High Quality Biodiesel and Glycerin from Fleshings*

by

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Abstract

Animal fleshings represent more than 50% of the total waste generated by the leather industry. Generally, the fleshings represent undesirable waste the elimination of which is often connected with expenses. However, this waste contains valuable protein and fat fractions. For this reason, a complex procedure for separation and utilization of both fractions was suggested. The method involves sodium chloride removal with subsequent protein and fat separation. The proposed desalting operation facilitated significant reduction of ash content and consequently the obtained protein fraction has acceptable properties for commercial application. A mathematical model of this process was worked out. The model enables to find the optimal conditions at which the practical desalting should be carried out. The obtained fat is deacidified and the resulting quality product is suitable for direct biodiesel production. The analyses of the prepared biodiesel confirmed high conversion of transesterification reaction and thus optimal purity of the feedstock. Even the sulfur content which could be an issue in fleshings utilization for biodiesel production was low enough to meet the biodiesel standard of quality EN 14 214.

Resumen

Descarnes de origen animal representan el 50% de los desperdicios totales obtenidos en la industria del cuero. En general, los descarnes representan un desecho indeseable asociado comúnmente con solo gastos. Este desecho sin embargo contiene componentes de proteínas y grasas potencialmente valiosos. Por esta razón, un complejo proceso ha sido sugerido para separar y utilizar ambos componentes. Este método consta en la remoción del cloruro sódico acompañado subsecuentemente con la separación de la proteína de la grasa. La propuesta operación con desalinación inicial facilita una reducción del contenido final de cenizas y consecuentemente la proteína obtenida demostró propiedades más aceptables para aplicación comercial. Un modelo matemático para este proceso fue desarrollado. El modelo permite encontrar las condiciones óptimas, bajo la cual la práctica la desalinación debe efectuarse. Por medio de una desacidificación de la grasa así obtenida, la calidad resultante es apta para la producción directa de combustible bio-diesel comercial. Los análisis del biodiesel así preparado, confirmaron la extensa transformación por medio de la reacción de transesterificación, a un componente combustible óptimamente purificado para su uso. Aún el contenido de azufre, que pudiese haber sido contraindicado en la producción de biodiesel basado en el descarne, resultó lo suficientemente bajo para ser aceptable bajo la norma de calidad EN 14214 para biodiesel.

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INTRODUCTION

Animal fleshings represent 50-60% of the total waste generated by the leather industry[1] and at the same time the major proteinaceous solid waste generated by the said industry[2]. They are produced during the fleshing operation to remove flesh and natural fats from the hides and skins. Fleshings can be obtained either before or after the liming treatment, being termed as green fleshings (or pre-fleshings) and limed fleshings, respectively.[3] Green fleshings consist of sodium chloride[4], high water portion (up to 87%) and a balanced content of protein, fat and carbohydrates.[1] The liming treatment alters the fat and protein content. The significant content of nitrogen compounds, i.e. proteins, considerably complicates further utilization of the fleshings since the protein part succumbs to quick decomposition and releases unpleasant odors. For this reason, large quantities of these wastes are subjected to thermal/chemical processes such as incineration and rendering, respectively, which are energetically and time demanding and give economically uninteresting products.[5] The incineration is usually charged and also bears health and environmental risks. The protein content leads to formation of toxic dioxins in the combustion products which makes this way of disposal environmentally disputable.

Several methods of more environmentally friendly processing of the fleshings and their utilization into useful end products were proposed. An alternative to chemical/thermal processes is enzymatic treatment, which is more favorable in terms of environment protection and can be carried out at low cost of energy, low temperature, and no other chemicals are needed. Furthermore, protein products obtained can be used as fertilizers, feed additives or are landfilled in sanitary conditions. [2,5] Another method combines enzymatic and ultrasound treatment.[6] Acid hydrolysis with a mixture of formic and propionic acid was proposed in,[7] with products applicable in livestock/aquaculture feeds. Microbiological method for utilization of hide trimmings, green and limed fleshings from leather manufacturing industries, for the production of value added products like enzymes, is an unconventional methodology compared to existing chemical and thermal methods for the disposal of solid wastes. In,[8] fleshings were used as the substrate for the production of alkaline protease by *Pseudomonas aeruginosa*. The production of a mesophilic protease with solvent stability in solid-state fermentation using a proteinaceous solid waste was studied in.[9] Kumaraguru *et al*.[10] hydrolyzed fleshings with pancreatic enzymes. The hydrolysate, as a protein source, was suggested to be used a feed formulation by mixing with other feed ingredients. According to the above described methods and also to,[1] the most frequent ways of utilization of the fleshing processing products are in agriculture (as fertilizers), as animal feed or for the production of amino acids or enzymes.

Special attention has been paid to the use of the fleshings (especially their lipid part) as an alternative source of energy. The extracted fat can be utilized as boiler fuel for steam production (electric power).[11] Tannery residues such as fleshings, trimmings, splits and effluent sludges were used in the production of biogas.[12] However, the waste material had to be admixtured e.g. with municipal solid waste prior to biogas production, otherwise a poisoning of the bacteria with ammonia may occur which leads to ceasing of the fermentation process.[13] For this reason, this method is not suitable e.g. for tanneries as a direct way of fleshing processing. The economically most interesting[14] and most intensively investigated areas is the possibility of utilization of the fleshings in biodiesel production, as an alternative to current production from vegetable oils. Canola oil is predominantly used in Europe, while soybean oil is prevalent in the United States. The high price of biodiesel (over double the price of diesel) mostly results from the high price of the feedstock.[15] On the contrary, tannery fats represent unpleasant waste the disposal of which is often charged. This makes this waste economically profitable in biodiesel production. However, there are some limitations which should be taken into account to make the biodiesel production economically viable.

The acid value of fleshings (the main waste fat produced by tanneries) usually exceeds 2 mg KOH/g. Therefore their direct processing via alkali-catalyzed transesterification is not suitable since the inorganic alkali catalyst (e.g. potassium hydroxide, sodium methanolate) is spent on free fatty acids (FFA) neutralization and the conversion of the transesterification reaction is not high enough. Moreover, salts formed during this reaction prevent easy separation of the methyl ester and glycerin phase; also simultaneously formed water decreases the transesterification yield.[16, 17] There are several references in literature to using animal fleshings for biodiesel production. In[18] fat was released from sheep pre-fleshings by boiling with water under high speed grinding, separated and used without further refining for the production of fatty acid methyl ethers, using potassium methanolate as a catalyst. Production of biodiesel from fleshing scrap using immobilized Lipase-catalyst was carried out and demonstrated successfully.[19] A technology was presented in[20] using refining melting process for the acid fat pre-treatment and strong organic alkalis as catalysts for the transesterification reaction. Crispim *et al*.[21] produced biodiesel from limed fleshings together with an economical evaluation of the process. The fat was obtained from the fleshings by digestion in water at 90°C, and refined by extraction with *n*-hexane. However, the pre-treatment procedure was stated to require further optimization to reduce investments and energy costs. Isler *et al*.[22] reported biodiesel production from raw fleshing oil using sodium hydroxide as transesterification catalyst. However, it was not known from the study, how the oil was separated from the original fleshings nor was described any possible pre-treatment prior to transesterification. A pre-treatment of the

acid fleshing oil using sulfuric acid and methanol was carried out in.[23] After reducing the FFA level of the fleshing oil to less than 1%, they performed the transesterification reaction with various alkaline catalysts (sodium and potassium methanolates, sodium and potassium hydroxides). The effects of catalyst type, catalyst amount and molar ratio of alcohol to fat on the fuel properties of produced methyl esters were investigated. The measured fuel properties of the fleshing oil methyl ester (FOME) were compared to EN 14214 and ASTM D6751 biodiesel standards. According to results, the cold flow properties of FOME should be improved and the sulfur content of FOME should be investigated in detail.

The overview given above shows that current attempts of processing animal fleshings into valuable products are mostly targeted either on the protein or fat fraction. However, from the economical but also environmental point of view it is advantageous to produce both fractions simultaneously. The protein content can be processed to gelatin or biostimulants[24] and biodiesel from the fat fraction is also very interesting. Therefore, complex technological procedures for the processing of fleshing wastes into added-value products should have the highest potential. Very few complex procedures have been reported in literature or by the industry, with little reference to the actual application of the products. Taylor *et al*.[25] presented a technology of enzymatic treatment of pigskin and cattlehide fleshings with several commercial enzymes. The enzymatic treatment gave protein and fat fractions, which were subsequently separated. The fat fraction had relatively low content of FFA and was meant for further processing. The protein fraction was stabilized with acid to eliminate the protein decomposition products. Naumann[26] subjected untreated fleshings to maceration, acidification with mineral acid to pH 2, and subsequent pumping under atmospheric pressure through a heat exchanger. After depressurizing, a hot mixture of 10–15% glutine solution, insoluble matter and fat was obtained and separated in a centrifuge. The fat had FFA content of 5–8% and was found suitable for splitting into glycerin and fatty acids. The insoluble matter, containing keratin, meat and some salts, can be dried and used as a component for animal feed. The Coming Industria e Comercio de Couros, (Brazil) presented their technology of the rendering of fleshings.[27] The fleshings are rendered on site to produce oils and protein, in conjunction with bones from the abattoirs. In the first step, the solids are macerated into small pieces. These pieces are rendered at 125ºC, to form liquid tallow and cooked recovered protein. These products are separated by gravity, and extruded from the recovered protein by screw pressing. The company reports that the recovered oil is used for pharmaceutical purposes and personal care, food additives, shampoo and soap manufacture. The lower grades are used in tyres for cars and biodiesel, and can be used as boiler fuel. The sterilized bone/protein meal product is used as feed for chickens, pigs and fish.

The complex technologies face several problems. One of them is high content of sodium chloride in the fleshing material. While it does not cause trouble in biodiesel production since most of the salt remains in the protein fraction, it becomes undesirable if also the protein is meant for commercially interesting products. For example, in some cases the use of enzymatic hydrolysis gives an arduously separable mixture with considerably lower added value than in the case of pure protein. For this reason, it is necessary to design a complex technology with special focus on the maximal purity of the obtained products.

The main objective of our study was to propose a complex technology for the processing of the pre-fleshings with regard to utilization of both fractions, i.e. protein and fat, to products with high added value. Our study deals with pre-treatment of raw fleshings with special attention paid to the achievement of suitable quality of the resultant gelatin or protein hydrolysate and refined fat. The effect of pretreatment procedure on the properties of crude products is discussed and the pre-treatment technology is presented. We also present economical and technological model of the desalting which enables us to determine suitable technological conditions to provide maximal profit.

THEORY

The suggested technology consists of desalting, deproteinization, refining melting and extraction deacidification processes. The purpose of the named processes is to prepare pure feedstock for consequent biodiesel production. Costs of this pre-processing must be lower than the price of vegetable oils to make the technology competitive on the market. To meet this target we worked out a mathematical model of desalting. This model is suitable for the optimization of the named process. The fleshings are mixed with cold water and small pellets are created. Mathematical model of desalting describes the diffusion of sodium chloride from the inner space of the pellets into the surrounding washing water.

Equation (1) together with boundary conditions (1a – 1e) represents the model itself. We received the dimensionless form of the model by introducing dimensionless parameters (2a – 2d). The solution of this dimensionless model is presented by equations (3 – 6). Equation (3) represents a non-stationary concentration field of sodium chloride in the pellets, expression (5) describes concentration of sodium chloride in the surrounding washing water and according to equation (6) the efficiency of desalting can be calculated. The q_n are roots of equation (4) and *Na* stands for the ratio of volume of washing water to the volume of fleshings; the parameter *Na* is so-called soaking number.

$$\frac{\partial c(r,\tau)}{\partial \tau} = D\left[\frac{\partial^2 c(r,\tau)}{\partial r^2} + \frac{2}{r}\frac{\partial c(r,\tau)}{\partial r}\right] \qquad \begin{matrix}\tau > 0 \\ 0 < r < R_1\end{matrix} \tag{1}$$

$$\frac{\partial c(0,\tau)}{\partial r} = 0 \tag{1a}$$

$$c(r,0) = c_p \tag{1b}$$

$$c_0(0) = 0 \tag{1c}$$

$$c(R_1,\tau) = \varepsilon c_0(\tau) \tag{1d}$$

$$-SD\frac{\partial c(R_1,\tau)}{\partial r} = V_0\frac{\partial c_0(\tau)}{\partial \tau} \tag{1e}$$

$$C = \frac{c_p - c}{c_p};\ C_0 = \frac{\varepsilon c_0}{c_p};\ Fo = \frac{D\tau}{R_1^2};\ R = \frac{r}{R_1} \tag{2a,b,c,d}$$

$$C = \frac{Na}{\varepsilon + Na} + \frac{2Na}{3\varepsilon}\sum_{n=1}^{\infty}\frac{\frac{\sin(Rq_n)}{Rq_n}\exp(-Foq_n^2)}{\sin(q_n)\left[\frac{1}{q_n} - \frac{Na\cdot q_n}{3\varepsilon} - q_n\right] - \cos(q_n)\left[1 + \frac{Na\cdot q_n^2}{3\varepsilon}\right]} \tag{3}$$

$$\operatorname{cotg}(q_n) = \frac{Naq_n}{3\varepsilon} + \frac{1}{q_n} \tag{4}$$

$$C_0 = \frac{\varepsilon}{\varepsilon + Na} - \frac{2Na}{3\varepsilon}\sum_{n=1}^{\infty}\frac{\exp(-Fo\cdot q_n^2)}{\left[1 - \frac{Na\cdot q_n^2}{3\varepsilon} - q_n^2\right] - \cot(q_n)\left[q_n + \frac{Na\cdot q_n^3}{3\varepsilon}\right]} \tag{5}$$

$$y = \frac{V_0 c_0}{c_p V} = \frac{NaC_0}{\varepsilon} = \frac{Na}{\varepsilon + Na} - \frac{2Na^2}{3\varepsilon^2}\sum_{n=1}^{\infty}\frac{\exp(-Fo\cdot q_n^2)}{\left[1 - \frac{Na\cdot q_n^2}{3\varepsilon} - q_n^2\right] - \cot(q_n)\left[q_n + \frac{Na\cdot q_n^3}{3\varepsilon}\right]} \tag{6}$$

The main unit processing costs of the desalting process involve a sum of electric power unit consumption necessary for mixing and the overall unit consumption of washing water.

$$N = K_E P\tau + K_v V_v(\tau) \tag{7}$$

The consumption of washing water (V_v) is an implicit function of time (τ) that is calculated according to equation (6) for specific required efficiency (y).

EXPERIMENTAL

Materials

The pre-fleshings were obtained in local tannery (Tarex, s.r.o., Otrokovice, Czech Republic), their properties are listed in Table I. Demineralised water was used in all experiments. HYDRANAL Solver (Crude) oil and HYDRANAL Composite 5 were used for water content determination and were purchased from Sigma-Aldrich. Sodium chloride and silver nitrate used in argentometry were obtained from IPL, s.r.o. and both were of analytical grade. All chemicals used in various analyses were of analytical grade. Solution of tetramethylammonium hydroxide (TMAH, 25 %w/w in methanol) was of electrotechnical grade and was purchased from Sachem, Inc. Methanol was obtained from IPL, s.r.o. and was of analytical grade.

Analytical Methods

Dry matter was determined according to the standard EN ISO 662, acid value according to the standard EN ISO 660, saponification value according to the standard ISO 58 8763, ash content according to the standard ČSN 58 8760, Total Kjeldahl Nitrogen (TKN) according to the standard ISO 1871, gel strength according to the AOAC 948.21 (all samples were extracted with petroleum ether prior this analysis in the same manner as for fat content determination – see the procedure below), content of glycerol and mono-, di- and triglycerides in the final biodiesel according to the standard EN 14 105, content of sulfur according to the standard EN ISO 20 846.

The fat content was determined by samples extraction with petroleum ether in Soxhlet apparatus. The extraction was repeated ten times in each analysis.

Water content was determined by Karl Fischer titration on volumetric titrator Mettler-Toledo V30.

The sodium chloride content was determined by argentometric titration, the equivalence point was visualized either by the Mohr method or was calculated from conductometric titration curve which was recorded with the Schott handylab LF12 conductometer.

Protein Separation without Prior Desalting

Fresh pre-fleshings (marked as I in Table I) in the amount of 3 kg were loaded into reactor together with 3 kg of demineralised water. The reaction mixture was slowly stirred and heated to the 80 °C. This temperature was kept during subsequent 3 hours. After this period the reaction mixture was settled in half an hour and it was then separated into two layers – the upper, refined fat layer and the lower, water gelatin layer. Next, the water layer was filtered through filtration cloth (four time folded filtration cloth with mesh size 150 μm) and was dried at laboratory temperature.

Desalting and Protein Separation

Fresh pre-fleshings (3 kg, marked as II in Table I) were loaded into reactor together with 12 kg of demineralised water. The reaction mixture was intensively mixed at laboratory temperature for one hour. After this period, the water layer (lower phase) was separated from the fat layer (upper phase) and samples were taken for sodium chloride content determination. This presents one cycle of decantation washing. In the next cycle, the 12 kg of demineralised water were added to the fat layer which came from previous cycle and the procedure was repeated. Totally, four cycles were done.

TABLE I
Properties of raw pre-fleshings.

	Unit	I		II		III	
		Value	S.D.	Value	S.D.	Value	S.D.
Dry matter	[% w/w]	46.4	2.5	49.3	2.6	58.6	2.0
Acid value[a]	[mg KOH/g]	15.5	0.7	1.56	0.16	15.8	0.2
Saponification value[a]	[mg KOH/g]	140.7	3.1	184	12	183.4	1.4
Ash content[a]	[% w/w]	6.1	0.3	5.8	0.6	2.5	0.4
TKN[a]	[% w/w]	2.20	0.07	1.23	0.06	3.47	0.05

Values are means from at least three replicates per sample
[a] values are expressed on moisture free basis

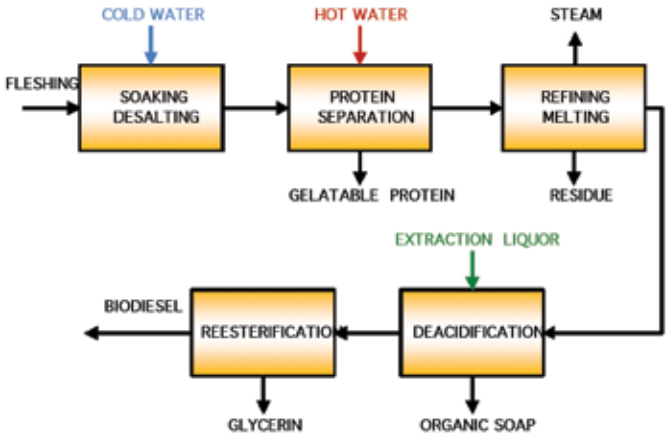

Figure 1. Simplified scheme of pre-fleshings processing technology.

2 kg of the final washed fat layer were loaded in the reactor, 1 kg of demineralised water was added and the reaction mixture was heated to 80 °C and slowly stirred. This temperature was kept for two hours and the reaction mixture was then settled during half an hour. Three products were obtained: refined fat (upper phase), transition layer – a mixture of unrendered fat, together with refined fat and water (gelatin) layer – this product was collected at the boundary between upper and lower phase and the third product – gelatin (lower, water phase). The transition layer was subsequently added to equal volume of water and boiled for 30 minutes. After this time, the reaction mixture was separated to upper (fat) phase and to lower (gelatin) phase.

TABLE II
Properties of gelatin obtained by different separation processes.

	Unit	Experiment without desalting		Experiment with desalting	
		Value	S.D.	Value	S.D.
Ash content[a]	[% w/w]	46.42	0.13	3.36	0.07
TKN[a]	[% w/w]	5.48	0.34	14.47	0.12
Gel strength[b]	[g Bloom]	32	3	158	2
Fat content[a]	[% w/w]	10.9	0.8	12.1	1.4

Values are means from at least three replicates per sample
[a] values are expressed on moisture free basis
[b] gel strength was measured after fat extraction

Biodiesel Synthesis from Refined Fat

The refined fat (see Table V) obtained by protein separation was extracted with methanol (50 % w/w) which contained equimolar amount of TMAH (with respect to free fatty acids content). The mixture was allowed to settle and the extract and deacidified fat were collected. 650 g of the final deacidified fat were then loaded into glass reactor with 150 g of methanol and 31 g of TMAH methanolic solution. The reaction mixture was then refluxed and stirred for two hours. Next, it was transferred into a separatory funnel where the clear separation of hot glycerin and biodiesel (methyl ester) layers was observed. The layers were allowed to cool at laboratory temperature and were then separated. The methanol present in biodiesel layer was further distilled in a vacuum rotary evaporator and a sample of this raw biodiesel (i.e. the distillation residue) was subjected to an analysis.

RESULTS AND DISCUSSION

The utilization of pre-fleshings is complicated by the fact that this feedstock is highly inhomogeneous. It is well documented in Table I, which offers comparison of pre-fleshings characteristics from pigskin collected in one tannery in different times within approximately a half year period. The dry matter content fluctuated around 50%, the acid value was highly dependent on the actual season (the fat decomposition is much faster in summer due to higher outer temperatures). In addition, the properties like ash and protein content (expressed as total Kjeldahl nitrogen – TKN) are largely dependent on the raw skin composition and also on the manufacture process in the specific tannery. As a result, the ultimate goal of the utilization of this feedstock is to design the technology in a robust way, so it is able to be easily adapted to the actual feedstock composition and consequently to ensure acceptable fluctuation of the final products quality.

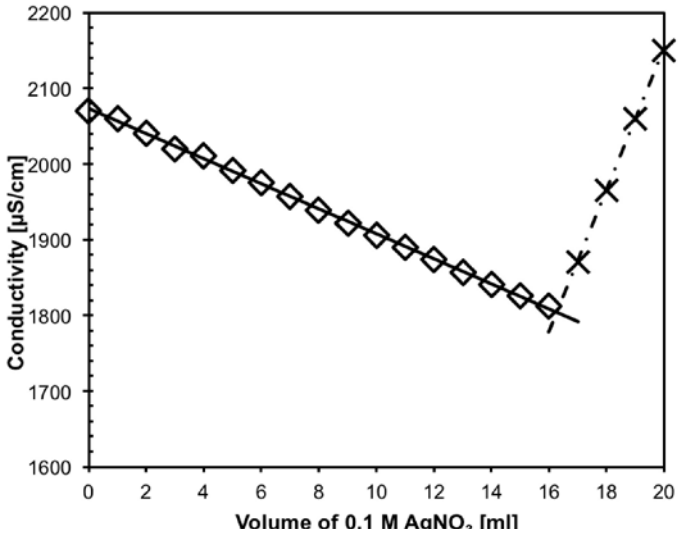

Figure 2. An example of typical conductometric titration curve for chloride content determination.

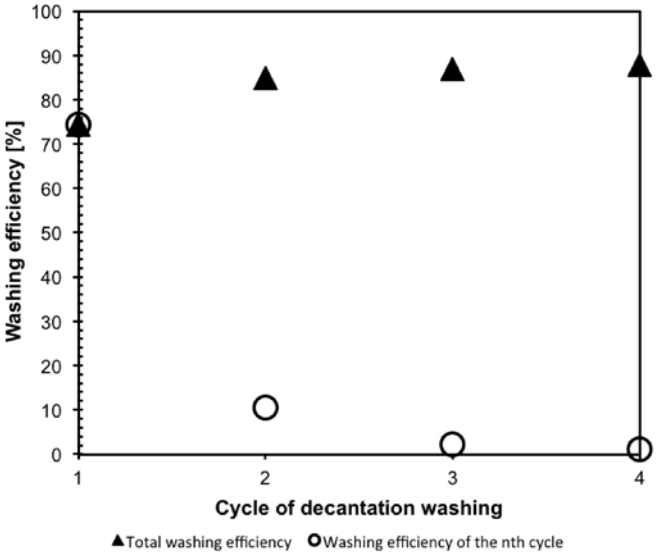

Figure 3. Efficiency of desalting during decantation washing.

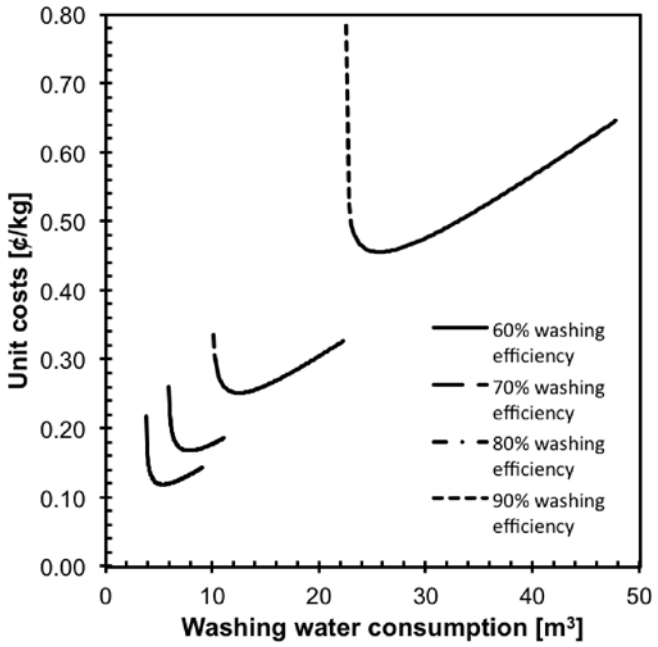

Figure 4. Dependency of desalting unit costs on washing water consumption.

TABLE III
Dry matter content of the spent washing water.

Cycle of decantation washing	1	2	3	4
Dry matter of washing water [% w/w]	0.530	0.214	0.079	0.034

TABLE IV
Input parameters of the desalting costs simulation.

Parameter	Value	Unit	Parameter	Value	Unit
ε	0.5	[1]	K_V	0.5	[USD/m³]
V	5	[m³]	P	40	[kW]
D	10^{-9}	[m²/s]	R_1	5	[mm]
K_E	0.07	[USD/kWh]			

The analyses illustrate that the pre-fleshings are composed of four main components – fat, protein, water and also hair. In addition, a considerable amount of sodium chloride is usually present, since this salt is commonly used as a preserving agent. The fat and protein represent valuable constituents; however, it is necessary to separate them before their further utilization. If the fleshings fat fraction is meant for biodiesel production, the impurities – namely sodium chloride, fibrous tissue, free fatty acids (FFA) and water – have to be removed or drastically reduced. The proposed complex technology therefore consists of desalting, protein separation, refining melting and extraction deacidification processes. Figure 1 shows simplified scheme of the technology. In the first step, sodium chloride is removed by washing with cold water, with the subsequent separation of protein fraction via extraction with hot water. In the next step, refining melting is employed during which the possible moisture is removed and quality of fat and protein separation is further increased. The refined fat is then subjected to extraction in ammonia, or possibly alkyl-ammonia methanol solution, which removes the free fatty acids. It should be noted that the deacidification step can be easily adjusted to the actual content of free fatty acids and therefore also feedstock with fluctuating acid value can be processed. The resulting high quality fat is ready to be used directly for biodiesel production. By-products of the described pre-treatment of waste fats are sodium chloride, gelatin of utilizable quality and the refining melting residue which can be used as a feed or reprocessed together with fresh pre-fleshings. The methanolic extract contains organic-ammonium, or possibly N-alkylammonium soaps. After methanol removal and dehydration, these soaps give respective amides of fatty acids which can serve e.g. as lubricants during plastic extrusion.

All separation experiments were done at a larger scale (nearly pilot-plant) in order to test the practical (industrial) potential of the processes. Firstly, the protein separation by water extraction was tested without prior desalting. The properties of

the final gelatin which was obtained by this procedure are listed in Table II. As can be seen, the ash content is enormously high. Also the fat which remains in the gelatin (approx 11%) must be removed from the final product. However, even after fat removal (done by extraction with solvent) the gel strength of the final gelatin is too low. This is of course caused by the ash content and this fact prevents practical application of such product. The ash content can be substantially reduced e.g. by utilization of ion exchange resins,[28] nevertheless the costs of such process are quite high especially when the ash content is high.

The preliminary analyses showed that the ash in the obtained gelatin was predominantly consisted of sodium chloride which originated from hide preservation operation. In order to decrease the amount of the sodium chloride, another experiment was conducted. The pre-fleshings were desalted by decantation washing with water prior the gelatin extraction. The pre-fleshings contained similar amount of ash compared to those used in the previous experiment (compare feedstock I and II in Table I). As can be seen in Table II, this procedure is able to substantially reduce the amount of ash in the final gelatin. As a result, the gel strength of the final product (after fat extraction) increased significantly, reaching the Bloom value of 158. Such gelatin represents a commercially interesting product. The fleshings protein utilization is of course not limited to gelatin. The obtained protein fraction can be further hydrolyzed and a variety of final products can be prepared – e.g. fertilizers or biostimulants. In addition, fat extraction from the crude protein fraction is usually not necessary in these agricultural applications.

TABLE V
Properties of refined fat.

	Unit	Value	S.D.
Dry matter	[% w/w]	97.0	0.4
Acid value[a]	[mg KOH/g]	13.16	0.17
Saponification value[a]	[mg KOH/g]	186.0	0.5
Ash content[a]	[% w/w]	0.18	0.05
TKN[a]	[% w/w]	<0.1	
Water content (KF titration)	[mg H_2O/g]	5.02	0.05

Values are means from at least three replicates per sample
[a] values are expressed on moisture free basis

TABLE VI
Properties of crude biodiesel from pre-fleshings.

	Unit	Achieved value	S.D.	limit prescribed by EN 14 214
Monoglyceride content	[% w/w]	0.497	0.011	0.8
Diglyceride content	[% w/w]	0.063	0.004	0.2
Triglyceride content	[% w/w]	<0.05		0.2
Free glycerol	[% w/w]	0.049	0.001	0.02
Total glycerol	[% w/w]	0.185	0.004	0.25
Sulfur content	[mg/kg]	8.3	0.4	10

Values are means from at least three replicates per sample

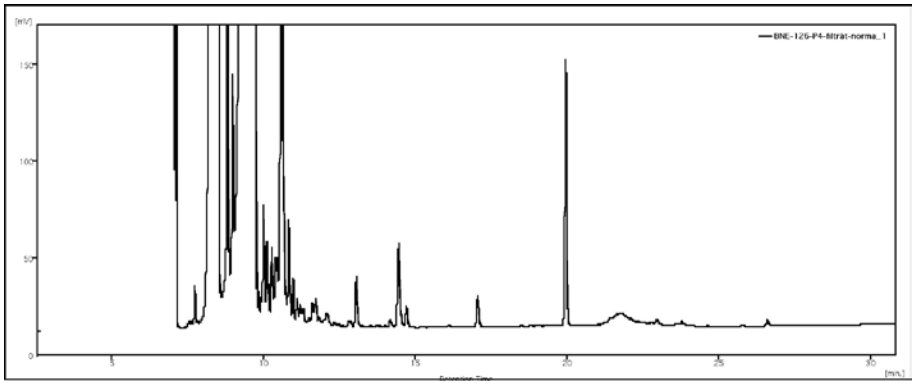

Figure 5. Chromatogram of crude biodiesel from pre-fleshings. Peak marked "A" belongs to glycerin, peaks marked "C" belong to monoglycerides and peaks marked "D" to diglycerides.

The efficiency of each washing cycle of pre-fleshings desalting was evaluated. Figure 2 illustrates typical conductometric titration curve from which the sodium chloride content was calculated. As can be seen, the indication of equivalence point by conductometry was clear. Since the sodium chloride content was determined also in the ash of the raw pre-fleshings, we were able to calculate the overall process efficiency. The progress of the desalting efficiency is summarized in Figure 3. As is shown, the most efficient was the first washing step during which 74% of the present salt was washed out from the feedstock. The second step increased the overall washing efficiency nearly to 85%. During the third and fourth step, only 2% and 1%, respectively, from the initial amount of salt were washed out. It therefore makes sense to perform only first two washing steps from the economical point of view. The dry matter of the spent washing water was determined as well. The results (Table III) confirm that practically only salt is washed out during the desalting and thus the losses of valuable protein and fat are negligible. We can conclude that the described desalting process presents efficient and simple method for significant lowering of the ash content of pre-fleshings protein fraction.

The unit processing costs of the desalting vary according to the design of this process. As was discussed in the Theory section, there is a relationship between water and electric power consumption (see equation 7). Figure 4 illustrates this dependency of unit processing costs on the water consumption and total washing efficiency calculated according to the suggested model. The input parameters of the unit costs simulation are summarized in Table IV. The figure documents that all cost functions have a minimum whose position is strongly dependent on washing water consumption. As a result, the suggested model can be helpful in the desalting process design and the practical desalting is advantageously performed at computed optimal conditions.

The second product of the separation process is refined fat. Probably its most perspective utilization lies in the area of biodiesel production[14] as was discussed in the introduction. If the biodiesel is to be used in standard diesel engines, it has to meet strict quality standards, e.g. EU standard EN 14 214 or US standard ASTM D6751. This means that also the feedstock must be of high purity in order to achieve high quality biodiesel. The properties of typical refined fat obtained from the described separation process are listed in Table V. The dry matter is very high, in fact the fat should not contain practically any water since the water can significantly reduce the conversion of transesterification reaction. The dry matter measurements are not precise enough in this case and therefore the water content was determined by Karl Fischer titration. Table V shows that the typical amount of water in the refined fat is approximately 0.5%. In the suggested process (see Figure 1) this resulting water is removed during deacidification step or its content can be reduced by the preceding fat rendering.

LIST OF SYMBOLS

c	Concentration of NaCl in pre-fleshings	[kg m^{-3}]
C	Dimensionless concentration of NaCl in pre-fleshings	[1]
c_0	Concentration of NaCl in the washing water	[kg m^{-3}]
C_0	Dimensionless concentration of NaCl in the washing water	[1]
c_p	Initial concentration of NaCl in pre-fleshings	[kg m^{-3}]
D	Effective diffusion coefficient of NaCl in pre-fleshings	[m2 s^{-1}]
Fo	Dimensionless time	[1]
K_E	Unit price of electricity	[USD/kWh]
K_V	Unit price of water	[USD/m^3]
N	Unit processing costs	[USD/kg]
Na	Soaking number	[1]
P	Input power of the stirrer system	[kW]
r	Space variable	[m]
R	Dimensionless space variable	[1]
R_1	Radius of pre-fleshings pellet	[m]
S	Area of pre-fleshings pellet	[m^2]
V	Volume of the pre-fleshings	[m^3]
V_0	Volume of the washing water	[m^3]
V_V	Consumption of washing water	[m^3]
y	Washing efficiency	[1]
	Greek symbols	
ε	Pre-fleshings porosity	[1]
τ	Time	[s]

Other symbols are explained directly in the text.

We have processed several batches of different pre-fleshings and the properties of the most of all of them achieved similar values as are listed in the table. However, there were few batches which had lower dry matter (around 90%). In such case, the dry matter and consequently the purity of the fat were increased to the desired level by repeating of the

separation process or by simple reheating of the fat (as is also described in Figure 1 – refining melting operation). Also the boiling of the fat with water as is described in the experimental section can facilitate the water removal. These findings were confirmed by the water content determination employing Karl Fischer method. At a larger scale, the transition layer could be advantageously treated in the same manner, i.e. together with the fresh pre-fleshings (so it is repeatedly rendered) as was mentioned above. The only parameter which had varied widely between refined fat batches was the acidity value (see also Table I). This parameter shows the content of free fatty acids (FFA) and it consequently indicates the degree of pre-fleshings deterioration. However, the FFA removal is facilitated during deacidification step and can be easily adapted to the actual acid value of the refined fat. The presence of protein fraction was not detected in the refined fat. To summarize, the composition of the refined fat (Table V) shows that the separation process is able to remove the protein fraction from the refined fat, substantially reduce ash and water content and consequently the obtained product is suitable for further processing to biodiesel.

The refined fat, the properties of which are listed in Table V, served as a feedstock for biodiesel synthesis. Its transesterification was performed after FFA removal in the deacidification step (see the scheme in Figure 1). The excess of methanol was removed from the obtained biodiesel by means of vacuum distillation and the crude biodiesel was then subjected to analyses. Table VI lists its properties related to the transesterification conversion and the sample chromatogram is presented in Figure 5. As can be seen, practically no fat (i.e. triglycerides) and very low amount of reaction intermediates (i.e. mono- and diglycerides) are present in the product and consequently the prepared biodiesel fulfils strict requirements of the EU standard EN 14 214 regarding to the reaction intermediates content. Furthermore, this means that the transesterification conversion was very high and consequently the feedstock was suitably refined since alkali catalyzed transesterification is particularly sensitive to FFA and water content.[16,17] The higher content of glycerin in the biodiesel was caused by the fact that we analyzed a crude product which was not further purified, e.g. by common water washing procedure.[17] The amount of sulfur present in the crude biodiesel was also determined because it was reported that sulfur content can present an issue in fleshings conversion into biodiesel.[23] The results (Table VI) proved that pre-fleshings treated by the suggested technology are able to fulfill the EN 14 214 requirements which limits the maximal amount of sulfur in biodiesel to concentration of 10 ppm.

Conclusion

A technology for complex processing of tannery fleshings has been proposed. The technology comprises several pretreatment steps. The purpose of these steps is to achieve separation of valuable fleshings contents – particularly protein and fat. In the first step, the fleshings are washed with cold water. As was shown, this process facilitated substantial reduction of fleshings sodium chloride content. As a result, protein fraction with low amount of ash and appropriate gel strength was obtained. Furthermore, the losses of protein and fat during the desalting operation were negligible. A mathematical model of this process was worked out. The model enables to find the optimal conditions at which the practical desalting should be carried out.

The next step leads to the separation of the named valuable fractions. It was observed that despite the fluctuating composition of the pre-fleshings, the quality of the final refined fat is practically constant. The only parameter which varied significantly was the free fatty acid content. However, subsequent deacidification can be easily adjusted to ensure practically complete removal of these free fatty acids. The refined and deacidified fat obtained by means of the said operations is suitable as feedstock for direct biodiesel production with comparable quality to conventional vegetable oils. The pre-fleshings were tested for biodiesel production and the results showed that the technology was able to ensure high conversion of transesterification reaction and consequently the prepared biodiesel met strict biodiesel quality standard EN 14 214 related to content of reaction intermediates which is the main indicator of the overall biodiesel quality. Moreover, the sulfur content issue was also investigated; it was found that the sulfur content in biodiesel from pre-fleshings was within the limits of the said standard.

To conclude, the proposed technology was able to convert the fleshings into several products with promising added value. The fleshings fat content was refined to a quality level suitable for direct biodiesel production at costs which are competitive to prices of conventional biodiesel feedstock (i.e. vegetable oils). The gelatin obtained from the protein fraction had acceptable quality for commercial application. Moreover, the protein fraction can be easily processed to biostimulants or fertilizers suitable for agricultural use.

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