Studies on Use of Fish Oil Methyl Ester for Chamois Leather Manufacture

by

N. Vedaraman[1]*, K.V. Sandhya[2], V. John Sundar[3], K. C. Velappan[1], C. Muralidharan[3]

[1]*Chemical Engineering Division, Central Leather Research Institute*
Adyar, Chennai-600 020, India

[2]*Chemical Technologists, St. Peters Engineering College*
Avadi, Chennai

[3]*Tannery Division, Central Leather Research Institute*
Adyar, Chennai-600 020, India

Abstract

Chamois leathers are conventionally made using fish oil. The fish oil is high in viscosity and due to this it takes a longer time for the oil to penetrate into the skin. Also, a significant quantity of oil is wasted in the drum during chamois tanning. In the present work, with the objective of study to reduce the fish oil viscosity, trans-esterification of fish oil was carried out using methanol with sulphuric acid as the catalyst. The esterified product, fish oil methyl ester, was used for tanning goat skins. The chamois leather thus obtained was tested for different properties such as sink test, water absorption and strength. This study shows the chamois leather made using fish oil methyl ester has better properties compared to conventional chamois with additional benefit of reduction in fish oil usage up to 25% on the total offer.

Resumen

Cueros al Chamois son convencionalmente fabricados utilizando aceite de pescado. El aceite de pescado es alto en viscosidad, y por esto el aceite toma un largo tiempo en la penetración a través de la piel. También una significante cantidad del aceite se desperdicia en el fulón durante el curtido convencional al chamois. En el presente estudio para reducir la viscosidad del aceite de pescado, trans-esterificación del aceite de pescado se efectuó, utilizando metanol con ácido sulfúrico como catalizador. El producto esterificado, metil ester de aceite de pescado, se utilizó para curtir pieles de cabra. El cuero Chamois, así obtenido se comprobó favorable en sus diferentes propiedades tales como son la prueba del hundimiento, absorción de agua y tenacidad. Este estudio demostró que un cuero curtido con el ester metílico de aceite de pescado, posee mejores propiedades que el proceso convencional del cuero, con la ventaja adicional de reducción de hasta de un 25% de la oferta total de aceite.

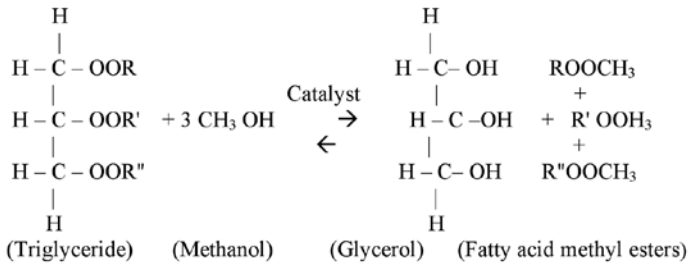
* Corresponding author e-mail: nvedaraman@yahoo.co.in, Tel: 0091-44-24916706
Manuscript received May 3, 2012, accepted for publication August 29, 2012

INTRODUCTION

Millions of animal skins are processed annually worldwide for production of Chamois leather and it is a type of porous leather that possesses exceptional absorption.[1] properties. Chamois leather can absorb water more than at least two times on its weight The water absorption properties arise from the effect of the oil matrix holding the protein structure apart, allowing it to interact with water.[2] It is extremely soft, flexible and good absorbent. Generally bulk of chamois leather is used as wash leather for cleaning windows, car bodies and similar surfaces where its softness and high water absorption are of importance. As wash-leather for cleaning, it must be very soft so that it does not scratch the surface to be cleaned. These leathers must wet back immediately on immersion in water in-order to discard the dirt and absorb a large bulk of water to wet and clean the surface. The dirt cleaned should be easily removed from the leather by simple rinsing and wringing in water. It is important that wet leather can be easily wrung out by hand. On subsequent drying it should retain these properties for repeated use.

Indian goat skins are considered suitable material and the skins having defects such as hair-slip, scratches and other such damages on the grain side are generally selected for making chamois leather.[3] The traditional method of making chamois leather is to impregnate the skins/splits with fish oil and then hang them in air or warm stoves to allow oxidation of the oil to occur. This oxidation process generally takes long time and in some cases, uses various oxidizing agents such as sodium per-carbonate and hydrogen peroxide having been attempted to shorten the time of oxidation tanning process.[4] A new approach on usage of ozone to oxidize oil treated leather has been found to reduce the oxidation time to 60 min from 10- 12 days without any impairment in quality was reported in the literature.[5] Fish oils are not only used in leather industry for oil tanning, in-addition, fish oil such as menhaden oil and cod oil are used for fat-liquoring leather.[6] Studies were also been reported in the literature on chamois tanning using modified fish oil to minimize the odor and improve the water absorption characteristics, by esterification of fish oil with various grades of poly ethylene glycol.[7] The fish oil was substituted by rubber seed oil in the chamois leather tanning in-order to avoid the odor of fish oil was also reported.[8] The viscosity of vegetable and marine oils is generally high and fish oils are tacky in nature because of this a significant quantity of oil goes waste during chamois leather manufacture. During chamois leather processing, a significant quantity of fish oil adhere to the processing drum and the un penetrated oils that remains on the surface of oil tanned skins is washed and discharged as waste.

Alkyl esters of oils are made by simple process called trans-esterification. Trans-esterifications is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. The process has been widely used to reduce the viscosity of triglycerides. If methanol is used in the above reaction, it is termed methanolysis. The reaction of triglyceride with methanol is represented by general equation:



In the present study, to reduce the viscosity of fish oil, trans-esterification of fish oil has been made using methanol and sulphuric acid as catalyst. The esterified product, i.e. fish oil methyl ester was then used for tanning goat skin.

EXPERIMENTAL

Procedure for Trans-esterification

Material Used: Raw Fish Oil commercial grade, (iodine value 135, acid value 15), Sulphuric Acid (AR grade, 98% (min)), Methanol, sodium bi-carbonate (AR grade)

Method: 100ml of raw fish oil, 30ml of methanol and 1ml of sulphuric acid was taken in a 500 ml 2 neck round bottom flask. A condenser fitted with a guard tube having calcium carbonate with cotton to prevent moisture entering into the reaction flask from atmosphere. The contents in the flask was stirred using magnetic paddle at a temperature of 65 ºC to 70 ºC for 16 hours. Then the contents were transferred in to a separating funnel and allowed to separate into two layers over 2 hours. The glycerol layer separates at the bottom and fish oil methyl ester layer rests at the top of separating funnel. Then the top ester layer was washed with sodium bi-carbonate solution to neutralize the free acid. This product was then dried in oven for 3 hours to remove traces of moisture and weighed. The fish oil and fish oil methyl ester were analyzed for different physical and chemical properties such as iodine value, acid value, and kinematic viscosity as per the standard methods. The fish oil methyl ester prepared by trans-esterification process was then analyzed for its contents using Gas Chromatography (GC).

GC analysis: The GC 1000 series system was used to identify composition of fish oil and fish oil alkyl ester. The GC conditions are: Column used-SGE S/N, FID detector, Carrier gas Nitrogen, Temperature programming: 160°C-hold for 0 min. 4°C/min till 210°C, hold for 6 min. The ester was dissolved in solvent and injected into the column at a split ratio of 1:11.

Chamois Leather Processing using Fish Oil and Fish Oil Methyl Ester:

The following procedure was adopted for processing animal skins into chamois leather using following chemicals and fish oil and fish oil methyl ester.

Raw material: Wet salted goat skins (average weight 1 kilogram per skin) having good substance and free from flesh defects were taken for processing. The skins were cut into halves and processed by the conventional method.

Soaking: The goatskins were trimmed and soaked in a paddle for 2 hours the skins were given a change of water and the paddle was run for another 30 mins after which they were piled for draining and weighed (soaked weight).

Unhairing by painting: The skins was painted with

Sodium sulphide	2%
Lime	10%
Water	20%

The above paint was applied on the flesh side of the skins and they were paired flesh to flesh and piled overnight and covered with wet gunny bags. They were unhaired on the next day.

Liming

The un-haired skins are limed with

Lime	10%
Soda ash	0.5%
Water	300%

The skins were handled in this bath twice a day for three days. On the day 5 (calculated from soaking), they were removed from the limed bath and washed in running water The skins were then machine fleshed and the fleshed weight was noted.

Deliming

The pelts were delimed with 1% ammonium chloride and 100% water in a drum for 45 minutes. The delimed skins were washed with a float of 200% water for 10 minutes. The completion of deliming was checked with phenolphthalein indicator.

Glutaraldehyde tanning

Glutaraldehye	2%
Water	100%

The glutaraldehyde was diluted with 10% water and mixed with 0.25% soda ash and added to the drum in 3 feeds at 30 minutes interval. Finally, the drum was run for 2 h. The pH of the bath was checked and adjusted to 8.5 by adding 10% soda ash solution. The skins were piled overnight. Next day, the skins were sammed and completely shaved on the grain side to ensure uniform thickness. Conventionally, in order to withstand the shaving operation, the pelts are first treated with aldehyde.[9]

The shaved skins were weighed, washed in running water.

Oil tanning

Fish oil - 20% (Experiment I)

Fish oil methyl ester - 20% (Experiment II)

Fish oil - 15% (Experiment III)

Fish oil methyl ester - 15% (Experiment IV)

were used for the studies. The calcium carbonate (5%) was mixed with oil and the mixture was uniformly applied on the both sides of the skins before loading the skins into the drum. The balance of the oil was also added to the drum and run for 6 h. The skins were then hung up in an airy place for 12 days to promote oxidation. Oxidation was at room temperature (34 – 36^{0}C).

Washing: The oxidized skins were first weighed and then wet back with 1000% water at 40^0 C for 40 mins in a drum. The skins were squeezed out and then treated with

Nonionic wetting agent	0.5%
Water	400%

The drum was run for 40 min. Then the skins were squeezed and washed twice with 1000% water at 45^{0}C for 10 min.

The skins were then treated with following for a further 40 min.

Soda ash	2%
Water	400%

The soda ash treatment followed by wetting agent treatment was given successively 3 times. In between these treatments and also in the end; the skins were washed thoroughly until the frothing ceased. The skins were then hung up for drying. When completely dried, the leathers were staked and trimmed. They were buffed with three different emery papers consecutively viz., 150, 240 and 400. After buffing, the leathers were dusted off and samples were taken for different

tests. Then oil tanned leathers were subjected to sink test, water absorption, and different strength properties such as tensile strength, tear strength and color value.

Water Absorption
The sample was cut as per the standard procedure. The conditioned sample was weighed and soaked in 25 ml of distilled water in a dish for 30 min. The sample was removed with forceps, drained the adhering water back into the dish for 2 min. The sample was weighed and the solution in the dish was evaporated to dryness and the residue weight was taken.

Sink Test
A sample was cut from the specified position of the leathers and was placed over water in a 2-L beaker and the time required for it to sink to the bottom was noted.

Strength Analysis
The tensile and tear strength of all the four samples were carried out as per official methods.[10]

Color value of chamois leathers:
Quantification of color values of the chamois leathers was made by reflectance measurements. Color values such as L^*, a^*, b^*, c, h were measured using Milton Roy Color mate HDS spectrophotometer

Where L^* = 0-100 Lightness / darkness

a^* = Redder

b^* = Yellower

c = Color concentration

h = Color angle

Differential Scanning Calorimetry (DSC)
Shrinkage temperature of the fish oil and fish oil methyl ester tanned chamois leathers were analyzed using differential scanning calorimetry (TA Instrument, Model no.-DSC 2910). The ramp heating was given as 10^0C/min.

Organoleptic Properties Of Leather
The leathers were subjected to organoleptic assessment for softness, fullness and general appearance by hand and visual examination by experts.

RESULTS AND DISCUSSION

Chemical and Physical Characterization of Oil
The fish oil and the fish oil methyl ester were analyzed for iodine value, acid value and kinematic viscosity. The results are shown in **Table I.** For fish oil, the iodine value was around 135 and it has not changed much after transesterification in to methyl ester, however, there was a significant reduction in acid value after transesterificaiton. There was a significant reduction in viscosity of fish oil after transesterification process.

TABLE I
Chemical and physical characterization of oil.

Experiment	Iodine value	Acid value	Kinematic viscosity, Cst
Fish oil	135	15	36
Fish oil methyl ester	133	0.05	6

Gas Chromatography Analysis
The gas chromatography analysis of raw fish oil and fish oil methyl ester is shown as **Figure-1 and Figure-2** respectively**.** The retention time and peak area of fish oil and fish oil methyl ester are noted in **Table II.** Fish oil is high in palmitic acid followed by eicosenpentanic acid and there is not much change in the composition of different fatty acid after transesterification process.

TABLE II
GC analysis data.

Components	Retention Time [min]	Area [%] Fish oil	Area [%] Fish oil methyl ester
Myristic acid	3.280	11.059	11.276
Palmitic acid	4.427	24.490	24.127
Palmitoleic acid	4.777	10.825	11.249
Stearic acid	6.033	5.319	5.405
Oleic acid	6.417	13.818	12.697
Eicosenpentanic acid	11.127	14.987	15.284
Decosahexanoic acid	13.963	9.233	9.405

The water absorption for fish oil and fish oil methyl ester tanned leathers is shown in **Table III**. The leathers tanned with fish oil methyl ester had slightly higher water absorption compared to fish oil tanned leather.

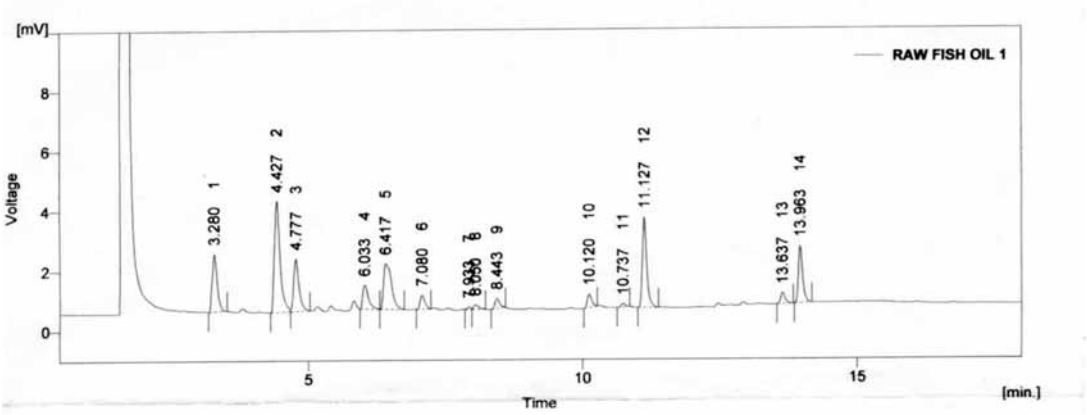


Figure 1. GC analysis of raw fish oil.

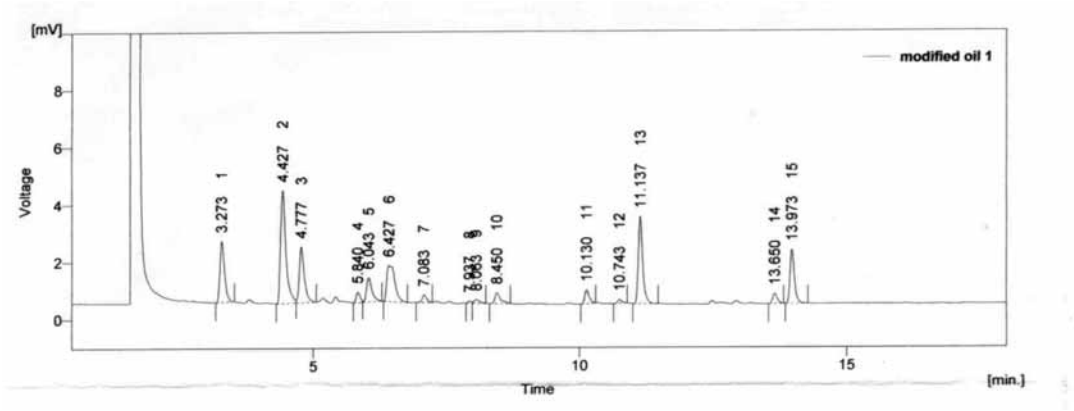


Figure 2. GC analysis of fish oil methyl ester.

TABLE III
Water absorption of leathers.

Experiment	% (W / W)
Fish oil control [20%]	360 ± 5
Fish oil methyl ester [20%]	375 ± 5
Fish oil [15%]	346 ± 5
Fish oil methyl ester [15%]	354 ± 5

This sink test results of various fish oil and fish oil methyl ester tanned leathers are shown in **Table IV**. The test results show that fish oil methyl esters absorb water faster compared to fish oil tanned leathers.

TABLE IV
Sink test of leathers.

Experiment	Sink Time (Sec)
Fish oil [20%]	65 ± 5
Fish oil methyl ester [20%]	48 ± 5
Fish oil [15%]	73 ± 5
Fish oil methyl ester [15%]	58 ± 5

Color Value of Leathers

The leathers were examined by three experts and the values are tabulated below in **Table V**. Visual assessment of leather tanned by four different system has acceptable color.

TABLE V
Color value of leather.

Color value	Fish oil [20%]	Fish oil methyl ester [20%]	Fish oil [15%]	Fish oil methyl ester [15%]
L	74.7	79.7	74.0	76.5
a	4.3	1.5	5.3	4.4
b	31.6	25.7	30.4	28.2
c	31.9	25.7	30.8	28.6
h	82.2	86.7	80.1	81.1

The tensile and tear strength analysis results are shown in Table VI. Test results show that leather tanned with higher amount of fish oil or fish oil methyl ester has higher strength and among fish oil and fish oil methyl ester, the fish oil methyl ester tanned leather had marginally better strength.

TABLE VI
Physical testing method.

Experiment	Tensile strength (N/ mm^2)	Tear strength (kgf/mm)
Fish oil [20%]	92.8	1.6
Fish oil methyl ester [20%]	98.5	1.8
Fish oil [15%]	86.7	1.6
Fish oil methyl ester [15%]	88.9	1.3

The DSC results are shown in Figure- 3 and Table VII. All the samples show a change in slope of thermo gram between 63-65 ºC, except leather tanned with higher amount fish oil methyl ester, which shows a high value of 73 ºC.

TABLE VII
Shrinkage temperature of leathers.

Experiment	DSC Temp (ºC)
Fish oil [20%]	64.5±1
Fish oil methyl ester [20%]	73.1±1
Fish oil [15%]	63.7 ±1
Fish oil methyl ester [15%]	64.0 ±1

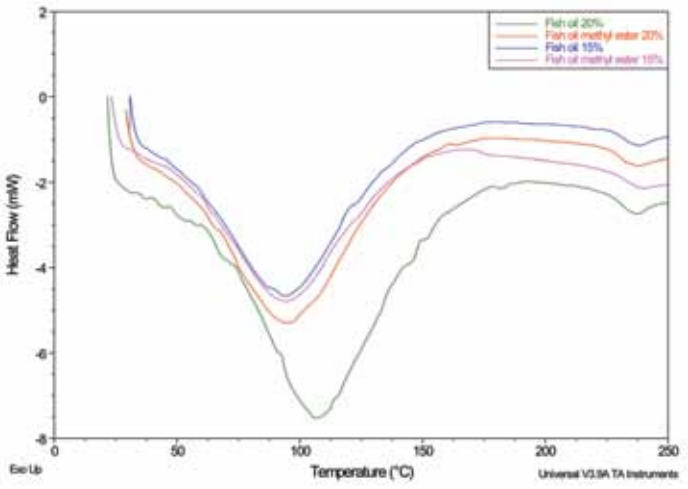


Figure 3. DSC of leathers.

The leathers were subjected to organoleptic assessment for softness, fullness and general appearance by hand and visual examination by experts and were rated based on a scale of 1 – 10 grade points for each functional property by experts. The higher grade points indicate better property for the subsequent end usage of leather, which are shown in **Table VIII**.

TABLE VIII
Organoleptic properties of leather.

Experiment	Softness	Fullness	General appearance	Odor
Fish oil [20%]	7	6	8	4
Fish oil methyl ester [20%]	7- 8	7	8	5
Fish oil [15%]	6- 7	6	7	6
Fish oil methyl ester [15%]	7	7	7	7

Scale 1 – Poor, 10 – Excellent

CONCLUSIONS

Chamois leathers are produced in large quantities mainly using fish oil. In this study fish oil has been converted to fish oil methyl ester by transesterification process. This ester was then used for tanning goat skin. The chamois leather thus obtained was tested for sink test, water absorption and strength properties and found that the fish oil methyl ester tanned chamois leather takes shorter time for sink test and there is a

marginal increase in water absorption compared to conventional fish oil tanned leathers. This study shows the chamois leather having better water absorption characteristics can be made using fish oil methyl ester instead of fish oil and in addition, up-to 25% reduction in fish oil usage can be achieved using fish oil methyl ester as oil tanning agent instead of fish oil.

References

1. M. S. Olivannan, Improved techniques for the manufacture of chamois leather from Indian goats skins and their utilization as garment leathers, *Leather science* **25**, 234-237, 1978.
2. Covington, A. D. Tanning Chemistry – the science of leather. Royal Society of Chemistry, Cambridge, 2009.
3. J.C.Deb, Manufacture of chamois leather by formaldehyde – sardine oil combination tannage, *Bulletin of CLRI* **6** (2), 81-84, 1959.
4. O. Suparno, E. Gumbira-Sa'id, Kartika, Muslich and S.Mubarak, An innovative new application of oxidising agents to accelerate chamois leather tanning, *JALCA* **106**, 360-366, 2011.
5. V. John Sundar, N. Vedaraman, P.A. Balakrishnan and C. Muralidharan, Chamois Leather – An approach for accelerated oxidation, *JALCA* **88**, 256-259, 2004.
6. Victor Mattei, William T. Roddy, The use of fish oils for fat liquoring leather. Menhaden oil and cod oil fat liquors, *JALCA* **54**, 12-30, 1959.
7. S. Hari Krishnan, V. John Sundar, N. Vedaraman, V. Hari Babu, C. Muralidharan, and S. Sadulla, Studies on chamois tanning – an investigation using modified fish oil, *JALCA* **100**, 61-65, 2005.
8. Ono Suparno, IKA. Kartika, Muslich, Chamois leather tanning using rubber seed oil, *JSLTC* **93**, 158-161, 2009.
9. Olivannan M. S, Iqbal G. Md., Suede and chamois leather, Some aspects of chamois tanning process, *CLRI Publications*, 45 – 54, 1984.
10. SLTC. Official methods of analysis. Society of Leather Technologists and chemists, Northamption, 1996.