SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF SARAWAK BLACK PEPPER OIL

Harcharan Singh, Masitah Hasan and Lim Jit Kang

Department of Chemical Engineering
University of Malaya
harcharan@um.edu.my

ABSTRACT

Given the demands for natural products that are inherently safe and environmentally compatible, the advancement in supercritical extraction has provided a better alternative for extracting low volume, high value product such as essential oil. In this study, supercritical carbon dioxide at 160 bar and 200 bar and both at 40°C was used to extract pepper oil from whole low density Sarawak pepper. At these conditions, the essential oil (light fraction) was extracted first followed by the oleoresin (heavy fraction). The solubility of the extracted oil obtained was 4.29 x 10^{-3} g oil/g CO_2 at 160 bar and 6.67 x 10^{-3}g oil/g CO_2 at 200 bar. Ground pepper oil was shown to have a significantly higher solubility. Increasing system pressure increased pepper oil solubility due to the increase of CO_2 density.

INTRODUCTION

Essential oil is a small portion of a plant material which consists mainly of terpenes and their derivatives responsible for the characteristic aroma and imparts the identifying flavor and odor most closely associated with the plant itself (Jirovetz et al., 2002). The delicate aroma of rose, the refreshing lift of pine or wintergreen, the pungent, sometimes offensive odor and flavor of garlic are the sensatory properties of these unseen oils. Different parts of the plants can be used to obtain essential oils, including the flowers, leaves, gums, seeds, roots, stems, bark, wood.

Supercritical CO_2 extraction of essential oils is a widely discussed application in supercritical fluid literature. Recently, Reverchon (1997) has summarised the use of supercritical fluid for the extraction and fractionation of essential oil and related products. Supercritical fluid extraction of herbal and natural product has also been reported as well (Lang and Wai, 2001). In most of these studies, supercritical fluid extraction has been identified as a promising method to extract essential oil out from natural matrix system. The numerous advantages of supercritical fluids extraction has been reported (Hauthal, 2001; Shivonen et al., 1999) and the application of supercritical fluid technology in a range of food industries has been reviewed by Palmer and co-workers (1994).

Many researchers have investigated Malaysian pepper (Allan, 1993; Tiong, 1986). Pepper has been cultivated in Malaysia for more than 100 years. It is an important agricultural crop which has put Malaysia as one of the leading pepper producer in the world. Sarawak is the state, which accounts for over 95% of pepper production in Malaysia and is follow by Johor and Sabah. Generally, there are two main types of pepper produced in Malaysia that is black and white pepper. The share of white pepper in the total production of Sarawak pepper is 25% to 30%. The decision to produce black or white pepper depends on various factors such as the premium in price for white pepper, the availability of water for processing white pepper, the customary practice of the farmer, the size of the berries harvested and the security of the farm against theft.

MATERIALS AND METHODS

Three different sources of black pepper [*Piper nigrum L.* (fam. Piperaceae)] are available as shown in Table 1. The density of pepper was measured using a gas pycnometer. However, only the low density Sarawak black pepper (provided by the Sarawak Pepper Board) was used for extraction using supercritical CO_2 because this pepper type contained the highest oil content. The carbon dioxide used in this study was supplied by Sit Tatt Sdn. Bhd. with a purity of 99.7%.

Table 1: Properties of different types of black pepper

Types of black pepper	Source	Essential oil (wt %)[1]	Density, ρ (g/cm^3)
Local pepper	Market	-	Varied
Low density Sarawak pepper	Sarawak Pepper Board	3 to 6	0.9301
High density Sarawak pepper	Market	2 to 3	1.276

1 Determined using steam distillation

The apparatus used for the extraction of pepper oil is shown in Figure 1. It consists of a 60 ml high pressure liquid extraction vessel (Jerguson sight gauge) immersed in a water bath which is controlled by a heater (Techne, model TU-16D). Collection of extracted essential oil (in a vial immersed in a cold trap at ~2°C) and the system pressure was controlled by a back pressure regulator (Jasco, model 880-81). A HPLC pump (Jasco, PU-980) was used to deliver liquid CO_2. The system conditions studied were at 40°C and 160 and 200 bar.

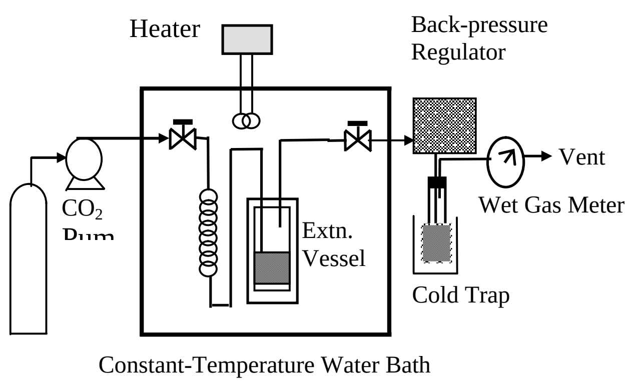

Figure 1: Schematic diagram of apparatus used

In a typical experimental run, 12 g of whole low density Sarawak black pepper was placed into the extraction vessel. Carbon dioxide was then fed into the system until a pressure of 140 bar was attained and the system temperature was set to 40 °C by the bath heater. The system was then left to equilibrate for about 30 minutes. Then liquid CO_2 was continuously delivered at a volumetric flow rate of 1.2 ml/min and the pepper essential oil extracted was collected in a cold trap located at the back pressure regulator. During the extraction, 5 to 7 pepper oil fractions were collected in the vial. Each fraction took between 2.5-3 hours to extract. The black pepper oil extracted contained both the essential oil (i.e. volatile, liquid like fraction) and oleoresin (heavy, solid fraction), where the initial fractions collected were mainly liquid like in nature.

The extraction of pepper oil was terminated when it was visually observed that no pepper oil was being collected in the vial and is termed as exhaustive extraction. The weight of each fraction collected was determined using a balance (Metler Toledo, model AG 204).

RESULT AND DISCUSSION

The density, total oil extracted, CO_2 consumed and total time taken for extraction of pepper oil at 40°C and 160 and 200 bar is shown in Table 2.

Table 2: System conditions and total pepper oil extracted at 40°C

Parameters	Pressure (bar)	
	160	200
Density (g/cm^3)	0.7660	0.8283
Total oil extracted (g)	0.1918	0.4404
Total CO_2 gas (l)	467.8	698.6
Total CO_2 liquid (ml)[1]	1044	1476
Extraction time (hr)	14.5	20.5

1. At system temperature and pressure

A plot of oil extracted with the amount of CO_2 consumed is shown in Figure 2. The general behavior at both conditions is the same with the difference being in the amount of oil extracted, CO_2 volume used and duration of the extraction. In any separation process, the solubility of a solute is greatly affected the solvent density. The solvent density is proportional to system pressure where at high pressure, high solvent density can be obtained resulting in higher extraction yields. At supercritical conditions, the density of a solute can approach that of a liquid as the system pressure is increased. It can be seen from Table 1 that as the system pressure increases from 160 to 20 bar, the solvent density increases by 8 %. However, the amount of pepper oil extracted increases by 130 % going from 160 to 200 bar as seen in Figure 2. It has to be noted that the pepper oil extracted at both conditions contained a mixture of essential oil and oleoresin. Thus at 200 bar, a higher oil extraction yield is most likely attributed to the larger amount of oleo resin being extracted. Most of the oil being extracted at the latter fractions (at both conditions) is expected to be made up mainly of oleoresins, which are not desired for use in the perfumery industry

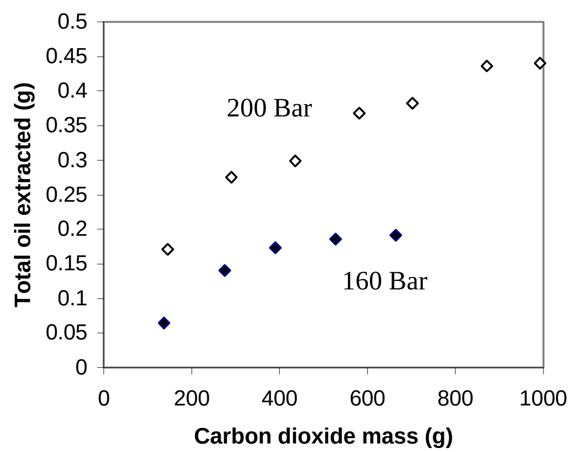

Figure 2: Total pepper oil extracted at 40°C

Ferreira et al. (1999) and Sovova et al. (1995) extracted essential oil from grounded black pepper (*Piper nigrum L.*) using supercritical CO_2 at various system temperatures and pressures. The grounded pepper used by these researchers was 0.25 mm and 0.05 mm respectively. In this study, whole pepper (~2.3 mm diameter) was used. A comparison between whole and grounded pepper at 40°C and 200 bar is shown in Figure 3. The pressure used by Sovova et al. (1995) was 280 bar.

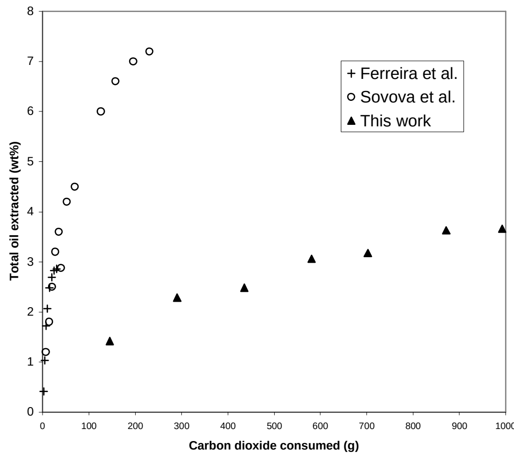

Figure 3: Comparison of pepper oil solubility with other studies at 40°C

CONCLUSION

This study showed that supercritical CO_2 at 40°C and 200 bar is able to extract much of the essential oil from whole pepper. The amount of oil extracted can be significantly increased by grinding the pepper. Supercritical carbon dioxide has the potential to extract both the volatile (liquid) and heavy (oleo resin) pepper oil fractions.

REFERENCES

T.C.K. Allan. 1993. Pepper products and its developments", chapter in Ibrahim, M.Y., C.F.J. Bong and I.B. Ipor (eds.), The pepper industry: problems and prospects, Kuching: UPM: 331-336

E. Reverchon. 1997. Supercritical fluid extraction and fractionation of essential oil and related products. J. of Supercritical Fluids 10: 1-37.

H. Sovova, J. Jez, M. Bartlova and J. St'astova. 1995. Supercritical carbon dioxide extraction of black pepper. J. of Supercritical Fluids 8: 295-301.

L. Jirovetz, G. Buchbauer, M.B. Ngassoum and M. Geissler. 2002. Aroma compound analysis of *Piper nigrum* and *Piper guineense* essential oil from Cameroon using solid-phase microextraction-gas chromatography, solid-phase microextraction-gas chromatography-mass spectrometry and olfactometry. J. of Chromatography A 976: 265-275.

M.V. Palmer and S.S.T. Ting. 1994. Application for supercritical fluid technology in food processing. Food Chemistry 52: 345-352.

M. Shivonen, E. Jarvenpaa, V. Hietaniemi, and R. Huopalahti. 1999. Advances in supercritical carbon dioxide technologies. Food Sci. and Tech. 10: 217-222.

S.R.S. Ferreira, Z.L. Nikolov, L.K. Doraiswamy, M.A.A. Meireles and A.J. Petenate. 1999. Supercritical fluid extraction of black pepper (Piper nigrum L.) essential oil. J. of Supercritical Fluids 14: 235-245

I.C. Tiong. 1986. The marketing of Malaysian pepper, chapter in Bong C.F.J. and M.S. Saad (eds), Pepper in Malaysia, Kuching: UPM: 169-18.

W.H. Hauthal. 2001. Advances with supercritical fluids [review]. Chemosphere 43: 123-135.