Rapid expansion supercritical solution (RESS) of CO$_2$ as a green technology method for pineapple peels solid oil particle formation

N A Zainuddin$^{1*}$, N D Mohamad$^2$, R M Rodzay$^2$,

$^1$Integrated Separation Technology Research Group (i-STRonG), Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor
$^2$Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor

Corresponding author email: nurain1465@uitm.edu.my

Abstract. Current development using the technique of Rapid Expansion Supercritical Solution (RESS) in solid oil particle formation pineapple peel contains a great deal active pharmacological which are anti-inflammatory, anti-oxidants, and anti-cancer agent. Many researchers use the conventional technique such as hydro-distillation, supercritical fluid extraction, and soxhlet extraction in order to extract the valuable component in oil formed. However, these techniques have several disadvantages such as long extraction time, high usage of solvent and produce toxic residual which can harm the environment. The RESS technique is not as time consuming as it will directly produce oil in particle formation, instead of conventional technique that need to undergo further technique such as spray drying in order to produce solid oil particle. In this study the extraction was conducted using temperature 40, 45, 50, 55, 60$^\circ$C and the pressure used were 3000, 4000, 5000, 6000 and 7000 psi at a constant flowrate of 24ml/min for 50 minutes extraction time. The extracted component in solid oil particle was analyzed using Gas Chromatography Mass Spectrometry (GCMS) and show that pineapple peels is rich in volatile components such as 1-Hexene, 4-methyl, Benzene, 1,1’-(1,2 cyclobutanediyl) bis-, trans, and 1-Buten-3-one, 1-(2-carboxy-4,4-dimethylcyclobutanyl).

1. Introduction
Pineapple (Ananas comosus) is a tropical plant belonging to the family of Bromeliaceae. Pineapple widely used in food, cosmetic, and therapeutic industries [1]. It is known to contain anti-bacterial, anti-inflammatory, anti-aging, anti-cancer properties and high source of antioxidant that can help body to fight free radical that can cause numerous disease. Sixty percent of fresh pineapple is edible and average yield in processing ranges from 45% to 55% [2]. The residue from pineapple left between ranges from 45% to 65% that shows serious organic-side stream disposal challenges which can cause environmental pollution if not treated well [2]. In previous studies residues of certain fruit can present a higher antioxidant than the pulp. Antioxidants such as flavonoids, phenolics, ascorbic acids are substances that are able to prevent or inhibit oxidation processes in the human body and food products. The residues of fruits are usually discarded, but actually it can be used as an alternative source of nutrients that initiate the nutritive value of poor people’s diets and to help reduce dietary deficiencies.
Previous research, the pineapple peel was used as therapeutic, land fertilizer and also act as reducing agent in the biosynthesis of metal nanoparticles. The pineapple peel has a high source of anti-oxidants, and it also has a lot medicinal values such as helping to fight intestinal parasites, helps to accelerate healing from surgery, helps to lose weight and fight cellulite. From this research, it is expected the bioactive component from the pineapple peel are lutein, zeaxanthin, α-carotene, β-carotene and cryptoxanthin [3]. Many of previous researcher uses conventional method to extract the valuable component. The conventional technique such as steam distillation, hydro distillation and solvent extract are mostly used for oil extraction. In addition, the conventional method is constrained by many disadvantages such as excessive solvent use and disposal, solvent trace residues, product property and particle size uniformity [4]. Replacing traditional organic solvents with more environmentally friendly materials could eliminate the disadvantages of conventional methods [5].

In this research, solid oil particle from pineapple (Ananas comosus) is being studied. Using pineapple waste which is peel is chosen to extract the solid oil particle using RESS method. RESS is a process which supercritical fluid mixture is expanded into an expansion vessel through specially designed orifice to obtain the desired mean particle size and particle size distributed. The RESS method is effective for making submicron sized particles and the advantage of this method is that only CO$_2$ is used in the procedure due to low critical temperature and pressure ($T_c = 311$°C and $P_c = 7.38$ MPa) [6].

The RESS method is also less time consuming seems it directly produce solid oil compared to the traditional method such as hydro distillation that can only extract oil and need to further other method to produce solid oil particle which cause high operation cost and time consuming. Currently, many involvements to produce the ultrafine particle drug, especially by pharmaceutical industries. RESS offers considerable promise as a means for the production of films, crystalline or amorphous powders with narrow and controllable particle size distribution. Furthermore, RESS process is environmental friendly and non-toxic [4]. Up to date, there are no documented data were found on study RESS-CO$_2$ for Pineapple peel solid oil particle formation. This research is conducted to determine the best operating condition that produces high yield of solid particle using RESS method and to identify the extracted component present in pineapple peels.

2. Materials and methods

2.1. Materials
The Ananas comosus (A. comosus) peels used in this study were collected from Klang Market. The peels were washed through distilled water to remove impurities and dirt. The peels were ensuring to have 1mm thickness. The peels were placed in the tray and undergo oven drying for 12 hours for 40°C to remove moisture content. The dried pineapple peels sample was blended using mechanical blender to form a powder and the powder were sieved through the 150µm siever plate.

2.2. Rapid Expansion Supercritical Solution Carbon Dioxide Extractions
The study of pineapple solid oil particle extracted from the pineapple peel at operating temperature of 40°C, 45°C, 50°C,55°C, and 60°C and operating pressure of 3000psi, 4000psi, 5000psi, 6000psi, and 7000psi. Value for operating condition were selected based on previous studies done by many researchers. Based on preliminary studies the extraction time chosen is 50 minutes. Each run was conducted with 6g of the sample. If the mass of the sample exceeds 8g it might have a problem at the extraction vessel seal that cause loose fitting thus disrupt the extraction process which lead to CO$_2$ leaking. The RESS equipment was designed to operate at ambient temperature from 30°C to 150°C with maximum operating pressure 10000psi [7].

The extraction pressure and temperature were set up and 6g of sample was placed in a cotton bag before putting into the extraction vessel. Ensured that the cotton bag not touch the top of the extraction vessel before sealing the top tight. After the extraction temperature achieved its desired value, the CO$_2$ pump was run to feed high pressure liquid CO$_2$. Then the liquid CO$_2$ will be converted into a supercritical condition when it is pumped into extraction vessel. After reaching 50 minutes of extraction time, quickly opened the restrictor valve to depressurize the supercritical solution for the separation of solute from
solvent. The depressurized CO$_2$ converted into gaseous form and purged into ambient. Extracted product was collected in collection vial. The extraction yield was determined based on the weight of collection vials before and after the RESS process.

2.3. Gas Chromatography - Mass Spectrometry (GC-MS)

The solid oil particle extracted from A. comosus peels were identified the component by using GC-MS. The amount of 0.04g sample of A. comosus peels solid oil particle collected in the collection bottle from the RESS-CO$_2$ process were diluted with 2ml of hexane, then the sample is placed in a glass vial provided with the septa. The instrument employed with the following condition. The GCMS with length 30 m thickness 0.25μm and diameter 0.25 mm. The analytical condition with sample injection (1µL), carrier gas is helium (99.999% pure) with a flow rate of 1mL/min, and split ratio used was 1:10 with the injector temperature of 250°C. The oven temperature was set at 50°C for 50 minutes, later increased at a rate 0°C/min to 80°C which was maintained for 1 minute, followed by the same at 50°C/min to 150°C and 230°C with 3.0°C/min hold for 3 minutes. The components were detected based on mass spectra survey by The National Institute of Standards and Technology (NIST) mass spectral program [8]. Summary of the research methodology can be referred in Figure 1.

![Figure 1: Summary of the research methodology for solid oil particle formation from pineapple peel using RESS method](image)
3. Results and discussion

3.1. The Effect of Moisture Content
In this study, the percentage of moisture content of pineapple peels after drying were calculated using equation (1). The determination of moisture content was based on Palm Oil Research Institute of Malaysia (PORIM) [9]. The percentage of moisture content was below than 10%. The drying process should not be taken too long as to ensure that no volatile compounds are lost and also no thermally degradation of thermally labile of component before RESS extraction is done [10]. Thus the moisture content removed below than 10%. High moisture content in the sample will interrupt the extraction process which will affect the solubility and kinetic of mass transfer between the sample and supercritical CO₂. Moisture will act as a barrier, thus prevent the sample from contacting with the CO₂ during the extraction process [11]. It is important to keep the moisture content below than 10% to have good efficiency during the extraction process, therefore the total moisture content of pineapple peels need to be determined properly before running the extraction process. After the moisture content determination, it is indicated that the pineapple peels took 12 hours drying with temperature 40°C for it to be completely dry.

\[
\text{Moisture content (\%)} = \frac{(m_1 - m_2)}{(m_1 - m_0)}
\]  

(1)

Where:

\( m_0 = \text{mass of dish (g)} \)
\( m_1 = \text{mass of dish with sample before drying (g)} \)
\( m_2 = \text{mass of dish with sample after drying (g)} \)

3.2. The Effect of Particle Size
Preliminary studies were performed in order to accomplish two objectives which are to determine the best extraction time and to determine the best particle size that produce high solid oil particle yield. Three samples with different sizes which are 150µm, 300µm and 500µm were undergoing the extraction process. 6g of pineapple peels powder were put into cotton bag and placed in extraction chamber. Only 6g of sample can only fit in the extraction chamber after being tried with 7g and 8g of the sample. Three different size sample was extracted with 60 minutes extraction time and the oil yield extract were recorded every 10 minutes. Each sample was run with 40°C with pressure 3000psi, 4000psi, 5000psi, 6000psi and 7000psi.

Figure 2 shows plotted graph for the best extraction time and particle size. From the Figure 2, the best extraction time was at the time of 50 minutes, and the particle size that extract high yield is 150µm. Smallest particle size can maximize the diffusion of CO₂ inside the pores, thus producing high yields of solid oil particle [12]. As can be concluded, for the next RESS extraction of other parameters were being run using particle size 150 µm with 50 minutes extraction time.

![Figure 2](image_url)

**Figure 2.** Graph of preliminary study for best extraction times and best particle size the effect of pressure on solid oil particle yield.
In this study, the effect of different extraction pressure on the solid oil particle yield (%) was studied using various pressures which are 3000, 4000, 5000, 6000, and 7000 psi, while, holding the constant temperature different extraction temperature 40, 45, 50, 55 and 60°C. The extraction time is running constantly for 50 minutes for each parameter running as discussed in preliminary study. Figure 3 shown the effect of different extraction pressure on yield extract with constant temperature.

**Figure 3.** Effect of different pressure on solid oil particle yield at constant temperature, and constant CO₂ flowrate (24ml/min) during 50 minutes of extraction time.

Figure 3 indicates the highest solid oil particle extraction is at 45°C with 6000psi followed by the temperature at 50°C with pressure 4000psi which recorded 0.27% and 0.19% respectively. At constant temperature 55°C recorded the lowest solid particle yield with varying operating pressure from 3000 to 5000psi where the solid oil particle yield is 0.06%, 0.04% and 0.01% respectively. This shows that as the pressure increased, solid oil particle yield is decreasing. According to Ben-Rahal et al [13] noted that recovery of oil yield decreased as a result of increase in the temperature and this might be arising from the effects of solvent density. Meanwhile, at 45 and 55°C, the solid oil particle yield is high at pressure 6000psi but decrease at 7000psi, in my opinion, the best operating condition should be below than 60°C in order to have high recovery of oil. Based on research conducted by Iglesias et al [14] conclude that at temperature 45°C and 55°C can extract highest yield with low operating pressure.

From Figure 3, the percent solid oil particle yield is decreased when reaching temperature 60°C except for the operating pressure 4000psi and 5000psi. In my opinion, as temperature increase from 40°C to 60°C, solvent density reduces and also the solubility of solute pineapple peels powder might reduce as well, this is might due to higher temperature that can lead the fluids start to behave like a gas. At pressure 3000psi, the solid oil particle starts to reduce from temperature 45°C until 60°C by 0.22% to 0.02%. Generally, from the Figure 3, increasing the temperature from 40°C to 60°C, extraction yield is reduced. Extraction yield at 45°C is much higher than extraction yield 60°C. Fluctuation of extraction yield occurred might due to factors of some changes in temperature at constant pressure is a bit sensitive compared to the change of pressure. Small changed in temperature has may influence the solute solubility [15].

### 3.3. The Effect of Temperature on Solid Oil Particle Yield

In this study, the effect of different extraction temperature on solid oil particle yield (%) were studied using various temperature, which are 40, 45, 50, 55 and 60°C while holding the constant temperature different extraction pressure 3000, 4000, 5000, 6000, and 7000 psi. The extraction time is constant for 50 minutes for each parameter running. Figure 4 shown effects of different extraction temperature on yield extract at constant temperature.
Based on the Figure 4, it shows that, at 40°C, 50°C and 60°C, the highest extraction yield is obtained at constant pressure 4000psi with 0.23%, 0.21% and 0.19% respectively. Meanwhile, at 45°C and 55°C the second highest yield extracted is at pressure 6000psi. The temperature 40°C, 50°C and 60°C with constant pressure 4000psi is the best condition to enhance the solubility of a solute of pineapple peels powder. It shows that, as the pressure increase from 4000psi to 6000psi, the solid oil particle yield is decreased. However, the operating condition at 40°C at 4000psi works well in producing high yields of solid oil particles. In addition, increase of the pressure will increase the fluid density and the solubility of solute [16]. However, as the pressure increase from 4000 to 6000 psi, the extraction yield starts to decline. Increase of pressure may reduce the diffusivity of the SCF of solvent which can reduce the contact with the pores of the solute of pineapple peels, thereby potentially reduce solute dissolution [17].

At operating temperature 45°C and 55°C with constant pressure 6000psi the extraction yield somehow is high at these conditions with 0.27% and 0.19%. As pressure increases from 4000psi to 6000psi, the extraction yield at from temperature 45°C and 55°C was increased. In some cases, an increase in temperature may cause the solid matrix to compact and the void fraction leads to unfavourable extraction outcomes [17]. As pressure increased from 4000psi to 6000psi, the solid oil extraction also reduced for temperature 40, 50 and 60°C and start to increase until 7000psi. According to research done by Nejad et al., [18], The solid oil particle yield is directly proportional to operating temperature, but the differences in our study, the solid oil yield has reduced as temperature increase from 50°C to 60°C. This finding is found in agreement with the study made by [18] due to a different flowrate of solvent CO₂. Therefore, flowrate of CO₂ also is important in affecting the result of solid oil particle yield.

At operating temperature 45°C and 55°C with constant pressure 6000psi the extraction yield somehow is high at these conditions with 0.27% and 0.19%. The trend starts to decrease from 3000psi to 5000psi and increase from 6000psi to 7000psi. In my opinion, the temperature at 55°C is not good working temperature for extraction at low pressure as the density of CO₂ might increase in this condition due to small increases of pressure. This result differs with from research done by Iglesias et al., [14]. The high amount of solid oil particle is recorded at a temperature 55°C with pressure 2446psi. This is may be due the rate of extraction works well at density 0.7 g/cm³ which of the supercritical condition. However, the differences result between this research and research conduct [14] is might due to different parts of pineapple.

3.4. Component Identification of Pineapple Peels

Figure 5 indicates the chemical components were found in extracted A. comosus peels using GC-MS. There are five was identified. Based on the peak, components that were mostly found are functional group of ketones, aromatic compound, and alkenes. Component A is a functional group of alkene. The composition of 1-Hexene,4-methyl is the highest among five components found. Meanwhile, for B, C, and D are functional group of ketone which are component N,N’-Bis (2,6-dimethyl-6-nitrosohept-2-en-4-one), 5-Hepten-2-one, 7-phenyl, 1-Buten-3-one, 1-(2-carboxy-4,4-dimethylcyclobutenyl)
respectively. Component E is Benzene, 1,1’-(1,2 cyclobutanediyl) bis-, trans- a group of aromatic compound. All these components found are called aroma volatile compound.

According to study done by Baretto et al., [19] using process hydro-distillation to extract the volatile component from pineapple residue taken from juice processing. The volatile component found is a functional group of alcohol. In this study, functional group of alcohol were not detected as using A. comosus peels. Meanwhile, previous research using method SFE to extract the components from pineapple husk. The components presents are the functional group of ketones, alcohol, and phytosterol. Functional group of ketone was founded in pineapple husk using method SFE, which is the functional group that found also in A. comosus peels. However, the functional group of phytosterol is not detected in this research seems different part of pineapples were used.

4. Conclusion
The solid oil particle from pineapple peels powder were extracted using the method of (RESS) with 50 minutes extraction times using the 150µm size of pineapple peels powder. The objectives of the study were achieved with the highest solid oil particle yield was at condition 45°C and 6000psi with 0.27%. Based on the study conducted, the smallest particle size of pineapple peels powder is one of the factors that affect the yield of solid oil particles. The identified component in pineapple peels was the functional group of ketones, alkenes and aromatic.

5. References
[1] Hossain M. A and Rahman, S. M. M. 2011 Total phenolics, flavonoids and antioxidant activity of tropical fruit pineapple. Food Research International. 44 672–76
[2] da Silva D. I. S, Nogueira G. D. R, Duzzioni A. G and Barrozo M. A. S. 2013 Changes of antioxidant constituents in pineapple (Ananas comosus) residue during drying process. Ind. Crops and Prod 50 557–62
[3] Lim Y.Y, Lim T.T and Tee J.J 2007 Antioxidant properties of several tropical fruits: a comparative study. Food Chem. 103 1003-08
[4] Huang Z, Sun G. B, Chiew Y. C, and Kawi S. 2005 Formation of ultrafine aspirin particles through rapid expansion of supercritical solutions (RESS). Powder Tech. 160 127–34
[5] Tandya A, Dehghani F and Foster N.R. 2006 Micronization of cyclosporine using dense gas techniques. J. Supercrit. Fluids 37 272–78
[6] Keshavarz A, Karimi-Sabet J, Fattahi A, Golzary A, Rafiee-Tehrani M, and Dorkoosh F. A. 2012 Preparation and characterization of raloxifene nanoparticles using Rapid Expansion of Supercritical Solution (RESS). J. Supercrit. Fluids 63 169–79
[7] Sapkale G. N, Patil S M, Surwase U. S, and Bhatbhage P. K. 2010 Supercritical Fluid Extraction: A Review. Int. J. Chem. Sci. 82 729–43
[8] Erukainure O. L, Ajiboye J. A, Okafor O. Y, Okoro E. E, Asieba G, Sarumi B. B and Zaruwa M. Z. 2017 Alcoholic lung injury: pineapple peel extract modulates antioxidant enzymes and attenuates lipid peroxidation in rat models. Clin. Phytoscience 2 1-7
[9] Lin S.W, Sue T T and Ai T.Y. 1995 Methods of Test For Palm Oil and Palm Oil Products, Volume 1. Palm Oil Research Institute of Malaysia
[10] Durante M, Lenucci M. S, and Mita, G. 2014 Supercritical Carbon Dioxide Extraction of Carotenoids from Pumpkin (Cucurbita spp.): A Review. Int. J. Mol. Sci. 1 6725–40
[11] Zainuddin N.A, Norhuda I.S, Adeib I.S, A.N. Mustapha and Sarjo S.H. 2015 Rapid Expansion Supercritical Solution(RESS) Carbon Dioxide as an Environmental Friendly Method for Ginger Rhizome Solid Oil Particles Formation. Int J Chem Mol Eng 5 1523-28
[12] Salud M.G.P, Caja M.M, Marta H and Guilermo S.M 2003 Supercritical Fluid Extraction of all-trans- Lycopene from Tomato, J. Agric. Food Chem. 51 3–7
[13] Ben Rahal N, Barba F.J, Barth D and Chevalot, I. 2015 Supercritical CO2 extraction of oil, fatty acids and flavonolignans from milk thistle seeds: Evaluation of their antioxidant and cytotoxic activities in Caco-2 cells. Food Chem. Toxicol. 83 275–82
[14] Iglesias S, Sánchez E, and Bolaños G. 2013 Extraction and Encapsulation in B-Cyclodextrine of Aroma from Pineapple Husk Using Supercritical Carbon Dioxide. Conf on Supercritical Fluids Cartagena de Indias (Colombia) 1–9
[15] Ghosh S, Chatterjee D, Das S. and Bhattacharjee P.2013 Supercritical carbon dioxide extraction of eugenol-rich fraction from ocimum sanctum linn and a comparative evaluation with other extraction techniques: Process optimization and phytochemical characterization. Ind. Crops Prod. 47 78–85
[16] Khaw K. Y, Parat M. O, Shaw P. N, and Falconer J. R. 2017 Solvent supercritical fluid technologies to extract bioactive compounds from natural sources: A review. Molecules 22 1-24
[17] Belwal T, Dhyani P, Bhatt I.D, Rawal R.S and Pande V. 2016 Optimization extraction conditions for improving phenolic content and antioxidant activity in berberis asiatica fruits using response surface methodology. Food Chem. 207 115–24
[18] Nejad-Sadeghi M, Taji S and Goodarznia I. 2015 Optimization of supercritical carbon dioxide extraction of essential oil from Dracophyllum Kotschyi Boiss: An endangered medicinal plant in iran. J. Chromat. A 1422 73–81
[19] Barretto L. C. D. O, Jesus J. De, Antônio J, Narain N and Anne R. 2013 Characterization and extraction of volatile compounds from pineapple (Ananas comosus L. Merrill) processing residues. Food Sci Technol 33 638–45

6. Acknowledgments
The authors are grateful for support received and facilities provided by the Universiti Teknologi MARA, Institute of Quality and Knowledge Advancement (InQka) and Integrated Separation Technology Research Group (i-STRonG), Faculty of Chemical Engineering, UiTM Shah Alam.