OLEIN PRODUCTION FROM PRE-FLESHING RESIDUES OF HIDES IN TANNERIES

G. P. S. PRIEBE and M. GUTTERRES
Federal University of Rio Grande do Sul (UFRGS), Chemical Engineering Departmen, Laboratory for Leather and Environmental Studies (LACOURO), Porto Alegre-RS, Brazil
priebe@enq.ufrgs.br, mariliz@enq.ufrgs.br

***Abstract*— Olein production from the residue constituents of hide pre-fleshing is carried out through the unit operations of extraction and subsequent fractionation of the fatty material (tallow). The residue was characterized and the content of fatty matter (31.83% by mass) revealed a high potential for its reuse. By the extraction/ digestion of tallow assays were carried out to quantify the effect of factors such as the presence of agitation, temperature and extraction time in terms of the efficiency of the extraction operation and acidity index of the tallows obtained. The oils were characterized according to the acidity index, iodine index, saponification index, water content, volatile matter content and fractions of saturated and unsaturated fatty acids. The oil composition was quantified using gas chromatography.**

***Keywords*— olein, tallow extraction and fractionation, tannery waste, pre-fleshing solid waste, design of experiments.**

I. INTRODUCTION

The generation of large quantities of solid waste related to the processing of hides in beamhouse operations is closely linked to the characteristics of the raw material. There is the possibility for the employment of simple technologies which allow the use of part of the waste constituents, in the form of byproducts, as inputs for other processing industries. Studies in this area aim to contribute to a significant reduction in the potential environmental impact of the sector, as well as to decrease the production costs associated with the disposal of the wastes generated. It is well known that there are several difficulties encountered in the establishment of corrective actions aiming to reduce the generation of waste at source, related to the characteristics of the raw material itself (pre-fleshing waste and hair).

The pre-fleshing step aims to remove subcutaneous tissue and promote a significant improvement in the diffusion properties of the chemical agents used in the process. This operation is characterized by the generation of large quantities of residues (between 7 to 23% of hide weight), which are basically comprised of subcutaneous tissue and trimmings, in which a high content of fatty materials, minerals, protein and water are present.

According to Aquim (2004), the quantities of solid waste generated in pre-fleshing operations are 6 kg of subcutaneous tissue per 26 kg of salted hide. Buljan *et al.* (2000) cites that the total waste generation after fleshing and trimming operations is of the order of 555 kg per 1000 kg salted hide or per 1500 kg limed hide.

A study by Simeonova and Daley (1996) shows that a tannery with a production capacity of 100 tonnes of green hide produces approximately 30 tonnes of pre-fleshing residue daily and this leads to the creation of serious environmental problems.

Gutterres and Osório (2004) reported the following salted hide characterization: 43.51% of water, 13.74% of ash, 4.08% of fats and 40.55% of collagen substance. The fat content is high due to the subcutaneous tissue. Also, according to Wist and Schmidt (1992), the fatty matter composition varies according to the type of animal, feeding and climate, and basically consists of: glycerides (50%), phosphatides (20%), fatty esters (10%), fatty acids (10%) and stearin (1%).

The basic molecule of oils and fats is triglyceride (Fig. 1), which is classified as being of animal or vegetable origin. Chemically, there are no functional differences between them. In the constitution of oils and fats, of either animal or vegetable origin, the same fatty acids are present, there being only a differentiated distribution of the acid fractions present.

In case of triglycerides (triacylglycerols) the three groups are esterified, unlike mono and diglycerides (partial esters) in which only one or two hydroxyl groups are in the form of esters. The positions at which the fatty acids are linked to glycerol are called alpha and alpha' in the external positions and beta in the internal position (Fig. 2).

Practically all natural oils contain fatty acids with a certain number of carbons. Short chain saturated fatty acids C-6, C-8 and C-10 are present in coconut, palm and milk fat, and C-12 fatty acids (lauric and lauroleic) can be observed in spermaceti oil. The fatty acid C-16 and C-18 are found in high fractions in animal fats and in many vegetable oils (Thorstensen, 1969).

The extraction of animal fats is, in general, carried out by applying steam for a short time period, separated by decantation and/or centrifugation and freezing. Some stages of processing are similar to those employed for vegetable oils, for example, refining and whitening. These oils are employed as the raw material for other chemical conversions intended for the production of

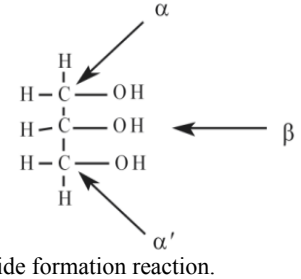

Fig. 1: Triglyceride formation reaction.

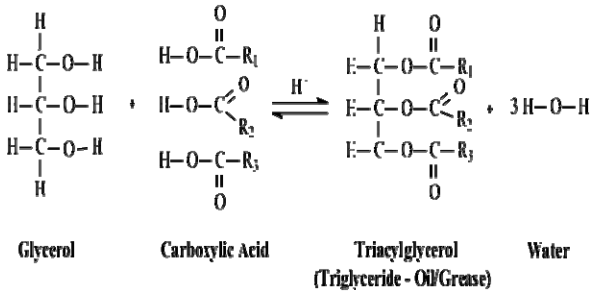

Fig. 2: Relative positions of fatty acids linked to glycerol.

soap and detergents obtaining from lards, and other fats and oils intended for food. They are widely used in paints as lubricants and in the manufacture of leather and fine soaps.

The refining of vegetable or animal oils for utilization as raw materials for other processes, from oil production to leather fatliquoring, requires a set of processes to transform the crude oils into a product with specific physical characteristics for their future use. Although there are some uses in which the oils are employed without refining, the majority of marketable oils and fats are subjected to these processes, seeking improvements in their appearance, smell and/or taste. According to Moretto and Fett (1998), the refining is performed aiming at the removal of the following components: colloidal substances, protein, and phosphatides and their decomposition products (free fatty acids and their salts, oxidized fatty acids, lactones, acetals, polymers); coloring substances (chlorophylls, xanthophylls, carotenoids); volatile substances (hydrocarbons, alcohols, aldehydes, ketones, esters of low molecular weight); inorganic substances (calcium salts and other metals, silicates, phosphates and others); and moisture.

After refining the oils are modified to obtain a product with the desired physical and chemical properties. In some cases it is necessary to mix several oils to achieve such characteristics. The degree of saturation of the carbon double bonds can be obtained through hydrogenation in addition to the employment of lipase in organic solvent dispersions to promote the hydrolysis and in teresterfication reactions of oils (Snape and Nakajima, 1996).

The final temperatures of the dry fractionation process vary between 5 and 10°C, according to the final specification of the oil product and the time periods employed are between 12 and 24 hours. After this process, the mixture is filtered or centrifuged to separate the phases formed. The percentage of saturated triacylglycerols present in raw oil is highly variable depending on the origin. Bailey (1979) cites percentage values of saturated fatty acids for pig fat of 36.1 to 41.5% and for cattle fat of 47.8 to 71.6% by mass.

Besides the evaluation of the fat content of this pre-fleshing residue and a thorough assessment of the processing method, this paper aims to show the clear interdependence between the characteristics of the oils obtained and the process parameters adopted. Moreover, there is an assessment of the reuse potential of the waste constituents (grease) as an alternative source of income (economic perspective), considerably reducing the environmental impact of the leather industry.

II. METHODS

Figure 3 shows a flowchart summarizing of the processes and activities related to olein production, highlighting the contributions of this study which aims to provide data related to the operations necessary to produce olein from the pre-fleshing waste of cattle hides.

A. Raw material, intermediary and final products

The study began with the collection of samples of the pre-fleshing waste from a tannery which uses diverse raw material sources (hides) and regularly carries out oil extraction operations. The residue used in the experiments came from bovine hides with average weight between 20 - 22 kg, of diverse origin, collected from different slaughterhouses.

Tallow is the term generally used for animal fat, and in this particular case, it is beef tallow, a mixture of fatty materials extracted from pre-fleshing waste. Samples

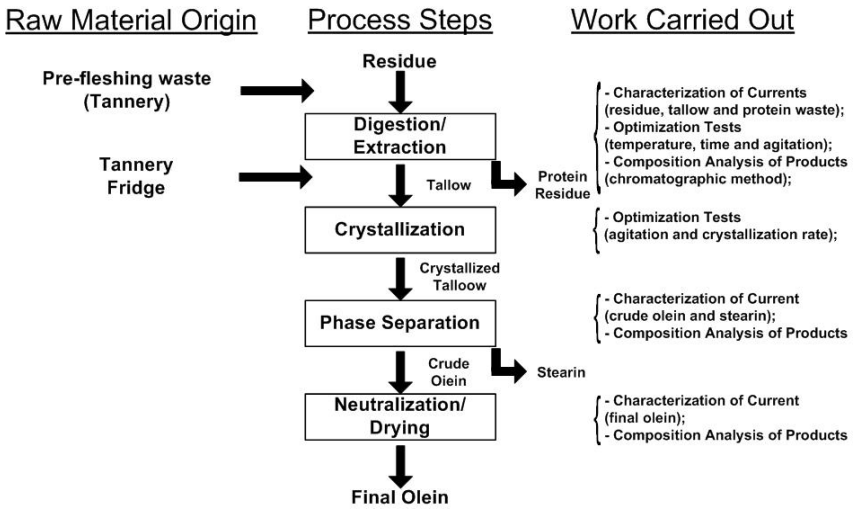

Fig. 3: Simplified flowchart of the process

of beef tallow were collected from a tannery. Immediately after its extraction the natural decomposition process begins, through the action of bacteria and enzymes, leading to changes in the quality characteristics of the tallow. The material degradation can be observed through its color and the free fatty acids content. Therefore, analytical quality differences are observed when comparing the tallow obtained from different tanneries.

The chemical and physical characteristics of the materials analyzed after each step are described below:

- Protein Residue: collected after the extraction of the fatty material (tallow) from pre-fleshing residue. It is rich in diverse organic materials. Besides the hydrolyzed collagen of the extraction process, it contains: hair remains, high salt content and other impurities present in the raw material. The presence of a high fat content in this waste indicates the low efficiency of the extraction process.
- Crude olein: oil obtained after fractionation of the tallow. It is composed of triglycerides comprising unsaturated fatty acids and oleic acid is the major component. Its main physical characteristics are a low melting point and yellowish color. This fraction is called crude olein because it needs to be refined in order to decrease the free fatty acid level and moisture content.
- Stearin: white grease fraction of higher melting point (solid at room temperature) resulting from the fractionation of tallow. It is composed of triglycerides of saturated fatty acids and is commonly used in soap production.

B. Characterization of Materials

The initial, intermediate and final process products from the extraction and processing of olein were analyzed with the following objectives:

- Analysis of pre-fleshing waste: to quantify the fatty matter contained in the pre-fleshing waste and to identify the potential for the obtainment of olein. Involves determination of the volatile matter (including water), the inorganic substances (chlorides and total ash content) and the protein material (nitrogen and hide substances content); and
- Analysis of intermediaries and final products: to estimate the degradation state of the triglycerides through the acidity index, to measure the degree of saturation of fatty acids in oils using the iodine index, to estimate the proportion of low molecular weight fatty acids through the saponification index, to quantify the volatile matter (including water), to determine inorganic substances through analysis of ash content, and to analyze the composition of oil (mass fractions) through its fatty acid formers by gas chromatography.

The analytical methodologies employed in the characterization analysis of residues were: ABNT NBR 11029 (2001); ASTM D 4653-87 (1998); ASTM D 2868-96 (1996); ASTM D 2617-96 (2001); ASTM D 3495-83. The following methods were employed in the analytical characterization of intermediate and final products: ABNT NBR 11115 (1998); ABNT NBR 10448 (2000); ABNT NBR 9231 (2002); water content according to Karl-Fischer method with titrations performed using 702 SM Titrino (Metrohm), and volatile matter content through evaporation in an oven under the same conditions used for the waste characterization.

The composition analysis of the different oils was based on methyl ester fractions of the various fatty acids that form the triglycerides. Thus, it was necessary to employ a methodology to crack the triglycerides and make a subsequent esterification of the resulting fatty acids with methyl alcohol. The mass percentages of each compound (methyl ester) of the tallow and the fractions obtained after dry fractionation were determined by gas chromatography with a flame ionization detector.

C. Study of Process Parameters

Extraction of tallow

The search for the extraction conditions able to achieve the highest efficiencies together with improved quality characteristics of the tallow obtained was carried out in a pilot plant. The experiments were performed as duplicates varying the temperature, time and presence of agitation (Tables 1 and 2).

Table 1 shows the levels considered and Table 2 shows the design used in each experiment. In these tests the acidity index of the tallow obtained and the fat content of the protein waste were considered as response variables. It should be noted that the temperatures of 143.4 and 158.7 °C refer to the saturated steam at 4 and 6 $kgf.cm^{-2}$. These levels were chosen due to the physical limits of the extraction plant taken as a case study, in which the boiler provides steam within this range.

Dry fractionation of tallow (winterization)

The experimental tests related to the beef tallow fractionation were conducted in laboratory scale based on the work of Cunha *et al.* (2002). The process of dry fractionation, known as "winterization", is carried out in three steps, namely homogenization, fractional crystallization and phase separation by filtration or centrifugation. The homogenization is performed by heating the material

Table 1: Parameter levels of extraction/digestion

Variables	Levels	
Temperatura (°C)	143.4 (4kgf/cm²)	158.7(6kgf/cm²)
Time (min)	30	90
Agitation (rpm)	0 (null)	6 (max)

Table 2: Extraction/Digestion operation

Process	T(°C)	t(min)	Agitation
1	143.4	30	yes
2	158.7	30	yes
3	143.4	90	yes
4	158.7	90	yes
5	143.4	30	no
6	158.7	30	no
7	143.4	90	no
8	158.7	90	no

Table 3: Parameters (factors) and their operation levels considered in the fractionation experiments

Factors	**Levels**	
	-1	**1**
Cooling rate (°C/h)	0.44	0.66
Agitation in crystallization (rpm)	0	20

Table 4: Experimental matrix (2^2)

Process	Agitation during Crystallization	Cooling Rate
1	1	1
1'	1	1
2	-1	1
2'	-1	1
3	1	-1
3'	1	-1
4	-1	-1
4'	-1	-1

Table 5: Pre-fleshing waste Characterization

Analysis	Mass Fraction(%)	Standard Deviation
Volatile Matter	49.37	3.68
TKN	1.54	1.62
Dermal Substances	8.67	9.08
Fats	31.83	11.48
Ash	9.93	3.38
Chlorides	9.70	2.83

until complete melting of triglycerides in the presence of agitation. In the next stage (crystallization), the tallow is cooled until crystallization of saturated triglyceride molecules occurs. The cooling rate and final temperature determine the purity of the crystals and the characteristics of the fractions obtained at the end of the process. The separation is commonly achieved through filtration, in which the filter medium used is a coarse cotton fabric.

In this case, the following variables were considered as fixed parameters: characteristics of the raw material (tallow of a single batch); stirring speed during pre-cooling and crystallization; volume and geometry of the beaker flasks used in the rapid cooling, pre-cooling and crystallization (250 mL); stirring speed of all stages (20 rpm); filter area (380 cm^2); mass/area proportion of diatom earth (0.5 $kg.m^{-2}$); cooling rate in the rapid cooling (60°C.h^{-1}); cooling rate in the pre-cooling (5°C.h^{-1}); final temperature (7°C); and the filtration vacuum of 600 mm Hg. In the fractionation experiments the following parameters were varied: cooling rate (0.66 and 0.44°C.h^{-1}) and stirring in the crystallization step (20 rpm) of the compounds present in the saturated tallow.

The response variables considered to represent the quality of the olein obtained at the end of fractionation were: iodine index and saturated triglyceride fraction, expressed as fatty acid formers. In the case of the iodine index, the aim was to obtain olein containing a maximum amount of compounds with unsaturated chains. The saturated fatty acids fraction was chosen according to the need to obtain an olein with low saturated triglycerides.

Table 3 gives the parameters (factors) used in the process control applied during the tests. The factors can be identified by the coding levels –1, for the lowest level, and +1, for the highest level. Table 4 shows the experimental matrix constructed to determine the tests to be run. The test order was randomized and procedure and equipment remained the same in all tests.

III. RESULTS

A. Characterization of Pre-fleshing Wastes

Table 5 shows the results for the chemical and physico-chemical analyses of the pre-fleshing waste collected from the tannery involved in this study. The same residue was used in the extraction/digestion experiments discussed below. These results are expressed on a wet basis. According to these results, it can be observed that the fatty matter (extractable) is high (31.83% by mass) which indicates a high potential for oil recovery from this residue aiming at its use as a raw material for other industries. It can be noted that almost all of the inorganic material comprises sodium chloride, the salt used in the hide conservation, which is supported by the results found for the total chloride content. The presence of hair and hide in the residue was observed as a protein content of 8.67% (by weight). This protein, after the extraction/digestion step, will be present in two forms, a part in the wastewater as hydrolyzed protein and the other as the protein residue, in its original form.

B. Extraction/Digestion Experiments

The analytical results obtained for the tallow and protein residues from the extraction/digestion step, for a constant time factor of 30 min and variable temperature and agitation factors, are shown in Fig. 4. In this case, the tests were performed at 143.4 and 158.7°C inside the digester, with and without agitation. The graph shows that there is a small variation in the fatty matter in the protein residue; however, there is no clear trend. A drop in the variable from 25.2% to 17.8% is observed when the temperature of the unshaken system is increased, but this trend needs to be further analyzed. The same behavior was not observed for the agitation factor. There was a significant increase in the acidity index of the tallow for the operating conditions of higher temperature with agitation. This represents a considerable drop in quality (8.4 to 19.7), since it indicates the degradation of constituent triglycerides of the tallow. In general, in a short extraction period, the temperature increase and the presence of agitation led to an increase in the acidity index, or further degradation of the material.

Figure 5 shows the results obtained from the extraction/digestion processes where the temperature and agitation are varied as in the previous case, but with the time factor remaining constant at 90 min. It can be observed from Fig. 4 and 5 that the presence of agitation in the system has a considerable negative effect, i.e. it causes a notable increase in the acidity index of the tallow. Therefore, even if a significant gain in the recovery of fatty material can be achieved with the presence of agitation, the losses due to tallow degradation are significant.

Figure 6 shows the results when the shaking was constant and the temperature and time were varied. It is clear from this graph that once again the negative influence of increased time on the acidity index can be noted. By comparing the cases in which the temperature is kept constant a sharp increase in the response variable can be observed. Unlike the previous graphs (Fig. 4 and 5), it is clearly shown through the conditions of constant temperature and constant time that shaking leads to a reduction in the fat content of the protein residue.

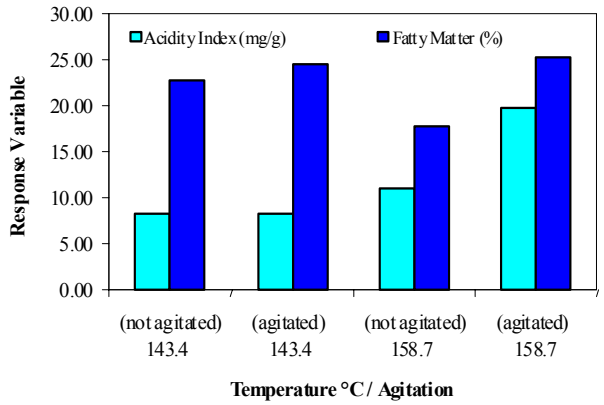

Fig. 4: Extraction/Digestion of tallow for 30 min extraction time.

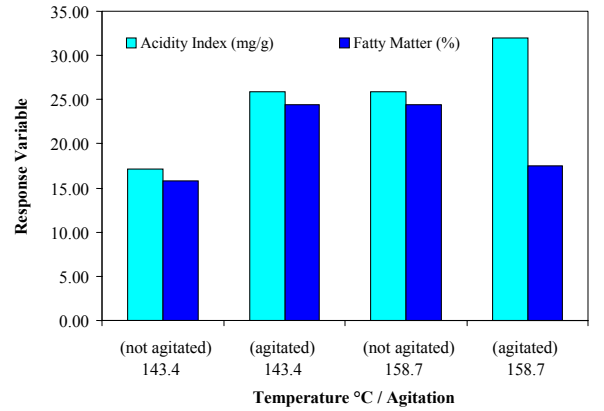

Fig. 5: Extraction/Digestion of tallow for 90 min extraction time.

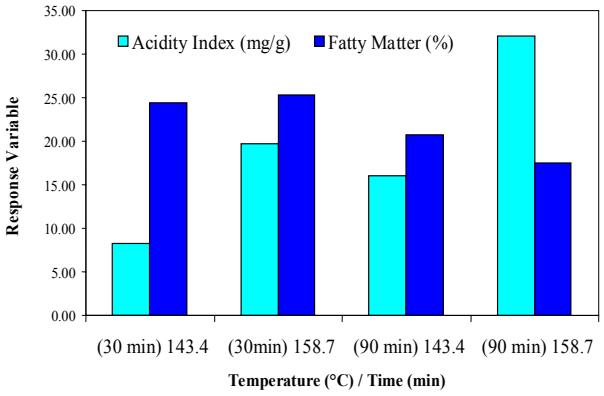

Fig. 6: Extraction/Digestion of tallow for the extraction under agitation.

C. Tallow Fractionation Process (Winterization)

The results obtained from the experimental design for the response variables iodine index and unsaturated fraction in the oleins are given in Table 6. Initial analysis of the data reveals that the values obtained from the repetition processes (case 1 and 1', for example) and for the duplicate samples analyzed are very close. Therefore, the determination of the significance of the results and the best process conditions is only possible through the use of statistical tools of the data collected. The saturated content is calculated from the sum of the mass fractions of the individual saturated fatty acids present in samples. The values for individual fractions are shown in Table 7. The notation used gives the number of carbons present in the fatty acids, C*xx*, and the number of unsaturated bonds present in the carbon chains.

The results for the tests performed to determine the effects of the manipulated variables on the crystallization of the tallow are presented again in Table 8 and 9 as average values of chemical analysis for each duplicate according to the different experimental conditions. It can be observed that the standard deviations calculated for the response variables, when analyzing both the replicates of the experimental conditions and the chemical analysis, have small absolute values. The data collected from the experimental design runs were analyzed statistically to establish the influence of the factors studied on the response variables of iodine index and saturated fraction in the final olein. The influence of parameter was calculated separately.

Table 6: Responses obtained in the application of experiments designed for the tallow fractionation process

Process	Agitation during Crystallization	Cooling Rate	Iodine Number (g/100g)	Saturated Fraction (%)
1	1	1	56.99	17.50
			57.72	17.83
1'	1	1	60.03	17.54
			59.72	17.45
2	-1	1	58.43	17.08
			58.02	17.66
2'	-1	1	57.43	17.87
			57.40	18.00
3	1	-1	58.78	15.35
			58.31	17.40
3'	1	-1	59.50	18.25
			59.92	19.28
4	-1	-1	58.99	18.46
			61.35	20.82
4'	-1	-1	59.43	21.82
			58.93	24.16

Table 7: Mass fractions of fatty acids present in the different oleins obtained from the tallow fractionation

Ester of fatty acids	Tratament			
	1	2	3	4
C14:0 Metil-Miristato	0.50	0.61	0.42	0.70
C16:1 Metil-Palmitoleato	5.12	5.25	4.73	5.63
C16:0 Metil-Palmitato	15.96	15.90	15.92	19.65
C18:2 Metil-Linoleato	4.71	5.65	4.93	4.56
C18:1Metil-Oleato	72.59	71.45	72.77	68.17
C18:0 Metil-Estearato	1.12	1.14	1.22	1.29
Σ Saturados	17.58	17.65	17.57	21.64
Σ Insaturados	82.42	82.35	82.43	78.36

Table 8: Results obtained for iodine index values for the process condition replicates

Process (number)	Iodine Number Test 1	Iodine Number Test 2	Mean	Standard Deviation
1	57,36	59,88	58,62	1,78
2	58,22	57,42	57,82	0,57
3	58,54	59,71	59,13	0,82
4	60,17	60,39	60,28	0,15

Table 9: Results obtained for the saturated fractions for the process condition replicates

Process (number)	Saturated (%) Test 1	Saturated (%) Test 2	Mean	Standard Deviation
1	17,67	17,49	17,58	0,12
2	17,37	17,93	17,65	0,40
3	16,38	18,76	17,57	1,69
4	19,64	21,32	20,48	1,19

The significance of the factors in relation to the two response variables studied were carried out using the program *SPSS 15*, through multivariate linear regression (MLR).

The results for the MLR applied shows that the level of factors in relation to the response variable iodine index are not significant (Sig.> 0.05) within a confidence interval of 95%, when considered together. Other important information can be extracted from the analysis of the model, such as the positive influence of the presence of agitation on the response, when evaluated separately. Similarly, the negative coefficient associated with the cooling rate of crystallization explains the tendency for the iodine index to decrease with an increase in the cooling rate.

The MLR used in the analysis of the influence of the factors on the response variable saturated content shows that the influence of the factors is significant (P <0.05) within the confidence interval of 95%. Furthermore, it can be observed a reduction in the saturated content in the presence of agitation and with a faster cooling rate, as expected.

IV. CONCLUSIONS

The main conclusions which can be drawn from the chemical and physico-chemical analysis of the prefleshing waste are: (a) the fatty matter content of this waste is high (31.83% by mass), which indicates the possibility for natural oil recovery; (b) the values for the total ash and total chloride contents are close, so that almost all of the inorganic material comprises sodium chloride employed to the hide conservation; (c) a large variability in the waste composition was observed, resulting from the non-uniformity of subcutaneous tissue thickness remaining in the hide. The experimental results to quantify the effects of the extraction process parameters allow the following conclusions: (a) the three parameters tested: time, temperature and the presence of agitation all influence the tallow acidity index. This influence is negative when the higher factor levels are used, i.e. more severe conditions tend to increase the degradation of triglycerides. Also, a major influence was observed for the factor time; (b) the influence of the parameters on the variable fatty matter leads to an increase in the extraction efficiency (lower fat levels in the protein residue) when the factor levels are raised. The opposite behavior was observed for the presence of agitation. The experimental results of Winterization leads to the following conclusions: (a) the response variable iodine index showed that the changes in factor levels are not significant within a confidence interval of 95%, when considered together; (b) There is a positive influence of the presence of agitation on the response, when evaluated alone and; the influence of factors on the saturated content is significant within the confidence interval of 95%.

ACKNOWLEDGMENTS

To the companies Curtume Bender S.A. and Anabe Com. e Rep. Ltda. To CAPES for the master's scholarship and to CNPQ for the Edict CTagro 40/2008.

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Received: February 27, 2011.
Accepted: May 18, 2011.
Recommended by Subject Editor Ricardo Gómez.