid in supercritical conditions may be analyzed in terms of its mobility which is evaluated very highly in supercritical conditions. As a result, it may be stated that the solubility in supercritical fluid is similar to solubility in liquid phase, while the capability to penetrate the constant matrix is close to transport properties of gas. This means that the process of extraction in supercritical conditions is a lot faster than processes of classic liquid extraction. At the same time, the possibility of directing the process parameters allows for conducting a separation of extraction products. The rate of extraction depends on the density of the supercritical fluid, while the fluid depends on pressure and temperature. The capability of the supercritical fluid to dissolve solids depends on the density and temperature. In conditions of higher temperatures and the same densities, the process of extraction occurs faster.

**Description of the supercritical extraction process**

More and more often supercritical fluid extraction (SFE) using carbon dioxide is used for obtaining extracts from plant materials [7, 8]. Carbon dioxide is a completely incombustible and nontoxic gas and is widely used for extracting valuable plant compounds. Its capabilities to dissolve various substances and change the process parameters may be easily controlled. This possibility is not offered by traditional extraction methods in the system solid body – fluid. Carbon dioxide does not dissolve certain compounds, e.g.: phenols, alkaloids or glycosides because of their polar character. A small addition of organic solvents, e.g. methanol, ethanol, acetone, acetonitrile, ether, dichloromethane, or water allows for increasing the efficiency of extracting polar compounds.

The extraction process is conducted in a high-pressure apparatus. The installation for extraction in supercritical conditions is constructed from the following basic elements: extractor R1, heat exchangers E1, E2a, E2b, E3, E4, circulation pump P1A, cooling system, separators S1 and S2, expansion valves. The extraction process is of a manufacturing nature. Each production cycle starts from feeding the material into the extractor, and then the apparatus is closed with a special lock, called quick lock. The next operation is a slow increase of pressure in the extractor, until the value of working pressure. The rate of heightening pressure is limited by the value of temperature inside the extractor and the output of the pump. The admissible temperature is determined in terms of technological requirements, specified for the processed material and because of admissible parameters of the extractor’s work; the temperature inside the extractor should not exceed the specified level given by the manufacturer of the extractor. After reaching a specified temperature level inside the apparatus, during the extraction process the feeding of the extractor should be slowed down or even temporarily stopped. The feeding process may be continued only after lowering the temperature to a safe level. After reaching a working pressure, a circulation of carbon dioxide is started up in the extractor. This is the start of the proper extraction process. Liquid carbon dioxide is fed into the circulation pump; it is cooled down to a suitable temperature in order to prevent cavitation and damaging of pump valves or pump whirls. The level of cooling down carbon dioxide depends on the pressure to which carbon dioxide is compressed. After reducing pressure, carbon dioxide may be cooled down using a suitable refrigerating unit or other cooling system (e.g. water cooling). A diagram of carbon dioxide circulation is shown in Figure 3. The extraction process lasts for a specified time, characteristic for a given material, until exhausting the deposit; then, the extractor is stopped and, after reducing the pressure inside the extractor to the level of the surrounding pressure and after opening the extractor, the deposit is discharged. Heat exchangers provide heat necessary for putting carbon dioxide into supercritical state, E4 and cool down the carbon dioxide stream, E3 fed to the high-pressure pump in order to prevent cavitation. Other exchangers deliver heat.

**Table 1.** List of physical and transport parameters

<table>
<thead>
<tr>
<th>Physical and transport parameters</th>
<th>Fluid</th>
<th>Supercritical fluid</th>
<th>Gas, t, p - surrounding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, kg/m³</td>
<td>600-1600</td>
<td>200-800</td>
<td>0.6-2</td>
</tr>
<tr>
<td>Viscosity, Zone</td>
<td>(0.5 – 1.0) (10^3)</td>
<td>(0.5 – 1.0) (10^4)</td>
<td>(10^4)</td>
</tr>
<tr>
<td>Diffusivity, m³/s</td>
<td>(10^3)</td>
<td>(10^3 – 10^4)</td>
<td>(10^4)</td>
</tr>
</tbody>
</table>
to extractor jackets or pipes, as well as separators and homogenizer, in order to prevent the extractor from depositing on apparatus or pipe walls. Expansion valves reduce pressure to a specified level and determine the stability of the installation's work.

**Fig. 3. Technological diagram of installation for extracting plant materials using CO₂ in supercritical conditions**

### Polish industrial installations for extracting plant materials in supercritical conditions

#### Installation for hop extraction

Breweries use mainly hop extracts which are concentrated extracts of resins and aroma oils from hops. Although hops contain many compounds, the most important include α-acids and β-acids. The object of trade is only α-acids and their amount decides about the profitability of hop production and processing. For this reason, those variants of hop which contain larger amounts of α-acids are the object of most interest. Varieties of hop with a low content of α-acids, even if they are valued by beer manufacturers because of the content of fragrant oils, undergo slow elimination from the plantation as less profitable. α-acids undergo isomerization during beer production and transfer into iso-α-acids which are the source of characteristic bitter taste. Iso-α-acids may undergo further unfavorable changes under the influence of light when storing beer; for this reason, beer with iso-α-acids are stored in dark bottles or metal cans.

The Institute of Fertilizers in Pulawy has developed a technology of hop extracts, as well as constructed and started an installation for processing hops according to this technology. The installation for hop extraction consists of four extractors, each with a capacity of approx. 2.6 m³. Carbon dioxide in supercritical conditions is used as solvent. The installation may work under a pressure of 250÷300 bars, at a temperature of approx. 35÷90°C. The process of hop extraction is a periodic process, because it is necessary to replace deposits in each extractor after its exhausting. The use of four extractors allows for conducting the extraction process in a continuous way, even with a short extraction cycle, by maintaining three extractors in motion and preparing the fourth extractor for work (discharge of extracted hop and loading of fresh material). Because of the necessity to often open the extractors, during extract production special closing solutions are used, so-called quick locks which enable the opening and closing of each extractor within a dozen or so seconds. Extractors are fitted with filtration systems which provide protection against the convection of solid hop particles. Extractors are connected with a system of pipes and valves which allow for work in a serial, parallel or mixed system. This is necessary when working with several extractors simultaneously. Upon introducing another extractor with fresh hop into circulation, the extractor in which the extraction process has finished is shut down. The loading of extractors occurs through a suitable charging system composed of a hoist, so-called big-bags. Discharge of the extracted hop occurs using pneumatic transport.

#### Universal scientific-production installation for extracting plant materials

The universal research-production installation for extracting plant materials is composed of two extractors with a working volume of approx. 2.2 m³ and a diameter of 1 m. It will be possible to introduce the material into extractors by means of two ways: using special baskets or by feeding directly into the apparatus. Depending on the adopted manner of feeding the deposit, the extractor will be properly prepared for work. When working with the use of a basket, filters are installed directly on baskets and no other liquid filtration is used after extraction. When working without baskets, grates are mounted in extractors from sinters, as well as filters in the outlet part from the extractors. The installation may work within a pressure range of 200÷530 bars, at a temperature up to 100°C. It has two separation stages: a stage of high-pressure separation up to 300 bars and a stage of low-pressure separation at a pressure of approx. 60 bars. Moreover, it has a low-pressure water separation stage, working at a pressure of approx. 60 bars. The installation is meant for extracting plant materials, especially pepper, berry fruit seeds, rice and cereal germs, as well as many other materials, containing especially unsaturated oils. The installation is not meant for extracting hop. The installation is fitted with refrigerating units for cooling carbon dioxide at the pump suction and for cooling CO₂ and its condensation, as well as for water separating. Thanks to this, the installation will be independent from the surrounding conditions and it will be possible to use it for the entire year.

**Fig. 4. View of extractors for hop extraction**

**Fig. 5. View of extractors**

### Summary

Poland is a significant agricultural producer in Europe. Favorable climate enables the production of high-quality fruit, vegetables and other plant materials. For this reason, plant products - unprocessed...
and processed — are readily purchased by domestic and foreign customers. Poland is also an important world manufacturer of processed plant products, e.g.: juices, paste, jams and other products of the agricultural-food industry. Plant materials (herbs), as well as remains after processing fruit (e.g. seeds and pulp skin) and vegetables may be further processed using extraction in supercritical conditions. The Institute of Fertilizers in Pulawy has developed a technology of hop extracts, as well as constructed and started up the first installation for producing hop extracts in Central and Eastern Europe. For several years it has also conducted studies on the application of other plant materials for obtaining valuable products for different industry branches. The extraction trials of berry fruit seeds in supercritical conditions, conducted at INS, have confirmed the presence of high-quality polysaturated oils and flavonoids. The obtained oils and natural pigments may be broadly used, e.g.: in the food, pharmaceutical, cosmetic and fodder industries. Extraction of plant materials in supercritical conditions using CO₂ is still intensively developed in the Institute of Fertilizers. A technology was developed and a universal research-production installation was constructed for processing plant materials, including materials containing oil extracts and oleoresins from pepper. Poland has a chance to become a leading manufacturer of high-quality components of cosmetics, food and drugs if it keeps up with the best and will continue working on broadening an offer based on supercritical extraction products.

Poland is currently the only manufacturer of hop extract on an industrial scale in Central and Eastern Europe, using extraction in supercritical conditions with carbon dioxide. The technology of extraction in supercritical conditions using CO₂ is an advanced technology, does not pollute the environment, does not generate harmful residues. Extraction products and post-extraction remains are sterile, without any harmful additives. Extracts may be stored for a long time, without a noticeable loss of precious qualities. Post-extraction remains may be used for further processing, e.g. in the food or fodder industry. There exists the possibility of using the extraction technology for producing extracts from many domestic natural materials, including plant materials. Natural extracts are an object of interest for companies from the food, cosmetic, pharmaceutical and fodder industry [11].

Literature