

# Parametric Evaluation for Extraction of Catechin from *Areca Catechu* Linn Seeds using Supercritical CO<sub>2</sub> Extraction

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## Article history

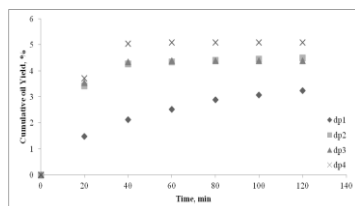
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## Graphical abstract



## Abstract

Supercritical fluid extraction is an advanced extraction technique which has been proven its efficiency and selectivity in numerous studies. Dense gas with diffusivity nearing liquid and viscosity closed to gas phase, supercritical fluid can provide better performance in the extraction of natural and heat sensitive active compounds. *Areca Catechu* Linn or commonly known as betel nut can be easily found in tropical country especially in south-east and south of Asia with India as its world largest producer. Phenolic compound present in *Areca Catechu* Linn are condensed tannins and also catechin. Catechin is a highly active compound with several properties such as anti-depressant, anti-oxidant, anti-viral, anti-inflammatory and anti-aging which are in demand by cosmetic and pharmaceutical industries. The aim of this study is to determine the best particle size, solvent flow rate, presence of modifier or co-solvent, and time of extraction for this pre-treatment study. Average particle size of 0.1774 mm ( $dp_1$ ) was detected as the best particle size for the extraction process with 3 mL/min solvent flow rate with 5% methanol added to solvent. Modifier presence enhances the extraction by improving the ability to extract more polar compound such as catechin. The best catechin recovery was observed at 3mL/min, solvent composition of 95:5 (SC-CO<sub>2</sub>:MeOH) at the temperature of 70°C and pressure of 30 MPa with 47.38 µg catechin/g extracts.

**Keywords:** Catechin; supercritical fluid extraction; pre-treatment; modifier

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## 1.0 INTRODUCTION

Supercritical condition is achieved when temperature and pressure exerted to the compound exceed the critical region. In this region, the compound cannot be compressed back to liquid form no matter how much pressure is applied to the compound. The compound possesses properties of both liquid and gases, with viscosity approaching gas phase and diffusivity approaching liquid phase. Supercritical fluid extraction (SFE) is an advanced extraction method that is used for selective extraction process. Commonly, SFE uses carbon dioxide (CO<sub>2</sub>) as solvent due to their relatively low critical condition. With critical temperature ( $T_c = 31.1^\circ\text{C}$ ) beneath body temperature, the extraction of heat sensitive material can be conducted. Furthermore, supercritical carbon dioxide (SC-CO<sub>2</sub>) greatest advantages are cleaner extracts and solvent free extracts compared to other extraction method such as steam distillation, soxhlet extraction, hydro distillation [1]. SC-CO<sub>2</sub> extracts are considered as green and consumable by the World Health Organization, WHO and European Food and Drug Association, EFDA [2, 3]. In addition to that CO<sub>2</sub> is selected because of their

properties of non-toxic, inflammable, non-hazardous, inert and also cheap [4].

*Areca Catechu* Linn or commonly known as 'pinang' in Malaysia is a tropical plant used majorly for interior landscaping. The leaves are traditionally used as food packaging for fruit paste or fried fish and the nut is traditionally used for consumption [5]. Its nut which is called betel nut or areca nut has been studied previously and it has been shown to contains catechin as the bio-active compound. Extraction by maceration technique with 50% ethanol for seven days yielded 14.4% extracts [6]. This result comply with the previous results that methanolic extracts or areca nut yield 118.3 mg/g sample of Phenolic content that contain condensed tannins and catechin as the major compounds [7]. Holdsworth *et al.*, in 1998 said that *Areca Catechu* Linn is the only species that contains alkaloid out of 54 *Areca* species in the world [8].

Catechin is commonly referred to (+)-catechin that contains anti-oxidant activities that can help repair oxidative damages caused by free radical and hydroxyl radical in human body system [9]. Anti-oxidant activity of catechin was ranked second prior to quercetin which contains anti-oxidant activity of 94.4%

while quercetin contains 95.3% when bioassay analysis was conducted to both compounds [10]. Catechin belongs to group of flavan-3-ol that if consumed regularly can hinder human disease such as arthritis, diabetes, cancer and Parkinson [11]. The presence of catechin can be easily detected with the colour of dark brown colour of the extracts.

In this study, the objective is to determine the optimum value of solvent flow rate, particle size, amount of modifier that will be used for extensive studies of effect of pressure and temperature on SFE extraction of *Areca Catechu Linn*. High Performance Liquid Chromatogram (HPLC) will be used to detect (+)-catechin presence in the extracts.

## 2.0 MATERIALS AND METHODS

### 2.1 Material

Sun dried *Areca Catechu Linn* seeds are hulled using hammer-grinding grinder (POLYMIX® PX-MFC 90D, Switzerland) into fine particle. Hulled sample are sieved to get several ranges of particle sizes ( $2.0 \text{ mm} > dp_1 > 0.71 \text{ mm}$ ,  $0.71 \text{ mm} > dp_2 > 0.5 \text{ mm}$ ,  $0.5 \text{ mm} > dp_3 > 0.355 \text{ mm}$  and  $dp_4 < 0.355 \text{ mm}$ ). These samples were used to determine the best particle size for extraction using SFE and were used for further determination of parameters. (+)-catechin standard were bought from Sigma-Aldrich.

### 2.2 Supercritical Fluid Extraction (SFE)

10 grams of hulled *Areca Catechu Linn* seeds are placed into the extraction cell. The cell was fitted into extraction cell that was then fitted into the SFE unit. CO<sub>2</sub> tank supplied the CO<sub>2</sub> needed for extraction process. CO<sub>2</sub> pump (Lab Alliance, Series II Pump) chills the gas into liquid and pumped it into the extraction cell that was fitted earlier according to the solvent flow rates. The pump was connected to an extraction cell placed inside an oven (Mettler) and finally connected to a back pressure regulator with a restrictor valve (JASCO, Model BP-2080). The extraction temperature was controlled via oven temperature by assuming the temperature inside of the extraction cell is equivalent to the temperature of oven, while the extraction pressure was controlled by the back pressure regulator. Oil extracted by CO<sub>2</sub> was collected in the collection vial attached to the restrictor valve. The extraction takes places for 2 hours extraction regime with 20 minutes fractionation to determine the optimum time of extraction. Experiment duration was reduced after obtaining the optimum extraction time. The extraction pressure and temperature were fixed at 30 MPa and 40°C respectively for consistency of response.

Three parameters were tested namely particle size, solvent flow rates and modifier determination. These parameters were selected to be studied in the pre-treatment stages to eliminate the effects of total surface area of sample subjected to solvent and polarity of solvent used. These factors were crucial to be fixed before studying the thermodynamics parameters of the SFE process.

In particle size determination, solvent flow rates were fixed at 3 mL/min (without modifier addition) while variation of particle sizes were tested namely  $dp_1$ ,  $dp_2$ ,  $dp_3$ , and  $dp_4$ . While in the solvent flow rate determination, the best particle size of sample obtained was used and no modifier was introduced. Solvent flow rate ranges from 2–6 mL/min. In modifier determination, the best particle size and best solvent flow rates were used but the solvent tested were pure CO<sub>2</sub> and 5% methanol used as modifier to the polarity of CO<sub>2</sub>. Several

experiments with various pressure and temperature were conducted to study the overview of extracts obtained and catechin content in the extracts. Operating pressure used were 20, 25 and 30 MPa while operating temperature were set to be 50, 60, 70 and 80°C

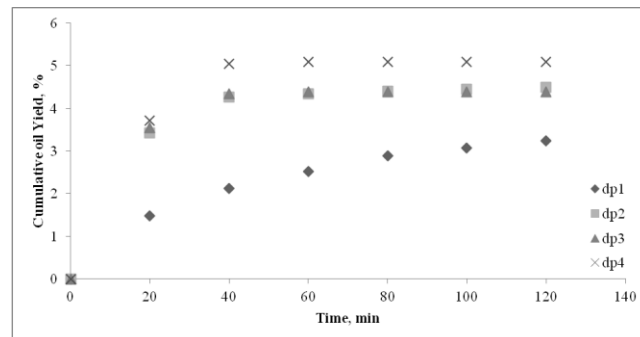
### 2.3 HPLC Analysis

The presence and amount of (+)-catechin were analyzed using HPLC (Perkin Elmer 200 Series) equipped with auto-sampler, pump, column oven, guard column, reverse phase C18 column (4.6 mm x 250 mm x 5 µm, Merck, Darmstadt, Germany–LiChrosper® 1100 NH<sub>2</sub>) and diode array detector. The mobile phases used were HPLC grade methanol (A) and 0.5% orthophosphoric acid in deionized water (B). Gradient program was used as follows: 0–5 min, starts with 20% A; 5–7 min linear gradient from 20–24% A; 7–10 min hold at 24% A and finally 10–15 min hold at 20% A, with 1 mL/min flow rate, detection wavelength at 210 nm, detection temperature at 30°C and injection volume of 10 µL. The (+)-catechin standard was prepared in several concentrations to construct a calibration curve. Extracts were diluted in 3 mL of methanol and 3 mL *n*-hexane and obtained two layers of solution. Methanolic extracts were analyzed using the HPLC to determine the presence of (+)-catechin in the extracts due to the fact that catechin is only soluble in methanol.

## 3.0 RESULTS AND DISCUSSION

### 3.1 Effect of Particle Size at constant pressure, temperature, flow rate and using pure CO<sub>2</sub>.

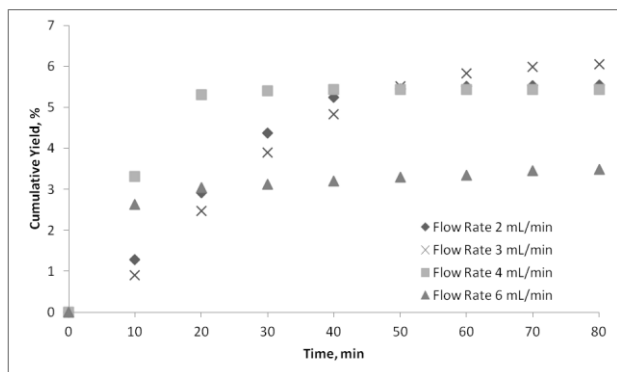
Figure 1 shows the effect of different particle sizes on the overall oil yield of *Areca Catechu Linn* when extracted at 30 MPa, 40°C and 3 mL/min of pure CO<sub>2</sub>. The highest average particle size,  $dp_1$  gives the lowest yield of 3.404 g oil/ 10 g sample while the lowest average particle size,  $dp_4$  give the highest yield of 5.091 g oil/ 10 g sample. For average particle size  $dp_1$ ,  $dp_2$  and  $dp_3$  most of its oil were extracted on the first 20 minutes of extraction time. The linear increment shows the solute is in equilibrium with the solvent. Excess amount of oil presence at the outer part of the sample particle was easily extracted by the CO<sub>2</sub>. Small particle size shows greater yield due to the higher surface area that were exposed to the solvent during the extraction process.



**Figure 1** Effect of particle sizes on oil yield of *Areca Catechu Linn* extracted at 30 MPa, 40°C and 3 mL/min of pure CO<sub>2</sub>

### 3.2 Effect of Flow Rate at Constant Pressure, Temperature, Particle Size and Pure CO<sub>2</sub>.

Solvent flow rate plays an important role in obtaining the asymptotic yield for the extraction of natural products. Solvent flow rates control the amount of solvent used for extraction in a specific extraction regime. Figure 2 shows the effect of solvent flow rate on the cumulative oil yield of *Areca Catechu Linn* when extracted using average particle size of 177.5  $\mu\text{m}$ , 30 MPa and 40°C. SC-CO<sub>2</sub> was supplied constantly to the extraction cell with several flow rates. Highest flow rates (6 mL/min) give the lowest yield with 3.49 %. This is due to the channeling effect which is caused by high flow rate. When the flow rate is very high, the solvent pass through the sample has low penetration power due to lack of contact time between samples and solvent. The reduction of contact time made the extraction process less effective thus produces a low yield. In contrast, lower flow rates give higher value of yield. The highest yield was observed at the flow rate of 3 mL/min, where the yield obtained was 6.06 %, an increase of 89% compared to the extraction done at 6 mL/min. Longer contact time allows longer penetration to the sample core resulting to the higher amount of extract being obtained. Results were coherent with previous research on the extraction on parsley seed oil and peach almond. Reducing the flow rate of solvent will give better results and higher extraction yield [12, 13]. At 2 mL/min, the extracts obtained were slightly lower due to the limited amount of solvent molecules to extract the solute from the sample matrix.



**Figure 2** Effect of solvent flow rate on cumulative oil yield of *Areca Catechu Linn* extracted using average particle size of 177.5  $\mu\text{m}$ , 30 MPa and 40°C

### 3.3 Effect of Modifier/Co-Solvent

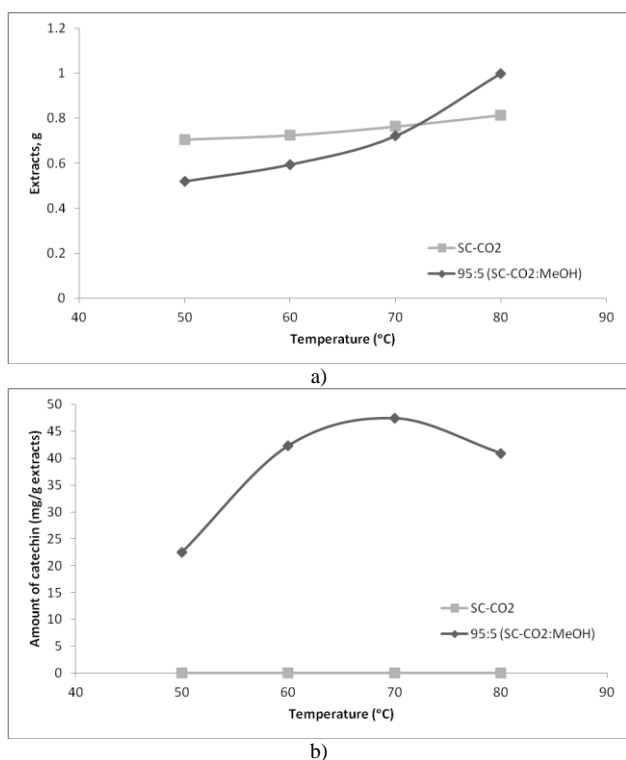
Modifier presence is critical in selective extraction process. Normal SFE extraction using pure SC-CO<sub>2</sub> is a selective extraction process. By altering the operating pressure and temperature, different compounds can be extracted with high quality. However, the downfall of the process is that normal SFE favours non polar or mild polar compound. This is due to the properties of CO<sub>2</sub>, which is a non polar compound and non polar solvent will extract non polar compound. For polar compound such as catechin, modifier is needed to increase the polarity of the solvent. Mixing the solvents with the right quantity will boost the selectivity of SFE with additional ranges of polar compound. In this research, modifier was introduced to the sample instead of mixing the solvent with SC-CO<sub>2</sub>. Modifier selected was methanol due to high polarity scale. Water was not selected to prevent corrosion in the extraction apparatus.

Amount of modifier usually used is in ratio to the total flow rate. In this research, the amount selected was 95:5 (CO<sub>2</sub>: methanol).

Comparing the results given by extraction using pure SC-CO<sub>2</sub> and SC-CO<sub>2</sub> with 5% methanol, only trace amount of catechin was detected when using pure SC-CO<sub>2</sub> as the solvents. On the other hand, high detection of catechin was obtained when using 5% methanol. The amount of catechin was determined using calibration curve. The calibration curve was obtained by plotting the peak area of standard catechin. Several concentrations were prepared and graph of peak area versus catechin concentration was plotted. With calibration curve of  $y = 92192x$  with  $y$  is the peak area ( $\mu\text{V.s}$ ) obtained using HPLC analysis and  $x$  is the concentration of standard catechin (ppm), the concentration of catechin in each experimental run can be quantified.

Figure 3 shows the effects of extracts in the presence of modifier in the flow rate at constant pressure of 30 MPa. At constant pressure, pure SC-CO<sub>2</sub> shows a steady increase in oil yield with highest yield of 0.8144 g extracts at 80°C as shown in Figure 3(a). Similar pattern is also observed during the extraction using 5% modifier. With the increasing of temperature, it also increases the amount of oil yield. The difference in the behaviour is that the exponential increment of oil is more rapid than pure SC-CO<sub>2</sub>. The highest yield was obtained by using 5% methanol as modifier, at 80°C with yield of 0.9985 g extracts.

Figure 3(b) shows that increasing amount of catechin can be observed with the highest amount of catechin obtained at 70°C, 30 MPa with 47.38  $\mu\text{g}$  catechin/g extracts when 5% methanol as modifier was used. However, extracts did not contain any trace of catechin when pure SC-CO<sub>2</sub> was used. This proves that catechin needs a polar solvent to extract it out from the sample matrix of *Areca catechu Linn* seeds. Higher temperature of extraction process shows a decrease in the amount of catechin extracted. Increasing the temperature greater than 70°C is not recommended for the extraction of bio-active compound. This is due to the compound heat sensitive properties that will degrade when exposed to high temperature for a period of time.



**Figure 3** Effect of modifier at constant flow rate (3mL/min), particle size ( $dp_4$ ) and pressure (30 MPa). (a) Effect on extracts (b) Effect on amount of catechin

Effects of modifier presence to the responses at constant temperature, 60°C is shown in Figure 4. At constant temperature, pure SC-CO<sub>2</sub> shows better results with higher oil yield at every selected pressure. Highest yield observed at 25 MPa with 0.7415 g oil using pure SC-CO<sub>2</sub> as solvent. Pure SC-CO<sub>2</sub> gives a better result due to the composition of the extracted compound is more to non-polar compound. As observed in the extract, only the pale yellowish colour which represents the oily part of the extracts were collected when extraction was using pure SC-CO<sub>2</sub>. Dark brown colour of catechin only can be observed when the extraction was using 5% methanol as polarity modifier to the solvent.

The increment of catechin can be seen when pressure is increased at constant temperature and no trace of catechin were detected when pure SC-CO<sub>2</sub> were used. The amount of catechin increases from 12.00 µg catechin/g extracts to 42.27 µg catechin/g extracts when pressure was increased from 20 to 30 MPa. As pressure increases, it also changes the polarity of the solvent.

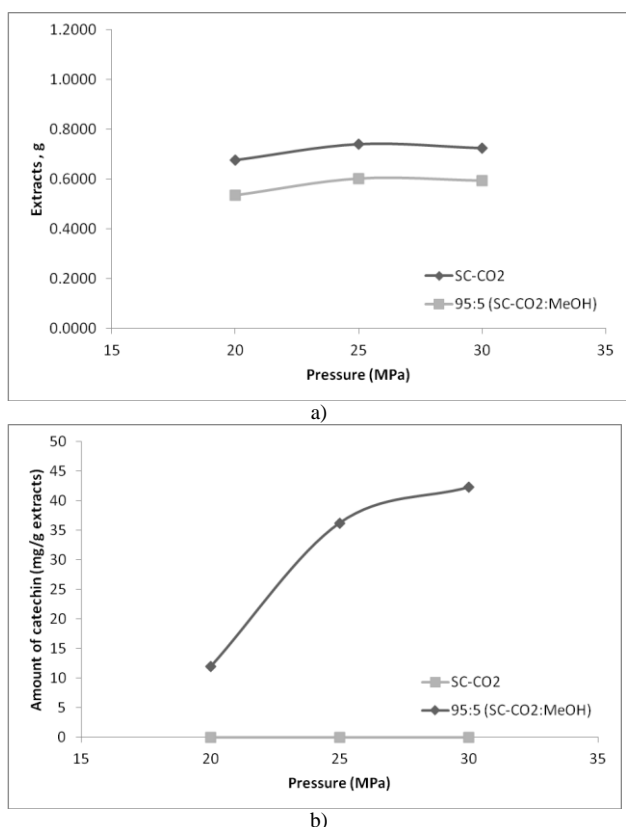
As collective effects take place in the extraction, when both pressure and temperature increase, polarity of solvents also increases. Previous researches show some fatty acids can only be obtained at higher operating pressure and temperature when the polarity scale of solvent is near the polarity scale of interest compound. In this case, catechin is a highly polar compound. Combination of high operating pressure and temperature with addition of methanol as polarity booster to SC-CO<sub>2</sub>, increases the amount of catechin that can be obtained using supercritical fluid extraction method. Theoretically, higher pressure and temperature will result in higher results. However, as the interest compound is biologically active with temperature and heat sensitive properties, it is not recommended to conduct the extraction in temperature higher than 80°C.

### 3.4 Effects of Pressure at Constant Temperature

As pressure increases from 20 to 30 MPa, the amount of extracts using both type of solvent increases as shown in Figure 4. Figure 4(a) shows that similar pattern of extracts was obtained when extraction was conducted using SC-CO<sub>2</sub> and SC-CO<sub>2</sub> with 5% modifier. SC-CO<sub>2</sub> extracts yield slightly higher with highest extracts obtained at 25 MPa with 0.7415 g extracts. On the contrary, no traces of catechin were obtained when SC-CO<sub>2</sub> extracts were analyzed as shown in Figure 4(b). Highest trace of catechin obtained at 30 MPa with 42.47 mg catechin/g extracts when 5% of modifier was introduced to the process. The presence of catechin in the extracts was due to the polarity of solvent that has been discussed earlier in section 3.3.

Increasing the pressure will increase the density of fluid used for extraction. Increasing the density also increase the penetration power or solvating power of supercritical fluid nearing the liquid state. Diffusivity of fluid increases and the ability of solvent to penetrate deeper into the sample matrices also increases. Better penetration also means that fluid is able to access solute located deep in the sample matrices that were not easily accessible compared to the solute that were available on the surface of the sample.

Sovová in 1994 detailed his theory in dividing the assumedly spherical particle into two different regions namely broken and intact cell [14]. Broken cell is defined as the broken part of the particle that contained free oil that is easily accessible by solute which is located at the outer part of the particle. This process takes place on the earlier part of the extraction regime. Broken cell was formed during the grinding process to obtain smaller particle size. Intact cell is defined as the inner part of the particle that is not being crushed in the grinding process. This intact cell contained solute that usually can be extracted at higher pressure. As higher pressure increases the solvating power of solvents, it can diffuse deep into the intact cell of the particle. This process takes place in the later part of the regime when all the free oil has been depleted by the earlier extraction process. This theory was also applied by Özkal *et al.* in 2005 in modelling the extraction of apricot kernel oil [15].



**Figure 4** Effect of modifier at constant flow rate (3mL/min), particle size ( $dp_4$ ) and temperature (60°C). (a) Effect on extracts (b) Effect on amount of catechin

### 3.5 Effects of Temperature at Constant Pressure

As temperature increases from 50 to 80°C, the amount of extracts increases gradually as shown in Figure 3. For both solvents, similar pattern was observed. As temperature increases so does the vapour pressure of solute in the plant matrices increases. Higher vapour pressure indicates that the solute can be easily attached to the solvent and carried out of the sample. Charstil *et al.* in 1982 stated that for an extraction process to take place, temporary bonding between solute and solvents needs to take place to form a solute-solvent complex [16]. This temporary bond is also determined by the operating temperature of the extraction process. Higher temperature normally increases the solubility of solute to the solvent which resulted in the increasing amount of extracts obtained.

## 4.0 CONCLUSION

Previous studies show that the extracts have big potential for cosmetics field in term of bio-active properties of the extracts. This study aims to enhance the quality of the extracts with the implementation of advance extraction process, while previous research only focused on conventional extraction process. Higher amount of catechin can be obtained by increasing the percentage of co-solvents from 5% to 15%. However, too high amount of modifier can cause the sample to be more compact and can result in blocking in the extraction cell. Because of the sample is too wet, the sample will form a concrete lump that will block the flow of solvents in the extraction cell. For supercritical fluid extraction of biologically active compound, it

is advised to operate at lower temperature due to the sensitivity of the active compound. While higher operating pressure can give better results, it is advised to operate below the safety limit of the equipment due to some safety precautions. In the extraction of polar compound using supercritical fluid such as catechin, modifier such as methanol or ethanol needs to be added to SC-CO<sub>2</sub> to assist the extraction process. If not, the yield will not contain any trace of the interest compound. Results in this study will be used for further study on the behavior of parameters in the solubility and mass transfer coefficient of the extraction using several models.

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## References

- [1] Araus, K., E Uquiche, and J. M. Del Valle. 2009. Matrix Effect in Supercritical CO<sub>2</sub> Extraction Oils from Plant Material. *Journal of Food Engineering*. 92: 438–447.
- [2] Tiek, N. L., and M. I. Mohd Azmi. 1997. Trade in Medicinal and Aromatic Plants in Malaysia. Forest Research Institute of Malaysia, FRIM Report. 71: 52–67.
- [3] Starman, D. A. J., Nijhuis, H. H. 1996. Extraction of Secondary Metabolites from Plant Material: A Review. *Trends Food Science Technology*. 7: 191–197.
- [4] Davarnejad, R., K. M. Kassim, A. Zainal, and S. A. Sata. 2008. Supercritical Fluid Extraction of B-Carotene from Crude Palm Oil Using CO<sub>2</sub>. *Journal of Food Engineering*. 89: 472–478.
- [5] Matan, N., W. Saengkrajang, and N. Matan. 2011. Antifungal Activities of Essential Oils Applied by Dip-Treatment on Areca Palm (*Areca Catechu*) Leaf Sheath and Persistence of Their Potency Upon Storage. *International Biodeterioration & Biodegradation*. 6: 212–216.
- [6] Bhandare, A., A. Kshirsagar, N. Vyawahare, P. Sharma, and R. Mohite. 2011. Evaluation of Anti-migraine Potential of *Areca Catechu* to Prevent Nitroglycerin-induced Delayed Inflammation In Rat Meninges: Possible Involvement Of NOS Inhibition. *Journal of Ethnopharmacology*. 136: 267–270.
- [7] Cai, Y., Q. Luo, M. Sun, and H. Corke. 2004. Antioxidant Activity and Phenolic Compounds of 112 Traditional Chinese Medicinal Plants Associated with Anticancer. *Life Science*. 74: 2157–2184.
- [8] Holdsworth, D. K., R. A. Jones, and R. Self. 1998. Volatile alkaloids from *Areca Catechu*. *Phytochemistry*. 48 (3): 581–582.
- [9] Kalender, Y., S. Kaya, D. Durak, F. G. Uzun, F. Demir. 2012. Protective Effects of Catechin and Quercetin on Antioxidant Status, Lipid Peroxidation and Testis-Histoarchitecture Induced by Chlorpyrifos in Male Rats. *Environmental Toxicology and Pharmacology*. 33: 141–148.
- [10] Katalinić, V., M. Milos, D. Modun, I. Musić, and M. Boban. 2004. Antioxidant Effectiveness of Selected Wines in Comparison With (+)-Catechin. *Food Chemistry*. 86: 593–600.
- [11] Gogoi, P., S. Hazarika, N. N. Dutta, and P. G. Rao. 2010. Kinetics And Mechanism of Laccase Catalyzed Synthesis of Poly (Allylamine)-Catechin Conjugate. *Chemical Engineering Journal*. 163: 86–92.
- [12] Louli, V., G. Folas, E. Voutsas, and K. Magoulas. 2004. Extraction of Parsley Seed Oil by Supercritical CO<sub>2</sub>. *Journal of Supercritical Fluids*. 30: 163–174.
- [13] Mezzomo, N., J. Martínez, and S. R. S. Ferriera. 2009. Supercritical Fluid Extraction of Peach (*Prunus Persica*) Almond Oil: Kinetics, Mathematical Modelling and Scale-Up. *Journal of Supercritical Fluids*. 51: 10–16.
- [14] Sovová, H. 1994. Rate of the Vegetable Oil Extraction with Supercritical CO<sub>2</sub>-I. Modelling of Extraction Curves. *Chemical Engineering Science*. 49(3): 409–414.

- [15] Özkal, S. G., M. E. Yener, and L. Bayindirh. 2005. Mass Transfer Modelling of Apricot Kernel Oil Extraction with Supercritical Carbon Dioxide. *Journal of Supercritical Fluids*. 35: 119–127.
- [16] Charstil, J. 1982. Solubility of Solids and Liquids in Supercritical Gases. *Journal of Physical Chemistry*. 86: 3016–3021.