SOLUBILITY OF TRIGLYCERIDES IN UNMODIFIED SUPERCRITICAL CARBON DIOXIDE

B. M. BOTHA* and R. I. McCRINDLE
Department of Chemistry and Physics
Technikon Pretoria
Private Bag X680
Pretoria, 0001, South Africa.
E-mail: bothabm@techpta.ac.za

SUMMARY

Mechanical pressing and subsequent solvent extraction of oil cake, succeeds in extracting most of the oil from sunflower seeds, peanuts and olives. Consumer demand for specialised oils such as avocado, evening primrose and grape seed is increasing and to produce these specialised oils requires a technique such as Supercritical Fluid Extraction, in order to yield a high quality product.

The triglycerides from destoned, dried avocado fruit were extracted with unmodified supercritical carbon dioxide. The extraction rate was found to be influenced, not only, by fluid flow rate, temperature, pressure and particle size but is strongly by the degree of entrainment in the fluid stream.

INTRODUCTION

Fuerte is an important avocado variety and, in South Africa, is used extensively for avocado production. Fuerte is a natural hybrid between the Guatemalan and Mexican groups (Lewis, 1978). The fruit is pear-shaped, small to medium in size, the skin is slightly rough, thin and not adherent to the flesh. The larger part of the flesh is yellow but green nearer to the skin. Throughout the mesocarp there are specialised oil cells, although small droplets of oil also can be detected in the parenchyma cells. The oil cells, or idioblasts, are distinguished by their large size and lignified walls (Werman and Neeman, 1987). The oil and water content of the avocado is dependent on the variety and stage of development but can be in excess of 30% oil and 65 to 80% water (Bizimana, Breene and Csallany, 1993).

Although human skin is generally not highly penetrable to oils, noticeable differences were observed in the ability of the oil from the avocado to penetrate the outer epidermis of the skin. Of the oils tested, avocado oil had the highest rate of skin penetration in a group that included soybean, almond and olive oils (Swisher, 1988). Avocado oil is ranked second best out of a list of ten oils tested for their effectiveness as sunscreens. Mink oil was ranked first, jojoba oil eighth and olive oil last (Grayson and Eckroth, 1979: 153). According to Jacobsberg (1988), avocado oil is used industrially in the soap manufacturing industry. The main outlet is, however, in the pharmaceutical and cosmetics industries, thanks to its high skin penetration coefficient and the specific biological action of its unsaponifiable matter. The edible uses of avocado oil are rather limited. This is mainly because of the price of the oil and it is also in direct competition with a well-established olive oil industry. However, if the oil is regarded as a by-product from unsaponifiable matter extraction, the price might become more attractive. Werman and Neeman (1986) claimed that large surpluses of avocado were likely to occur in the future. This is especially true when seasonal variations may result in a glut of fruit, or the production of fruit that is not suitable for export or consumption by the local population.

Literature regarding the Supercritical Fluid operating conditions for the extraction of triglycerides is conflicting (Mangold, 1983; King, Johnson and Eller, 1995; Botha and McCrindle, 1999). Extraction results from evening primrose oil indicated that an increase in the pressure generated a significant increase in triglyceride solubility in supercritical carbon dioxide. Rapid extractions at high efficiencies were achieved by operating at 60 ºC and 700 atm, but even extractions conducted at 40 ºC and 300 atm yielded over 75% of the available oil in only 55 min (Favati, King and Mazzanti, 1991). The extraction of avocado oil was shown to yield more than 95 % of the extractable oil within 60 min at 40 ºC and 450 atm (Botha and McCrindle, 1999).

At 50 ºC and 544 atm, the triglycerides were found to be only partially soluble in unmodified supercritical carbon dioxide, while at 80 ºC and 816 atm they were completely miscible (List, Friedrich and King, 1989). Walker, Bartle and Clifford (1994) extracted oil from oven dried rapeseed material (virgin rapeseed, meal and rapeseed cake) at 340 atm and 90 ºC. The authors reported that a higher pressure than 340 atm should result in greater solubility of the triglycerides and reported that an increase of flow rate should reduce the extraction time. The increase of extraction rate at higher fluid flow rates is indicative of a system with low solubility.

Complete miscibility between the solute and solvent yields a faster extraction rate than in the case when the solute is only partly miscible with the solvent. This implies that a commercial unit for the extraction of triglycerides should preferably be operated at 70 ºC and 819 atm in order to minimise the time associated with an extraction cycle. The cost of the equipment, capable of operating at these more extreme conditions is excessive and decreases the economical viability of the application. It can be expected that a degree of solvation of the triglycerides will occur in the carbon dioxide at pressures where total miscibility is not yet obtained. Traditional wisdom does, however, not predict the reported degree of extractability (95% avocado oil and 75% evening primrose oil) at pressures less than half of that required to obtain complete miscibility

EXPERIMENTAL

Liquid carbon dioxide, purity 99.995% from Air Products SA was used without any further purification. A home build apparatus was constructed and a high-pressure pump (ISCO 100 DX) was used with a non-return valve between the fluid supply and the pump. The temperature of the pump head was maintained at 16 ºC by water circulation from a chiller (Labotec, Model 432). A 10 ml extraction cell and a 10 ml pre-heating column

(Keystone Scientific, Bellefonte, PA, USA) were placed in a Carlo Erba Fractovap (Model 2700) gas chromatograph oven. The temperature control of this oven was modified by replacing the original thermocouple by a Pt-100 thermocouple and a Shinko FCS 13-A controller (WIKA). All extractions were performed by this combination of cell volumes. Slip-free finger tight connectors (Keystone Scientific) were used on the end caps of the extraction and preheating cells.

The SFE system was constructed with three shut-off valves (Type ss1, Anatech). The first valve was prior to the preheating cell, the second valve between the preheating- and extraction cells and the third valve just after the extraction cell. These shut-off valves were fitted on the outside of the oven in such a manner that it required the minimum length of tubing exposed to atmospheric conditions. A back pressure regulator (Rheodyne, Cotati, CA USA) was fitted between the third shut-off valve and a micro-metering valve (Autoclave, model A3) encased in a copper housing 45 cm (width) by 60 cm (height) by 45 cm (depth). Each half was hollowed to fit the exterior of the micro-metering valve and the two halves were bolted together to enclose the valve. This assembly was fitted on the outside of the oven via ceramic spacers and was heated by two electrical cartridge heaters, placed in holes drilled in the copper housing. The temperature of this assembly was controlled at 130 ºC by a Shinko FCS 13-A controller (WIKA) and the internal thermocouple of the cartridge heater. At the exit of the valve 200 mm peek tubing (Upchurch Scientific, 0.005 inch internal diameter) was used to transport the extracted oil to a 10 ml glass container (culture tube, ISCO).

Avocado fruit, variety Fuerte and of unknown origin, was purchased from a local market. The fruit was allowed to ripen before processing. Dried avocado slices were prepared by oven drying destoned, unpeeled, fresh fruit at 80 °C for 24 hr. Dried avocado was ground to less than 2 mm by means of a Kenwood food processor (Model PFP 32) and stored in a freezer at 4 ºC until analysis.

Extractions were performed at 37 ºC / 350 atm, 37 ºC / 540 atm and at 81 ºC / 350 atm, 81 ºC / 540 atm. The fluid flow rate was kept constant at 4.5 ml/min, measured at the pump head and controlled by a heated needle valve. All extractions were performed on 4.000 g ripe oven dried avocado mesocarp samples in a 10 ml vertical tube extractor with flow direction, vertical up-flow.

Extractions were continued for 2 hr or until a consecutive extraction of 15 min resulted in a mass increase of less than 0.001% (m/m) at which point the extraction was considered to be exhaustive. Extracts were collected in a glass collection vessel without any solvent to assist collection. Prior to gravimetrical analysis, the extracted oil was subjected to vacuum evaporation for 30 min in order to remove water and dissolved carbon dioxide.

RESULTS AND DISCUSSION

The influence of flow rate was evaluated by carrying out avocado oil extractions at 60 ºC and 540 atm. Examples of extraction profiles, not hindered by blockages, are represented in Figure 1.

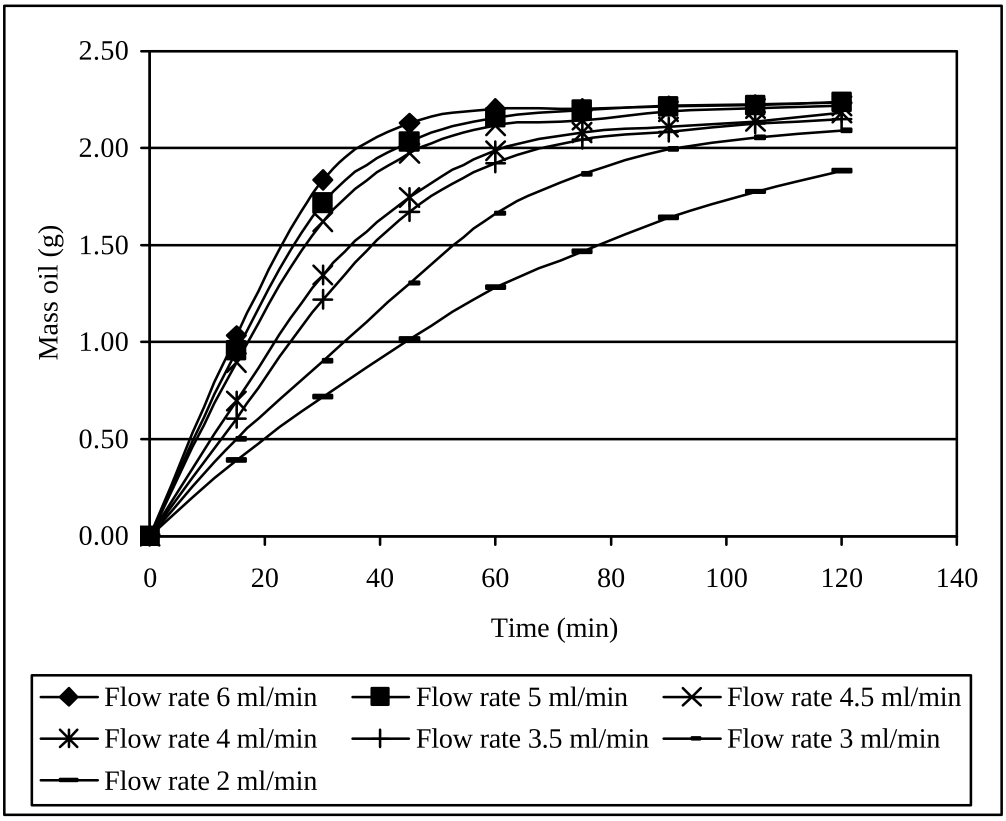

Figure 1 Extraction profiles for the extraction of avocado oil from solid avocado material at 60 ºC and 540 atm at different carbon dioxide flow rates.

These results showed that a higher flow rate is beneficial to the kinetics of the extraction. This is in accordance with the findings of King (1989) and Walker, Bartle and Clifford (1994) that reported an increased flow rate would shorten the extraction time of triglycerides. A constant flow rate of 4.5 ml/min was chosen as the fluid flow rate to be used during all extractions because freezing of the restrictor valve occurred at flow rates in excess of 4.5 ml/min resulting in erratic extractions. Although a flow rate setting at

4.5 ml/min did not yield the most favourable extraction rate it resulted in the same percentage oil extracted than that obtained by flow rates in excess of 4.5 ml/min.

The results as contained in Figure 1, furthermore indicate that some of the liberated avocado oil could have been entrained in the fluid and thus not extracted because of solubility of the oil. As an example, consider the mass obtained after 40 min for a flow rate of 3 ml/min (approx. 0.9 g). If it is assumed that the SCF is saturated with oil over the range of flow rates investigated then it would be expected that approximately the same mass of oil should be obtained after 20 min for a flow rate of 6 ml/min. In Figure 1, it can be seen that the mass of oil after 15 min, at 6ml/min was about 1.35 g and this was much higher (50 %) than the expected 0.9 g. If it is assumed that the SCF is not saturated at 3 ml/min then it would be expected that the mass obtained at 6ml/min should be lower than 0.9 g. It was thus possible that entrainment occurred.

The influence of temperature and pressure on the extraction of avocado oil was evaluated at 37 ºC / 350 atm, 37 ºC / 540 atm and 81 ºC / 350 atm, 81 ºC / 540 atm with a fluid flow rate of 4.5 ml/min, measured at the pump head. The extraction results are presented in Figure 2.

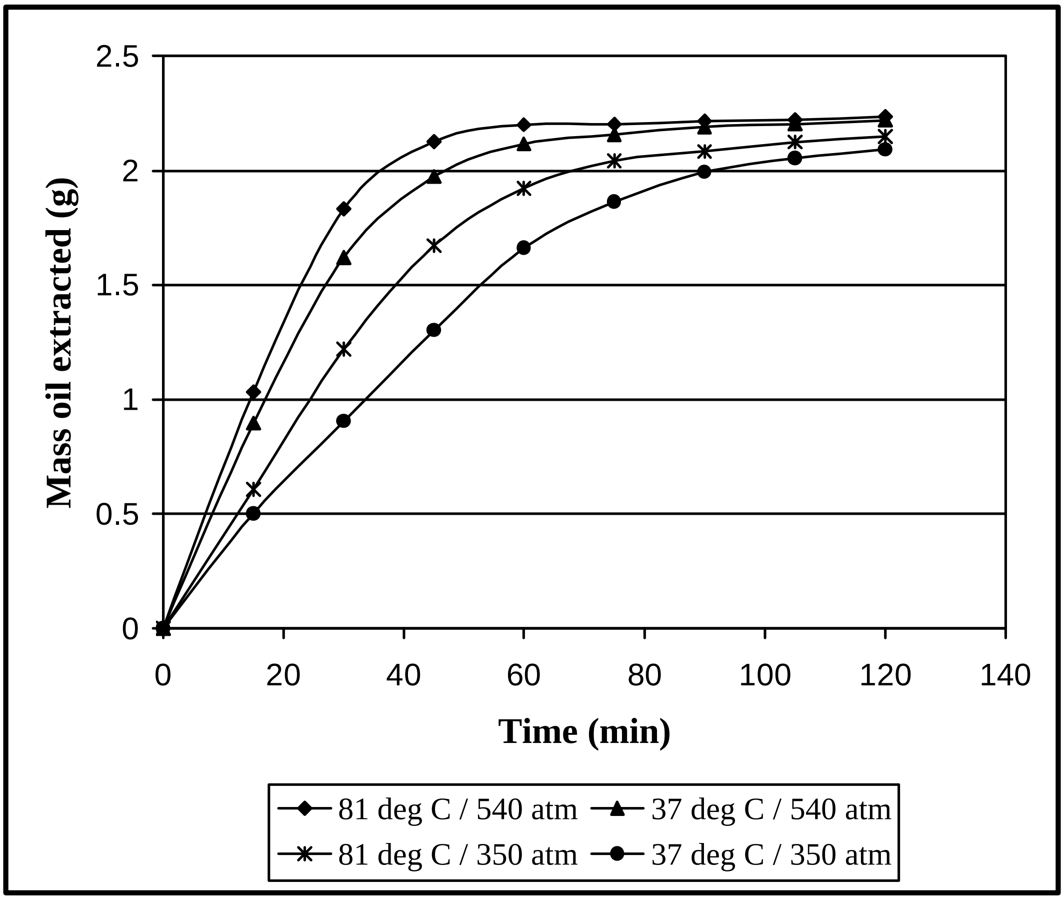

Figure 2 Yield of avocado oil obtained under different temperatures and pressures.

At both 37 and 81 ºC the yield of the avocado triglycerides in unmodified carbon dioxide increased with increased pressure. After 120 min there was only a difference of about 0.1 g between the highest lowest yields. However, at 37 ºC after 50 min, the increased pressure (from 370 to 540 atm) resulted in an increase of about 50% in yield. The percentage increase was less for the higher temperature (29%). This is in accordance with the findings of List, Friedrich and King (1989) who investigated the influence of temperature and pressure on an extraction.

High pressures will result in higher yields of triglycerides with carbon dioxide but should also be beneficial to the extraction of avocado oil because of the physical effect that pressure will have on the oil-bearing cells in the mesocarp. The oil in avocado is carried in idioblast cells with strong lignified walls. Increasing pressure will assist in breaking the walls of the cells, so that the oil is more easily available.

An important feature to note regarding the results as presented in Figure 2 is that at 37 ºC and 350 atm 94% of the total extractable avocado oil was obtained within 120 min, when taking the maximum yield to be obtained at 81 ºC and 540 atm. This was the maximum that could be extracted with available instrumentation. The obtained yield at 350 atm is of great economical importance because of the capital investment associated with an industrial system operating at 350 atm instead of 540 atm.

CONCLUSION

At 350 atm the triglycerides were not expected to be soluble, and yet, a high yield (94% after 2 hr) was obtained. Based on the findings with regard to optimisation of the flow rate and the expected low solubility of the triglycerides (King, 1989 and List, Friedrich & King, 1989) it was concluded that the extraction was governed by the entrainment of the oil in the fluid and not by it’s solubility.

Unmodified carbon dioxide can be used to extract avocado oil from the dried fruit. The extraction can be conducted at 350 atm and a yield of 94% obtained within 120 min.

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