Multi-Product Fractionation of Roasted Peanuts using $scCO_2$: An Evaluation of Process Alternatives

Z Siqungathi, T. F. N Madzimbamuto, and T. V Ojumu

Abstract—Supercritical fluid extraction has emerged as an attractive separation technique due to growing demands for cleaner products, free of residual chemicals. This process obviates disadvantages presented by conventional methods. In this study, the techno-economic feasibility of roasted peanuts extraction using supercritical fluids is proposed, for simultaneous separation of multiple products of: aroma compounds, fatty acids, triglycerides and waxes. Literature shows that a triglyceride rich vegetable oil fraction can be extracted at 25-30 MPa and 40 – 60 °C. However, the simultaneous separation of the constituents has not been reported. For this process, operating conditions are estimated using thermodynamic predictions. A process model will be developed and validated using experimental data to explore possible conditions for a feasible process. Preliminary results indicate plausibility of removing aroma and wax fractions from the triglycerides in a single pass while the simultaneous separation of fatty acids is rather complicated.

Keywords— Feasible processes, Supercritical fluid extraction, Thermodynamic predictions, Process model, Conventional methods

I. Introduction

According to Grain Legumes (2015) peanuts are crops grown for their edible seeds and have thus received much attention in different industries due to their high oil content and nutritional value. Similarly, they are an important source of edible oils, aroma compounds and fatty acids, particularly oleic (18:1) and linoleic (18:2) acid. Industrial uses for high oleic peanut oil include engine lubricants, oleo-chemicals, and hydraulic fluids. The marked improvement in oxidative stability offered by high oleic peanuts and oil should stimulate commercialization [1].

In industry, peanut oil is commonly extracted from peanuts with an expeller or a solvent [3]. Nonetheless, the extraction of oil from peanuts typically involves a series of steps which include cracking into small pieces, mechanical pressing, and solvent extraction. Occasionally, roasting is also included as an important preparatory step depending on the range of products required. The mechanical pressing removes approximately 50% of peanut oil and the remaining oil is extracted using hexane [2]. Solvent extraction using hexane is commonly used in industry for the extraction of peanut oil extraction. This method has been regarded with circumspection due to an intractable problem of persistent solvent remaining in the product and physical methods.

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Methods such as cold pressing has drawbacks attached to it in that, it does not provide a way of selectively extracting the oil from peanuts and thus require another process step after fractionation called degumming, Because the oil produced from these methods contain several impurities, it needs to be sent to refining plant for further processing. Consequently, Supercritical Fluid extraction has merged as an alternative extraction separation technique due to a need for natural processes that do not introduce any residual organic chemicals in the final product. This process uses supercritical carbon dioxide as a solvent because of its unique properties for separating antioxidants, pigments, flavours, fragrances, fatty acids, and essential oils from plant and animal materials[4].

This method is believed to produce products of superior quality due to selective extraction of desirable oil fractions and preclude drawbacks presented by conventional methods and thus making it cheaper and environmentally friendly[3]. This study focusses on the single step techno-economic feasibility of separation for the extraction of peanut oil from roasted peanuts using $scCO_2$ through evaluating and comparing process alternative routes based on; product quality, product value and energy requirements. The study is expected to produce the highest extraction yield of commercially marketable products in a single step fractionation unit. In order to achieve this aim, a few objectives will be followed: a theoretical prediction of the feasibility of separation of pure fractions from a model mixture composed of triglycerides, fatty acids, and aroma compounds, based on the phase behaviour of binary mixtures of the model compounds with $scCO_2$.

Vapour –liquid equilibria of the relevant binary systems will be represented as thermodynamic equations of state fitted to experimental binary VLE data found in the literature. Flash calculations will be performed with a model mixture containing a representative sample of the components in the same ratios as they are present in the raw material. The calculated distribution coefficients of each component between the liquid and vapour phases will enable the determination of separation factors between any two of the components. The range of parameters spanning the feasible region will be noted. A likelihood of a feasible separation will be indicated by a selectivity deemed comparable to that achieved in similar industrial processes.

Additionally, any separation deemed theoretically feasible will be tested experimentally at pilot plant scale. Several approaches will be adopted, including (i) the total extraction of all soluble material followed by their separate deposition in three separators, and (ii) sequential extraction at progressively increasing solvent density. Kinetic data will be recorded and

fitted to a suitable extraction kinetics model. The feasible options achieved at this stage will be used to develop a plant-wide process model, whose performance will be fitted to the experimental data, and validated with additional experimental data. The resultant model will enable the rapid exploration of the performance of the process at a much wider range of conditions than could be performed experimentally. In addition, the kinetic data will enable a batch-wise extraction system to be simulated, sized and scaled to achieve a given production capacity, and the economic performance of the resultant system to be investigated and optimized.

II. Experimental Method

Fig 1 shows a schematic diagram of the system which consists of a solvent pump that delivers the fluid throughout the system, an extraction cell, according to the system configuration (solids) and separators in which the extract is collected and the solvent is depressurized.

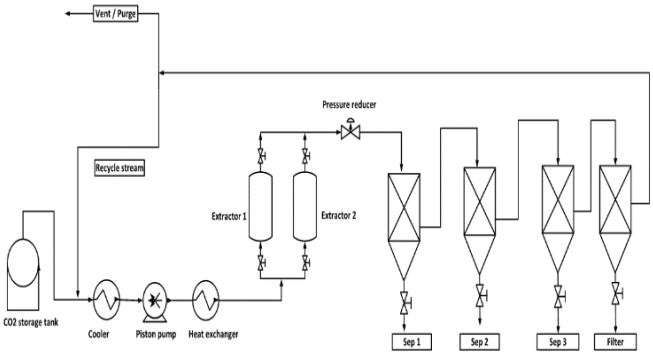

Fig. 1: Schematic for Supercritical Fluid pilot plant

A. Chemicals

The chemicals and standards used in this work are bought in different companies. Supercritical carbon dioxide which is used as a solvent is a source of Air Liquide with a purity of 99.997% and the standards are ordered from Sigma Aldrich.

B. Sample preparation

The feed investigated is an agricultural product supplied by Alibaba. The material was firstly rinsed in room temperature water to remove any form of dust. The material was then dried in an oven using a tray dyer in Cape Peninsula University of Technology, CPUT at a temperature of 80 °C over a period of 24 hours, this was done to keep peanuts at constant moisture content. The specific drying time was not determined experimentally, hence the drying kinetics was not obtained.
The tray was filled uniformly flat at the top to maintain constant drying and the peanuts were then sealed in a container until further use.

C. High pressure extraction procedure

The equipment used for the extraction is a typical supercritical fluid extraction. The experiment is carried out in the SEPAREX pilot plant located in the high pressure laboratory in the Chemical Engineering Department of CPUT. The SEPAREX SFE-5 pilot plant is designed for the processing of both solid and liquid feed using a supercritical solvent, carbon dioxide (sCO2). The plant consists of two parts; an extraction section to process solids, and a counter-current fractionation section to process a liquid feed. The two sections use the same separation vessels for the disengagement of the extract from the solvent. For this reason, the two sections cannot be operated simultaneously. In this research, only the extraction section will be used because the feed is a solid.

D. Supercritical fluid extraction

The system is first allowed to reach different steady states, specifically the present operating temperature before pressurization. In order to ensure a liquid feed to the piston pump, the subcooled solvent ($scCO_2$) stored in the cylindrical vessel is drawn and passed through a chiller. From the pump, it is heated in an exchanger above its critical temperature changing its phase to a vapor before it is fed at the bottom of the extraction vessel, for extraction. Ranges of process parameters were chosen to keep the solvent close to its critical point to avoid a thermal degradation of thermally labile compounds. The pressure was chosen starting from 200 bar and above because any pressure below this doesn't allow for increase in the total yield of peanut extracts. The mass flow of the solvent was kept between 10 and 15 kg/hr. The solid matrix of roasted peanuts was unsealed, weighed and loaded into the extraction vessel and the system was gradually pressurized until the desired pressure. To assure that the solvent was saturated with the extract, it was only after 60 minutes of stabilized pressure that the outlet valve was opened to start the extraction process. After pressurizing the vessel, the peanuts were statically soaked, and the solvent was fed at the bottom of the extraction vessel to begin the experiment. The static interval allowed peanuts to soak so that CO_2 can penetrate the matrix and extract the oil from the peanuts. Extracts were collected in different separators which were set at different temperature ranges and constant bottle pressure (50 bar) and these samples were taken at 30 minutes intervals.

E. Analysis

For characterization of the collected extracts, analysis will be performed using NMR, HPLC and FTIR. For NMR, different deuterated solvent will be used to dissolve the different extracts and peaks will be used to identify the extracts accordingly.

III. Results

From the preliminary run, process conditions were selected to separate free fatty acids, triglycerides, aroma compounds and waxes from protein rich peanuts. The influence of pressure (20–30 MPa), temperature (40°C) and solvent flowrate (10-15 kg/hr) on the yield and composition of products was

determined. In the range studied, separation was found to be feasible and the highest values of temperature and pressure gave the highest extraction rates and yield. Currently, a process model for the system has not been done. The results below were taken during a preliminary experimental run and graphs to interpret the results were plotted and discussed.

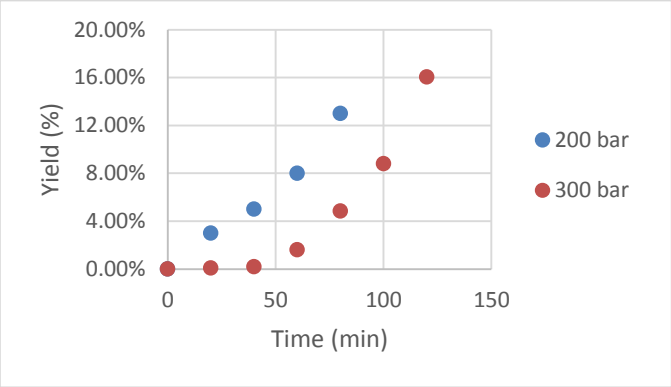

Fig. 2: Extraction yield versus pressure over time

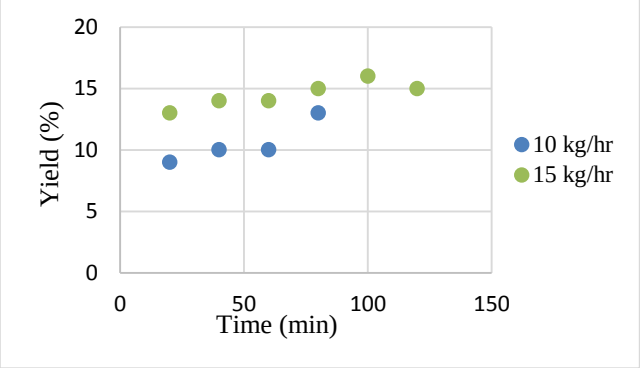

Fig. 3: Extraction yield versus solvent flowrate over time

IV. DISCUSSION

A. *Effect of pressure:*

From Fig 2, it is noticed that the extraction yield decreased by increasing pressure at constant temperature over time. Generally, it would be expected an increase in pressure results in an increase in the fluid density which decreases the distance between the molecules thereby increasing the solvent power and the solubility of the extract thereby giving an increase in the yield. However, the opposite was noted. In order to obtain a higher yield, it is advisable that when CO_2 is compressed at high operating pressures, the temperature be increased in order to obtain an increase in the solute/solvent attractive interactions that result in an increase in the extraction yield. From the results, the highest yield obtained was as 16% at 300 bar. However it can be concluded that the experiments for both pressures were not complete, the yield did not reach a point where it levelled off.

B. *Effect of temperature:*

In the extraction of peanut oil from roasted peanuts, temperature was kept constant. But literature has shown that an increase in temperature would result in a decrease in the extraction yield and this is because of the decrease in the solvent density which decreases the solubility and therefore the solvent power. However, in this experiment, it would be expected that an increase in extraction temperature would result in a decrease in the solute vapor pressure thereby increasing the solvent solubility This is similarly reported by (Papamichail et al., 2001; Louli et al., 2004) emphasizing the effect of increasing extraction temperature on the yield.

C. *Effect of solvent flow rate:*

Fig 3 show the effect of CO_2 flowrate on the extraction yield of peanut oil from roasted peanuts. The yield was noticed to increase with an increase in the solvent flowrate meaning that the amount of peanut oil extracted increased with increasing CO_2 flowrate. The increasing flow rate generally caused a shorter residence or contact time between the solvent and the solute, however, the number of CO_2 molecules contacting with the solute and the number of CO_2 molecules per unit volume entering the extractor increased, thus increasing inter-molecular interaction between the CO_2 and the solute, and therefore increasing the solute dissolution.

V. CONCLUSION

A. *Figures and Tables*

From the observations discussed above, it can be deduced that in order to shorten the time it takes to reach maximum extraction yield, an increase in solvent flowrate would be advisable. However, the flowrate needs to be increased in such a way that it doesn't affect the contact time between the solute and solvent. Three hours would be best for a full experiment to obtain enough results.

REFERENCES

[1] G. R. List, *Processing and Food Uses of Peanut Oil and Protein*. Elsevier Inc., 2016. https://doi.org/10.1016/B978-1-63067-038-2.00015-0

[2] M. Matricardi, R. Hesketh, and S. Farrell, "Effect of Operating Conditions on Static/Dynamic Extraction of Peanut Oil Using Supercritical Carbon Dioxide," pp. 1–8, 2015.

[3] J. W. Goodrum and M. B. Kilgo, "Peanut oil extraction using compressed CO2," *Energy Agric.*, vol. 6, no. 3, pp. 265–271, 1987. https://doi.org/10.1016/0167-5826(87)90007-6

[4] S. E. E. Profile, "IMPORTANCE OF SUPERCRITICAL FLUID EXTRACTION TECHNIQUES IN," no. January 2015, 2016.

[5] M. Herrero, 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 Chem.*, vol. 98, no. 1, pp. 136–148, 2006. https://doi.org/10.1016/j.foodchem.2005.05.058

[6] S. C. Kupski, E. J. Klein, E. A. da Silva, F. Palú, R. Guirardello, and M. G. A. Vieira, "Mathematical modeling of supercritical CO2 extraction of hops (Humulus lupulus L.)," *J. Supercrit. Fluids*, vol. 130, no. June, pp. 347–356, 2017. https://doi.org/10.1016/j.supflu.2017.06.011