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# SUPERCRITICAL FLUID EXTRACTION OF VEGETABLE MATERIALS

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**Abstract**. The paper presents the base and conditions for the extraction of organic materials with solvents in the supercritical state with particular attention to use of $CO_2$ as the extraction agent. The advantages and disadvantages of this process are described. The examples of extraction of organic materials using supercritical of $CO_2$ are presented.

**Keywords**: carbon dioxide, supercritical fluid extraction, vegetable materials.

## 1. Introduction

A wide use of supercritical gas extraction (SGE) or supercritical fluid extraction (SFE), as an extraction or separation method, in fuel and energy, chemical, food production or pharmaceutical industries as well as methods of separating mixtures or extractions of substances in analytic technology was possible because of the discoveries and research results carried out in second half of 19th century.

In 1822 C. Cagniard de la Tour [1] noticed that beyond a certain temperature some substances do not undergo the process of evaporation and condensation, but occur in the form of supercritical fluid having specific properties. In the 1870s Andrews [2] considerably expanded the knowledge concerning supercritical phenomena. For the first time he called the temperature above which substances obtained the characteristic of a supercritical fluid, a "critical point". In 1879 Hannay and Hogharth [3] proved that supercritical fluids have high potential to dissolve solid matter and fluid. The above discovery was used as supercritical extraction approx. 100 years later in numerous industries.

Already in 1920s attempts were made to use compressed gases (supercritical fluids) in refinery industry to separate heavy oil fractions from petroleum residue using *n*-pentane in supercritical state – so-called ROSE method [4, 5]. A little later attempts were made to separate mixtures in appropriate columns using supercritical fluids [6, 7]. In the 1960s Zosel *et al*. [8] designed the basics for the technology of extraction of natural components using carbon dioxide ($CO_2$) in supercritical state. In food industry this technology was used in 1970s in the process of the decaffeination of coffee and work on decaffeination of tea as well as extraction of oils from hop. In 1980s in Europe, USA and Australia the technologies using supercritical extraction were developed on an industrial scale. At that time the first unit was built for complete fractioning, and the first spices obtained *via* this method were admitted to market.

In 1970s the search for new ways of processing coal to obtain synthetic crude oil led to intensified research on extracting them with fluids in supercritical state – SGE process. Researches on the new method of liquefaction of coal, by extraction of coal using gaseous solvents, compressed to high densities, at temperatures higher than their critical point [9], were initiated by the National Coal Board in Great Britain [9-11]. The researches were carried out between 1970s and 1990s with various intensity in a number of government and industrial research centres of the world [11-13], including centres in Poland, mainly the Institute of Chemistry and Technology of Petroleum and Coal, Wroclaw University of Technology, (currently the Division of Chemistry and Technology of Fuel). In this particular University research centre supercritical phenomena have been used in numerous research areas [14-20].

Apart from industrial uses, the technology is applied in analytic chemistry, analysis of biological and environmental samples such as water, soil, flue ash, biological tissue and other materials, to separate relevant

organic compounds from matrix, as an alternative for solvent extraction.

Huge interest in supercritical phenomena and their practical use led to considerable increase in publications and patents, which was expressed by publication of the first international scientific journal (in 1988) "The Journal of Supercritical Fluids", devoted to results of work on SFE process.

A wide use of this extraction technology is related to its high capability of dissolving various substances by compressed gases in supercritical conditions. The fluid or gas in supercritical state (supercritical fluid) is dense and capable of being dissolved by liquid solvents while the speed of diffusion, viscosity and penetration ability is comparable to that of gases. The connection of high ability to dissolve supercritical fluids and the penetration ability represent the main advantage of the supercritical extraction process over the traditional solvent extraction or traditional distillation as a form of separation.

## 2. Basics of Supercritical Extraction of Organic Materials

### 2.1. General Principles of the Extraction Process

The process of extracting organic material using supercritical solvents is based on the dissolving effect of compressed gases compared to the condensed phases, *i.e.* solid matter and liquids, expressed by the increase in saturated vapour pressure over solid matter or liquid $p/p^o$, induced by the presence of compressed inert gas. This increase in saturated vapour pressure being the measure of deviation from the Dalton law, often reaches very high values of $10^7$ [21, 22].

The deviation from the Dalton law is present in most real systems and it is the sense of SGE or SFE extraction. The use of this phenomenon creates the possibility of obtaining (from various materials) substances of very low volatility, *i.e.* low saturated vapour pressure. A quantitative description of solubility of solid matter and liquids in compressed gases was first introduced by Poynting [23]. It allowed to describe experimental data mostly only in a qualitative method [24-26], and the attempts to modify it did not result in a material improvement of anticipated concentrations of gas solutions with experimental data.

In 1950s scientists derived an equation of solubility in compressed gases for real systems based on a virial equation of real gas state [27-30]:

$$\ln \frac{c}{c_0} = \frac{V^s - 2B_{12}}{V} \tag{1}$$

where $c/c^o$ is a measure of an increase in concentration of component 1 in gas phase over the $c^o$ value attributable to a single-component, *i.e.* with no presence of inert gas; $V^s/V$ ratio corresponds to Poynting effect and this expression does not depend on the type of gas, and only shows the impact of total pressure in the equation on $c/c^o$ value; the second 'mixed' virial $B_{12}$ coefficient is the function of temperature. The ratio $2B_{12}/V$ depends both on the character of gas and the substance in its compressed phase. Thus it takes account of individual features of the components creating the system in question.

Above the relationship allows with some deviations [30], only to describe experimental results obtained in simple, defined two-component system. Nevertheless the dependence allows formulating general rules of conducting gas extraction.

High concentration of gas solutions occur when molar volume of $V$ mixture goes to low values. Having assumed that inert gas is the main component of a mixture, it can be concluded that it will be more effective at higher molar density $1/V$, *i.e.* at higher pressure. With the constant pressure set, gas density decreases as temperature rises, therefore extraction temperature should be the lowest possible. Practically it means that gas extraction should be conducted in temperatures close to the gas critical temperature.

In the above equation there is also another virial coefficient $B_{12}$, *i.e.* the function of temperature. The paper of Prausnitz [29] shows that the decrease in temperature of gas extraction although results in increase of $c/c^o$ quotient, but it is not a sufficient condition to obtaining higher concentration in gas phase. The saturated vapour pressure over the concentrated phase $p^v$ or corresponding molar concentration $c^v$ in the presence of inert gas, in certain ranges of total pressure significantly decreases with temperature [30]. Therefore the choice of extraction temperature must be a compromise between the influence of temperature on the $c/c^o$ and the impact of temperature on the standard $c^o$ value.

The provided theoretical description of solubility in compressed gases do not result in any limitations regarding the applied pressure in extraction process carried out above the critical temperature of the extraction solvent.

As it was mentioned above, the derived equation of solubility in compressed gases for real systems based on a virial equation of real gas state equation, does not allow to estimate concentrations of the extracted substance in the case of multi-component mixtures. An attempt to predict "solubility" of coal in gas extraction based on the solubility parameter Hildebrand ð, was made by Giddings [31-33]. Basing on experimental data, Giddings suggested

that the power of supercritical extraction is directly related to their solubility parameter ð. Basing on the van der Waals equation he obtained for different solvents almost a linear correlation between the solubility parameter and efficiency of the extract.

The attempt to obtain a quantitative description of the SFE process is also affected by the occurrence (in the case of using a mixture of two or more solvents, in which one of the components of the mixture is a polar solvent, *e.g.* toluene or methanol) of synergetic effect. In such a case having a specific content of individual components in the mixture, it is possible to achieve higher efficiency of extracts, compared to efficiency of extracts obtained from only individual components [32, 34].

## 2.2. Parameters of Extraction Process

Yields of SFE process, properties and chemical composition of extracts depend both on the type of the supercritical fluid, and the parameters of the process: temperature, pressure, extraction time and the method of extracted material contact with the solvent in the supercritical condition. The higher the extraction solvent density (*i.e.* the higher pressure of the process), the higher its ability to dissolve solids and liquids in supercritical conditions. Typical solvents include simple paraffin hydrocarbons (pentane, hexane), aromatic (benzene, toluene), alcohols (methanol, isopropanol, *n*-butyl alcohols) and their mixtures, and some gases (carbon dioxide, ethylene, propane) are used. When choosing a solvent for SFE process, the key parameters include its temperature and critical pressure, hydrogen donor solvent properties and polarity. Table 1 shows critical parameters of selected extracting agents.

In the relevant literature concerning supercritical extraction of coals an important problem for the economics of the process and yields, properties and chemical composition of coal extracts is the problem associated with the decomposition of the solvent (*e.g.* alcohols) or connection of solvent molecules to extracted organic substances and residues (*e.g.* simple aromatic hydrocarbons). The scale in which the solvents are decomposed depends on the temperature of the process and the type of the used solvent and may reach up to 5 % of the mass in the case of toluene and up to 35 % in the case of butanol.

Generally, supercritical fluids are non-polar and are better in dissolving non-polar substances. In most cases a supercritical fluid dissolves ionized substances. *i.e.* those ones with dissociated acidic and basic groups and mineral salts, as well as polar compounds. In such a case two main strategies are applied involving the increase in polarity of the solvent, or the decrease in polarity of the substance being extracted [37]. A substance which will modify polarity of the supercritical fluid, *e.g.* ethanol to $CO_2$, can be applied as well. In addition operation parameters of the process influence the effectiveness of extraction of polar compounds – the decrease of pressure enhances the process [37].

The process of extraction performed under supercritical conditions also allows fractioning of soluble substances. Separation of components from a gas mixture is achieved through the change of temperature and/or pressure in a separation system. The result is the change of individual components solubility allowing their progressive precipitation [37, 38]. An appropriate choice of temperature makes it possible to keep in the extractor only one component; more volatile components may leak out to a separator. According to this method one can precisely separate and concentrate individual components.

*Table 1*

**Critical parameters of selected extracting agents [32, 35]**

| Solvent | Critical temperature $T_C$, K | Critical pressure $P_C$, Pa | Critical density $q_C$, kg/m³ |
|---|---|---|---|
| *n*-Hexane | 507.9 | 2989087.5 | 234 |
| Decane | 621.2 | 2148090.0 | 231 |
| Cyclohexane | 554.1 | 4053000.0 | 270 |
| Benzene | 561.8 | 4863600.0 | 304 |
| Toluene | 593.8 | 4215120.0 | 292 |
| Alcoholes:<br>  Methanol<br>  Ethanol<br>  Isopropanol<br>  Butanol | <br>513.0<br>516.5<br>516.0<br>559.7 | <br>7974277.5<br>6393607.5<br>5370225.0<br>4914262.5 | <br>272<br>276<br>274<br>270 |
| Water | 647.4 | 22139512.5 | 318 |
| Carbon dioxide | 304.2 | 7396725.0 | 468 |

# 3. Supercritical Extraction of Organic Material

## 3.1. Characteristics of Carbon Dioxide as an Extracting Agent

Carbon dioxide ($CO_2$) occupies a special position among applied extraction solvents. It is easily accessible, cheap and creates no problems typical for toxic waste; it is characterized by low critical temperature ($T_k = 304$ K) and relatively high critical pressure ($p_k = 7.39$ MPa) (Table 1, Fig. 1). It also offers low viscosity and high diffusion which allows deep penetration of the substrate to obtain all desirable components from the raw material; it is non-corrosive and non-flammable [39, 40]. In addition, under normal conditions it is a gas which facilitates its removal from the product after the extraction process. In environmental terms, carbon dioxide can be obtained from production surplus in other industries [41].

Taking into account $CO_2$ properties in supercritical conditions, it is a Lewis base with a polarity comparable to that of *n*-hexane. Therefore in polar extractions of substances, organic modifiers enhancing solubility of $CO_2$ should be used (its mixture with the modifier). Solubility of compounds in supercritical carbon dioxide decreases along with the increase in their polarity (Fig. 2), aromatic feature (Fig. 3), number of carbons in a homologous series and molecular mass [43].
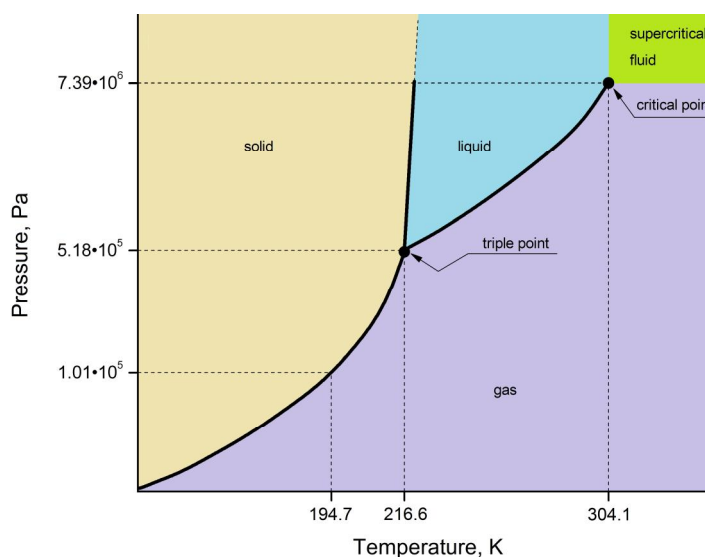


**Fig. 1**. Phase diagram of carbon dioxide [42]



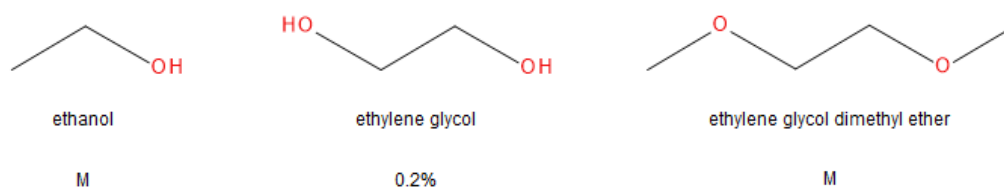**Fig. 2**. Influence of polarity compound on its solubility
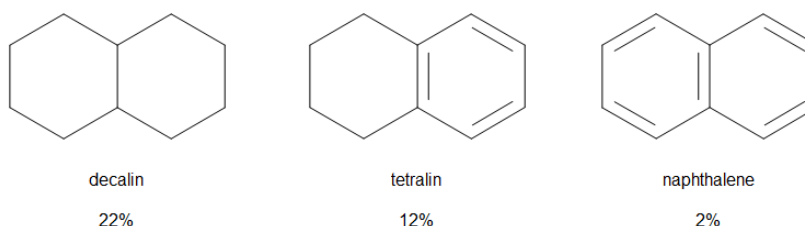in supercritical $CO_2$ (M-miscible with liquid $CO_2$) [43]



**Fig. 3.** Decrease in compound solubility in supercritical $CO_2$ along
with an increase in their aromatic features [43]

Solubility increases with the increase in degree of branching and unsaturation of the hydrocarbon chain. Supercritical carbon dioxide is well dissolved with extracting compounds with low molecular mass and polarity, aliphatic hydrocarbons having less than 12 atoms of carbon in a molecule, saturated mono-hydroxyl aliphatic alcohols having less than 6 atoms of carbon in a molecule, saturated aliphatic carboxylic acids having less than 9 atoms of carbon in a molecule, esters such as analogous acids, saturated aliphatic aldehydes having less than 8 atoms of carbon in a molecule, glycerides in a mono < tri < di, resulting from decreasing polarity corresponding to the increase in the degree of esterification, but with increasing molecular mass [43]. Aromatic hydrocarbons and macromolecules, as well as polar compounds, such as salts, glycerol, sugars and protein are non-soluble in supercritical carbon dioxide.

Undoubtedly the application of the high-pressure equipment has an impact on the price of obtained products.

The advantage of extraction in supercritical state over liquid extraction is mainly more effective and more precise separation of a solution from post-extraction residue, associated with large differences in viscosity and density of the supercritical phase and residue. In liquid extraction multicomponent extracts without individual chemical components are usually obtained.

## 3.2. Method of SFE Process Realization

The equipment for SFE process comprises a pump for compressing the solvent or a compressor, pressure and temperature measurement system, pressure extractor and separators. Extraction is periodic. Each production cycle begins by loading material to the extractor and then the extractor is closed with a special lock.

Another operation involves slow increasing pressure in the extractor to the working pressure value. The speed of increasing pressure is limited by the temperature inside the extractor and capacity of the pump. The admissible temperature is established based on technological requirements concerning the processed material and admissible extractor operational parameters.

After a specific level of temperature inside the extractor is reached during the extraction process, its loading process should be slowed down or even stopped. The filling process can be resumed only after the temperature is lowered to a safe level.

After the working pressure is reached in the extractor, circulation of carbon dioxide is initiated. This is the beginning of the proper extraction process. Liquid carbon dioxide is cooled to the required temperature and added to the circulation pump, in order to prevent cavitation and damage of valves or pistons of the pump.

The level of carbon dioxide cooling depends on a pressure to which $CO_2$ is compressed. After pressure reduction carbon dioxide can be cooled using special cooling unit or using a different cooling system (*e.g.* water cooling). The extraction lasts as long as required for the used specific material. After finishing the process the extractor is stopped. After reducing the pressure inside the extractor to the ambient pressure, the extractor is opened and the post-extraction residues are removed.

In the case of multi-component materials the separation is carried out gradually, decreasing pressure or temperature. In such a way it is possible to selectively separate several components of the extract.

## 3.3. Extraction of Vegetable Materials with Carbon Dioxide in Supercritical State

Based on the analysis of results published in worldwide scientific literature in 2000 – 2013, Melo *et al.* [44] presented an interesting publication concerning the current state of knowledge and research on supercritical extraction of vegetable materials. It includes the analysis of the used plants and obtained products, processing conditions under which they were obtained, including solvents and co-solvents (modifiers), optimization and modelling methods, as well development level of individual processes in terms of their industrial use.

The above-mentioned publication describes more than 300 raw materials, 28% of the works relates to the extraction of seeds, 17 % – leaves, 10 % – fruit, 7 % – roots, 5 % – flowers, 3 % – rhizome and 32 % – other materials, including their mixtures [44]. SFE extracts obtained from vegetable matrices are typically mixtures of the following compounds: triglycerides, fatty acids, fatty alcohols, terpenoids, phytosterols, tocopherols, tocotrienols and phenolics [44].

It is worth noticing that a large part of the material is plant biomass. Many obtained extracts and pure compounds from this biomass are used for human nutrition and health purposes, the others represent potentially new applications, involving plants [44].

As it was mentioned above, one of the efficient ways of obtaining oils, including special oils from nuts, seeds or grains of various plants or fruit, fragrant roots and flavorings for food, pharmaceutical and cosmetic industries, is their extraction using carbon dioxide in supercritical conditions. These oils contain for example bioactive substances soluble in fats (plant sterols, carotenoids and vitamin E). The process is currently being developed in fat industry as an alternative for conventional refining, separation or fractioning methods. A historic fact is the use of this method in food industry

for decaffeination of coffee and tea as well as extraction of oils from hop [45, 46]. The extract product contains bitter acids, fatty parts and essential oils (10 vol %) [47-48]. It contains no pesticides. The application of carbon dioxide instead of currently applied dichloromethane or methylene chloride [47] allows conducting the process at relatively low temperature and anaerobic conditions. As a result, active components are not decomposed and oxidized and their organoleptic quality is not deteriorated.

An example of special oils obtaining is supercritical $CO_2$ extraction of Canola seeds. Under the pressure of 10–35 MPa, at the temperature of 313–333 K, using 6–26 kg $CO_2$ for 1 kg of raw materials, with 9–57 wt % yield one can obtain oil which may be less stable than refined or crude canola oil due to its higher free fatty acid content and polyunsaturated fatty acid level. However, it requires less refining to remove undesirable compounds such as chlorophyll pigments. Quantification of total phytosterol and tocopherol levels suggests healthier oil than refined oil [49].

Carbon dioxide is often used in extraction of oil fractions from specially prepared seeds (pre-macerated with water). Plant oils are the mixtures of fatty acid glycerides and free fatty acids. Individual compounds differ in solubility regarding $CO_2$. At the temperature above 238 K and pressure of 20 MPa they well dissolve in supercritical $CO_2$. In terms of efficiency and quality of the product the parameters for running extraction process every time must be adjusted experimentally.

One of the reasons that SFE-obtained oils are rancid is their low content of phospholipids which are poorly soluble in $CO_2$ [50, 51]. Improvement in their solubility in supercritical $CO_2$ can be achieved by increasing its polarity by adding ethanol. The fact that oils obtained by extraction have low content of phospholipids was used to produce good quality lecithin [52]. It is produced by double step phase extraction, involving the use of $CO_2$, then extraction of the oil to 15 wt. % of its content in the material, and then extraction using supercritical $CO_2$ with 10 % ethanol. This allows to obtain oil with over 5 wt % of phospohlipids from which lecithin is produced. In this process a mixture of solvents can be used simultaneously. This type of extraction involves the use of both polar and non-polar solvents [53]. The polar one which usually contains a mixture of methanol, ammonia and water, dissolves low-molecular sugars, non-protein nitrogen compounds, hydrating phospholipids and glucosinolates, which improve the quality of both pellets and oil [54].

Supercritical $CO_2$ extraction is also used to remove strong volatile compounds and essentials oils. This method is an attractive alternative for traditional separation methods such as distillation or solvent-based extraction. Essential oils mainly contain hydrocarbons and oxidised terpenes or sesquiterpenes. They are used as flavour additives in food. Their share in oily plants is low – from 1 to 3 wt %. They can be separated using supercritical $CO_2$ extraction which guarantees their best solubility (9–20 MPa, 313–323 K). Solubility of essential oils in supercritical carbon dioxide is much stronger compared to other substances tested for extraction under low pressure. Another example can be the extraction of lemon aroma [55]. Limonene contained in the peel of lemon belongs to the group of essential oils characterized by good solubility in supercritical $CO_2$. It is extracted at 7–10 MPa and 323 K. Under similar conditions lemongrass is extracted [56]. Another interesting material for obtaining fragrance substances is spices. The efficiency of taste-fragrance extraction from spices depends on the processing conditions, *e.g.* for ginger it is 4.5 wt %, for pepper – 12 wt % [45].

Another group of material is herbs, which are especially reach in essential oils but also contain anthocyanins. Method is applied in research on extraction of natural colouring agents ($\beta$-carotene, astaxanthin), and removing animal fat from milk and egg yolk [37]; also in deodorizing of fat and oils, separation of phosphatide (lecithin), extraction of oil essences from mint, garlic and oregano, extraction of aromas and tastes (tropical and citrus fruits) [37, 57, 58].

Pomace from fruit juice production plants, especially from berry fruits can be equally useful in obtaining many unsaturated oils, as well as polyphenol, TCP and carotenoids [59]. They serve as antioxidants necessary for proper functioning of human body.

Algae and water plants or those from plantations are rich in excellent bioactive compounds. Extracts from algae are particularly used in cosmetic and pharmaceutical industry, and as valuable source and supplements of diets. Algae can be extracted using supercritical $CO_2$. Extracting efficiency may reach 95 %. The process should be conducted under pressure of at least 60 MPa, to obtain the desirable efficiency [60].

## 4. Conclusions

Extraction of organic materials using carbon dioxide in supercritical condition has numerous advantages compared to other industrial methods. It allows to obtain with high efficiency and purity the individual components or mixture of a number of useful compounds, *e.g.* bioactive compounds, colouring agents, essential oils and special oils. However this technology requires installation of high-pressure equipment. Nevertheless, the cost of manufacturing various products using SFE compared to traditional methods (*e.g.* producing essence using distillation with water vapour) is lower.

# References

[1] de La Tour C.: Annales de Chimie et de Physique, 1822, **21**, 127.

[2] Andrews T.: Philosophical Transactions of the Royal Society (London), 1869, **159**, 575.

[3] Hannay J. and Hogarth J.: Proc. Roy. Soc. London, 1879, **30**, 484.

[4] Brunner G.: J. Supercrit. Fluid., 2015, **96**, 11.

[5] Subramanian A. and Floyd A.: Pat. US 2011/0094937 A1, Publ. Apr. 28, 2011.

[6] Sihvonen M., Jarvenpaa E., Hietaniemi V. *et al.*: Trends Food Sci. Technol., 1999, **10**, 217.

[7] Czechowski F., Stolarski M. and Simoneit B.: Fuel, 2002, **81**, 1933.

[8] Zosel K.: Pat. US 4247570, Publ. Jan. 27, 1981.

[9] Whitehead J. and Williams D.: J. Inst. Fuel, 1975, **48**, 182.

[10] Pitt G. and Millward G.: Coal and Modern Coal Processing: An Introduction, Academic Press, London 1979.

[11] Maddocks, R.R., Gibson J. and Williams D.F.,: Chem. Eng. Prog., 1979, **75**, 49.

[12] Bartle K., Calimli A., Jones D. *et al.*: Fuel, 1979, **58**, 423.

[13] Tugrul T. and Olcay A: Fuel, 1978, **57**, 415.

[14] Rutkowski A. and Slomka B.: Koks, Smoła, Gaz, 1979, **24**, 4.

[15] Slomka B., Rutkowski A. and Stolarski M.: Koks, Smoła, Gaz, 1982, **27**, 97.

[16] Surygala J. and Stolarski M.: Koks, Smoła, Gaz, 1986, **31**, 205.

[17] Stolarski M. and Szczygiel J.: Fuel, 1991, **70**, 1421.

[18] Stolarski M., Machnikowski J. and Machnikowska H.: Fuel, 1993, **72**, 1497.

[19] Rutkowski A. and Slomka B.: Pat. PL 10900282, Publ. Jan. 31, 1981.

[20] Stolarski M., Szuba J. and Walendziewski J.: Karbo, 2003, **3**, 142.

[21] Eiesenbeiss J.: A basic study of the solubility of solids in gases at high pressures. Southwest Res. Inst., San Antonio 1964.

[22] Slomka B.: Doctoral thesis, Wrocław University of Technology, Wroclaw 1982.

[23] Poynting J.: Phil. Mag., 1881, **IV**, 32.

[24] Bartlett E.: JACS, 1927, **49**, 65.

[25] Wiebe R.: JACS, 1941, **63**, 475.

[26] Robin S.: J. Chim. Phys., 1951, **48**, 501.

[27] Paul P. and Wise W.: The Principles of Gas Extraction. M and B. Monographs, CE/5 London 1971.

[28] Jepson W.: J. Chem. Phys., 1955, **23**, 1599.

[29] Prausnitz J.: AIChE., 1959, **5**, 16.

[30] Ewald A., Jepson W. and Rowlinson J.: Disc. Far. Soc, 1953, **15**, 238.

[31] Randall L.: Separ. Sci. Technol., 1982, **17**, 1.

[32] Vasilakos N., Dobbs J. and Parisi A.: ACS, Division of Fuel Chemistry, 1983, **28**, 4.

[33] Amestica I. and Wolf E.: Fuel, 1984, **63**, 227.

[34] Lisicki Z., Majewski W., Cendrowska B. and Eybinski W.: Chem. Ind., 1985, **XXXVII**/Juni, 404.

[35] Poradnik Fizykochemiczny. Praca zbiorowa. B 81-84, WNT, Warszawa 1974.

[36] Luque de Castro M. and Tena M.: Trends Anal. Chem., 1996, **15**, 32.

[37] Janiszewska E. and Witrowa- Rajchert E.: Żywność. Nauka. Technologia. Jakość, 45, **5**, 2005.

[38] Brunner G.: J. Supercrit. Fluid., 2009, **47**, 574.

[39] Brunner G.: J. Food Eng., 2005, **67**, 21.

[40] Diaz-Maroto M., Perez-Coello M. and Cabezudo M.: J. Chromatogr. A, 2002, **947**, 23.

[41] Chin K., Crabb Ch., Ondrey G. *et al.*: Chem. Eng., 1998, **10**, 32.

[42] McCoy S.: PhD thesis, Carnegie Mellon University, Pittsburgh, PA 2008.

[43] Steytler D.: Supercritical Fluid Extraction and its Application in the Food Industry [in:] Grandison A. and Lewis M. (Eds.), Separation Processes in the Food and Biotechnology Industries: Principles and Applications, Woodhead Publishing, 1996.

[44] Melo M., Silvestre A. and Silva C.: J. Supercrit. Fluid., 2014, **92**, 115.

[45] Duarte C., Moldao-Martins M., Gouveia A. *et al.*: J. Supercrit. Fluid., 2004, **30**, 155.

[46] Knez Z., Markovicz E., Leitgeb M. *et al.*: Energy, 2014, **77**, 235.

[47] Valcarcel M., Tena M. and Fresenius J.: Anal. Chem., 1997, **358**, 561.

[48] Li H., Wu J., Rempel C. *et al.*: JAOCS, 2010, **87**, 1081.

[49] Khattab R., Rempel C., Suh M. *et al.*: Am. J. Anal. Chem., 2012, **3**, 966.

[50] List G. and Friedrich J.: JAOCS, 1989, **66**, 98.

[51] Buskov S., Sorensen H., Sorensen J. *et al.*: J. Food Nutr. Sci., 1997, **6/47**, 115.

[52] Dunford N. and Temelli F.: JAOCS, 1995, **72**, 1009.

[53] Diosady L. and Rubin L.: GCIRC Congress, Canada, Saskatoon 1991, 776.

[54] Thobani M. and Diosady L.: JAOCS, 1997, **74**, 207.

[55] Rozzi N., Phippen W., Simon J. *et al.*: Lebensm.-Wiss. u.-Technol., 2002, **35**, 319.

[56] Sun Y., Liu Z., Wang J. *et al.*: Sep. Purif. Technol., 2008, **64**, 221.

[57] Grajek W. and Lukaszynski D.: Przemysł Spoż., 1993, **11**, 307.

[58] Jung J. and Perrut M.: J. Supercrit. Fluid., 2001, **20**, 179.

[59] Roj E., Dobrzynska-Inger A., Kostrzewa D. *et al.*: Przem. Chem., 2009, **88**, 1325.

[60] Roj E.: Ekstrakcja surowców roślinnych w warunkach nadkrytycznych z użyciem CO₂, rozdział 22, Inst. Nawozów Sztucznych, Puławy 2013, 413-428.

## НАДКРИТИЧНА ФЛЮЇДНА ЕКСТРАКЦІЯ РОСЛИННИХ МАТЕРІАЛІВ

**Анотація.** Приведені основні положення і умови екстракції органічних матеріалів розчинниками в надкритичному стані. Особливу увагу акцентовано на використанні CO₂ як екстрагента. Описані переваги і недоліки процесу. Розглянуто приклади екстракції органічних матеріалів з використанням надкритичного CO₂.

**Ключові слова:** діоксид вуглецю, надкритична флюїдна екстракція, рослинні матеріали.