

PROCESSING OF CASHEW NUT (*Anacardium occidentale L.*) AND CASHEW NUT SHELL LIQUID WITH SUPERCRITICAL CARBON DIOXIDE AND WATER

Setianto W.B, Smith R.L*, Inomata H. and Arai K.

Department of Chemical Engineering, Tohoku University
Research Center of Supercritical Fluid Technology
Aoba-ku, Aza Aramaki, Aoba-04,
Sendai 980-8579 Japan

smith@scf.che.tohoku.ac.jp ; FAX: +81-22-217-5863

In this work, our objective was to examine methods for processing cashew nut shell liquid and cashew shell with carbon dioxide and water. Supercritical CO₂ was applied for extraction of split cashew shells and near-critical water was applied for reaction of the cashew shell material. In the extractions, it was found that a pressurization-depressurization step that was approximately 1 h gave extraction yields as high as 60%. Extraction of ground shell material gaved extraction yields as high as 90%. Composition of the extracted CNSL showed that it was similar to expressed oil so that it can be concluded that extraction with supercritical CO₂ leads to an oil of high quality. Reaction of the shell material in near-critical water with a diamond-anvil cell technique showed that the material could be liquefied at 334 °C and that the liquefaction products dissolved into water at about 358 °C. From these results, it can be concluded that CO₂ and water can be used to extract CNSL and process cashew shell material for the purpose of developing a new green chemical process.

INTRODUCTION

Future green processes are destined to use agricultural resources as feedstocks and green chemistry for product manufacture [1]. This means that a significant number of processes will to develop methods to use non-traditional bioresources and will most likely have to use clean solvents that are compatible with the earth's biosphere. In this work, we consider cashew nut shell liquid (CNSL) and cashew nut shell as an agresource and its processing with solvents carbon dioxide and water. Carbon dioxide and water are two possible solvents that have been proposed for use in natural product processing, resource conversion, and materials production [2].

CNSL represents a significant source of phenolic compounds according to production data for cashew nuts [3] and it contains a number of useful compounds. Anacardic acids contained in CNSL have been found to have an uncoupling effect on oxidative phosphorylation [4] and technical grade CNSL has been used in automobile brake fluids, paints and polymer formulations [5]. The chemical structure of the anacardic acids is made up of salicylic acid with a 15-carbon chain that contains various degrees of unsaturation. Application of heat causes the ring to decarboxylate and the anacardic acids to convert to cardanol or polymerization to occur [5]. In previous

research [6-7], we reported on supercritical extraction of CNSL from cashew with carbon dioxide with pressurization-depressurization (PD) technique. In this work, our objective was to examine variations of the PD step technique and the effect of temperature on the extraction of CNSL with supercritical CO₂. Further, we also examined the use of near-critical and supercritical water to process the cashew shell materials.

MATERIALS AND METHODS

Materials

Samples were Indonesian cashew nuts obtained from BPP Teknologi (Indonesia). Carbon dioxide (99.9% purity) was supplied by Nihon Sanso and used as received. The cashew shells used in the experiments were prepared by cutting whole cashew nuts-in-shell in half with a micro-saw and then removing the kernel and testa. Ground cashew shells were prepared by loading 20 pieces (about 110 g) of whole cashew nut-in-shell (NIS) into a stainless-steel container and freezing with liquid nitrogen. After the NIS became frozen and all of the liquid nitrogen evaporated, the NIS were cracked and broken into small pieces by carefully hitting each NIS with a hammer. The shells were separated from the nuts with tweezers. Shells were ground to have an average particle size of 0.2-0.4 cm in diameters. Analysis of extracted CNSL was performed with method propose by Tyman et al. [8].

Apparatus for Extraction

The apparatus, which has been described in previous works [2-4], consisted of a 500 mL extractor that had a maximum working pressure of 40 MPa at 100 °C. The extractor was controlled to within ± 0.1 °C with a water bath. Liquid carbon dioxide from a cylinder was chilled and liquefied at 0 °C and then compressed to extraction pressure and pumped through a heat exchanger into the extractor. Pressure in the system was controlled with a back-pressure regulator. Effluent CO₂ solvent from the extractor that contained the extracted solute was sent through a metering valve that was maintained at 60 °C. The stream was depressurized through this metering valve. The depressurization at the control valve caused the dissolved CNSL to precipitate and this was collected in a trap that was cooled with ice-water. The amount of carbon dioxide used was measured with a dry gas meter. The gas used was corrected to STP conditions.

Method of Extraction

Two methods were used for extracting CNSL. In the first method, extractions were performed by pressurizing the system and then flowing CO₂ through the extractor at constant temperature. Solute was collected by depressurizing the effluent solvent mixture through a control valve. This is called typical extraction method in this work. In the second method, the pressure of the system was brought to a given value of pressure and then the pressure was released slowly to atmospheric pressure. Then, the pressure was increased and the extraction was resumed. This is called the pressure profile method in this work. Some experiments used more than one pressurization-depressurization (PD) step. During the time at atmospheric conditions, the extractor and trap were isolated from the surroundings by closing all of the valves to prevent possible contamination such as water from entering the system. In both methods, the mass of CO₂ reported in the experiment includes the amount of CO₂ required to pressurize the extraction vessel at the given conditions.

Apparatus for Reaction

The reaction apparatus was a diamond anvil cell (DAC) that allowed complete view of the full cell contents that contained cashew shell and water. Details of the experimental arrangement can be found in ref. [8]. Briefly, the DAC apparatus consists of two diamonds are held in place by tungsten carbide supports and surrounded by upper and lower microheaters. The diamond anvils with about 1 mm faces are pressed against a thin piece of metal that has a 0.5 mm hole that serves as a sample chamber. Cashew and water samples were loaded into the sample chamber and heated to a given temperature. The chamber volume was 50 nL and the cell material was inconel.

Method of Reaction

First, a small cut of cashew nut shell was loaded into the chamber with the aid of a microscope. Then, a drop of water was placed on the upper anvil and held there by the surface tension. The two diamonds were then pressed against the gasket. For a successful loading, the shell sample would remain in the cavity and the water would not leak upon heating. Samples were heated and the images were recorded by CCD and microscope along with digital video. The time course of the images represents the reactive phase behavior of the sample.

RESULTS AND DISCUSSION

Effect of PD step time

Setianto et al [6] reported that application of one Pressurization-depressurization (PD) step prior extraction gave greatly increasing of CNSL extraction yield and this was followed-up by a later report [7]. **Table 1** and **Figure 1** show the effect of a PD step time on the extraction yields. These yield values were remarkably much higher than those reported in other literature [9]. From these results, we could understand that a certain contact time was needed before depressurization and repressurization was performed.

Table 1 Data for extraction of CNSL with pressure profiles for single PD steps at various times. Extraction conditions: 60 °C; CO₂ flow rate: 5 L/min at STP. Depressurization was always to 0.1 MPa

	Time	Pressure	Total CO ₂ Used [kg]	W _{whole nut} [g]	W _{shell loaded} [g]	W _{CNSL extracted} [g]	Yield [%]
	[h]	[MPa]					
T-9a	PD : 0.1 Ext : 4	30 30	3.26	56.49	36.18	2.89	28.43
T-28	PD : 1 Ext : 4	30 30	4.57	55.15	35.29	5.62	56.66
T-6	PD ₁ : 4 Ext : 4	30 30	4.59	64.50	41.31	6.13	53.92
T-35	PD : 7 Ext : 4	30 30	6.37	53.48	34.23	5.51	57.24

PD = Pressurization-depressurization step.

Ext = Extraction step.

Trial T-9 is the result of an extraction with a 5 min PD step. Trials T-6, T-29, and T-35 all had much longer PD step times from 1 h to 7 h. In trial T-9, the yield increased as expected in the extraction step, but the ultimate yield was lower than the other trials, which were performed with longer PD step times. In trial T-9, the extraction yield reached a plateau of about 28.4% yield. This probably means that the contact time 5 min was insufficient for CO₂ to penetrate into the shell and

make good contact and dissolve into the CNSL. The trials showed large differences in the amount of CO₂ used and in the time at which the extraction yields began to increase. These differences might be explained by considering CO₂ and CNSL contact time. However, the differences in contact time did not seem to affect the ultimate yields that were obtained which was about 55% for PD step times greater than 1 h. From these results, it could be concluded that after depressurization, that about 1h is sufficient to allow the CNSL to expand from the shell material while 5 min is too short a time.

Effect of temperature

Extractions at 40 to 60 °C were made with 1 h PD steps. In initial stages of the trials, before a PD step was performed, the extraction temperature did not have a significant effect on the yield. This means that probably only a very small amount of CNSL was available to the solvent. After a PD step was performed, however, the results for the various temperatures changed greatly with the higher temperature giving the higher yields for a given amount of CO₂ than for yields obtained at lower temperatures.. Once that the CNSL became in good contact with the CO₂, the temperature influence on the CNSL–CO₂ phase behavior became more important.

Effect of PD step on ground sample extraction

Figure 2 shows extraction of ground cashew shell with the typical extraction method and extractions made with a single 1-h PD step denote as the pressure profile method. For both methods, extraction yields greater than 90% could be obtained. Further, as shown in Figure 2, there was no difference between the typical extraction method and the pressure profile method for the case of ground samples. Therefore, it can be concluded that grinding the shell breaks the CNSL-bearing membranes and allows good contact

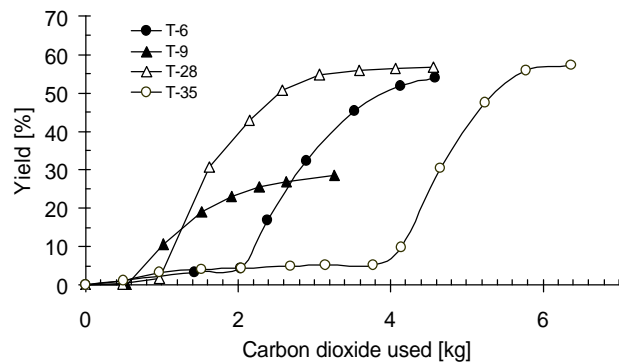


Figure 1 Extraction results for pressure profiles with single PD steps for various PD step times.(see Table :1 for extraction conditions)

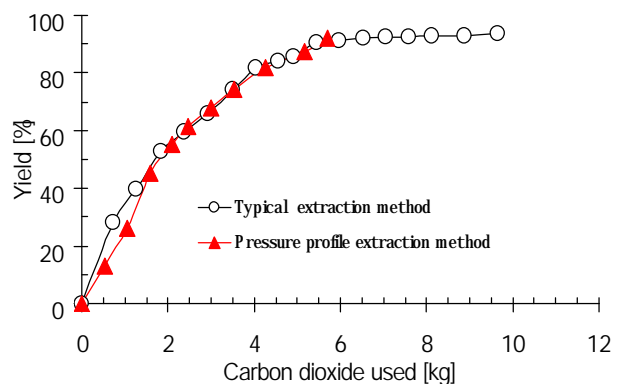


Figure 2 Extraction of ground samples with SC-CO₂ at 60 °C, 30 MPa, 5 L/min CO₂ flow rate

between CO₂ and the CNSL. Further, it can be implied that the PD step in the previous results, plays a similar role as grinding since the PD step must promote contact between CO₂ and CNSL.

HPLC analysis results

In the analyses, anacardic acids, cardols, and cardanols were found to be the main components. Sample analyses of the extracted CNSL gave average composition of about 52.% anacardic acid, 28% cardol and 20% cardanol. For comparison samples of CNSL obtained by expression were analyzed and gave result of similar composition with those obtained from CO₂ extraction process.

Reaction of Shell Material

Figure 3 shows the direct visual observations of the reacting shell material in water as it the mixture is heated to near-critical conditions. Pressure can be estimated to vary from about 30 MPa to 400 MPa from equation of state calculations. Remarkably, the shell material changes shape and seems to liquefy before totally dissolving. Most likely, cellulose oligomers and sugars such as glucose and fructose were formed. Sasaki et al. [10] found that crystalline cellulose could be completely dissolved in water without acids, bases, or other catalysts as mixtures were brought to supercritical conditions. The mechanism of dissolution was surface hydrolysis and homogeneous reaction that gave a product distribution that favored formation of hydrolysis products (cellobiose, erythrose, glucose) rather than pyrolysis products. The study here, differs however, in that the cashew material is crude biomass and can be expected to contain lignin and possibly aromatic compounds including anacardic acids.

CONCLUSIONS

Cashew nut shell liquid (CNSL) can be extracted from cashew shells with supercritical CO₂. The efficiency of the extraction is greatly enhanced through the use of a single pressurization and depressurization (PD) step. The PD step is thought to break the oil-bearing membranes and to create channels in the cashew shell honey-comb matrix. Extractions made at various temperatures showed that temperature only had a significant effect on the extraction yields after the PD step is made. This is probably due to CNSL - CO₂ contact and CNSL solubility. During the extractions, composition analyses made show that the content of anacardic acids, cardols, and cardanols do not change greatly. Reaction experiments on cashew shell and water show that the material can be liquefied and dissolved into near-critical water at high pressures.

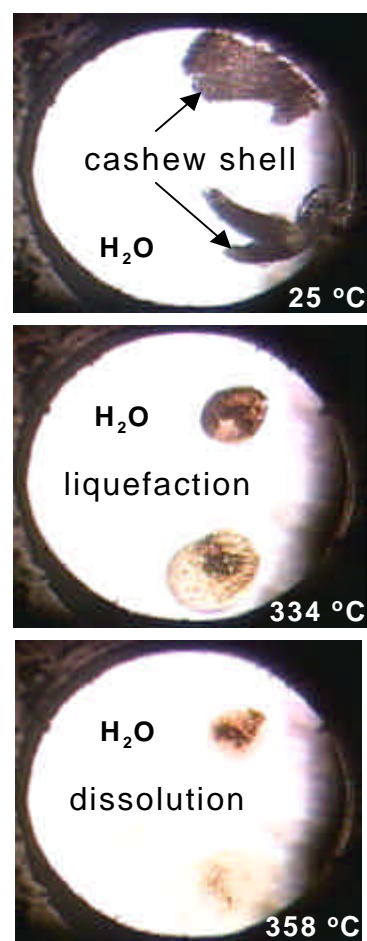


Figure 3 Reactive phase behavior of cashew shell in water at a density of 1010 kg/m³. Reaction time was 132 s.

REFERENCES :

- [1] National Research Council, Biobased Industrial Products: Research and Commercialization Priorities, National Academy Press, **1999**, pp. 1-14.
- [2] Arai, K., Adschiri, T, Fluid Phase Equilibria 158-160, **1999**, 673.
- [3] Food and Agriculture Organisation (FAO) Yearbook, Food Statistics Series No. 148, 52, **1998**, 167.
- [4] Toyomizu, M.; Okamoto, K.; Akiba, Y.; Nakatsu, T.; Konishi, T. Biochim. et Biophys. Acta-Biomembranes 1558(1), **2002**, 54.
- [5] Tyman, J. H. P. Synthetic and Natural Phenols, Studies in Organic Chemistry 52; Elsevier, Amsterdam, **1996**.
- [6] Setianto, W. B., Smith, Jr., R. L., Inomata, H., Published proceedings of the Japan Oil Chemist's Society, 40th annual meeting, Sendai, October 4-5, **2001**, paper 1E-05, . . (in Japanese).
- [7] Smith, Jr., R. L., Malaluan, R. M., Setianto, W. B.; Inomata, H.;Arai, K. Bioresource Technol., 8, **2003**, 1.
- [8] Fang, Z., Smith, Jr., R. L., Inomata, H., Arai, K.,. J Supercritical Fluids 15, **1999**, 229.
- [9] Shobha, S. V.; Ravindranath, B. J Agric Food Chem , 39, **1991**, 2214.
- [10]. Sasaki, M.; Kabyemela, B.; Malaluan, R. M.; Hirose, S.; Takeda, N.; Adschiri, T.; Arai, K. J Supercritical Fluids, 13, **1998**, 261-268.