FAT CONTENT REDUCTION IN PIG-SKIN SHEETS BY EXTRACTION WITH SUPERCRITICAL CARBON DIOXIDE

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Background

Collagen is the most abundant protein in animals. This fibrous protein is widely used in the Food Industry for various applications. Most often, it is obtained from cattle skin. However, it is always advisable to count on some alternative sources to eliminate strong dependences on one of them. Pig skin could be such an alternative; however, it has a high fat content that needs to be reduced to meet the specifications required by some of the applications of the food industry. Although there exist some methods to eliminate or reduce the fat content of animal skin, we propose in this work a mild method that can achieve very high reductions or even total elimination of the fat contained in pig skin to achieve a protein concentrate that can be used for most industry processes that need these type of proteins as raw material. This method consist in using supercritical carbon dioxide as a solvent that can selectively extract the fat without affecting the protein.
Supercritical fluid extraction (SFE) is a clean technique that can use low temperatures. Fat and oil extraction with supercritical fluids is widely reported in the literature from a large variety of natural sources such as different types of seeds, spices, meat or marine products (King et al., 1989). The most commonly used supercritical fluid is carbon dioxide due to its mild supercritical temperature and pressure and because it is a gas under ambient conditions what allows an easy separation of the processed products. It is also cheap and achievable with high purity; it is non toxic, non corrosive, non inflammable etc.CO_2 presents a large number of nice features to be used as a solvent for extraction processes. Its main inconvenient is its lack of polarity that makes it a poor solvent of polar solutes. However, it is a good solvent of fat (Bamberger et al., 1988), which is the solute whose removal from pork skin is to be studied in this work.

Objectives

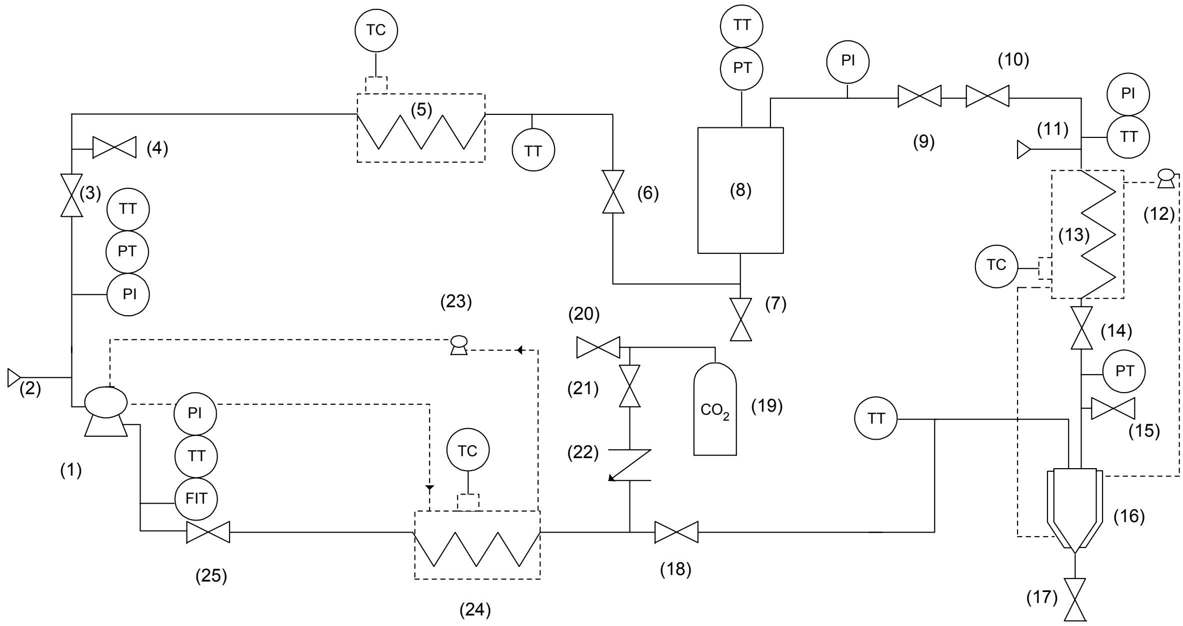
The objective of the work was the search of the process conditions that allowed the highest yield for reducing the fat content of pig skin by using supercritical carbon dioxide. The skin was defatted as part of the treatment for its conditioning to be used as raw material to obtain the collagen paste that is used as casing of Frankfurt-type sausages. Different experiments were carried out to identify the resistance controlling the extraction process and to search for the process conditions that overcame such resistance and gave a high extraction yield.

Materials and methods

The experimental study was made in a semi-pilot SFE-plant whose flowsheet is presented in Figure 1. Pig-skin sheets, around 5 mm thick, were placed in the extractor. The skin could not be ground since, by doing so, the later treatment necessary to obtain the desired collagen paste could not be carried out. The solvent, CO_2, was pressurized up to the extraction pressure and then, it was circulated with a certain flow (F) through the skin trying to achieve a good contact skin-solvent for the extraction to be faster. The solvent was recycled after removing the solute in a separator where the solvent power of CO_2 was reduced by reducing pressure and increasing temperature.
Two types of experiments were carried out. In a first set of experiments, the extraction was carried out continuously during a certain extraction time in order to evaluate the influence of extraction pressure, temperature and time, and initial water content on the extraction yield. In a second set of experiments the extractor was depressurized several times during the extraction experiment in order to take a sample of the raffinate whose analysis allowed to follow the course of the extraction.

Results and discussion

The first set of experiments were designed to study the influence of the extraction pressure (p), temperature (T) and time (t) on the extraction yield as well as the influence of the initial water content. The influence of pressure and temperature on fat extraction is showed in Figure 2. It can be observed that fat extraction increases slightly with temperature and pressure, but a maximum yield of around 40% was obtained. The maximum temperature assayed was 40 ºC since collagens experience denaturational transitions at temperatures above 40ºC (Privalov et al., 1979). The large error bars in the data are a consequence of the heterogeneity of the fat content of the skin. The results of some additional experiments carried out to study the influence of the extraction time are presented in Figure 3, where it can be observed that even fairly large extraction times did not allow a limit of 60% yield to be overcame.



High pressure pump (1)
Rupture disks (2, 11)
Check valves (23)
Purge valves (4, 15, 21)
Shutoff valves (3, 6, 9, 14, 19, 22, 26)

Thermostatic baths (5, 13)
Discharge valves (7, 17)
Extractor (volume = 2 L) (8)
Expansion valves (10, 18)

Separator (16)
CO_2 storage (20)
Cooling bath (25)
Circulation pumps (12, 24)

Figure 1. Flowsheet of the SFE semi-pilot plant of the Chemical Engineering Area of the University of Burgos. Maximum specifications: T= 200 ºC, p = 65 MPa and solvent flow, F = 20 kg/h.

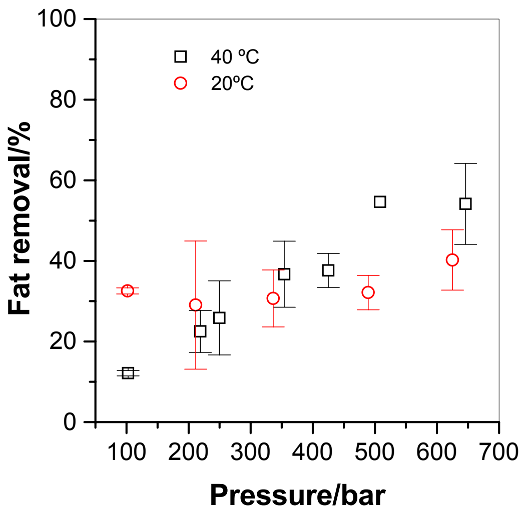


Figure 2. Fat extracted (%) versus pressure. F = 10 kg CO_2/h, skin sheets size = 2 cm × 14 cm, t = 60 min.

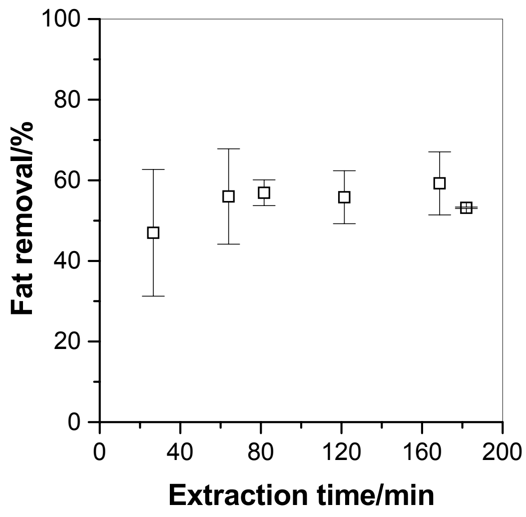


Figure 3. Fat extracted (%) versus extraction time. T = 40 ºC, p = 65 MPa, F = 10 kg CO_2/h, skin sheets size = 2 cm × 14 cm.

The influence of the skin water content on the fat extraction yield was also evaluated. The water content of the pig skin was reduced to different levels in a drier unit. The fat extraction yield obtained when using dried skin was also limited to an approximate value of 60%. Therefore, the study so far, proved that supercritical CO_2 removed the fat from pig skin, but the final concentration of fat was too high for this skin to be used to obtain the collagen-paste of interest. As an extraction temperature increase was not advisable and an extraction pressure or extraction time increase did not produce the required efficiency, a different extraction procedure needed to be assayed.

The fat is located all along the pig skin from the epidermis to the dermis and hypodermis (Compte, 1996). Therefore, it is reasonable to think that, when the skin is not ground, the external fat must be easily removed by the solvent but it must be much more difficult to extract the internal fat. In order to confirm or reject this assumption, some experiments were carried out to follow the course of the extraction process by determining the remaining amount of fat in the pig skin at different extraction times. In this experiments, the extractor was depressurized after some extraction time (called "cycle time") in order to take the skin sample necessary to determine its fat content.

The first observation made when analyzing the results obtained with this new experimental procedure was that the extraction yield of 60 %, that was the maximum obtained when working without depressurizing the extractor, was overcame and even total elimination of fat was achieved in some cases. That is, the successive and rapid depressurizations of the extractor seemed to be "exploding" the fat cell membranes and making the fat accessible to the solvent that extracted the fat much better. Therefore, two new variables that are going to influence the yield of the process have to be taken into account, i.e.: the number of cycles and the cycle time. Besides these variables, the influence of the initial fat content of the pig skin and of the solvent flow on fat removal was evaluated

Figure 4 shows the fat removal as a function of the number of cycles (a) and as a function of the total extraction time (b) for different cycle times. The experiments for cycle times of 10 minutes and 60 minutes were repeated to check for reproducibility of the tendencies. In the first 10 min cycle time experiment, sampling was made after every depressurization of the extractor and in the second experiment, after every three depressurizations. The two experiments carried out at a cycle time of 60 min differed on the initial amount of fat that is expressed in Fig, 4 as grams of fat per grams of protein. Figure 4a shows that fat removal increases when increasing the cycle time up to a cycle time of 60 minutes but larger cycle times do not improve fat removal. Therefore, a cycle time of 60 minutes was considered as the ideal time for the solvent to diffuse into the fat cells, so they explode with depressurization, and for extracting most of the fat accessible to the solvent after the previous rapid depressurizations performed in the extractor. A shorter cycle time required a larger number of depressurizations leading to a substantial loss of on-stream time, and a larger cycle time did not increase the extraction efficiency. Figure 4b shows that the tendencies were much more similar in all cases when the total extraction time was considered. Yields between 90 % and 100% were obtained in all cases after 4 hours of extraction.

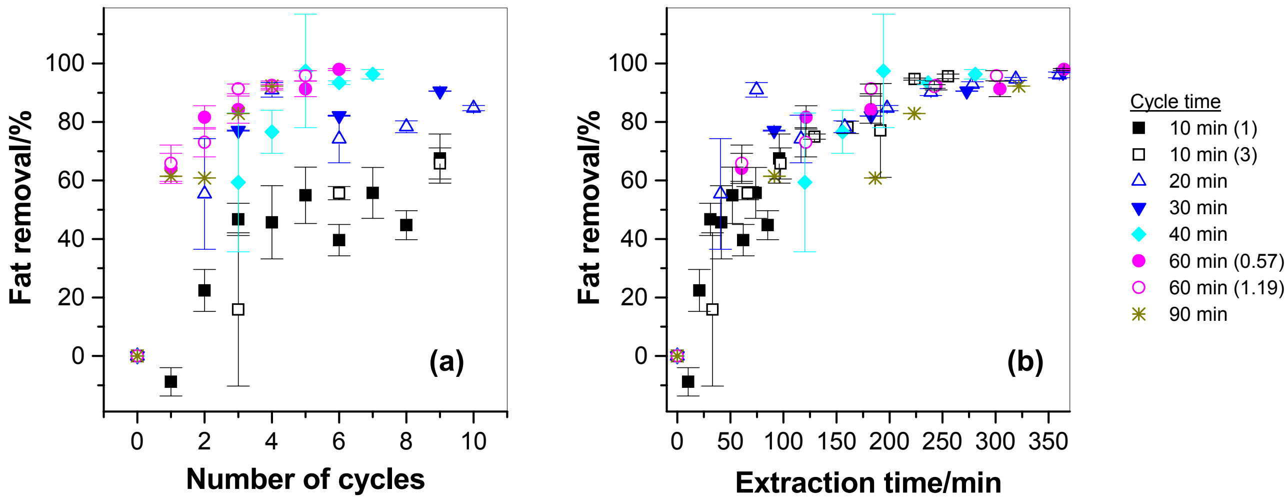


Figure 4. Percentage of fat removed against number of cycles for different cycle times (a) and as a function of total extraction time (b). T = 40 ºC, p = 35 MPa, F = 10 kg CO_2/h. skin sheet size = 15 cm × 14 cm.

Figure 5 presents the amount of fat in the skin, in a protein bases, as a function of the extraction time for different skin sheets with different initial fat contents. If fat removal was considered, there was no distinction between the two experiments indicating that the percentage of fat removed in a certain time is similar in both cases; however, Figure 5 shows that the fat content in the skin only reaches similar values for the two experiments after three hours of extraction. These experiments lead to the conclusion that the initial fat content in the skin is a variable to take into account. Therefore, the better the mechanical fat removal was performed, the lower the extraction time was for a given final fat content.

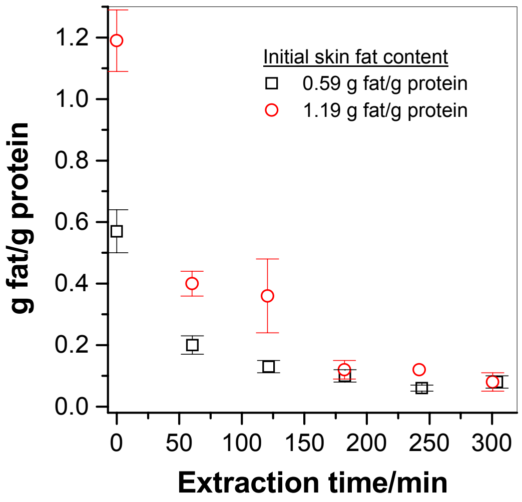


Figure 5. Fat content as a function of extraction time for different initial skin fat contents. T = 40 ºC, p = 35 MPa, F = 10 kg CO_2/h, skin sheet size = 15 cm × 14 cm, cycle time = 60 min

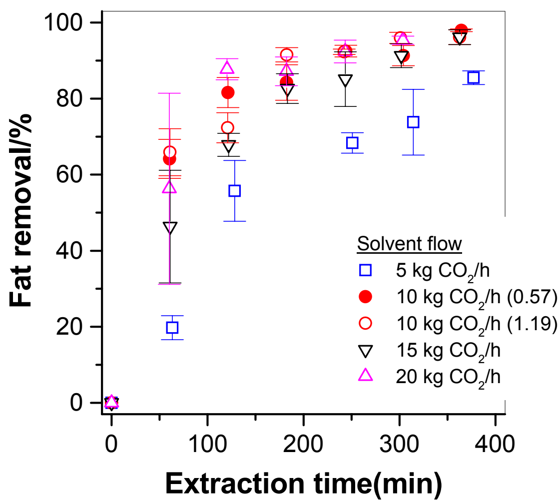


Figure 6. Fat removal as a function of extraction time for different solvent flows. T = 40 ºC, p = 35 MPa, skin sheet size = 15 cm × 14 cm, cycle time = 60 min

Figure 6 shows the fat removal as a function of extraction time for different solvent flows. It may be observed that when the solvent flow was low (5 kg/h) the extraction efficiency was also lower than in the rest of the cases indicating that the external matter transfer was important in the case. When the flow was equal or larger than 10 kg/h, the external matter transfer resistance seemed to be eliminated. Therefore it is recommended to work with a solvent flow of 10kg/h since using higher flows would only mean the use of a larger amount of solvent but not an improve of the extraction efficiency..

Conclusions

The results obtained showed that the internal matter transfer was the mechanism controlling the process; therefore, such resistance needs to be reduced or eliminated. A way of doing so, without grinding the skin, could be by "exploding" the fat cell membranes through rapid decompressions of the extractor where the skin sheets were previously swollen by the pressurized carbon dioxide. The optimum process conditions obtained after analyzing the influence of the process parameters were: extraction temperature 40 ºC, extraction pressure 350 bar; cycle time 60 min and solvent flow 10 kg/h.

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