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Mass Transfer and Solubility of *Hibiscus cannabinus* L. Seed Oil in Supercritical Carbon Dioxide

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Abstract: Solubility of *Hibiscus cannabinus* L. seed (particle size 400 μm) oil in supercritical carbon dioxide was determined at pressure of 34.47-48.26 MPa, temperature of 50-80°C and constant flow rate of 5 mL min^{-1}. It was found that the solubility of *Hibiscus cannabinus* L. in supercritical carbon dioxide increased with the increased of temperature. The extraction yield increased with increased in temperature and pressure. The maximum yield was 8.66% at 48.26 MPa and 80°C for 40 min of extraction. The mass transfer coefficients for *Hibiscus cannabinus* L. oil was found to be 0.0072 sec^{-1} at 48.26 MPa and 80°C.

Key words: Supercritical carbon dioxide, extraction, solubility, mass transfer, oil seed

INTRODUCTION

Hibiscus cannabinus L. plant or Kenaf as its local name is from Malvaceae family is composed of multiple useful plant parts and each of these plant parts produced variable usable portions. One of the useful plant parts is the seeds. The seeds can produce oil that is believed to be edible and very useful in the cosmetic industries. Mohamed *et al*. (1995) did an extraction on *Hibiscus cannabinus* L. seeds conventionally by using hexane as the solvent for the extraction process. He found out that the oil content inside the *Hibiscus cannabinus* L. seed was 23.7%. The oil consists of phospholipids, sterol and fatty acids. The oil content is similar to that of cottonseed oil which then he suggested that the *Hibiscus cannabinus* L. oil may and was suggested to be an excellent source of edible oil for human consumption.

The production of organic seed oil is based on technical processes that respect the principles of the organic agriculture. These principles stated that the process should avoid the use of pollutant, pesticides and toxic that may have adverse health effects. Therefore, it is unwise to use toxic and pollutant organic solvents, such as hexane.

For this case, Supercritical Fluid Extraction (SFE) is the technique that will be used to extract the oil. The extraction uses carbon dioxide (CO_2) as the solvent to extract the oil out from the *Hibiscus cannabinus* L. seed. There are quite a few remarkable advantages for which CO_2 has been the most attractive solvent for supercritical fluid extraction. It is inexpensive, non-toxic, non-flammable and available in high purity. It has sometimes been called the cleanest solvent. Besides that, this substance has the status of Generally Recognized As Safe (GRAS) (Sahu, 2003).

Advantages of using SFE are that this technique is a mild technique, ideally no organic solvents needed i.e., environmentally friendly and cheap and can give fast extractions. Besides that, with 100% CO_2, no solvent removal step is needed and the solvating power varies with the operating pressure (Mukhopadhyay, 2000).

The objectives of this study are to determine the solubility and mass transfer at best operating pressure for highest oil yield which is at pressure of 48.26 MPa and at range temperature of 50-80°C. Besides that, the effect of temperature and pressure on oil yield and solubility is observed.

The value of mass transfer coefficient of *Hibiscus cannabinus* L. seed oil is important as for design or sizing of SC-CO_2 extractor since the value regulates the rate of mass transfer during the extraction process. Besides that, the role of mass transfer coefficient is essential to enhance the extraction rate of *Hibiscus cannabinus* L. seed oil using SC-CO_2.

MATERIALS AND METHODS

Hibiscus cannabinus L. seeds was obtained from Malaysian Agricultural Research and Development Institute (MARDI), Serdang. *Hibiscus cannabinus* L. seeds shown in Fig. 1. Seed samples were ground by using mechanical grinder and passed through a siever of 0.5, 0.45 and 0.4 mm pore size. Prior to the seeds being ground, a moisture content analysis experiment was

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conducted. The equipment used for the extraction process is called the SFT-100, supercritical fluid extractor by Supercritical Fluid Technologies, Inc. which uses CO_2 as its solvent. The CO_2 used is analytical grade with 99.99% purity.

Moisture content determination: The moisture content of *Hibiscus cannabinus* L. seed was determined by using the PORIM Test Method, 1995(Lin *et al*., 1995). In this test, the sample is ground in a mechanical mill to a meal size of 2 mm maximum dimension. Ten gram of the sample is weighed in a glass dish that has been previously dried in an oven and is weighed after cooling. The material is dried in an oven, at 103± 2°C, for 4 h and is weighed after it has been cooled.

Fig. 1: *Hibiscus cannabinus* L. seed

Super Critical Carbon Dioxide (SC-CO_2) extraction: A laboratory-scale supercritical-fluid extraction system (SFT-100) was used for this study. The CO_2 with 99.99% purity is continuously fed into the extractor with fixed solvent flow rate of 5 mL min^{-1}. The pressure and temperature of extractor are maintained constant at pressure of 34.47-48.26 MPa and temperature of 50-80°C. The pressure within the extraction vessel was built up with constant CO_2 flow rate at 24 mL min^{-1} and regulated by automated back pressure regulator. The supercritical fluid extraction was initiated after the desirable temperature and pressure were achieved. The entire process lasted for 40 min and the yield of the oil was measured after every 10 min interval. After the extraction was completed, the CO_2 was depressurized and the oil was collected. The total oil obtained from the extraction was calculated through the accumulation of interval yields. The extraction yield was determined gravimetrically by measuring the weights of the collection vials before and after extract collection. The flow sheet of the apparatus is shown in Fig. 2. In the extraction, 5 g of ground

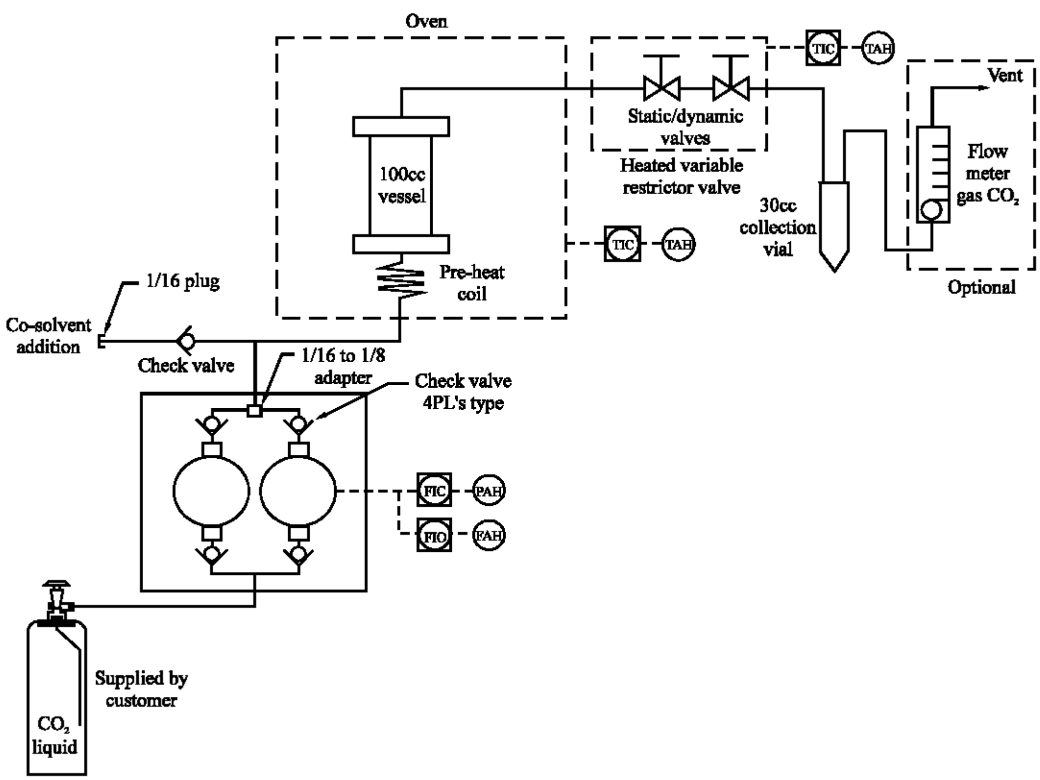

Fig. 2: Flowsheet of the supercritical fluid extraction unit

Hibiscus cannabinus L. seed sample with moisture content of 9.18% was extracted with SC-CO_2 at pressure of 34.47, 37.92, 41.37, 44.81 and 48.26 MPa and at temperature of 50, 60, 70 and 80°C.

Soxhlet extraction: The procedure of Soxhlet experiment is based on the PORIM Test Method, 1995 (Lin *et al.*, 1995). The test portion should be representative of the analysis sample. Ten gram of test sample is weighed into a thimble and the latter is plugged with cotton wool.

Extraction was conducted with 150 mL of solvent for 6 h. The thimble is removed from the extraction apparatus and it is placed in a current of air in order to expel the greater part of the residual solvent. The extract was dried at atmospheric pressure and 103±2°C for 2 h. The flask was allowed to cool at room temperature. The oil and hexane collected in the flask were then fed to rotary evaporator to separate the oil and the solvent, hexane. The process will take about an hour for the oil and hexane to be fully separated. Then the oil is weighed.

Solubility determination: Solubility of *Hibiscus cannabinus* L. oil in SC-CO_2 was estimated from a correlation given by Chrastil (2005), who proposed this semi-empirical equation to determine the solubility of stearic acids and oleic acids in SC-CO_2 as shown in Eq. 1,

$$c = \rho^{a_1} \exp\left(\frac{a_2}{T} + a_3\right) \quad (1)$$

where, c is solubility in kg m^{-3}, ρ is the density of CO_2 in kg m^{-3} and T is temperature in K.

However, Del Valle and Aguilera (1988) proposed an improved version of Chrastil's equation allowing the determination of solubility of vegetable oils in SC-CO_2, as given below:

$$y_r = \frac{\left[\exp\left(40.361 - \frac{18708}{T} + \frac{2186840}{T^2}\right) \times (0.001\rho)^{10.724} \pm 2.7\right]}{\rho} \quad (2)$$

where, y_r is solubility (kg oil/kg CO_2), T is temperature (K) and ρ is density of CO_2.

According to Del Valle and Aguilera (1988), this correlation is valid for temperature range of 20-80°C and pressures ranging. From minimum value 150-200 atm up to the temperature-dependant upper limit 800 atm at 20-60°C, 750 atm at 70°C and 680 atm at 80°C.

In addition, Adachi and Lu (1983) used Eq. 3 to find the solubility of 27 solutes such as stearic acid and oleic acid in SC-CO_2.

$$c = \rho^{(a_1 + a_2\rho + a_3\rho^2)} \exp\left(a_4 + \frac{a_5}{T}\right) \quad (3)$$

Table 1: Constants for solubility equations

Equation	Constants a_1	a_2	a_3	a_4	a_5
Chrastil (1)	8.45	-5480	-38.4		
Adachi-Lu (3)	-19.90	75.2	-48.2	18.3	-4919

which contains five constants, where c is solubility in kg m^{-3}, ρ is the density of CO_2 in kg dm^{-3} and T is temperature in K.

The constants of Eq. 1 and 3 are shown in Table 1. Therefore, Eq. 1 to 3 were used to describe the solubility behaviour of *Hibiscus cannabinus* L. oil.

Mass transfer determination: The kinetic model by Andrich *et al.* (2001) was used in this study to describe the unsteady state mass transfer as:

$$\frac{dm_e}{dt} = k(m_{s,t} - m^*_{s,t}) \quad (4)$$

Where:

- m_e = Amount of oil extracted in grams at time t
- k = Mass transfer coefficient in sec^{-1}
- $m_{s,t}$ = Amount of unextracted oil at time t
- $m^*_{s,t}$ = Amount of unextracted oil at time t if equilibrium between two phases has been reached

Assuming $m^*_{s,t}$ is negligible, because pure solvent continuously fed to the extractor and $m_{s,t}$ is equal to the difference between oil initially present in the sample ($m_{s,0}$) and oil extracted at time t, than Eq. 4 becomes:

$$\frac{dm_e}{dt} = km_{s,t} = k(m_{s,0} - m_e) \quad (5)$$

After integration, it gives,

$$\ln\left(\frac{m_{s,0}}{m_{s,0} - m_e}\right) = kt \quad (6)$$

Slope of the straight line passing through the origin of the axes t and ln ($m_{s,0}$/$m_{s,0}$-m_e) gives k, which is the mass transfer coefficient. The amount of oil extracted at time t is:

$$m_e = m_{s,0}(1 - e^{-kt}) \quad (7)$$

The extraction yield in g oil/g sample was calculated by dividing Eq. 7 by the amount of sample.

RESULTS AND DISCUSSION

Oil yield measurements and extraction curves: The oil yield from SC-CO_2 extraction is calculated by dividing

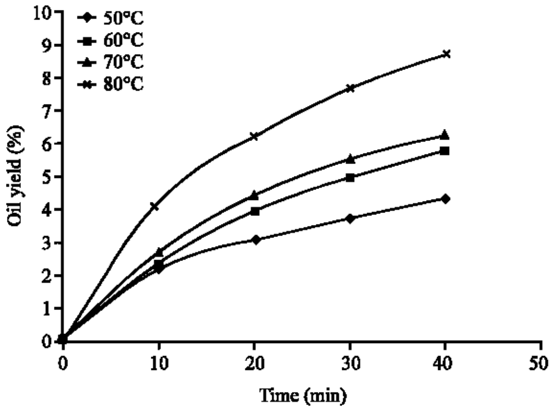

Fig. 3: Oil yield (%) of *Hibiscus cannabinus* L. oil vs. time of extraction at constant pressure of 48.26 MPa at various temperature

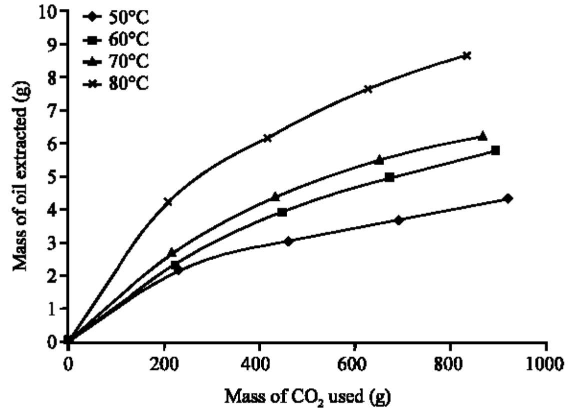

Fig. 4: Mass of oil extracted (g) vs Mass of CO_2 used at constant pressure of 48.26 MPa at various temperatures

weight of oil extracted (g) over weight of the solid sample (g). The oil content from Soxhlet extraction is found to be 27.1%. Extraction curve is a plot of total mass of oil extracted versus total CO_2 used. A typical extraction curve of vegetable oil is initially linear with time with a slope close to the value of oil solubility in SC-CO_2 (Ozkal *et al*., 2005). The linear region is referred as the constant mass transfer rate from solid matrix to the SC-CO_2 at high solute concentration in the solid matrix. This region of the extraction curve is also referred as the steady state or solubility-controlled mass transfer region (Beis and Dunford, 2006).

The easily accessible oil from the surface of the seed particle is extracted first and the slow extraction of inaccessible oil inside the solid particles follows.

Results of percentage of *Hibiscus cannabinus* L. oil extracted from *Hibiscus cannabinus* L. seed was plotted against time of extraction at constant pressure of 48.26 MPa with temperature range from 50 to 80°C and is shown in Fig. 3. From Fig. 3, it can be seen that the highest oil yield (8.66%) is at the highest temperature of 80°C at 48.26 MPa. This behavior is similar in trend of other related studies on seed oil using SC-CO_2 (Perrut *et al*., 1997; Reverchon *et al*., 1999; Aleksovski *et al*., 1998).

Effect of pressure and temperature: From the experiments conducted as shown in Fig. 3 and 4, it is found that, pressure and temperature control the oil yield. As the temperature increased, the solvent density also decreased. Thus, the solubility of the seed oil in the SC-CO_2 increased. Furthermore, saturation pressure of the solute in supercritical fluid increased with temperature thus improved the solubility.

Table 2: Values of solubility from experiments and from Del Valle and Aguilera, Adachi and Lu and Chrastil correlation

P (MPa)	T (°C)	Solubility (experiments)	Del Valle and Aguilera	Adachi and Lu	Chrastil
		($g\ g^{-1}$)			
48.26	50	0.0212	0.0226	0.0161	0.0148
	60	0.0302	0.0308	0.0207	0.0202
	70	0.0338	0.0345	0.0236	0.0251
	80	0.0477	0.0499	0.0256	0.0302

Similar findings can be found by Ozkal *et al*. (2005), Salgin *et al*. (2006), Perrut *et al*. (1997) and Reverchon *et al*. (1999). The extraction rate increases significantly with pressure, due to the increase of the solubility of the oil components. Thus the mass transfer also increased as the pressure and temperature increased.

Solubility data: The solubility of *Hibiscus cannabinus* L. oil in SC-CO_2 at each condition was determined from the slopes of the linear parts of extraction curves which were drawn as mass oil extracted versus mass of CO_2 used at the beginning of each extraction (Beis and Dunford, 2006). This result maybe due to the oil that was located on the particle surface of the solid matrix which is easily extracted by the SC-CO_2. In addition, during the initial state of extraction, solubility of oil in SC-CO_2 is the dominant factor that controls the extraction and mass transfer resistance was actually in the solvent (fluid) phase (Ozkal *et al*., 2005). The experimental data was compared with model developed by Del Valle and Aguilera (1), Adachi and Lu (2) and Chrastil (3). It was found out that the Del Valle and Aguilera (1), Adachi and Lu (2) and Chrastil (3), are in good agreement with the experimental data with correlation of coefficient (r^2) of 0.99, 0.98 and 0.94 respectively as shown in Table 2.

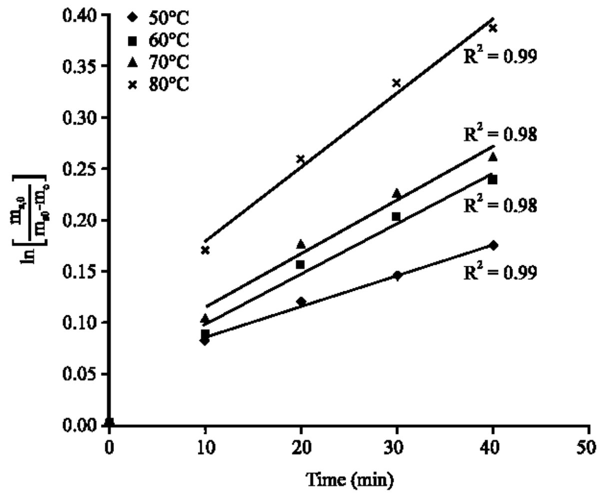

Fig. 5: Mass transfer behavior at constant pressure of 48.26 MPa and at temperature of 50-80°C

Table 3: Values of mass transfer coefficients

P (MPa)	T (°C)	Mass transfer coefficient (k) (sec^{-1})	Coefficient of correlation (r^2)
48.26	50	0.0030	0.99
	60	0.0049	0.98
	70	0.0052	0.98
	80	0.0072	0.99

Mass transfer coefficients: The mass transfer coefficients evaluated from the experimental data in Fig. 3 and 4 was determined from the slope of the straight line passing through the origin of the axes time and ln ($m_{s,0}/m_{s,0}$-m_e) as shown in Fig. 5.

Table 3 shows the value of mass transfer coefficients, k from the experimental data of constant pressure of 48.26 MPa and temperature range of 50-80°C. As shown in Table 3, the mass transfer coefficient increased with temperature at constant pressure of 48.26 MPa. The kinetic model used in Eq. 7 was successful in describing the mass transfer behavior with coefficient of correlation (r^2) value above 0.9.

The highest value of mass transfer coefficient, k is 0.0072 sec^{-1} at highest temperature of 80°C and at constant pressure of 48.26 MPa.

CONCLUSIONS

From the experiments conducted it was found that, temperature and pressure plays a crucial role in determining the oil yield. Both temperature and pressure affect the solubility of the oil in the extraction process. The solubility model proposed by Del Valle and Aguilera (1988), Adachi and Lu (1983) and Chrastil (2005) was found to be in good correlation with the experimental data with coefficient of correlation (r^2) above 0.9. The highest value of overall mass transfer coefficient was found to be 0.0072 sec^{-1} at the highest temperature of 80°C and pressure 48.26 MPa. The values of mass transfer coefficients determined in this work could provide good information especially on design or sizing of actual extractor SC-CO_2 plant or during industrial operation to evaluate the extraction time required for given yield at different temperatures and pressures. In addition, the oil extracted can be a new product for human consumption in Malaysia.

ACKNOWLEDGMENT

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