Pecan Kernel Breakage and Oil Extracted by Supercritical CO_2 as Affected by Moisture Content

M. Li, D.D. Bellmer, and G.H. Brusewitz

ABSTRACT

During supercritical CO_2 extraction of oil from pecans, kernel breakage frequently occurs when the depressurization time is short. The purpose of this study was to investigate the effects of initial moisture content of pecan kernels and moisture equilibration time on pecan breakage and oil recovery when extracting with supercritical CO_2. Initial pecan moisture content, adjusted to 3.5% to 11.0%, had a significant effect on breakage when using a short depressurization time. With higher pecan moisture, less kernel breakage occurred. Increasing moisture equilibration time from 1 to 48 h reduced kernel breakage and produced an average of 30% more oil during extraction. Moisture content did not significantly affect the amount of oil extracted.

Key Words: supercritical CO_2, pecans, oil extraction, moisture

INTRODUCTION

THE HIGH OIL CONTENT OF PECANS CONTRIBUTES TO PECAN flavor, but the oil is especially vulnerable to oxidation, causing off-flavor (Santerre, 1994). The development of off-flavor and subsequent further quality deterioration shortens product shelf life and reduces pecan marketability. Storage stability might be improved by reducing the oil content of the pecan meats. Lowering the oil content of pecans could extend shelf life, prolong high quality, and provide a new lower-fat food product (Passey and Patil, 1994).

Fat removal from seeds is traditionally done by either mechanical compression or solvent extraction. The primary disadvantage of compression is destruction of the pecan structure. Solvent extraction may leave undesirable residues in the final edible product and is not effective without first grinding the pecan. Supercritical fluid extraction with carbon dioxide (SC-CO_2) is an alternative to such conventional procedures. Supercritical fluid extraction (SFE) is performed in the critical region where the fluid has physical properties in between a gas and liquid and exhibits significant solvent strength (McHugh and Krukonis, 1994). The use of CO_2 as a solvent in the food industry is advantageous because it is inexpensive, nontoxic, and is easily and completely removed from the final product.

For longer pecan shelf life, Zhang et al. (1995) investigated the feasibility of using SFE to remove oil from pecans. Up to 77% of the initial oil was extracted from intact pecan halves during 160 min at 80 °C and 68.9 MPa. In those extractions, serious breakage of pecan kernels occurred whenever pressure was released quickly after oil collection. Alexander (1996) examined the effects of extraction pressure, temperature, and CO_2 flow rate on the amount and composition of pecan oil recovered. The optimum temperatures for the micrometering valve and the collection vessel were investigated to reduce extract loss. Pecan breakage was observed during fast depressurization; and a long depressurization time (at least 1 h) was required to avoid kernel breakage.

Kernel breakage was reported during SFE of peanut oil. Passey and Patil (1994) found that pretreating peanut kernels to 8% to 11% moisture content before extraction reduced the extent of kernel breakage. Borges and Peleg (1997) found that increased water activity increased the break deformation of almonds or hazelnuts, which implied that a higher moisture content softened their texture. The moisture content of pecans is typically adjusted prior to nut cracking and shelling operations to minimize breakage, suggesting that water pretreatment might be useful for preventing the breakage that occurs in pecans during SC-CO_2 extraction. The effect of moisture content on oil extraction has been studied with a number of products, including soybeans, cardamom seeds, and canola rapeseed (Snyder et al., 1984; Gopalakrishnan and Narayanan, 1991; Dunford and Temelli, 1997).

Although several studies have been conducted to optimize extraction of pecan oil with SC-CO_2, none have addressed the effect of moisture content. This study was conducted to investigate the possibility of using a short depressurization time in order to preserve the integrity of pecans. The specific objectives were to determine the effect of initial moisture content and moisture equilibration time on pecan breakage and oil yield during SC-CO_2 extraction, and to examine the effect of depressurization time on pecan breakage after SC-CO_2 extraction.

MATERIALS & METHODS

WESTERN SCHLEY PECAN HALVES WERE OBTAINED FROM Young Pecan Co. (Las Cruces, N.M., U.S.A.) and were kept in a refrigerator (4 °C) until use. Our storage time was less than 5 mo. When received, pecan halves had 3.5% moisture content (MC) and 64.2% oil content (both by weight). Moisture content was determined by oven drying pecan halves at 130 °C for 6 h, and oil content was measured by quantitative SFE of pecan oil from ground pecans (Maness et al., 1995). Moisture contents of intact pecan halves were modified by two methods (humidification and exposure to sprayed water) to achieve specific levels for extraction. All broken pieces and damaged kernels were removed by hand. After extraction, unbroken pecan halves and broken pieces were separated to determine the degree of kernel breakage.

A Spe-ed™ SFE Model 680 BAR system (Applied Separations, Allentown, Pa., U.S.A.) was used for pecan oil extraction. This extraction unit consisted of a pump module, a control and collection module, an oven module and a 300-mL extraction vessel rated at 68.90 MPa (Thar Designs, Pittsburgh, Pa., U.S.A.). A CO_2 cylinder with 14 MPa helium head pressure and a dip tube was attached to the main extraction unit to provide liquid CO_2 (Air Products and Chemicals Inc., Allentown, Pa., U.S.A.). A schematic of the system is shown in Fig. 1.

Adjustment of pecan initial moisture content

Humidification. Pecans were placed in a screen-bottom tray in an environmental chamber at 90% RH and 30 °C. After 9 h, 2 d,

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and 5 d, moisture content increased to 4.9%, 6.4%, and 7.4%, respectively. Higher moisture content could not be achieved by humidification as mold appeared after pecans had been in the chamber for more than 5 d.

Spraying water. This method was used to obtain a moisture content of 11.0%. The water was sprayed on the kernel surfaces as uniformly as possible with a hand-held atomizer spray bottle (capacity 300 mL), and the excess water drained through the screen bottom of the tray. Sprayed pecan halves were then stored in Zip-Loc™ freezer bags for at least 24 h to allow moisture to become more evenly distributed before extraction.

In addition to the original 3.5%, 4 further initial moisture levels were attained for the experiments: 4.9%, 6.4%, 7.4%, and 11.0%. All pecan halves were stored in Zip-Loc™ freezer bags at 4 °C for the extraction tests. Refrigerated pecans were brought back to room temperature (around 25 °C) at least 30 min before each extraction experiment.

Effect of moisture equilibration time after spraying

Water was added to pecan halves using a spray bottle to achieve a range of moisture contents. The added water was absorbed into pecan tissues within minutes so that no excess water remained on the pecan surface. The humidification method was not used in this experiment because the moisture equilibration time needed to be controlled for all moisture levels. Pretreated pecans were sealed in Zip-Loc™ bags and kept at room temperature. Extraction was conducted after 1 h and after 48 h to determine whether there was a relationship between moisture equilibration time and pecan breakage and oil yield. Our assumption was that water was more uniformly distributed after 48 h. The test was conducted at 6 different moisture contents: 6.1%, 7.0%, 7.5%, 7.7%, 8.5%, and 11.6%.

Extraction

Thirty-five pecan halves (around 20 g total) were used in each extraction. Weighed pecans were filled into the 300 mL extraction vessel with Pyrex™ glass wool plugging at both ends to retain pecans and prevent clogging of the extraction system.

The oven extraction conditions were held at 62.0 MPA pressure and 3.0 L/min CO_2 flow rate. Temperatures throughout the system were 75 °C for the vessel, 100 °C for the micrometering valve, and 0 °C for the collection tube. These extraction conditions were chosen based on previous work by Alexander (1996). During extraction, the micrometering valve was opened and served as a restrictor to control flow. Supercritical CO_2 flowed through the pecan samples, dissolved the oil from pecans, and the mixture was separated at a collection tube (13 mm × 100 mm, with a septum in the screw cap) due to a reduction in pressure. A glass wool plug was inserted at the top of the collection tube to trap entrained oil in the exiting CO_2. When pecan oil had been extracted for 60 min, the collection tube was removed and depressurization was conducted.

Depressurization

The supercritical fluid extraction process consisted of a 60-min pressurization period followed by depressurization for either 10 or 20 min. When opening all release valves, the pressure of 62 MPa in the extraction vessel dropped to 0 MPa in 20 min. The initial decrease from 62 to about 7 MPa occurred within the first minute of depressurization and was around 2 MPa after 10 min (Fig. 2). For the 10-min depressurization test, the remaining 2 MPa pressure was released instantly by disconnecting the gas inlet tubing. After depressurization, the vessel was removed from the oven and opened to obtain access to the pecans.

Analysis of pecan breakage

The extracted pecans were poured out of the extraction vessel and sealed in a plastic bag and allowed to cool to room temperature. To measure pecan breakage, the unbroken pecans were counted as they were taken out of the bag. Standard U.S. No. 4 (Opening: 4.75 mm) and No. 8 (Opening: 2.36 mm) sieves were used in series to separate the pecan pieces into groups of large, medium, and very small pieces. The pecans were placed onto the sieves and shaken gently by hand for a few seconds to determine the particle size of the broken pieces.

Determination of oil extracted

The weight of the collection tube was measured before and after extraction. Since water was co-extracted along with the oil, the pecan oil needed to be dried. The extracted oil in the tube was poured into an aluminum dish, and both the tube and the dish were placed into a forced convection oven at 56 °C. Samples were dried for at least 5 h, at which time the weight remained constant (Li, 1998).

Experimental design

The independent variables in this study were pecan initial moisture content, depressurization time, and moisture equilibration

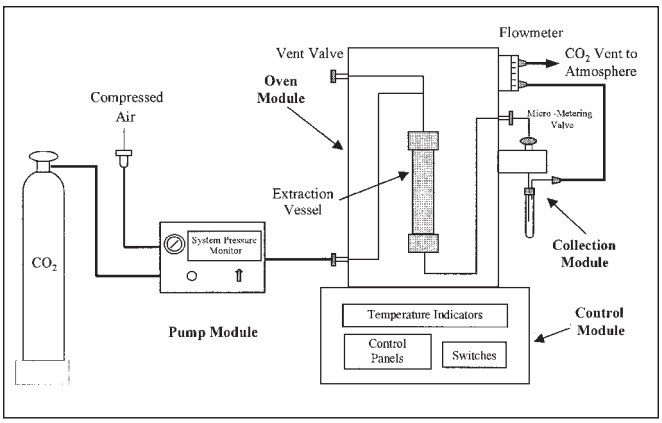

Fig. 1—Schematic of the Spe-ed™ Supercritical Fluid Extraction system.

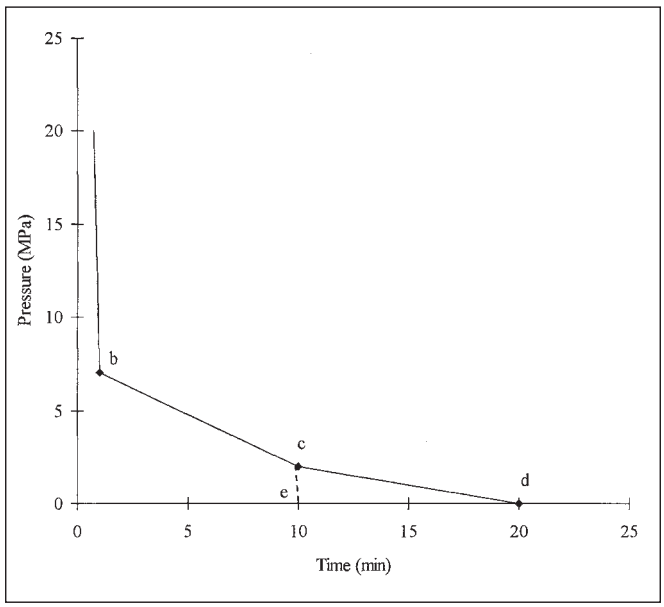

Fig. 2—Vessel pressure vs time when release valves are opened during depressurization. Starting at 62 MPa, the 10-min depressurization followed the path from b-c-e while 20-min depressurization went from b-c-d.

time. For the experiment on pecan initial moisture content, 5 levels of moisture content were prepared with 3 extraction replicates at each level. Each replicate was a separate extraction run requiring 3 to 4 h for a single complete test. To distinguish the effect of depressurization time, 2 depressurization times (10 and 20 min) were tested and the interaction between depressurization time and pecan moisture on pecan breakage was examined. For the experiment on moisture equilibration time, 2 moisture equilibration times (1 h and 48 h) were selected and tested at 6 different moisture levels without replicates at a given moisture content. The resulting pecan breakage and oil extracted were determined. The statistical differences were tested using analysis of variance, the General Linear Model procedure of SAS (SAS Institute Inc., 1989), and multiple comparisons of means by LSD (least significant difference) at $\alpha = 0.05$.

RESULTS & DISCUSSION

Depressurization time

With a depressurization time of 20 min, virtually no pecan breakage was found. When extracted pecans were removed from the vessel, the pecan halves were entirely intact; only their color became darkened. However, significant pecan breakage occurred when using a 10-min depressurization time. The interaction between depressurization time and pecan initial moisture content on pecan breakage was significant ($P < 0.05$).

Since no kernel breakage occurred with a 20-min depressurization time, this suggests that the end of the depressurization is crucial in causing pecan breakage, in spite of the 55-MPa pressure drop during the first minute of depressurization. Since depressurization was conducted above the critical temperature of CO_2 (T_c = 31.1 °C), the CO_2 experienced a phase change from a supercritical state to a gas during high pressure release. The saturated CO_2 in the extraction system remains in a supercritical state when pressure releases from 62 MPa to 7 MPa, but from 7 MPa to 0 MPa the supercritical CO_2 will change to a gas. After 10 min of depressurization, the pressure gauge indicated a pressure of 2 MPa in the extraction system. Although this is below the critical pressure, the CO_2 inside pecan kernels may still remain in a supercritical state under this condition if CO_2 is bound to the cell structure or if the pressure inside kernels is actually higher than the system pressure of 2 MPa. During the 10-min depressurization, a sudden release in pressure causes CO_2 to transition from a supercritical to a gas state rapidly so that gas flushes out substantially from the inside of kernels. Another possibility is that this gas transition during the 2 to 0 MPa depressurization may contribute to the release of CO_2 that was dissolved in water, inducing a strong internal mechanical stress on the structure of the pecans. When the kernel structure cannot withstand this stress, pecan kernels will break. Therefore, a fast depressurization rate is inconsequential while CO_2 remains in a supercritical state, but a slow rate is required in order to avoid breakage when the CO_2 changes from a supercritical state to a gas state.

Since pecan breakage occurred during the 10 min of depressurization, further tests were conducted with this depressurization time to determine conditions which produce less breakage.

Effect of initial moisture content

The particle size distribution of the pecans after extraction at different moisture contents is shown in Fig. 3. Increasing the pecan initial moisture content tends to increase the percentage of large pieces (No. 4 sieve) and decrease the percentage of fines, indicating that more pecan breakage occurs at lower moisture contents. There was a nearly linear increase in weight of large particle sizes as moisture content was increased as shown in Fig. 4 ($r^2 = 0.86$). An analysis of variance showed that there was a significant difference among the 5 moisture contents (P-value < 0.05). For large pecan pieces, the effects of 7.4% and 11.0% MC are different from each other and the other 3 moisture levels, but the particle size at 3.5% MC was not different from that at 4.9% and 6.4% MC.

The effect of water content on pecan breakage can be explained by the pecan texture change with water. Related studies have shown that the mechanical properties of pecans vary with water content (Shult, 1996). After absorbing water, pecan kernels become soft and pliable, which may be attributed to a change in their tissue structure. Pecan tissues consist of proteins and carbohydrates, which are the main hydrophilic components of the structure. Changes in the moisture content may affect the plasticization of proteins and carbohydrates and alter the physical properties of

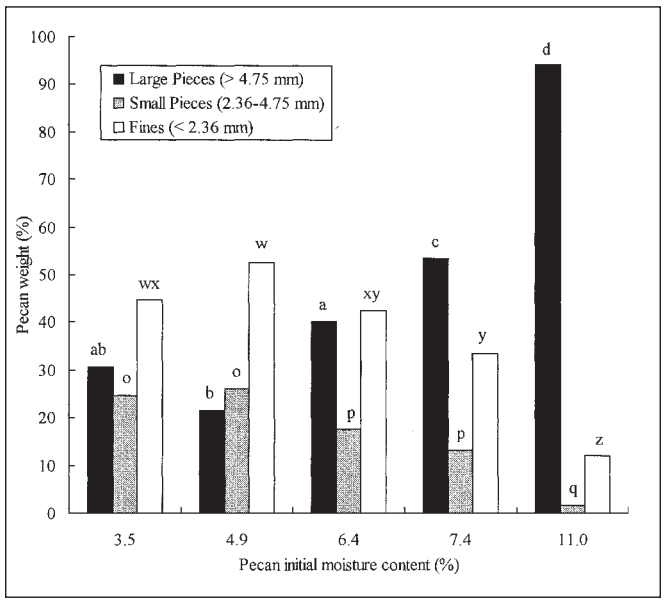

Fig. 3—Particle size distribution of pecans after a 1-h extraction at 75 °C, 62.0 MPa, and 3.0 L min^{-1} CO_2 flow rate followed by depressurization in 10 min. Data shown are averages of 3 replications. a, b, c, d = Means of large pecan pieces in a column with the same letter are not significantly different ($P < 0.05$). o, p, q = Means of small pecan pieces in a column with the same letter are not significantly different ($P < 0.05$). w, x, y, z = Means of fines in a column with the same letter are not significantly different ($P < 0.05$).

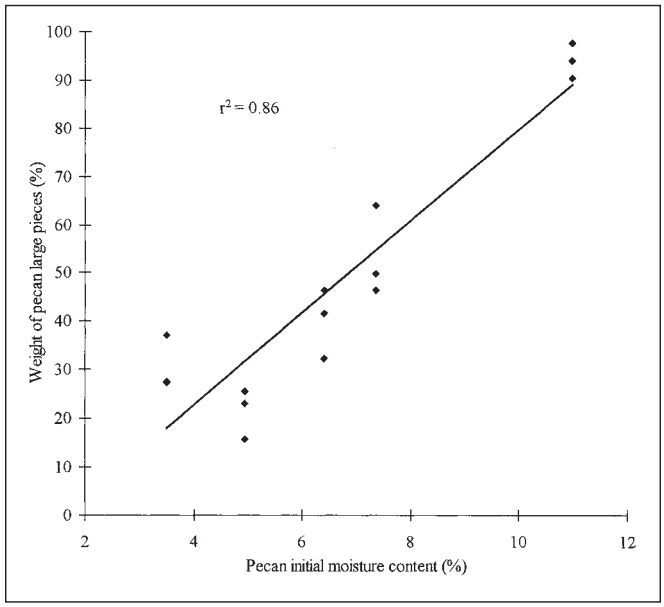

Fig. 4—Weight percent of large pieces (those remaining on No. 4 sieve) after a 1-h extraction at 75 °C, 62.0 MPa, and 3.0 L min^{-1} CO_2 flow rate followed by depressurization in 10 min.

the tissues. A limber and more flexible pecan structure is formed at higher moisture contents, and its resistance to rapid pressure release is improved, thus reducing kernel breakage. With higher-moisture pecans, an additional drying process following oil extraction would be necessary for use in pecan products.

The effect of pecan initial moisture content on the amount of oil extracted is shown in Fig. 5, where the percentage of extracted oil is defined by dividing the weight of extracted oil by the total amount of oil in unextracted pecans. After 1 h of extraction, oil recovered ranged from 14% to 21%, which was consistent with the experiments of Alexander (1996). Moisture content showed no discernible effect on oil recovery.

Water affects SC-CO_2 oil extraction primarily by swelling the pecan structure to change oil accessibility. The addition of water and diffusion into the pecan causes an expansion of the pecan structure. Rai and Kumar (1995) demonstrated this expansion by measuring porosity and grain volume changes in moisture content. The expansion of cell walls could make the cell membrane more permeable so that both oil and CO_2 can pass more easily. At this point, oil extractability should be improved by adding water because the swelling effect of the water increases the contact between the oil and CO_2. However, excess water in pecans could also impede the reciprocal diffusion of oil and have a negative effect on oil accessibility. These 2 opposing effects of water on pecan oil extraction seemed to balance each other, leaving no significant effect of moisture content on oil yield.

Effect of moisture equilibration time

The percent of large pecan pieces (those remaining on the No. 4 sieve) after extraction with short and long moisture equilibration times is shown in Fig. 6. Extraction of oil from pecans after a long moisture equilibration period produced less breakage than a short moisture equilibration time period. In the 6.1% to 7.7% MC range, the 48-h moisture equilibration time produced almost twice the amount of large pecan pieces as the 1-h equilibration time. These results imply that water changed the pecan texture as it penetrated further into the tissue. As moisture content was increased to 8.5%, the effect of the moisture equilibration time decreased, and the difference between 1 h and 48 h was negligible at 11.6% MC. Fig. 7 shows the oil extracted with long and short moisture equilibration times for the 6 different moisture levels. The amount of oil extracted after a 48-h equilibration time was about 30% higher than the amount extracted after a 1-h equilibration time period.

After spraying water on the pecan surface, a water concentration gradient is developed, and water starts to diffuse from the pecan surface to the interior. As water gradually penetrates toward the pecan interior, more of the microstructure of the pecan is modified. Eventually, it is likely that equilibrium will be attained, and the amount of added water will determine the degree of structure modification. As expected, less pecan breakage occurred after extraction with the 48-h treatment due to the pecan structure being altered more than that of the 1-h treatment. The water in the kernels was likely more evenly distributed after the longer time period so that the whole kernel structure was expanded by swelling.

The amount of water sprayed on the pecans also affects the time of attaining equilibrium. A larger amount of water on the pecan surface accelerates the speed of water imbibition because water osmotic pressure is higher. Therefore, the number of unbroken pecans was almost the same at 11.6% MC for either longer or shorter moisture equilibration time.

Water co-extraction

During extraction of higher-moisture content pecans, the collected oil contained more water, was cloudy, and exhibited a yellow color. About 0.1 mL of water was visible at the bottom of the collection tube when oil was extracted from pecans with 11% MC, and the oil floated on the top of the water. As the pecan initial moisture content was increased, there was a linear increase in the amount of co-extracted water (Fig. 8). The water content of extracted oil from pecans having initial moisture levels of 3.5% and 12.0% were 0.7% and 11.7%, respectively, indicating that a large amount of water was co-extracted from those pecans having a higher moisture content. An increase in the amount of water co-extracted with increasing pecan initial moisture content indicates that water extraction is an equilibrium-controlled phase extraction process. In this case, the highest water solubility in SC-CO_2 was calculated to be about 0.12 g water per 100 g CO_2, which is much lower than pure water solubility of 0.68 g/100 g CO_2 based on the data of Wiebe and Gaddy (1941) at 75 °C and 62 Mpa. This was

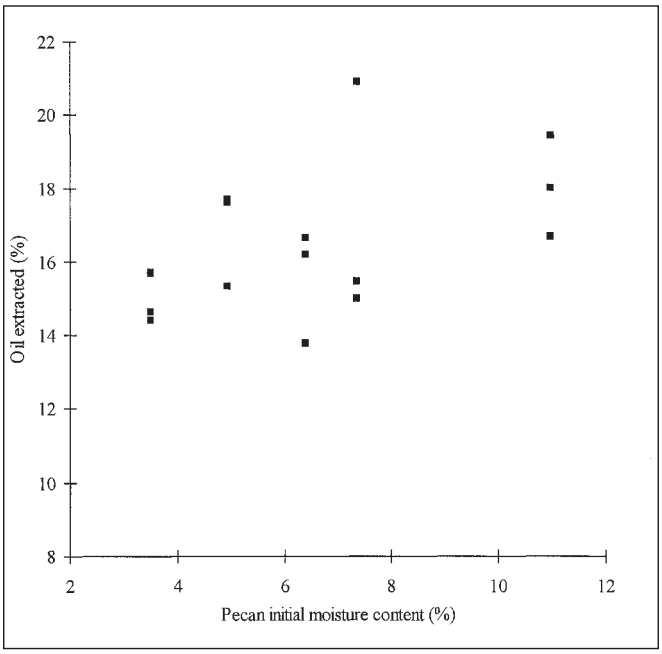

Fig. 5—Percentage of extracted oil versus pecan initial moisture content after a 1-h extraction at 75 °C, 62.0 MPa, and 3.0 L min^{-1} CO_2 flow rate followed by depressurization in 10 min.

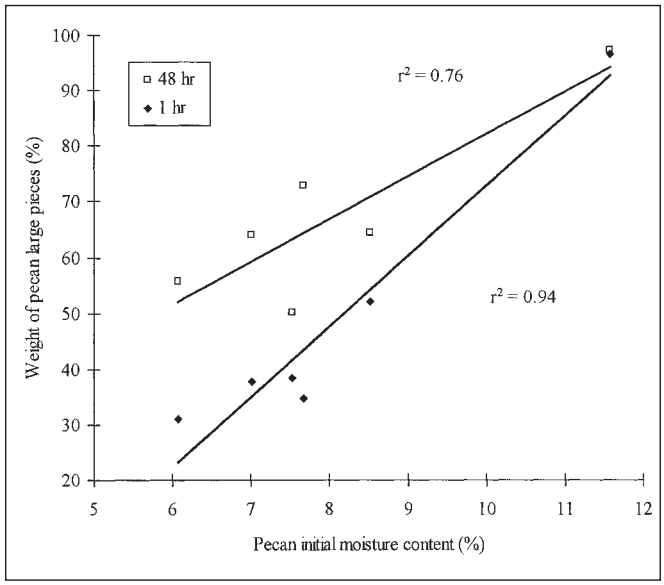

Fig. 6—Percent of large pieces of pecans (those remaining on No. 4 sieve) after extraction at 75 °C, 62.0 MPa, and 3.0 L min^{-1} CO_2 flow rate with short (1 h) and long (48 h) moisture equilibration time followed by depressurization in 10 min.

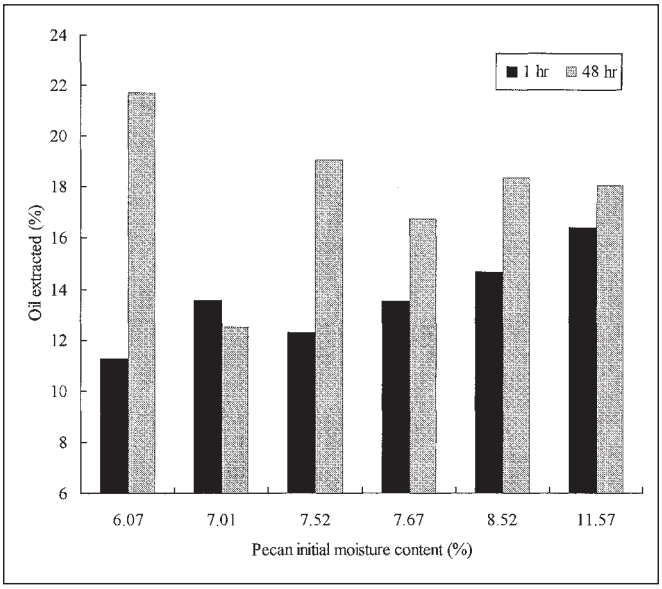

Fig. 7—Effect of moisture equilibration time and pecan initial moisture content on pecan oil extracted at 75 °C, 62.0 MPa, and 3.0 L min^{-1} CO_2 flow rate. Depressurization time = 10 min.

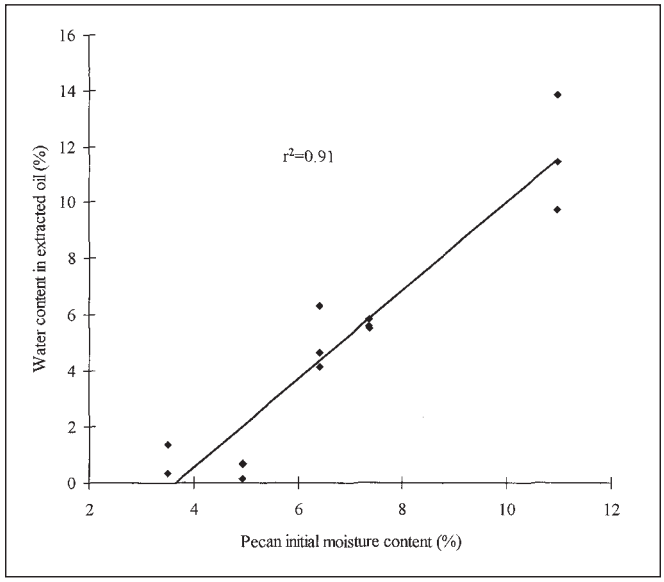

Fig. 8—Effect of pecan initial moisture content on water content in extracted oil at 75 °C, 62.0 MPa, and 3.0 L min^{-1} CO_2 flow rate followed by depressurization in 10 min.

similar to the report of Dunford et al. (1998), where co-extraction of water with oil from fish was determined at 35 °C and 34.5 MPa. Reverchon et al. (1995) computed the equilibrium solubility of water to be 0.03 g/100 g CO_2 in sage oil extraction, which is about 4 times less than the water solubility in pecan oil extraction. This difference can be accounted for mainly by the different extraction conditions: sage oil was extracted at 20 MPa and 40 °C, while pecan oil was extracted at 62 MPa and 75 °C.

CONCLUSIONS

THE ADJUSTMENT OF PECAN MOISTURE CONTENT PRIOR TO SC-CO_2 extraction of oil reduced the amount of pecan breakage. As expected, a higher initial moisture content of pecans produced less breakage. Moisture equilibration time also had a significant effect on pecan breakage. Allowing added water to penetrate into the pecan for 48 h reduced breakage, especially for lower moisture levels, and increased oil recovery by 30%. This study shows that water pretreatment is a feasible method for keeping kernel integrity when a short depressurization time is required. The short depressurization is desirable for industrial SC-CO_2 extraction because it reduces process time. This makes possible the simultaneous production of 2 valuable products: pecan oil and intact low-fat pecans.

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