International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:12, No:9, 2018

Optimization of Soybean Oil by Modified Supercritical Carbon Dioxide

N. R. Putra, A. H. Abdul Aziz, A. S. Zaini, Z. Idham, F. Idrus, M. Z. Bin Zullyadini, M. A. Che Yunus

***Abstract*—**The content of omega-3 in soybean oil is important in the development of infants and is an alternative for the omega-3 in fish oils. The investigation of extraction of soybean oil is needed to obtain the bioactive compound in the extract. Supercritical carbon dioxide extraction is modern and green technology to extract herbs and plants to obtain high quality extract due to high diffusivity and solubility of the solvent. The aim of this study was to obtain the optimum condition of soybean oil extraction by modified supercritical carbon dioxide. The soybean oil was extracted by using modified supercritical carbon dioxide (SC-CO_2) under the temperatures of 40, 60, 80 °C, pressures of 150, 250, 350 Bar, and constant flow-rate of 10 g/min as the parameters of extraction processes. An experimental design was performed in order to optimize three important parameters of SC-CO_2 extraction which are pressure (X_1), temperature (X_2) to achieve optimum yields of soybean oil. Box Behnken Design was applied for experimental design. From the optimization process, the optimum condition of extraction of soybean oil was obtained at pressure 338 Bar and temperature 80 °C with oil yield of 2.713 g. Effect of pressure is significant on the extraction of soybean oil by modified supercritical carbon dioxide. Increasing of pressure will increase the oil yield of soybean oil.

***Keywords*—**Soybean oil, SC-CO_2 extraction, yield, optimization.

I. Introduction

THERE are many extraction processes that can be used to extract and carry out oil and bioactive compounds inside of solutes. However, supercritical carbon dioxide extraction is a green alternative technology compared to conventional processes such as accelerated Soxhlet extraction and hydrodistillation [1]-[3]. Moreover, the benefits of using supercritical carbon dioxide as solvent are inexpensive and non-toxic solvents that can be easily separated from the extracts. From the previous research, the supercritical carbon dioxide extraction process has been successfully used to extract bioactive compounds from herbaceous plants. Other applications include the extraction of oils from avocado, rosehip, *Pithecellobium jiringan* (Jack), Prain seeds, peanut skin and ginger [4]-[8]. Additionally, the supercritical CO_2 extraction process can be applied in investigating the matrices of plants and herbs [9]-[11].

Soybean or its scientific name *Glycine Max* is classified as an oilseed. Soybean has history in all parts of the world as a major crop and is widely consumed as an alternative source of protein. Some examples of soy related products are soy vegetable oil, soy milk, and others. Previous studies showed that conventional extraction processes have been already applied on the extraction of soy bean such as Soxhlet extraction and ultrasound-assisted extraction [12], [13]. Extraction time, amount of solvent, and toxicity of solvent are the problems in the extraction of *Orthosiphon stamineus.* Therefore, supercritical carbon dioxide extraction is one of the solutions for extraction of soybean because supercritical carbon dioxide extraction has short extraction time, low consumption of solvents, and non-toxic solvent [14]-[17]. However, due to its limited polarity, supercritical CO_2 can only extract non-polar bioactive compounds from plants and herbs matrices [18], [19]. To overcome this problem, modification of the supercritical CO_2 process is needed to enhance the polarity of solvents used for the extraction of bioactive compounds. The modification process involves the addition of ethanol as a modifier during extraction [4], [20], [21]. The choice of ethanol as a modifier is due to its low toxicity compared to methanol and ethylene glycol [18], [19]. Therefore, the objective of this study is to investigate and optimize the effect of process parameters on supercritical carbon dioxide extraction with oil yield of soybean as a response.

Nicky Rahmana Putra is with the Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia (e-mail: nickyrahman1309@ gmail.com).

Ahmad Hazim Abdul Aziz, Ahmad Syami Zaini, Zuhaili Idham, Fadillah Idrus, Muhammad Zahid Bin Zullyadini, and Mohd Azizi Che Yunus were with the Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia (e-mail: azimaziz_utm91@ yahoo.com, ahmadsyahmizaini@gmail.com, zuhaili@cheme.utm.my, faadilaidrus@gmail.com, zahidla.zz@gmail.com, azizi@cheme.utm.my).

II. Materials and Methods

A. Plant Material

The sun-dried soybean was powdered using dry-mill grinder with the aim of increasing the samples' surface area [22], [23]. The dried powdered plants were then sieved by using sieve trays with particle size of 300 µm. The chosen size was made based on the preliminary result which showed that particle size of 300 µm was the optimum size for extraction process. At the end of this stage, the material's powder was put inside the sealed plastic bag and stored in a refrigerator at temperature −20 °C to maintain the freshness of samples before being used for extraction [24].

B. Chemicals

Liquid carbon dioxide (99% purity) was used in the supercritical extraction apparatus purchased from Kras Instrument, Johor Bahru, Malaysia. An analytical grade of ethanol (99.86%) was purchased from Permula Sdn Bhd, Johor Bahru, Malaysia.

C. Modified Supercritical Carbon Dioxide Extraction

The procedure of SC-CO_2 extraction process is discussed in detail. To begin with, the collection vials were prepared, labelled and weighted. Meanwhile, the oven and chiller were turned on. The chiller and heater temperature were set at 5 °C and 50 °C, respectively. Next, 15 g of powdered soybean that has been processed through the sampling process was placed into the vessel. The extraction vessel was then fixed properly in the oven. The investigated values of pressure and temperature conducted in this experiment were: pressure of 150, 250 and 350 bar; temperature: 40, 60, and 80 °C and each set of extraction processes were run for 3 hours. Then, the back pressure regulator (Tescom 10000) had been controlled while the temperature was adjusted by setting the oven (France Etuves H555) temperature. Next, the CO_2 gas was pumped into the system continuously with supercritical pump (Separex Piston Pump P200GP50) at flow rate of 10 g/min while ethanol as modifier was pumped into the system at flow rate of 0.5 g/min. The extract was collected for every 15 minutes of the extraction process. The extract oil obtained was placed in the collection vials, sealed and stored in the chiller at 2.7 °C to prevent any possible degradation of the product.

D. Analysis of Oil Yield Percentage

The comparison of oil yield percentage of soy bean oil was expressed in terms of mass percentage of the samples:

$$\text{Percentage of Oil Yield} = (m_1/m_2) \times 100\% \qquad (1)$$

where, m_1 is the mass of extracted oil (g) and m_2 is the mass of sample (g).

E. Experimental Design

An experimental design was performed in order to optimize three important parameters of SC-CO_2 extraction which are pressure (X_1), temperature (X_2) to achieve optimum yields of soybean oil. Box Behnken Design was applied for experimental design.

TABLE I
FACTORS AND LEVELS TESTED FOR THE EXPERIMENTAL DESIGN

Factors	**Low Level**	**Medium Level**	**High Level**
Pressure, (X_1, MPa)	-1	0	+1
Temperature, (X_2, °C)	-1	0	+1

Response surface methodology (RSM) was applied to optimize the operating parameters of SC-CO_2 for the extraction of soybean oil. RSM model or regression equation which includes linear and quadratic variables as well as interaction terms was used to fit the first and second-order polynomial equation based on the experimental data as follows:

$$Y = B_0 + \sum_{i=1}^{k} B_i X_i + \sum_{i=1}^{k} B_i X_i^2 + \sum_i \sum_j B_{ij} X_i X_j \qquad (2)$$

where Y is the predicted response, B_0 is a constant, B_i, B_{ii}, B_{ij} are the interaction of effect, X_i and X_j are the coded value of factor. Finally, the response surfaces of the variables inside the experimental domain were analyzed by analysis of variance (ANOVA).

III. RESULTS AND DISCUSSION

Optimization of extraction process was conducted using three main parameters: the effect of pressure, temperature, and rate of co-solvent. extract yield and high antioxidant activity on peanut skin extract. The two variables were investigated by using second order polynomial statistical model. Preliminary studies were needed to determine fixed variables of the optimization. The quadratic effect of the treatments variables, their interactions, and coefficients on the response variables were obtained by ANOVA. Experimental design was made by using Box Bhenken design as shown in Table II.

TABLE II
VARIABLES AND RESPONSES OF EXTRACTION OF SOYBEAN OIL BY MODIFIED SUPERCRITICAL CARBON DIOXIDE

Run	Variables		Responses	
	Pressure, Bar (X_1)	Temperature, °C (X_2)	Oil Yield, gram (y_1)	Model, gram
1	60	350	1.929	2.423
2	80	250	2.145	2.181
3	40	350	2.463	2.142
4	80	350	2.874	2.704
5	60	150	0.582	0.817
6	40	250	2.084	2.426
7	60	250	2.381	2.304
8	40	150	1.534	1.342
9	80	150	0.334	0.293
10	60	250	2.607	2.304

From Table II, shows that the optimum condition to extract oil from soybean was at pressure 338 Bar and temperature 80°C with response oil yield 2.713 gram. Moreover, the maximum oil yield obtained was 2.874 gram at condition pressure 350 bar and temperature 80 °C. Furthermore, the minimum soybean oil yield was 0.334 gram at condition pressure 150 bar and temperature 80 °C

The ANOVA is presented in Table III where soybean oil yield is a response, and pressure and temperature are the variables. Based on the statistical analysis, a quadratic equation successfully optimized the extract yield of soybean. The analysis showed that both models were statistically significant (sig. <0.05) at 95% confidence. The coefficient of determination, R^2, of quadratic model was 0.893 and adjusted coefficient of determination was 0.803. From the coefficient of determination, the quadratic model has successfully fitted the experimental data.

Fig. 1 shows that the experimental data vs. predicted quadratic model of extraction soybean oil by modified supercritical carbon dioxide. Fig. 1 indicates that quadratic model has successfully fitted the experimental data due to the R^2 and adj R^2. The quadratic model of extraction soybean oil by modified supercritical carbon dioxide is shown in (3).

$$Y = -0.594 - 0.0564\,X_2 + 0.0302\,X_1 + 0.002014\,X_1 X_2 - 0.0000684 X_1^2 \qquad (3)$$

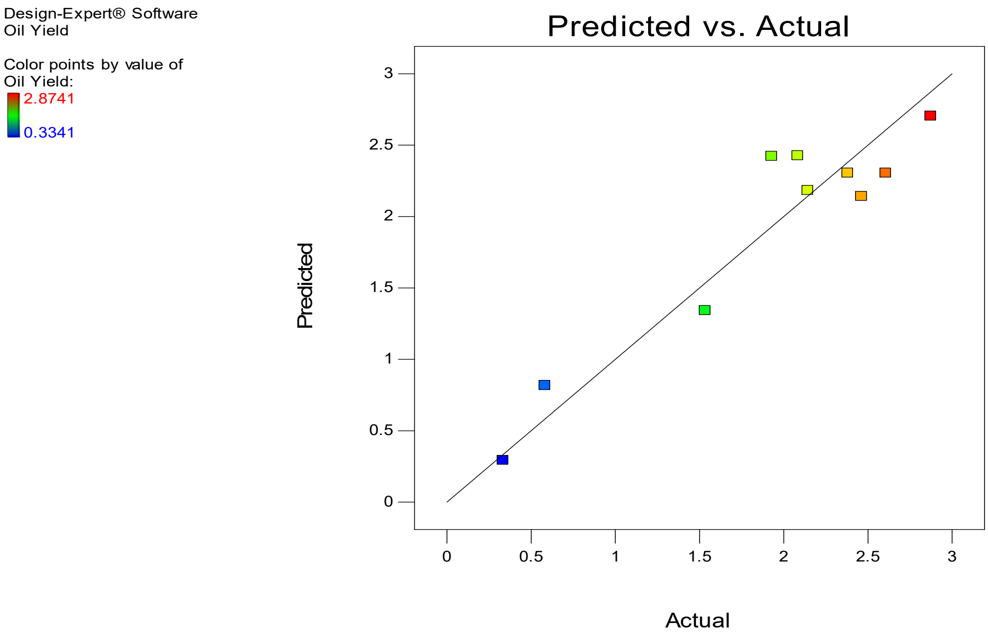

Fig. 1 The experimental data vs predicted quadratic model of extraction soybean oil from modified supercritical carbon dioxide

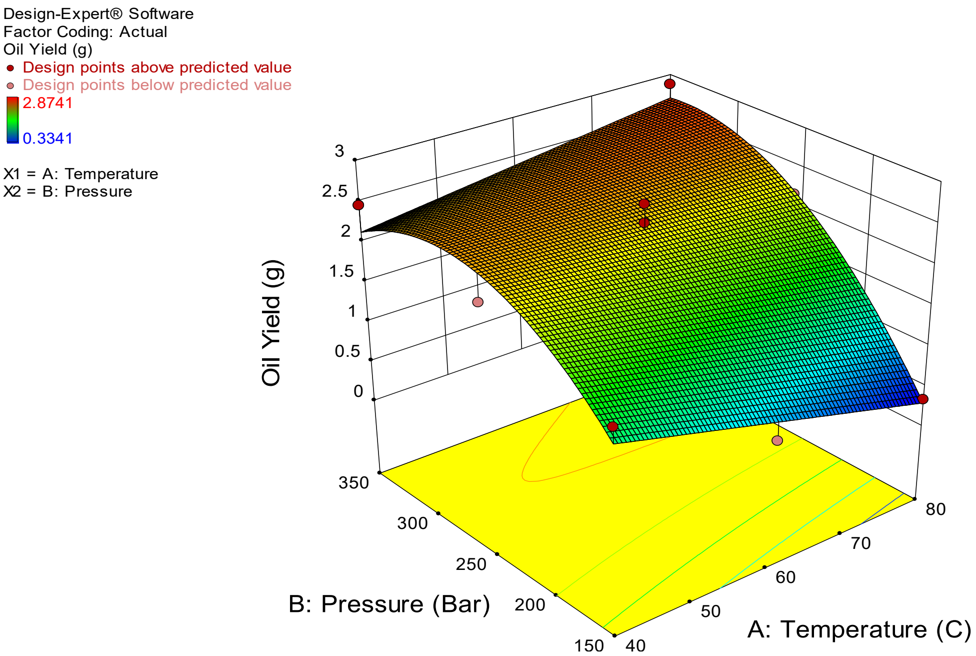

Fig. 2 3-D contour plot of the experimental data extraction soybean oil from modified supercritical carbon dioxide

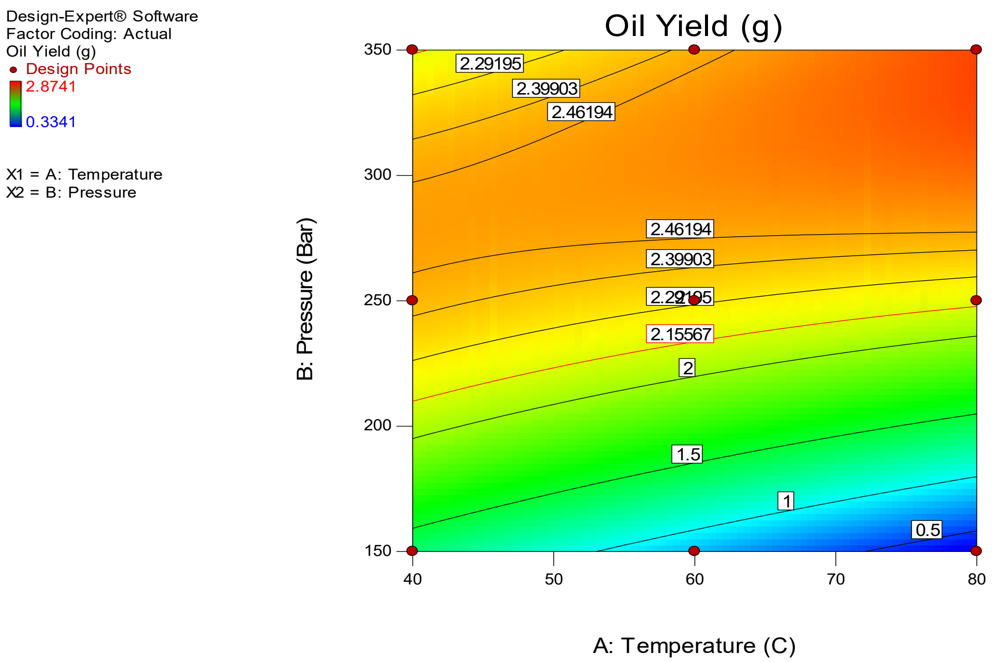

Fig. 3 Contour plot of the experimental data extraction soybean oil from modified supercritical carbon dioxide

TABLE III
ANOVA TABLE OF EXTRACTION OF SOYBEAN OIL BY MODIFIED SUPERCRITICAL CARBON DIOXIDE

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	5.78	5	1.16	7.30	0.0385	significant
X_1-Temperature	0.089	1	0.089	0.56	0.4958	
X_2-Pressure	3.87	1	3.87	24.41	0.0078	
$X_1 X_2$	0.65	1	0.65	4.10	0.1128	
X_1^2	0.052	1	0.052	0.33	0.5984	
X_2^2	1.17	1	1.17	7.42	0.0528	
Residual	0.63	4	0.16			
Lack of Fit	0.61	3	0.20		0.2533	not significant
Pure Error	0.025	1	0.025	7.98		
Cor Total	6.41	9				

From the coefficient of quadratic model on (3) shows that temperature gives a big influence on the extraction of soybean oil due to the highest coefficient model followed by pressure (0.564 > 0.0301).

From Figs. 2 and 3, it can be summarised that increasing pressure (150 bar- 350 bar) and temperatures (40–60 °C) increased the soybean oil yield. Increasing pressure will increase the density of supercritical CO_2. This is because the increase in interaction between CO_2 molecules and soybean as solute enhance the dissolution of oil into the solute [24]. Furthermore, the increase in density increases the solubility and diffusivity of extraction process [25]. This is similar to the result for extraction of prain seeds by modified supercritical carbon dioxide which reported that increasing of pressure will increase the prain seeds oil yield [6]. Increasing of pressure will increase diffusivity and solubility of solvent to extract soybean oil from the solute [24]. Furthermore, increasing of temperature enhances the soybean oil yield at a constant highest pressure (350 Bar). However, the increasing temperature decreases the soybean oil yield at a lowest constant pressure. At the highest pressure condition, the effect of vapour solute condition is significant during modified supercritical CO_2 [6]. Furthermore, at lowest constant pressure, increasing of temperature decreases the soybean oil extract. This is because increasing of temperature at a constant pressure will degrade the quality of extract and vaporize the extract [26]. This is similar to the result of extraction peanut skin oil by modified supercritical carbon dioxide where increasing of temperature will decrease the oil yield of peanut skin oil [24]. Increasing of temperature will decrease the solubility power of solvent to extract the oil from the solute [27].

IV. CONCLUSION

In this study, the quadratic model was successfully fitted to experimental data of extraction of soybean oil by supercritical carbon dioxide. The optimum recovery of soybean oil yield was 2.713 g at conditions 338 bar, 80 °C. However, the optimum temperature for extraction was not deduced. Nevertheless, the increase in pressure enhanced the yield of soybean oil at constant temperature condition.

ACKNOWLEDGMENT

The authors acknowledge the Centre of Lipid Engineering and Applied Research (CLEAR) for the use of equipment. The financial support from Universiti Teknologi Malaysia for professional development research university grant (R.J130000.7709.4J260) is gratefully acknowledged.

REFERENCES

[1] Koszegi, K., G. Vatai, and E. Békássy-Molnár, "Comparison the Soxhlet and Supercritical Fluid Extraction of Nettle Root (Urtica dioica L.)". *Periodica Polytechnica. Chemical Engineering*, 59(3): p. 168, 2015.

[2] Bimakr, M., R. A. Rahman, F. S. Taip, A. Ganjloo, L. M. Salleh, J. Selamat, A. Hamid, and I. Zaidul, "Comparison of different extraction methods for the extraction of major bioactive flavonoid compounds from spearmint (Mentha spicata L.) leaves". *Food and bioproducts processing*, 89(1): p. 67-72, 2011.

[3] Guan, W., S. Li, R. Yan, S. Tang, and C. Quan, "Comparison of essential oils of clove buds extracted with supercritical carbon dioxide and other three traditional extraction methods". *Food Chemistry*, 101(4): p. 1558-1564, 2007.

[4] Corzzini, S. C., H. D. Barros, R. Grimaldi, and F. A. Cabral, "Extraction of edible avocado oil using supercritical CO 2 and a CO 2/ethanol mixture as solvents". *Journal of Food Engineering*, 194: p. 40-45, 2017.

[5] Machmudah, S., Y. Kawahito, M. Sasaki, and M. Goto, "Supercritical CO2 extraction of rosehip seed oil: Fatty acids composition and process optimization". *Journal of Supercritical Fluids*, 41(3): p. 421-428, 2007.

[6] Yunus, A., NH, S. Zhari, Z. Idham, S. Setapar, and A. Mustapha, "Effect of supercritical carbon dioxide condition on oil yield and solubility of Pithecellobium Jiringan (Jack) Prain seeds". *J. Teknologi*, 60: p. 45-50, 2013.

[7] Putra, N. R., A. H. A. Aziz, L. N. Yian, W. D. Ramli, and M. A. C. Yunus. *Optimization of Supercritical Carbon Dioxide and Co-solvent Ethanol Extraction of Wasted Peanut Skin Using Response Surface Methodology*. in *MATEC Web of Conferences*. 2018. EDP Sciences.

[8] Zancan, K. C., M. O. Marques, A. J. Petenate, and M. A. A. Meireles, "Extraction of ginger (Zingiber officinale Roscoe) oleoresin with CO 2 and co-solvents: a study of the antioxidant action of the extracts". *The Journal of supercritical fluids*, 24(1): p. 57-76, 2002.

[9] Duarte, M. C. T., G. M. Figueira, A. Sartoratto, V. L. G. Rehder, and C. Delarmelina, "Anti-Candida activity of Brazilian medicinal plants". *Journal of ethnopharmacology*, 97(2): p. 305-311, 2005.

[10] Gião, M. S., C. I. Pereira, S. C. Fonseca, M. E. Pintado, and F. X. Malcata, "Effect of particle size upon the extent of extraction of antioxidant power from the plants Agrimonia eupatoria, Salvia sp. and Satureja montana". *Food Chemistry*, 117(3): p. 412-416, 2009.

[11] Herrero, M., A. Cifuentes, and E. Ibañez, "Sub-and supercritical fluid extraction of functional ingredients from different natural sources: Plants, food-by-products, algae and microalgae: A review". *Food chemistry*, 98(1): p. 136-148, 2006.

[12] Jokić, S., S. Svilović, Z. Zeković, and S. Vidović, "Mathematical modelling of soybean oil solubility in supercritical carbon dioxide". *International journal of food science & technology*, 46(5): p. 1031-1037, 2011.

[13] Lummaetee, K., H. M. Ku, W. Wongrat, and A. Elkamel, "Optimization of supercritical fluid extraction of isoflavone from soybean meal". *The Canadian Journal of Chemical Engineering*, 95(6): p. 1141-1149, 2017.

[14] Mohamed, H. B., K. S. Duba, L. Fiori, H. Abdelgawed, I. Tlili, T. Tounekti, and A. Zrig, "Bioactive compounds and antioxidant activities of different grape (Vitis vinifera L.) seed oils extracted by supercritical CO 2 and organic solvent". *LWT-Food Science and Technology*, 74: p. 557-562, 2016.

[15] Kopcak, U. and R. S. Mohamed, "Caffeine solubility in supercritical carbon dioxide/co-solvent mixtures". *The Journal of supercritical fluids*, 34(2): p. 209-214, 2005.

[16] Marongiu, B., A. Piras, and S. Porcedda, "Comparative analysis of the oil and supercritical CO2 extract of Elettaria cardamomum (L). Maton". *Journal of Agricultural and Food Chemistry*, 52(20): p. 6278-6282, 2004.

[17] Salleha, L. M., H. M. Nasira, H. Yaakobc, and M. A. C. Yunusa, "Determination of Supercritical Carbon Dioxide Extraction Parameters for Quercus infectoria Galls and the Effects on Extraction Yield and Antioxidant Activity". *J. Teknol*, 67: p. 1-4, 2014.

[18] Ikushima, Y., N. Saito, M. Arai, and K. Arai, "Solvent polarity parameters of supercritical carbon dioxide as measured by infrared spectroscopy". *Bulletin of the Chemical Society of Japan*, 64(7): p. 2224-2229, 1991.

[19] Freed, B.K., J. Biesecker, and W. Middleton, "Spectral polarity index: a new method for determining the relative polarity of solvents (1)". *Journal of Fluorine Chemistry*, 48(1): p. 63-75, 1990.

[20] Machmudah, S., A. Shotipruk, M. Goto, M. Sasaki, and T. Hirose, "Extraction of astaxanthin from Haematococcus p luvialis using supercritical CO2 and ethanol as entrainer". *Industrial & engineering chemistry research*, 45(10): p. 3652-3657, 2006.

[21] Trabelsi, D., A. Aydi, A.W. Zibetti, G. Della Porta, M. Scognamiglio, V. Cricchio, E. Langa, M. Abderrabba, and A. M. Mainar, "Supercritical extraction from Citrus Aurantium amara peels using CO 2 with ethanol as co-solvent". *The Journal of Supercritical Fluids*, 117: p. 33-39, 2016.

[22] Snyder, J., J. Friedrich, and D. Christianson, "Effect of moisture and particle size on the extractability of oils from seeds with supercritical CO2". *Journal of the American Oil Chemists' Society*, 61(12): p. 1851-1856, 1984.

[23] Yunus, M., M. Hasan, N. Othman, S. Mohd-Septapar, M. Ahmad-Zaini, Z. Idham, and S. Zhari, "Effect of particle size on the oil yield and catechin compound using accelerated solvent extraction". *J. Teknol. (Sci. Eng.)*, 60: p. 21-25, 2013.

[24] Putra, N. R., A. H. A. Aziz, Z. Idham, M. S. H. Ruslan, and M. A. C. Yunus, "Diffusivity optimization of supercritical carbon dioxide extraction with co-solvent-ethanol from peanut skin". *Malaysian Journal of Fundamental and Applied Sciences*, 14(1), 2018.

[25] Putra, N., L. Yian, H. Nasir, Z. B. Idham, and M. Yunus. *Effects of process parameters on peanut skins extract and CO2 diffusivity by supercritical fluid extraction*. in *IOP Conference Series: Materials Science and Engineering*. 2018. IOP Publishing.

[26] Hasmida, M., M. Liza, A. Nur Syukriah, Y. Harisun, C. Mohd Azizi, and A. Fadzilah Adibah, "Total Phenolic Content and Antioxidant Activity of Quercus infectoria Galls Using Supercritical CO2 Extraction Technique and Its Comparison with Soxhlet Extraction". *Pertanika Journal of Science & Technology*, 23(2), 2015.

[27] Danlami, J. M., M. A. A. Zaini, A. Arsad, and M. A. C. Yunus, "Solubility assessment of castor (Ricinus communis L) oil in supercritical CO 2 at different temperatures and pressures under dynamic conditions". *Industrial Crops and Products*, 76: p. 34-40, 2015.

Nicky Rahmana Putra was born in Indonesia (1994), holds a BS. Degree from Institut Teknologi Sepuluh Nopember (Indonesia), respectively. He is currently working on his doctoral program at the Department of Chemical Engineering with Universiti Teknologi Malaysia (Malaysia). Currently, the author has published 5 SCI Journal in term of supercritical fluid extraction, separation process, modelling and optimization**.**

Ahmad Syahmi Zaini was born in Malaysia (1994), holds a BS. Degree from Univertisi Teknologi Malaysia (UTM), Malaysia. He is currently working on his master's degree under Department of Chemical and Energy Engineering, UTM, Malaysia. Right now, the author already published 1 international conference paper at International Conference on Engineering, Science, and Industrial Applicantions (Bangkok, Thailand, ICESI, 2017) and 1 journal paper at Malaysia Journal of Fundamental and Applied Sciences (Johor, Malaysia, MJFAS, 2018).

Ahmad Hazim Abdul Aziz is a doctoral candidate of Chemical Engineering at Universiti Teknologi Malaysia (UTM) supported by the UTM Zamalah scholar. His current study focuses specifically on the extraction of natural product using supercritical fluid. He has MSc of Science in Safety, Health and Environment, and a Bachelor of Chemical Engineering which both from UTM. Before undertaking doctoral studies in 2016, Hazim worked as a research assistant at Centre of Lipids Engineering and Applied Research (CLEAR), UTM for six months; he and his team were granted research fund from Johor State Government and UTM about RM 100, 000 by winning the best of the best award for an INATEX 2016. Currently, he also involved on the production of health supplement product from the extraction of Orthosiphon stamineus.

Fadillah Nur Idrus was born in Malaysia (1994), holds a BS. Degree from Universiti Putra Malaysia (Malaysia) and M.Sc Degree from Universiti Sains Malaysia (Malaysia), respectively. He is currently working on his doctoral program at Department of Chemical Engineering with Universiti Teknologi Malaysia (Malaysia).

Muhammad Zahid Zullyadini was born in Malaysia (1994), holds a BS. Degree from Universiti Teknologi Malaysia (Malaysia). Currently, he also involved on the production of health supplement product from the extraction of soybean oil.

Zuhaili Idham was an Research Officer with Universiti Teknologi Malaysia, Malaysia. He spent approximate 5 years of his life on academic research in food industry. Being a professional scientist in the field of food engineering. The author had contributed at least 12 research papers in term of chemical engineering, food engineering, optimization and separation process.

Mohd Azizi Che Yunus (1963) was an associate professor with Universiti Teknologi Malaysia, Malaysia. He spent approximate 20 years of his life on academic research in food industry. Being a professional scientist in the field of food engineering, chemical engineering, bioseparation technology. The author had contributed at least 60 research papers in term of chemical engineering, food engineering, optimization and separation process.