Supercritical Carbon Dioxide Based Skin Preservation: Solving the Soak Liquor Effluent Crisis of the Leather Industry

by

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Abstract

Salt-based preservation of hides/skins contributes to about 50% total dissolved solids (TDS) in tannery wastewaters. In this study, raw skins have been preserved by exposing them to a continuous flow of supercritical carbon dioxide ($SCCO_2$) in a pressurized reactor. The process was carried out in reactors of two different capacities to ensure scalability. The skins thus dried could be stored at room temperature for a period of 30 days. The $SCCO_2$–dried skins were less conducive for microbial growth than wet-salted skins. The soak liquor of $SCCO_2$–dehydrated skin showed a 90% reduction in chloride content and significantly lower BOD and COD levels than soak liquor from wet-salted skins. The leathers produced from $SCCO_2$-preserved skins and wet-salted skin had no significant quality differences. As $SCCO_2$ systems have been reported as alternatives to all other unit operations, establishing $SCCO_2$–based preservation will complete the circle of total leather manufacture with $SCCO_2$.

Introduction

The leather industry is considered to be one among the most polluting and lot of research has gone into the reduction of effluents from tanneries by process modifications.[1] In spite of improvements that have been made the leather industry is still considered to be a serious threat to the environment, especially to water bodies and soil.[2] Most of the efforts in reducing tannery effluents have focused on the chrome and sulphide[3] content. Besides chromium, sulphide and other chemicals, salinity of the effluent is a major concern for tanneries.[4] Sodium chloride based skin preservation is the most common method for animal skin preservation used in the tanning industry with around 40% (w/w) being applied to hides/skins. High salinity/TDS load even after secondary effluent treatment has forced the tanners to choose reverse osmosis (RO) based technology for controlling TDS. Hence, elimination of salt in the preservation process will greatly reduce the salinity/TDS of the final effluent which will be a great step forward in making the leather industry more eco-friendly.

The problem of using a high amount of salt for preservation has been well known and suitable alternatives are very much essential. Chemical methods, where common salt is substituted by other chemicals, have been tried in the past, however there are some difficulties.[5] While successful in preserving the hides, these chemicals come with environmental concerns of their own. Green hide processing has been mooted as one of the methods to overcome the usage of salt.[6] However, this method applies only in those cases where the leather processing unit is in the immediate vicinity of the slaughterhouses. This is something that cannot always be ensured due to practical difficulties and thus would put the quality of the leather produced at risk which would be unacceptable for a leather manufacturer. Chilling is effective and does not have any environmental concerns,[7] but its infrastructure and power requirements make it difficult to implement on a large scale. But these methods either require low salt usage or give only short term protection and will still give considerable load in soak liquor.

An ideal way forward to design a preservation process that reduces the final effluent load from a leather manufacturing unit is to keep in mind both economic and environmental concerns, which is not easy to do. Any technique that demands a leather manufacturer to set up new infrastructure for a salt-free preservation process is bound to meet with resistance due to the costs involved. Therefore, if all leather manufacturers are required to invest in a process that ensures salt-free preservation, it has to be one that will also contribute to other processes in leather manufacture. $SCCO_2$ is considered to be the first green alternative to organic solvents. It is colorless, non-flammable, non-toxic and is compressible and inert and can be used for processing a variety of materials which makes it an attractive option for industrial applications.[8] $SCCO_2$ has been successfully used in tanning[9] and dyeing[10] applications and has been accepted as a low-discharge system. All unit operations involved in leather manufacture have been successfully demonstrated using $SCCO_2$ technology. Degreasing,[11] fiber separation,[12] deliming and fatliquoring[10] have been proven to be more efficient in terms of chemical usage and recovery, effluent parameters and quality of the leather produced. Even though involving huge initial investments, it

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is being seen as a method which can drastically reduce the effluent from the leather industry and can also reduce the expenses incurred in downstream processing of effluent. In the future, a state-of-the-art leather manufacture unit might be required to carry out all its operations using $SCCO_2$. The only process in leather manufacture that is yet to be established using $SCCO_2$ is preservation. As mentioned above, soak liquor contributes to about 60% of the TDS in the effluent stream. Therefore, it would be ideal to look at ways in which this problem can be eliminated. It is towards this goal that we have tried to initiate the removal of excess water from hides and skins using supercritical carbon dioxide technology.

Experimental

Curing with $SCCO_2$

For all curing experiments using $SCCO_2$, a sample of equal area taken from an adjacent portion of the same skin was subjected to conventional salt curing and used as a control in all subsequent analyses.

Fresh sheep skin was taken straight from the slaughterhouse, cut into uniform 10 × 5 cm pieces, and one such piece was taken to the $SCCO_2$ reactor (TharProcess Inc. PA USA) with a capacity of 250 ml. The sheep skin was completely wrapped in a polyester cloth to avoid loose hair from being carried into the narrow tubes of the $SCCO_2$ reactor which could lead to clogging of the tubes and build-up of pressure. The skin sample weighing approximately 7 g was placed in the reactor vessel and CO_2 was purged through the reactor at a rate of 20g/min. Throughout the process, the conditions were stringently maintained at a pressure of 20.5 MPa and a temperature of 37-40°C. Also, collagen is known to denature at around 41°C which is another reason why higher temperatures were not tried in this experiment.[13] The reactor was stopped every two hours and the weight of the skin sample was measured. The process was stopped when the weight of the sample was seen to be almost the same in two consecutive intervals. This experiment was carried out over 8 intervals, i.e. a total of 16 hours.

A similar experiment was carried out in a 1.5-L reactor. A skin sample weighing approximately 36 g (approx. 15 × 10 cm) was used in this reactor. The temperature and pressure were maintained at approximately the same level as the previous experiment. The flow rate of carbon dioxide through the reactor vessel was 1 kg/min. As the dimensions of the extractor vessel were comparatively larger, the skin sample was loosely wrapped around a perforated metal rod and inserted longitudinally into the reactor in order to allow full contact between skin and $SCCO_2$. Also, to ensure uniform distribution of $SCCO_2$ throughout the reactor vessel, the vessel was filled with glass beads. The considerable increase in sample size in this experiment allowed us to collect the removed moisture at the exhaust end of the system. The experiment was stopped when the exhaust failed to yield appreciable amounts of water for a few minutes. Here, because the system used was larger, with a higher CO_2 flow rate than the previous experiment, frequent stops were not possible. Therefore, the profile of moisture removal over different time intervals of the $SCCO_2$ driven drying process could not be evaluated in this trial.

Acetone as a Cosolvent

In order to study the effect of a cosolvent on the effectiveness of the $SCCO_2$-driven drying process, acetone was used. Ideally, acetone should have been pumped in to the reactor along with $SCCO_2$, by means of a cosolvent pump. In this case, 8 mL of acetone, approximately 0.0006% (w/w) of total carbon dioxide used, was uniformly spread on the skin sample and it was placed in the reactor at the start of the extraction process.

In all the above cases, before the start of the experiment, a portion of the skin sample was set aside for moisture analysis. After drying, the experimental skins and controls were stored at ambient conditions and periodically evaluated for hairslip and foul smell which are indications to evaluate proper curing/preservation. Wet-salted skin and unpreserved skin samples of approximately the same size, obtained from the same specimen, were stored in the same conditions and subjected to the same subsequent evaluations as the $SCCO_2$-dried skin. All experiments were performed in triplicate.

Moisture Analysis of Skin

To measure the moisture content of a skin sample, it was first weighed and then placed in a hot air oven (Memmert Type) at 105°C for 8 h. At the end, the sample was weighed again and the difference between the initial and final weights gave the total moisture content of the sample and the % moisture content was then calculated. The skin samples subjected to this analysis were taken from portions adjacent to the ones that were utilized for the experiments, and thus gave the closest possible estimate of the total moisture content of the samples inside the reactor.

Microbial Analysis

In order to analyze the effectiveness of the preservation process, the microbial load on the skin samples was enumerated.[14] A known surface area of the skin sample, usually 1 × 1 cm, was cut and dipped in a known volume of sterile saline, which was then serially diluted and inoculated via the pour plate method on nutrient agar. Appropriate dilutions were selected for colony count.

Leather Processing

The preserved skin samples were processed into leather after 30 days according to conventional leather manufacture methods and the procedure is given in the Appendix. All samples were processed together in the same process vessel to ensure same process conditions for both conventional and $SCCO_2$ aided preserved skins.

Leather Quality Analysis

The leathers produced from all the three samples were analyzed for comparison and to check for any significant differences in quality. This evaluation was done both at the wet blue as well as crust stages.

Measurement of Shrinkage Temperature

The shrinkage temperature of all three wet-blue samples was tested using a SATRA STD 114 shrinkage tester.[15] Specimens of equal size were cut out from each sample and attached to the shrinkage tester and the temperature was gradually raised by means of a flame. The temperature at which the sample shrunk noticeably compared to its original length was noted and that was considered as the respective sample's shrinkage temperature.

Evaluation of Chrome Content

The chrome content of the samples was tested after the post-tanning processes. Chrome content was estimated using previously established procedures.[16]

Evaluation of Physical Strength and Organoleptic Properties

The physical strength properties such as tensile strength, elongation at break and tear strength of the finished un-dyed crusts were analyzed. The specimens for physical testing were conditioned for 24 h at 25 ± 1°C and 65 ± 2% relative humidity. The crust leathers were also evaluated for various organoleptic properties such as softness, fullness and grain smoothness by hand and visual examination by two leather technologists who were blind to the experiment. They were rated on a scale of 1–10, where a higher point indicates better properties.

Examination of Surface Morphology and Cross Section

The surface morphology and cross sectional view of the leathers produced from the three samples (experimental and its corresponding control) were analyzed using a hand-held digital microscope at 10 fold magnification in the reflectance mode. The pictures thus obtained were visually analyzed for grain distribution and uniformity of chrome penetration.

Emission Parameters

The soak liquors obtained after the wetting process of both CO_2 and salt-preserved skin were subjected to analysis to check for differences in emission parameters. The parameters checked were Chemical oxygen demand (COD), Biological oxygen demand (BOD), total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), and chloride content. The BOD, COD and solids content of the soak liquor were measured following standard procedures.[17] The chloride content in the soak liquor was estimated using the Mohr Argentometric method, where chloride ions were titrated against silver nitrate using potassium chromate as indicator with formation of brick red precipitate being the end point.[18]

Results and Discussion

Moisture Content of Raw Skin

The total moisture in the skin was calculated as the difference between the weight of the skin before and after being kept in a hot air oven at 105° C for 8 hours. Based on this difference, the total moisture in the skin was found to be approximately 64% and 60%, respectively, for the samples used in the 250-mL and 1.5-L reactor.

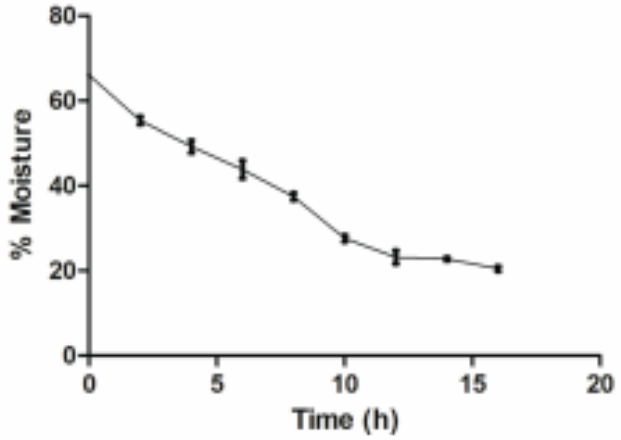

Figure 1. Effect of $SCCO_2$ with time on moisture removal from raw goat skin

$SCCO_2$ Drying of Skin – 250 ml Reactor

The moisture content of the sample placed in the reactor was analyzed and found to be 64%. This sample was subjected to $SCCO_2$ drying, at a CO_2 flow rate of 20 g/ min. The weight of the skin sample within the reactor was measured every 2 h to quantify the amount of cumulative moisture removed during that interval. From Figure 1, it can be seen that the moisture content of the skin sample has fallen from approximately 66% to 19-20% over the 16 h period. Fig 1 shows the fall in % moisture content of the sample with time. From this, it can be seen that the bulk of the moisture removal happened during the first 10 h of the process. The rate of moisture removal remained almost constant throughout the first 10 h of the process (Fig 1).

$SCCO_2$ Drying of Skin – 1.5-L Reactor

Here, a sample of 36 g was placed in the reactor and subjected to a CO_2 flow rate of 1 kg/min. The moisture content of the sample was 60%. The moisture removed from the skin was periodically collected at the exhaust end. The exhaust yielded very little moisture at the end of the 90th min, and therefore the CO_2 flow was terminated at a run time of 100 min. It should be noted that, because of the size of the equipment, around 20 min had elapsed before the desired pressure was achieved inside the reactor. The final moisture content of the sample was found to be 26-27%.

In another experiment in the 1.5 L reactor, 8 mL of acetone was uniformly spread on the flesh side of the skin sample before being set in the reactor. All other conditions were same as that of the previous experiment. Here too, the CO_2 flow was terminated after a run time of 100 mins. At the end of the 100 min period, the final moisture content of the dried skin was 24-25%. A co-solvent was used along with $SCCO_2$ here to enhance the solubility of water. $SCCO_2$ has a highly non-polar character and it is a well-established practice to introduce other solvents to improve the polar nature of the mixture for effective extraction.[19] It is known that supercritical carbon dioxide is used for the extraction of lipids from various sources. However, the removal of fats from the skins used in these experiments were not observed because the temperature and pressure ranges used

in these experiments is far lower than the ideal pressure ranges reported earlier for fat removal, which is around 24.0 MPa.[20] At 20.5 MPa, the pressure used in the current experiments, the degreasing efficiency is expected to be below 25%.

Microbial Load on Preserved Skin

The two dried skin samples, obtained after the processes in the 1.5 L reactor, along with corresponding control samples, were then stored at room temperature for 21 days to check the storage stability. The microbial load on each of these samples was estimated on days 10, 20 and 30 of storage. Over this period, the $SCCO_2$-dried skin samples had become slightly stiffer, indicating further moisture loss. It was seen that on the 10th day the microbial count was lowest on the salt-preserved skin sample. On the 20th day, the microbial load on all samples was almost equal. All samples showed an increase in the microbial load, with the quantum of increase being greatest for the salt-preserved skin. By the 30th day, the microbial load on the salt-preserved skin samples had exceeded that of the $SCCO_2$-dried samples. Both the $SCCO_2$-dried samples showed a much reduced microbial count than on the 20th day. At the end of the 30th day, all skin samples showed no signs of putrefaction or hair slip (Fig. 2) and were suitable for leather processing. The microbial load present in various skins are given in Table I. It can be said from these results that the $SCCO_2$ drying for skin preservation is comparable or even better than the conventional salt preservation method.

Fig. 2: Photographs of grain and flesh sides of preserved skin samples after 30 days storage at ambient conditions. a. CO_2, b. CO_2 + acetone, c. wet-salted

Table I

Microbial load of skin samples on 10th, 20th and 30th day of storage

Preservation Method	Microbial Load Colony count (CFU/mL) on		
	Day 10	Day 20	Day 30
$SCCO_2$-dehydration	2.2×10^5	2.87×10^6	2.1×10^5
$SCCO_2$-acetone-dehydration	2.9×10^5	3.01×10^6	3.03×10^5
Wet-salted	1.06×10^4	2.84×10^6	2.9×10^6
Unpreserved	1.26×10^9	–	–

Chemical and Physical Characterization

The chemical and physical characteristics of the leathers, i.e. shrinkage temperature, chrome content and tensile strength, made from the all the three samples, were analyzed and the results are shown in Tables II & III. The leathers were found to be comparable on all the three parameters. The shrinkage temperature was almost same for all three, whereas there was a minor variation in chrome content. The tensile strength was highest for the $SCCO_2$-dried skin, whereas the $SCCO_2$-acetone-dried skin was the lowest.

Table II

Physical characterization of leather samples produced after different preservation methods

Preservation Method	Shrinkage temperature (°C)	Tensile strength (MPa)	Elongation at break (%)	Extension at maximum load (mm)
$SCCO_2$-dehydration	104±1	14.01±1.34	51.67	25.83
$SCCO_2$-acetone-dehydration	104±1	11.51±1.22	70.16	35.08
Wet-salted	103±1	13.67±1.14	53.83	26.92

Table III

Chemical characterization of leather samples produced after different preservation methods

Preservation Method	$SCCO_2$-dehydration	$SCCO_2$-acetone-dehydration	Wet-salted
Chrome content (%)	3.08±0.12	3.43±0.25	3.15±0.25

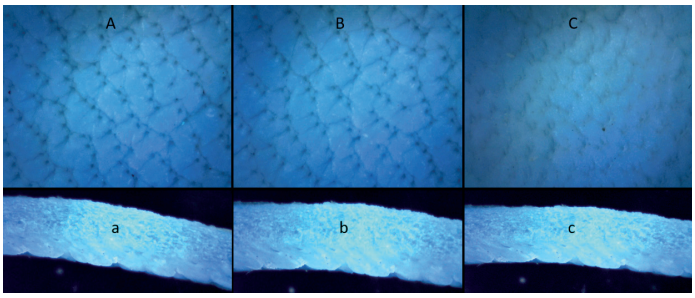

Figure 3. Surface view of leather produced from A. CO_2 dried, B. CO_2 + acetone dried and C. wet-salted skin, and their corresponding cross-section view (a, b and c) using optical microscope (10 fold magnification).

Surface Morphology and Cross Section View

There had been no significant difference in the appearance of the wet blue leathers tanned from both the control and experimental skins. The surface morphology and the cross sectional view of the leather tanned with both experimental $SCCO_2$ preserved and conventional wet salted raw material were observed and found to have a similar grain distribution pattern (Figure 3).

Organoleptic Properties

The leather from $SCCO_2$-dried skin was able to match the leathers produced from wet-salted skins in terms of organoleptic properties. The $SCCO_2$-acetone-dried skin, however, seemed to be slightly lower, although not a great difference, than the other two in terms of grain smoothness. In terms of softness and fullness, the three samples can be considered more or less equal. The ten point grading assigned to each leather sample by the assessors are given in Table IV.

Emission Parameters

The soak liquors of CO_2-preserved and salt-preserved skin were considerably different in appearance with the latter being far more turbid. Consequently, a significant difference in the solid content of the liquors was expected. The total solid content of soak liquor from salt-preserved and CO_2-preserved skins was calculated to be 228.3 and 56.6 g of solids per Kg of skin processed. The difference is huge, with CO_2-preserved skin showing a solid content that is less than 25% of that shown by salt-preserved skin. Even more significant is the difference in total dissolved solids, where salt-preserved skins showed 140 g/Kg of skin, whereas CO_2-preserved skin showed an almost negligible 10.8 g/Kg of skin, a difference of more than 90%. This is along expected lines as most of the dissolved solids in the soak liquor is contributed by the sodium chloride used in the conventional salt-preservation process. CO_2 preservation showed an advantage, even though not huge, in terms of BOD and COD also in soak liquor. This is probably due to the effect of sodium chloride removing soluble proteins like albumin from the skin matrix.[21] The most significant difference however was seen in terms of chloride content in soak liquor, a reduction by more than 90% for CO_2 preservation, which is a very significant step in reducing the effluent load generated from the soaking process. Even though no salt is used in the process proposed here, there is a small amount of chloride in the soak liquor. This can be attributed to the ground water that was used for the soaking process. The ground water was used in order to keep the process as close as possible to the common tannery practices. Details of all emission parameters can be seen in Table V.

Table IV

The scores awarded by independent assessor I and II to the three crust leather samples on the basis of feel and texture

	Softness		Fullness		Grain Smoothness	
Preservation Method	**I**	**II**	**I**	**II**	**I**	**II**
$SCCO_2$-dehydration	8	8	9	9	8	8
$SCCO_2$-acetone dehydration	8	7	8	8	7	8
Wet-salted	9	9	8	7	9	9

Legend: 10 point scale: 0 – Poor; 10 - Excellent

Table V

Emission parameters of soak liquor in terms of gram per kilogram of hide processed

Preservation method	BOD	COD	Total Solids	Total Dissolved Solids	Chlorides
Wet-salted	12.30±0.76	33.289±2.35	228.3±12.35	140±5.63	83.5±6.5
$SCCO_2$-dehydration	8.42±0.54	24.177±2.05	56.6±3.54	10.8±0.35	8.0±0.54

The results show that moisture removal using $SCCO_2$ is an effective means of preserving hides and skins to be further processed into leather. There are no obvious disadvantages with respect to the quality of the leather produced using skin preserved through this process. A significant reduction in terms of solids and chloride content in soak liquor has been achieved. This is the most significant outcome of this work and is very relevant to one of the most pressing problems faced by the leather sector, i.e. high chlorides and TDS in soak liquor thus making leather manufacture a cleaner and greener process. Additionally, we have proven that skins dried using $SCCO_2$ can be stored at ambient conditions. Hence, $SCCO_2$ technology can be considered on par to the traditional preservation process in terms of leather quality but low TDS and chloride content generation. The only problem that might be encountered in the implementation of this technology is the additional initial investment.

Conclusion

We have been able to prove through this work that $SCCO_2$ based preservation can significantly reduce TDS and chloride loads in tannery effluent without affecting the quality of the final leather. Physical and organoleptic properties of the leather produced from $SCCO_2$-preserved skin were comparable to that of leather produced

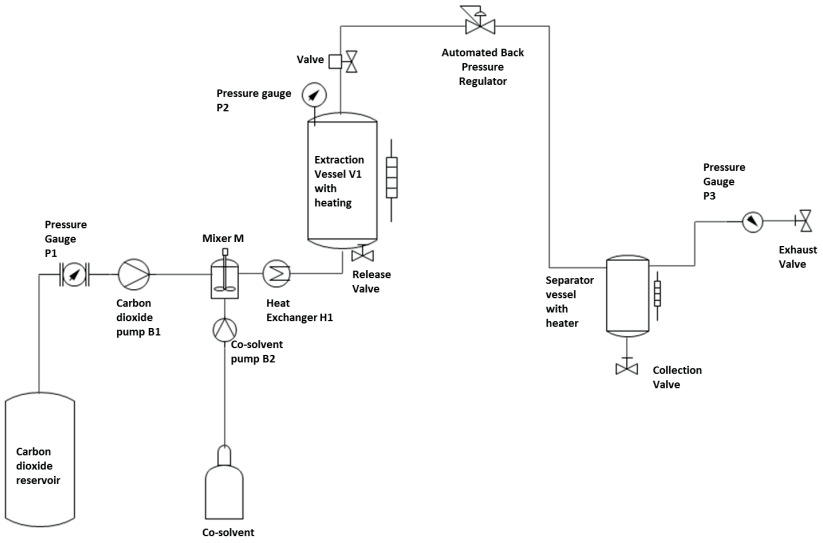

Figure 4. Schematic representation of $SCCO_2$ reactor set up.

from conventional wet-salted skin. It has also been proven that the skins preserved by this method can be stored at ambient conditions for up to 30 days. $SCCO_2$ technology is being touted as the future means of leather manufacture and processes such as tanning, finishing and beamhouse operations are already in various stages of development. It is possible that in the future the same reactor vessel can be used for preservation as well as subsequent operations. Other salt-free methods like silica gel preservation, plant extracts, chemicals etc. pose challenges of their own in the effluent stream. The method will guarantee minimal to zero discharge into the effluent stream.

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