Translated from *Uspekhi Khimii* **60** 2412–2421 (1991) U.D.C. 542.61

Supercritical extraction and prospects for the creation of new waste-free products

A A Pichugin, V V Tarasov
Mendeleev Moscow Institute of Chemical Engineering

ABSTRACT. The principal ideals underlying a new separation procedure—supercritical extraction—are described and its advantages and disadvantages are considered. The properties of supercritical gases such as solvent power and selectivity are discussed. The possibilities of supercritical extraction in the solution of applied problems in the protection of the environment are demonstrated: purification of waste waters, regeneration of sorbents, detoxification of toxicants.

The bibliography includes 32 references.

Contents

I.	Introduction	1249
II.	Properties of supercritical phases as extractants	1249
III.	Organisation of the supercritical exraction process	1251
IV.	Applications of supercritical extraction	1253

I. Introduction

The tasks faced by modern chemical engineering in connection with the problems concerning the protection of the environment can be performed only on the basis of the ecological optimisation of the existing and the creation of new low-energy low-waste chemical processes. One of the promising aspects of the creation of such processes, which has been attracting increasing attention by investigators and technologists during the last decade, is based on the use of supercritical gases as extractants and solvents for the extraction, separation, and purification of substances and also as a medium for various chemical reactions.[1] Although the first studies on the application of supercritical gases as solvents were published as early as the past century,[2] systematic fundamental and applied research in this field dates back to the 1970s, which is associated with the increasing urgency of energy saving and environmental protection problems. Among studies carried out hitherto on these lines, the vast majority are devoted to supercritical extraction (SE) of various substances both from the standpoint of the investigation of the physicochemical features of supercritical extraction and from the standpoint of its chemical-analytical and technological applications.

Supercritical extraction is a method for the extraction of components of solid or liquid mixtures into a supercritical gas phase, which plays the role of an extractant in this case. The supercritical gas (*supercritical fluid*) is a substance in a supercritical state, i.e. at a temperature and pressure above its critical point. By virtue of their low critical temperatures, carbon dioxide, ethane, ethylene, propane, sulphur hexafluoride, etc. have found the greatest number of applications in research and technological practice as extractants. Among them the greatest popularity is enjoyed by supercritical CO_2 because of its high solvent power in relation to many organic substances, ready availability, low cost, non-combustibility, and non-toxicity. A significant advantage of supercritical gases (SG) compared with the usual liquid solvents (extractants) is that the solvent power of such gases exhibits a marked dependence on temperature and pressure, which makes it possible to regulate extremely (i.e. by varying the temperature T or the pressure p) the selectivity of the supercritical extractants and also to achieve the complete regeneration of the extractant without resorting to reagent methods or distillation. Another attractive aspect of the application of supercritical gases is that high molecular diffusion coefficients (higher by 1–2 orders of magnitude than for the usual liquids) and low viscosities (approaching the usual gases in terms of order of magnitude) are characteristic of such substances.

Although supercritical extraction is a new and relatively expensive process, the results of a whole series of resarch studies have already found industrial applications and have been commercialised. For example, certain new technological processes based on supercritical extraction in the USA include the regeneration of the adsorbents and catalysts, the extraction of certain toxic organic substances from aqueous solutions and the soil, the elimination of asphaltenes from heavy petroleum fractions, the removal of sulphur from coal, the extraction of caffeine from coffee grains, the extraction of certain biologically active substances from plant raw material, etc. The range of industrial applications of supercritical extraction has been gradually expanding.

Supercritical extraction has been finding increasing applications in analytical chemistry as a selective method for the separation and concentration of components of complex mixtures of organic substances.

Bearing in mind that it is impossible to cover fully in a single article the present state of research into the field of supercritical extraction, which has recently acquired an interdisciplinary character, and also the fact that no reviews have so far been published on this topic in Russian scientific literature, the aim of the present study is to give an account of the main ideas underlying supercritical extraction and its practical importance and in addition to reflect certain latest tendencies in the development of this promising field.

II. The properties of supercritical gases as extractants

Supercritical gases occupy, as it were, an intermediate position between the usual gases and the usual liquids, combining the properties of both and possessing at the same time their own intrinsic properties. The supercritical state is a qualitative state of

matter in which the gaseous and liquid state become indistinguishable.[3] It is shown on the phase diagram (Fig. 1) that, on moving along the path (indicated by an arrow in Fig. 1) passing through the supercritical region, it is possible to achieve a transition from the liquid to the gaseous state and conversely without first-order phase transitions (in this instance this would be evaporation and condensation).

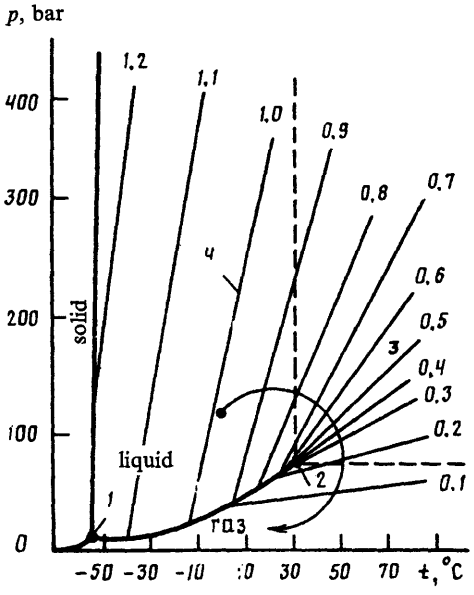


Figure 1. Temperature–pressure diagram for CO_2 with an indication of constant density lines: *1*, triple point; *2*, critical point (critical temperature −31.06 °C; critical pressure 73.8 bar); *3*, supercritical region; *4*, density lines.

One of the most important qualities of a supercritical gas as an extractant is its solvent power. It is determined by the molecular structure and density of the supercritical gas and can be characterised qualitatively by the solubility parameter δ (the square root of the cohesion energy density). This quantity can be rigorously calculated from thermodynamic properties by using the Hildebrandt theory.[3] The solvent power of a supercritical gas increases with increase in temperature at a constant density and with increase in density (pressure) at a constant temperature. The pressure dependence of the solubility parameter is illustrated in Fig. 2 for gaseous, liquid, and supercritical CO_2. Evidently δ for gaseous CO_2 is close to zero and at a temperature below the critical value (in the given instance $t = -30$ °C) the entire variation of δ with increasing pressure consists in an abrupt rise of δ until the attainment of a certain pressure p, which is caused by the condensation of CO_2. The parameter δ for liquid CO_2 differs only slightly from the value for organic solvents, for example solvents such as toluene, hexane, etc.[3,4] At a temperature exceeding the critical value (the cases corresponding to 32 and 70 °C are illustrated), increase in p does not induce a first-order phase transition and there is a possibility of a smooth regulation of the solvent power (δ) within wide limits by means of relatively small changes in temperature or pressure. The greatest changes in δ (as well as in the density—see Fig. 1) are observed in the vicinity of the critical point, since the compressibility becomes virtually unlimited at the critical point. The possibility of regulating the solvent power of a supercritical gas and hence the solubility of the components being extracted by varying the pressure or temperature is a unique characteristic quality of supercritical gases from the standpoint of their use as extractants.[5]

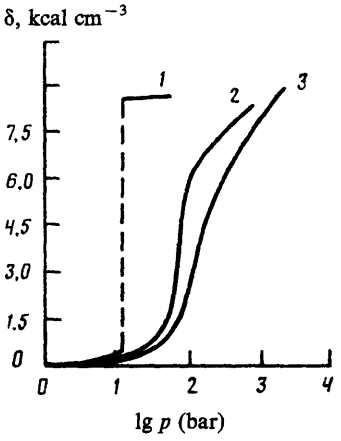


Figure 2. Dependence of the solubility parameter (δ, kcal$^{1/2}$ cm$^{-3/2}$) on pressure for CO_2 at different temperature (°C); *1*, −30; *2*, +32; *3*, +70.[1]

The solubility of the extracted components in a supercritical gas is determined by the characteristics of their partition between the phases in contact at equilibrium. Modern thermodynamics makes it possible to describe fairly reliably and in many instances with a high degree of accuracy the phase equilibria in various systems involving a supercritical gas. A detailed description of such problems may be found in the literature.[5–10] Here we shall deal only with the fundamental features important for the understanding of which factors determine the solubility of substances in a supercritical gas and the selectivity of the supercritical extraction.

We shall consider the relatively simple case of the equilibrium distribution of the components i between the solid (s) and supercritical (sp) phases. The equality of the fugacities of the ith component in the phases corresponds to the state of equilibrium:

$$f_i^s = f_i^{sp}. \quad (1)$$

The fugacities of the components can be determined using the fugacity coefficients ϕ_i:

$$f_i = y_i \phi_i p. \quad (2)$$

In Eqn. (2), p is the pressure and y_i the mole fraction of the component i in the supercritical phase or the vapour. For the

simplest case, where the solid phase consists of the component i, one can write[8]

$$y_i^{sp}\phi_i^{sp}p = \phi_i^s p_i^s \exp\int_o^p (V_i^s/RT)dp, \quad (3)$$

where p_i^s is the vapour pressure of the component i at a temperature T, ϕ_i^s the fugacity coefficient of the component i corresponding to the pressure p_i^s, V_i^s the molar volume of the component i, and ϕ_i^{sp} the fugacity coefficient in the supercritical phase. If the molar volume V_i^s is independent of p, then Eqn. (3) becomes

$$y_i^{sp}\phi_i^{sp}p = \phi_i^s p_i^s \exp\left(\frac{V_i^s(p-p_i^s)}{RT}\right). \quad (4)$$

Hence it is possible to find the solubility of the component i in the supercritical phase:

$$y_i^{sp} = \frac{p_i^s}{p}\left[\frac{\phi_i^s}{\phi_i^{sc}}\exp\left(\frac{V_i^s(p-p_i^s)}{RT}\right)\right]. \quad (5)$$

The multiplier in square brackets in Eqn. (5) is the intensification factor E, which shows by what factor the real solubility of the component i in the supercritical phase (y_i^{sp}) is greater than in an ideal gas (p_i^s/p):

$$E = \frac{\phi_i^s \exp\left(\frac{V_i^s(p-p_i^s)}{RT}\right)}{\phi_i^{sp}}. \quad (6)$$

The numerator in Eqn. (6) characterises the influence of pressure on the fugacity of the compound i, while the denominator (ϕ_i^{sp}) reflects the influence of the intermolar interactions in the supercritical phase and of the density. The quantity ϕ_i^{sp} may be found from equations of state such as the Soave–Redlich–Wang or Penn–Robinson equations.[3] It follows from Eqn. (6) that a component with a greater molar volume V_i^s is characterised also by a greater factor E for the same p and T and for identical intermolecular interactions in the supercritical phase. In terms of order of magnitude, the factor E is usually in the range 10^4-10^7 for substances of different types. Fig. 3 presents the dependences of E on the density of the supercritical CO_2 for a series of polar organic compounds with different functional groups.[11] Evidently the factor E varies in the series of these compounds approximately within the limits of one and a half orders of magnitude. At the same time, it has been shown[11] that the range of solubilities in the series of these compounds is much greater and corresponds to several orders of magnitude because the solubility is determined not only by the intensification factor, characterising the solvent–solute interactions, but also by the vapour pressure [Eqn. (5)]. The influence of the vapour pressure on the solubility and hence on the selectivity is illustrated in Fig. 4, which shows the dependence of the solubility of tetracyclic sterols having similar properties in supercritical CO_2 on the density of the latter. The solubility of cholesterol is greater by two orders of magnitude than that of ergosterol. This finding can be explained by the fact that the two compounds, having similar values of E, have very markedly different (by approximately two orders of magnitude) vapour pressures, that of cholesterol being higher, although they are both very low ($<10^{-10}$ bar).[12] Thus the selectivity of the supercritical extraction is proportional to the ratio of the vapour pressures although, the latter can in fact be negligibly low. With increase in p_i^s, the solvent–solute interactions, i.e. the factor E, make an increasing contribution to the selectivity.

The initial addition to the supercritical gas, for example to CO_2, of hydrocarbons and polar organic solvents is an extremely effective procedure for increasing the solubility of the extracted components in the supercritical phase and of the selectivity of the extraction.[5,13] This method has been widely used in research and technology because it significantly extends the limits of the applicability of supercritical extraction.[14] The most frequently employed additives (modifiers) of this kind in CO_2 are propane, hexane, alcohols (methanol, ethanol, octanol), acetone, tributyl phosphate, etc.[14] Such modifiers not only make it possible to increase the solubility and selectivity but in the vast majority of cases increase the dependence of the solvent power of the extractant on the pressure and temperature and make it possible to reduce the working pressure p and temperature T and also to reduce the amount of extractant consumed. The mechanism of the action of modifiers varies and depends on their nature. For example, propane, which has a high solvent power in relation to petroleum products, sharply increases their solubility in a CO_2–propane mixture compared with pure CO_2.[14] In contrast to supercritical CO_2, which is a lipophilic solvent with a very low dielectric constant ($\varepsilon = 0.5$ at $t = 50$ °C and $p = 250$ bar), polar organic substances are capable of forming donor–acceptor complexes of the extracted components, which affect the solubility and selectivity to a much greater extent than might have been expected on the basis of their fugacities alone.[13] Certain examples of an increase in solubility in the presence of polar modifiers are presented in Table 1. The last two rows of the table are noteworthy. They show that even ionic surfactants, in the given instance sodium 2-ethylhexyl sulphosuccinate, can be used as modifiers. Even ethanol-modified supercritical CO_2 is incapable of dissolving large amounts of hydrophilic substances. However, as can be seen from Table 1, in the presence of surfactants CO_2 is able to solubilise hydrophilic molecules as a result of the formation of reverse micelles or microemulsions.[1]

In many cases components entering into the composition of a complex mixture treated by the supercritical gas can play the role of modifiers. In this instance, being dissolved in the supercritical phase, some components increase the solubility of others, as happens, for example, on treatment of a naphthalene–benzoic acid mixture with supercritical CO_2.[15] A synergistic effect is observed in this case (Fig. 5), i.e. the solubility in the ternary system (two solutes, one solvent) exceeded the solubility in the binary system (one solute, one solvent).

III. Organisation of the supercritical extraction process

The organisation of the supercritical extraction process is illustrated schematically in Fig. 6.[16] The extractant (supercritical gas) passes in a continuous stream through the extractor (a mixer or a column apparatus), where it comes into contact with the solid or liquid mixture to be treated, extracting the soluble components. After emerging from the extractor, the extractant containing the dissolved target components is then subjected to a treatment, the main purpose of which is to isolate the target product from the extract and hence regenerate the extractant. This is achieved by a controlled decrease in temperature or pressure. Subsequently the parameters (p and T) of the regenerated extractants are adjusted to the required values and the extractant is again directed to the extractor, the circulation of the extractant being thereby achieved. Fig. 7 illustrated schematically the separation of components A and

B when component A is completely miscible with the supercritical gas. Evidently the complete separation of A and B can be achieved only when the extractant and component B are not infinitely miscible. A number of principal advantages and disadvantages of supercritical extraction as a technological process are presented below.[14,17,18]

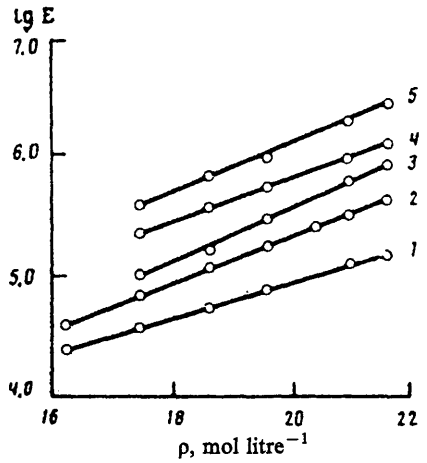


Figure 3. Dependence of the intensification factor E on the density (ρ) of supercritical CO_2 (t = 35 °C) for various substances: *1*, hexamethylbenzene; *2*, naphthol; *3*, phthalic anhydride; *4*, anthracene; *5*, acridine.[11]

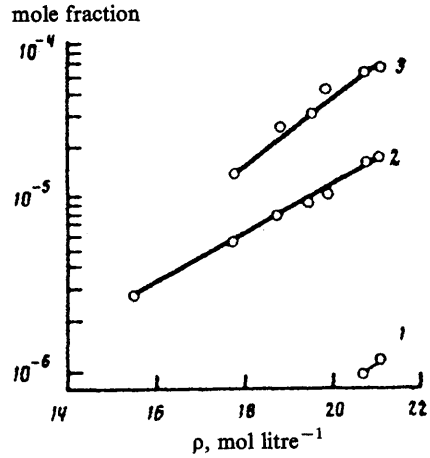


Figure 4. Dependence of the solubilities of various sterols in supercritical CO_2 (t = 35 °C) on its density: *1*, ergosterol; *2*, stigmasterol; *3*, cholesterol.[12]

Advantages: in terms of solvent power, supercritical gases are comparable to liquid organic solvents; the solvent power of supercritical gases and the solubility of the extracted components can be varied by altering p or T; it is possible to regenerate the extractant fully by altering p or T; high diffusion coefficients and low viscosities of supercritical gases; low working temperatures; low energy consumption in the process.

Table 1. The influence of modifiers on the solubilities of the extracted components in supercritical CO_2 at 35 °C.[13]

Extracted component	Modifier	F*
Acridine	Methanol (3.5%)	2.3
2-Aminobenzoic acid	Methanol (3.5%)	7.2
Cholesterol	Methanol (3.5%)	100
Hydroquinone	tri-n-butyl phosphate (2%)	300
ditto	Ethanol (5%)+surfactant** (0.5%)	>200
Tryptophan	Ethanol (5%)+surfacant (0.5%)	>100

* F is a parameter showing by what factor the solubility increases in the presence of the modifier.

** The surfactant employed was sodium di-2-ethylhexyl sulphosuccinate.

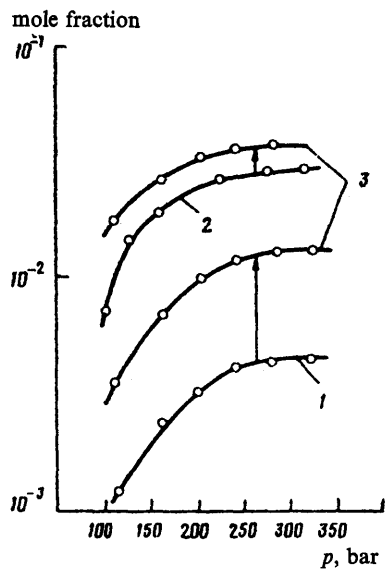


Figure 5. Mutual influence of naphthalene and benzoic acid in their extraction by supercritical CO_2 (t = 35 °C); dependence of the solubility in supercritical CO_2 on pressure in different systems: *1*, benzoic acid–CO_2; *2*, naphthalene–CO_2; *3*, (naphthalene + benzoic acid)–CO_2.[15]

Disadvantages: increased working pressure; high cost of equipment; unusual process conditions for many undertakings; complex character of the phase equilibrium in systems with supercritical gases.

IV. Applications of supercritical extraction

As shown by the analysis of the literature, among the wide variety of aspects of the technological applications of supercritical extraction, the aspects concerned with the protection of nature are nowadays of perhaps greatest interest because in this field the advantages of supercritical extraction make it extremely attractive for the solution of a wide range of applied problems.

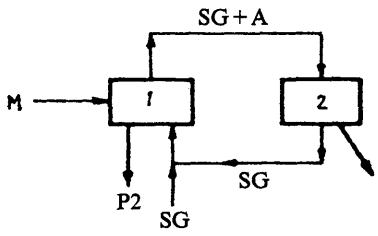


Figure 6. Schematic illustration of the supercritical extraction process: *1*, extraction; *2*, regeneration of the extractant and isolation of the products; M—mixture of components A and B undergoing separation: P1—product enriched in component A; P2—product enriched in component B.

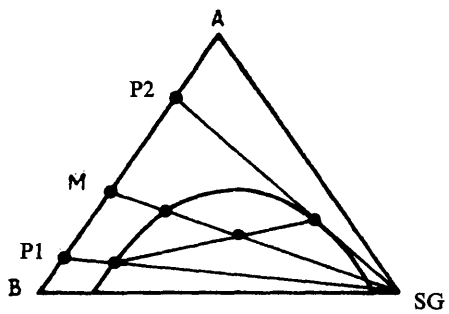


Figure 7. Schematic illustration of a binary mixture M of components A and B by supercritical extraction in conformity with the scheme presented in Fig. 6.

The processes based on the application of supercritical gases can be arbitrarily divided into three categories: single-stage separation, two-stage separation, and separation with simultaneous chemical conversion of the extracted components. In the single-state separation, the initial treated material is brought directly into contact with the supercritical gas, for example, in order to remove toxicants or to extract valuable components. In the two-stage separation, the initial treated material, for example water contaminated by organic toxicants, is brought into contact not with the supercritical gas but with an extracting phase of another type, usually a sorbent. Next, the sorbent is regenerated by being treated with the supercritical gas. In processes of the third category, the initial treated mixture is brought into direct contact with the supercritical gas, which functions not only as a solvent (extractant) but serves at the same time as a medium for the occurrence of chemical reactions, for example, such as oxidation of organic toxicants.

The single-stage separation is most suitable in those cases where the concentration of the extracted components in the mixture is relatively high. For example, processes involving the extraction of phenol, alcohols, aldehydes, and ketones from aqueous waste solutions by supercritical CO_2 and hydrocarbons have been developed for such cases.[19–23,27] The extraction of pyrethrin, for example, from plant raw material by means of supercritical CO_2 has proved extremely effective. Pyrethrin is extremely toxic to insects and is almost harmless to warm blooded animals. This substance is unstable and does not accumulate in the environment, in contrast to pesticides. The use of supercritical extraction for such purposes has made it possible to reduce almost by a factor of two the capital and operating costs compared with the usual multistage liquid extraction.[24,25] Another example of a single-stage process is the extraction of highly toxic organic substances, such as chlorine-containing pesticides and polychlorinated biphenyls from the soil and solid waste by supercritical CO_2.[24,26] The efficiency of the single-stage separation increases significantly when modifiers, increasing solvent power, are introduced into the supercritical gas.

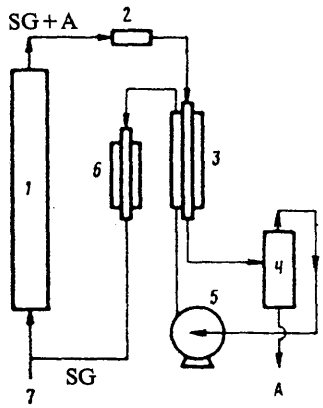


Figure 8. Schematic illustration of the sorbent regeneration process with the aid of supercritical extraction: *1*, apparatus in which the adsorbate is extracted from the sorbent by the supercritical gas; *2*, reductor; *3*, heat exchangers; *4*, separator; *5*, compressor; 6, heat exchanger; *A* = adsorbate.

The two-stage separation is extremely effective at low concentrations of the contaminant. In this case, supercritical extraction provides excellent possibilities for the regeneration of widely used sorbents such as activated charcoals and synthetic polymeric sorbents.[28–30] The usual regeneration methods, such as treatment with live steam and heat treatment, involve an extremely high energy consumption and are expensive. Compared with these methods, the use of supercritical extraction makes it possible, for example, to reduce by a factor of two the cost of regeneration of the sorbent in the purification processes for the waste waters from the industrial manufacture of pesticides involving the removal of contaminants such as atrazine, dinitrobutylphenol, alachlor, etc.[29]

An extremely important advantage of supercritical extraction is also the many-fold increase in the useful life of the sorbent, because it does not lose appreciably its properties even after many regeneration cycles. Fig. 8 illustrates schematically the regeneration of the sorbents by supercritical CO_2.[28]

The use of supercritical gases as a medium for chemical reactions has great potential possibilities. Supercritical water has attracted increasing attention of investigators and technologists in this connection. On passing to the supercritical state, the properties of water are radically altered and it becomes similar to non-polar organic solvents in terms of its solvent power. Supercritical water hardly dissolves in organic ionic substances and is completely miscible with hydrocarbons.[31] In supercritical water ($t > 374$ °C, $p > 218$ atm), organic toxicants can be oxidised by atmospheric oxygen to simple products such as CO_2, etc.[31] The study of the properties of supercritical water had made it possible to develop an effective process for the removal from waste waters of toxic organic components such as chlorine-containing pesticides, polychlorinated biphenyls, trichloroethane, perchloroethylene, etc.[31,32] The only reagent used in this process is compressed air. The degree of conversion of all the toxicants investigated into simple products as a result of oxidation was more than 99.99%, which exceeds significantly the degrees of conversion achieved in the combustion of toxic waste. The fact that, in contrast to combustion, the oxidation of, for example, chlorinated aromatic hydrocarbons in supercritical water does not involve the formation of dangerous toxicants such as dioxins and dibenzofurans is also important. Technical-economic estimates have shown that the cost of combustion exceeds significantly the cost of the process involving the use of supercritical water, which is associated with the lower consumption of fuel in the latter case. Fuel is necessary only in the initial stages of the process in order to establish the required temperature, which is then maintained as a result of the exothermicity of the oxidation reaction.

Another important example of the use of supercritical gases both as solvents and as reactants is the desulphurisation of coals by supercritical ethanol. Suphur-containing organic compounds are extracted into supercritical ethanol and are reduced there to products such as ethyl sulphide, and ethyl disulphide, thiophene, etc. Such treatment makes it possible to reduce the sulphur content in coal by a factor greater than 2.[24]

References

1. K P Johnston *Supercitical Fluid Science and Technology*, ACS Symp. Ser. 400, Washington, 1989, p.1
2. J B Hannay, J Hagarth *Chem. News.*, 1979, **40** 256
3. R Reid, J Prausnitz, T K Sherwood *The Properties of Gases and Liquids* (Translated into Russian), Khimiya, Leningrad, 1982, 591 pp
4. A W Fransic *J. Phys. Chem.*, 1954, **58** 1099
5. M A McHugh, U J Krukonis *Supercritical Fluid Extraction. Principles and Practice*, Boston, 1986
6. C T Lira *Supercritical Fluid Extraction and Chromatography. Techniques and Application*, ACS Symp. Ser. 366, Washington, 1988, p. 1
7. K P Johnston, D H Ziger, E C Eckert *Ind. Eng. Chem. Fundam.*, 1982, **21** 191
8. R T Kurnik, S J Holla, R S Reid *J. Chem. Eng. Data*, 1981, **26** 47
9. R A Van Leer, M E Paulaitis *J. Chem. Eng. Data*, 1980, **25** 257
10. K P Johnston, E C Eckert *Am. Inst. Chem. Technol. J.*, 1981, **27** 773
11. J M Dobbs, K P Johnston *Ind. Eng. Chem. Res.*, 1987, **26** 1476
12. J M Wong, K P Johnston *Biotech. Progr.*, 1986, **2** 29
13. K P Johnston, S Kim, J Combes *Supercritical Fluid Science and Technology*, ACS Symp. Ser., Washington, 1989, p. 52
14. G Brunner *Ion Exchange and Solvent Extraction* (Edited by J A Marinsky, Y Marcus), Marcel Dekker, New York, 1988, Vol. 10, p. 105
15. R T Kurnik, R C Reid *Fluid Phase Equilib.*, 1982, **8** 93
16. F Bohm, R Heinish, S Peter, E Weider *Supercitical Fluid Science and Technology*, ACS Symp. Ser., Washington, 1989, p. 499
17. *Supercritical Fluid: Chemical Engineering Principles and Applications*, ACS Symp. Ser. 329 (Edited by T G Squires, M E Paulaitis), Washington, 1987
18. U J Krukonis *Supercritical Fluid Extraction and Chromatography. Techniques and Application*, ACS Symp. Ser. 366, Washington, 1988 p. 26
19. R K Roop, R K Hess, A Akgerman *Supercritical Fluid Science and Technology*, ACS Symp. Ser. 400, Washington, 1989, p. 468
20. M S Kuk, J C Montagna *Chem. Eng. at Super Fluid Conditions* (Edited by M E Paulaitis), Ann Arbor Science, Ann Arbor, Mich., 1983, p. 101
21. T Suzuki, N Tsuge, K Nagahama *Abstracts of the International Solvent Extraction Conference 1980 (ISEC'90)*, Kyoto, Japan, 1990, p. 295
22. Z Knez, F Pesel, I Krmelj *Abstracts of the International Solvent Extraction Conference 1980 (ISEC'90)*, Kyoto, Japan, 1990, p. 296
23. G Brunner, R Dorhn *Preprints ISEC '86*, Munich, 1986, Vol. 3, p. 783
24. E C Eckert, J G Van Alsten, T Stoicos *Environ. Sci. Technol.*, 1986, **20** 319
25. G Bunzenberger, R Marr *Preprints ISEC'88*, Moscow, 1988, Vol. 3, p. 386
26. F C Knopf, B Brady, F R Groves *CRC Crit. Rev. Environ. Control*, 1985, **15** 237
27. Z Knez, U Ozin, P Sencar *Preprints ISEC'88*, Moscow, 1988, Vol. 1, p. 252
28. R P Fillippi, R J Robey *Supercritical Fluid Regeneration of Adsorbents, EPA–600/52–83–038, EPA, Washington, 1983*
29. R D Pricht *Am. Inst. Chem. Eng. Symp. Ser.*, 1982, **78** 136
30. J W King, R L Eissler, J P Friedrich *Supercritical Fluid Extraction and Chromatography*, ACS Symp Ser. 366 (Edited by B A Carpenter and M R Sevenants), Washington, 1988, p. 63
31. J Josephson *Environ. Sci. Technol.*, 1982, **16** 548
32. H E Barner, C Y Huang, T Johnson *Supercritical Water Oxidation — an Engineering Technology: Preprints ACHEMA 91*, Frankfurt-Main, 1991