EXTRACTION OF HERBAL
COMPONENTS – THE CASE FOR SUPERCRITICAL FLUID EXTRACTION

Andri Cahyo Kumoro, Masitah Hasan *)

Abstract

Malaysia is rich in heritage of sources for herbs and medicinal plants. The increasing public awareness of the health, environment and safety hazards associated with the use of organic solvents in herbals processing and the possible solvent contamination of the final products have pointed out the need for the development of new technologies for the processing of medicinal products. This becomes the challenge for the application of supercritical fluid extraction to enhance the economic value of Malaysian herbs. Therefore, the development of affordable, high-capacity, continuous-feed supercritical extractors in conjunction with research demonstrating its effectiveness and advantages over conventional techniques should be seriously taken as a consideration.

Keywords: extraction, organic solvents, herbs, medicinal products, supercritical fluid

The Malaysian Herbs Diversity, Current Usages And Proposed Extraction Method

Herbs have been used throughout human history as sources of food, medicines, beauty enhancers, and fragrances. The use of herbs as medicine has a long history starting from the Greek civilisation in the West to the Arabic, Chinese, and Indian civilisation in the East. There is a growing trend of people moving from synthetic allopathic drugs to herbal cures. Among the reasons for this shift include a preference for wellness oriented self administered healthcare, the prevalence of chronic illnesses that cannot be cured by conventional drugs, and the high pace of life, which involves higher stress and reduced free time. Many allopathic medicines, which are produced synthetically, are also derived from plants such as quinine for malaria and quinidine for heart arrhythmia from *Cinchona* spp, and digoxin for heart failure from *Digitalis* spp. About 25 % of drugs prescribed worldwide come from plants, where 121 such active compounds being in current use (Rates, 2001).

Malaysia is well positioned to be a key global player in the herbal medicine industry with its rich biological heritage, cultural background, and trade links. Malaysia is listed as the 12th most bio-diverse nation in the world and 4th is Asia with over 15,000 flowering plants and over 3000 species of medicinal plants. Of the 3000 listed medicinal plants, only about 50 are used and even less are being investigated scientifically for their medicinal properties, and many more have yet to be catalogued extensively through ethnobotanical research. The Tongkat Ali (*Eurycoma longifolia*), Kacip Fatimah (*Labisia pumila*), Hempedu Bumi (*Andrographis paniculata*), Dukung Anak (*Phyllantus amarus*), Misai Kucing (*Orthosiphon stamineus*), and Pegaga (*Centella asiatica*) are some good examples of the premier Malaysian traditional medicinal plants as shown Figure 1 (Arif, 2002).

Figure 1: The premier Malaysian medicinal plants

*) Staf Pengajar Jurusan Teknik Kimia Fakultas Teknik Undip

Tongkat Ali has been used as aphrodisiac, general tonic, anti-malarial, and anti-pyretic. It has been scientifically proven to have anti – tumour, anti oxidant and biochemically shown to increase testosterone production as well as overcome impotence. Kacip Fatimah is a herb used in the treatment of post partum mothers, gonorrhoea, rheumatism, pile and bone diseases. Hempedu Bumi is used for anti-pyretic, anti-fertility, treatment of appetite loss, anti-diabetes, anti-hypertensive etc. Dukung Anak is used to eliminate gallstones and kidney stones as well as to treat colic, diabetes, malaria, dysentery, fever, flu, tumours, jaundice, vaginitis, gonorrhoea, and dyspepsia. Based on its long documented history of use in the region, the plant is generally employed to reduce pain, expel intestinal gas, to stimulate and promote digestion, to expel worms, as a mild laxative. Misai Kucing can be used for kidney related and joint ailments such as gall stones, diabetes, arthritis, rheumatism, and gout. Pegaga is a long used Asian herb for its anti aging and overall beauty enhancement properties.

There is an increasing public awareness of the health, environment and safety hazards associated with the use of organic solvents in herbals processing and the possible solvent contamination of the final products. The high cost of organic solvents and the increasingly stringent environmental regulation, together with the new requirements of the medical industries for ultra- pure and high added value products, have pointed out the need for the development of new technologies for the processing of medicinal products. Over the past four decades, supercritical CO_2 has been used for the extraction and isolation of valuable compounds from natural products (Mansoori et al., 1988). Supercritical fluid extraction has proved effective in the separation of essential oils and its derivative for use in food, cosmetics, pharmaceutical and other related industries, producing high-quality essential oil with commercially more satisfactory compositions (lower monoterpenes) than obtained with conventional hydro-distillation (Ehlers et al., 2001; Ozer et al., 1996). Therefore, supercritical fluid extraction using carbon dioxide (CO_2) as a solvent has provided an excellent alternative to the use of chemical solvents to extract the bioactive components from herbs and other medicinal plants.

Supercritical Fluid (Scf)

A supercritical fluid (SCF) is any compound at a temperature and pressure above the critical values. The critical temperature of a compound is defined as the temperature above which a pure, gaseous component cannot be liquefied regardless of the pressure applied. The critical pressure is then defined as the vapour pressure of the gas at the critical temperature. The temperature and pressure at which the gas and liquid phases become identical is the critical point. In the supercritical environment only one phase exists. The fluid, as it is termed, is neither a gas nor a liquid and is best described as intermediate to the two extremes. This phase retains the solvent power common to liquids as well as the transport properties common to gases. Figure 2 illustrates the relationship between pressure and temperature on the phase of carbon dioxide (CO_2), including its supercritical region. For CO_2, its critical temperature and pressure are 31.1 ^oC and 73.8 bar, respectively. In the supercritical state, CO_2 has properties resembling both a gas and liquid. It is the gas-like high diffusion coefficient and low viscosities, in addition to the liquid-like high solvating power properties, that make supercritical fluids good solvents (Clifford, 1993)

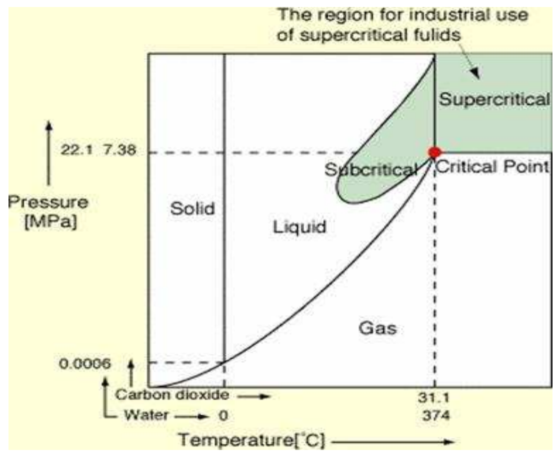

Figure 2: Phase diagram of CO_2

Supercritical Co_2 - The Safe And Economical Choice

Although there are many other compounds (e.g., ammonia, water, nitrous oxide and fluoroform) that could be used to perform supercritical extractions, the toxicities, reactivity, including explosiveness and corrosiveness, and cost prelude their widespread use. Carbon dioxide on the other hand, has the best of overall combination of properties and is by far the most widely used supercritical fluid (Eller, 2002).

Carbon dioxide is the king of extraction solvents for botanicals. It is good to all natural products, which leaves no toxic residues behind and is non flammable, therefore safe for personnel and the environment with no waste solvent disposal costs. It is relatively inert and does not react with the material involved in the extraction, which includes both the material being extracted and the equipment being used. Its extraction properties can be widely and precisely manipulated with subtle changes in pressure and temperature. It is inexpensive and widely available as a by-product of ethanol fermentation in food grade quality. Its relatively low critical pressure and temperature are readily attained. Its high vapour pressure, relative to typical organic solvents, makes it easy to separate from the desired extract and it leaves no hazardous residue in the extracts. The capability of processing botanicals skilfully with CO_2 gives a company an added edge of status and prestige.

The Fundamental Of Supercritical Fluid Extraction (Sfe)

The basic elements required for conducting SFE have been described as shown in Figure 3 (Hawthorne, 1993). The simplest system includes: a fluid source (e.g., a pressurised tank of CO_2), a compressor to pressurise and pump CO_2, an extraction vessel to hold the material to be extracted, a back-pressure regulator or flow restrictor to allow a drop in pressure, which will allow the separation of the extracted material from the CO_2, and a collection device.

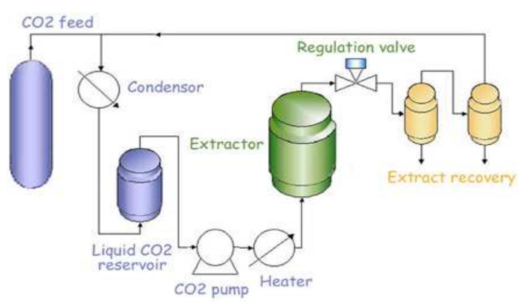

Figure 3: The Supercritical CO_2 Extraction Unit

Collection of the extract is an important step although often overlooked during optimisation of extraction methods. The important aspect of sample collection and maximising collection efficiency, including techniques such as cooled collectors, liquid traps and inert (e.g., sand or glass beads) and active solid traps (e.g., C18 solid-phase adsorbents) have been discussed (Taylor, 1996). Collection can be accomplished by simply allowing the CO_2/extract mixture to depressurise completely to atmospheric pressure whereby the CO_2 is vaporised and dissipated leaving only the extracted material in a collection vessel. Alternately, the pressure could be reduced only enough to decrease the solubility of the extract in the CO_2, without complete depressurisation, in a separation vessel held above atmospheric pressure. In this way, the can be recycled and the energy costs associated with pressurising the CO_2 saved.

The Sample Preparation

The sample preparation prior to extraction is extremely important. Usually, the material is dried and ground because dry and smaller particles are generally extracted more quickly as well as more completely. Although the presence of water is useful during the extraction of caffeine, in general water tends to adversely affect the extraction of fat or lipid and protein derivatives. A patent describes the use of pelletised diatomaceous earth as an extraction aid to dry and disperse samples prior to SC - CO_2 extraction (Hopper and King, 1992). The utility of this invention has been demonstrated by the various dispersing agents sold by the major manufacturers of analytical SFE equipment (Eller, 2002).

The Use Of Modifiers

Supercritical CO_2 is generally considered a more selective solvent than organic solvents and by proper control of the temperature and pressure; it is possible to vary the selectivity slightly as well. The facts that SC-CO_2 is a good solvent for non-polar and moderately compounds makes it an excellent choice for extracting fats, oils and other bio-active components without co-extracting other undesirable more polar components (Eller, 2002). However, in order to extract polar components, some sort of modifier or co-solvent must be added to SC-CO_2. Although there are many potential numbers of modifiers, the most common modifier used is ethanol and it increases the polarity of SC-CO_2 to allow the extraction of more polar compounds not removed by SC-CO_2 alone. It is good choice because of it's generally regarded as safe status, availability and cost (Langenfeld et al, 1994).

The Extracts Analysis

The extracts obtained from supercritical fluid extraction with carbon dioxide are clean, therefore their analysis can be performed without any additional clean-up by GC-MS after derivatisation or directly by HPLC-diode array detection (Anastassiades and Schwack, 1988). The samples are usually treated as common samples prior to HPLC or GC analysis.

Analytical – Scale Sfe

There has been much attention of research in the analytical scale SC-CO_2 extraction of herbs from medicinal plants for determining bioactive components content and the application of SC-CO_2 extractions to bioactive components analysis has been highly successful. The There are many advantages of SFE over soxhlet extraction using standard organic solvents such as hexane, ether or methylene chloride. One such advantage is the speed of the extraction due to the more rapid extraction that occurs in supercritical fluid opposed to conventional liquid solvents. Additional timesaving can be realised when using SC-CO_2 because there is no need to remove the solvent after the extraction as with hexane, which must be distilled off. Supercritical extractions can also be automated.

The greatest disadvantage for using SC-CO_2 to extract herbs is the relatively more expensive extractor required, which is a function of the high pressures involved and the complexity of the equipment.

Process- Scale Sfe

The difference between analytical-scale SFE and the process-scale SFE is primarily a matter of scale and both require the same basic elements described earlier. One basic difference, however, is that in analytical-scale SFE, the material is easily extracted in a batch-type process, i.e., one extraction vessel at a time is connected to the CO_2 flow path. The connection of large –scale vessels is much more complex (McHugh and Krukonis, 1994). Although current process-scale SFE is done in batch mode for hops extraction, the scales operation and product value in this operation can support the use of batch SC-CO_2 extraction.

Conclusions

The heritage of abundant sources in herbs and medicinal plants in Malaysia and the increasing public awareness of the health, environment and safety hazards associated with the use of organic solvents in herbals processing and the possible solvent contamination of the final products have become the challenges for the application of supercritical fluid extraction to enhance the economic value of the Malaysian herbs. However, there is a need to overcome the resistance to using this method in industries unaccustomed to high pressures as well as the reluctance towards innovation from conservative industries that adhere to established methods. Therefore, the development of affordable, high-capacity, continuous-feed supercritical extractors in conjunction with research demonstrating its effectiveness and advantages over conventional techniques should be seriously taken as a consideration.

References

1. Anastassiades, M. and Schwack, W., 1988, Analysis of carbendazim, benomyl, thiophanate methyl and 2,4-dichlorophenoxyacetic acid in fruits and vegetables after supercritical fluid extraction, *J. Chromatogr. A*, 825(1):45-54.

2. Arif, M. T., 2002. Traditional/Complementary Medicine in the Malaysian Healthcare System, 4th International Conference for Traditional/Complementary Medicine, Sunway Convention Centre, Kuala Lumpur.

3. Clifford, A. A., 1993, Introduction to Supercritical fluid Extraction in Analytical Science, S. A Westwood (ed.), Supercritical fluid Extraction and Its Use in Chromatographic Sample Preparation, CRC Press, Boca Raton, Florida, pp. 1-39.

4. Ehlers, D., Nguyen, T., Quirin, K. W., and Gerard, D., 2001, Analysis of Essential Basil Oils – CO_2 extract and steam distilled Oils, *Deutsche Lebensmittel – Rundschau*, 97, 245-250.

5. Eller, F. J., 2002, Supercritical Carbon Dioxide Extraction of Fat, Business Briefing: Food Technology, 1- 4.

6. Hawthorne, S. B., 1993, Methodology for Off-line Supercritical fluid Extraction, S. A Westwood (ed.), Supercritical fluid Extraction and Its Use in Chromatographic Sample Preparation, CRC Press, Boca Raton, Florida, pp. 39-64.

7. Hopper, M. L. and King, J. W., 1992, Supercritical Fluid Extraction Enhancer, US Patent 5, 151, 188.

8. Langenfeld, J. J., Hawthorne, S. B., Miller, D. J. and Pawliszyn, J., 1994, Role of modifiers for analytical scale supercritical fluid extraction of environmental samples. *Anal. Chem.* **66**. 909-916

9. Mansoori, G. A., Schultz, K and Martinelli, E., 1988, Bioseparation Using Supercritical Fluid Extraction/Retrograde Condensation, (Feature Article) Bio/Technology, 6, 393-396.

10. McHugh, M. A. and Krukonis, V. J., 1994, Supercritical Fluid Extraction (2nd ed.), Butterworth-Heinemann, Massachusetts.

11. Ozer, E. O., Platin, S., Akman, U, and Hortaqsu, O., 1996, Supercritical Carbon Dioxide Extraction of Spearmint Oil from Mint-Plant Leaves, *Can. J. Chem. Eng*., 74, 920-928.

12. Rates, S. M. K., 2001. Plants as source of drugs. Toxicon, 39: 603-613.

13. Taylor, L. T., 1996. Supercritical Fluid Extraction, John Wiley & Sons, New York, pp. 1-6.