Paper D8

Fatliquoring from a Viewpoint of Sustainability

Christine Fischer[1], Francina Izquierdo[2], Peter Mähner[1], Josef Drexler[1], Ivo Reetz[1], Ramon Segura[2]

[1]Pulcra Chemicals GmbH, Isardamm 79-83, Geretsried, Germany, Phone: 49-8171 628-218, Fax: 49-8171 628-440, e-mail: ivo.reetz@pulcrachem.com

[2]Pulcra Chemicals S.L. Polig. Ind. Sant Vicente, Castellbisbal, Spain, Phone: 34-93 81-71-69, Fax: 34-93 81-71-11, e-mail: francina.izquierdo@pulcrachem.com

ABSTRACT

In leather fatliquoring, a variety of natural and synthetic oil sources may be used.

Being traditionally the most important raw material for leather fatliquors, fish oil has in the past years increasingly been replaced by oils from vegetable sources. As fatliquor producers, we had various reasons for the search for alternatives, such as the questionable sustainability of fish oil, or the increasing shortage of fish oil provoked by the tremendous demand of fish oil for aquaculture. Still over 90% of the world fish oil production, which is based mainly on an excessive catching of wild fish, is used for aquaculture. Being one of the fastest growing food-producing sectors, aquaculture demand of fish oil will surely keep its supply tight in the future.

Vegetable oils are a very good alternative for fish oil in leather fatliquoring, which apart from having excellent properties and fastnesses give leathers with an improved eco-profile and a better overall sustainability. In our work we have assessed the overall sustainability of selected vegetable oils and have analyzed the positive effect fatliquors based on these oils have on leather character, such as softness, ageing stability and smell of treated leathers. Especial focus is given on car-upholstery leathers, were low emission and long-lasting stability of the leathers at harsh conditions is of foremost importance.

Introduction

Fatliquors for leather are usually very complex products. The major part of a leather fatliquor consists typically of processed natural oils or components derived from them. Furthermore, there can be emulsifiers, crude oils, antioxidants and various components accelerating the penetration of lubricating components and/or improving the stability of the formulation.

For the part of natural oil, the traditional raw material used for fatliquors has for many decades been fish oil. The main advantage of fish oil in application is, that, due to the high amount of long carbon chains with relatively high number of insaturations, they give very good softness to the leather. By means of sulfitation or sulfation, fish oil can easily be transformed into the anionic, lubricating components, which effectively prevent the leather fibers from sticking together.

With the premises to produce eco-friendly leather articles, one has to ask, how sustainable is the use of fish oil in comparison with its most prominent alternative, vegetable oils? The present paper gives an overview on the sustainability of both oils and the advantages of replacing fish oil by alternatives with a better eco-profile.

Sustainability of fish oil vs. vegetable oils

Fish oil is normally derived from small, wild marine fish with no direct nutritional value for humans. Notably, from the totally ca. 80 million tons of marine fish captured yearly [1] ca. 30% is destined for non-food uses, including the production of fish oil. For obtaining the oil, the fish is boiled, pressed, and the liquid separated into an oily and aqueous phase by centrifugation. The amount of fish oil produced annually world-wide has been pretty stable over the last decades at ca. 1 million tn/year except during El Nino years, and in spite of the fact that the introduction of precautionary quotas and increased use for direct human consumption has resulted in reduced volumes of whole fish going for fish oil [2]. However, extrapolation of the present situation leads to the forecast of declining global catches, expansion of bottom fisheries into deeper waters and thus a serious impact on biodiversity [3].

Regarding the use of fish oil, nowadays nearly 90% are used as component of feed for aquaculture, and only 7% for industrial applications, what includes leather fatliquors [4]. In light of aquaculture being still a strongly rising sector and driven by the fact that the fish-based nutrition sources are insufficient, there are many efforts to replace fishmeal and fish oil in aquafeed by non-fish products, especially vegetable oils [5-7].

In comparison to the annual 1 million ton of fish oil, almost 60 million tons of rape seed oil or 30 million tons of soy bean oil are produced annually. Both oils are potential precursors for leather fatliquors. Main application of these vegetable oils include again animal feed, direct human consumption, and of course, with increasing importance, the production of bio-fuel.

Regarding the ecological impact of fish vs. vegetable oil, many media-catching slogans can be brought into discussion, with overfishing being the main argument against fish oil, and monoculture and transformation of natural landscapes into farmland as an argument contra the use of vegetable oil. The fact that both materials are potentially valuable sources for direct human consumption makes another view that would imply not to use them for industrial applications at all.

The sustainability of fish oil vs. vegetable oil has been analyzed by other authors [8,9] by means of Life Circle Assessment (LCA), a ISO-standardized accounting framework used to calculate the environmental impacts of distinct life cycle stages, including the production of a material, its processing, transport and possibly its consumption. In LCA, the biophysical impact of a material is expressed with adequate impact categories giving information on the overall environmental impact the product, or a production has. In the mentioned study, calculations have been done with the idea to assess the environmental effect which canola (rapeseed oil) of local production has vs. fish oil (imported from Peru), for an aquaculture feed mill (cradle-to-mill gate) situated in British Columbia, Canada. A very similar set-up would be applicable for most global leather fatliquor producers, which can decide on the oil source for the production of their fatliquors. Results of the study [8] are given in Tab. 1.

Regarding the energy necessary for production, processing and delivery, rape seed oil is a real energy saver: it needs ca. 65% less energy than fish oil. To understand this figure it has to be taken into account that the yield of fish oil from fish can be as low as 5%. Therefore, the energy used for catching the fish, including the production and maintenance of the equipment used for that, and the processing, referred to the very amount of fish oil is much lower than in the case of rape seed oil. For the latter, the oil/plant yield is ca. 40%, consequently all energy use is related to a much higher yield. When the rape seed oil is from an organic production, the energy consumed is even less, only ca. 60% of the normal rape seed oil.

		Rapeseed Oil	Organic Rapeseed Oil	Fish oil
EU	MJ equiv.	9.860	5.980	27.000
GWP	kgCO2 equiv.	1.260	643	1.830
AP	kg SO2 equiv.	9,2	6,5	12,1
EP	kg PO4 equiv.	4,6	3,0	6,7
MEAP	kg 1,4-DCB eqv.	41.600	49.000	79.700
BRU	kg C	887	887	37.340

Tab. 1. Results for LCA for rape seed oil, organic rape seed oil and fish oil (Peruvian) [8]. EU = energy use, GWP = global warming potential, MAEP = marine aquatic ecotoxicity potential, AP = acidification potential, EP = eutrophication potential, BRU = biotic resource use.

Not very different is the result of this analysis for global warming potential (i.e., the emission of green house gases), acidification potential (emission of acidifying pollutants (SO2 or NOx)), Eutrophication potential (emission of macronutrients, such as nitrogen or phosphorus), and Marine Aquatic Ecotoxicity Potential (toxic substances emitted into marine ecosystems). In all these cases the figures for rape seed oil are better than for fish oil, and are mostly even lower for organically planted rape seed oil. Factors influencing these parameters are fuel used for production or processing, pesticides and fertilizers, or, as a curious example, the copper based anti-foaling paints used on fishing vessels having its impact on eco-toxicity [10].

Most importantly, the use of biotic resources is more than 40 times higher for fish oil than for rape seed oil. The rape plant directly converts CO_2 into organic matter, part of which is the oil. Being at least one trophic level higher, and having, due to a far more energy-consuming metabolism, a lower net production efficiency, in the case of fish oil only an infinite fraction of the originally produced organic matter is actually employed.

Factors which also have to be taken into account are the loss of marine biodiversity directly by the fishing, or indirectly, since many species depend on the small plegiatic fish as food [11]. All together, there is much scientific proof that vegetable oils from the view-point of eco-sustainability are the clear winner over fish oil. Thus, for producing more eco-friendly leather articles, it is worthwhile to think about switching from fish oil base fatliquors to high-quality vegetable fatliquoring agents.

But: can one get the same leather performance with fish oil than with vegetable oil in fatliquor?

Leather properties and how they can be influenced

Due to the long chains and high number of double bonds, fish oil is known to give good softness to leather. However, in our work we have found that, by optimization of formulation and reaction conditions, virtually the same softness can be obtained with vegetable oils as with fish oil. The secret lies in processing and formulation. In sulfation, reaction temperature, the ratio of oil / sulfating agent, and possible fatty additives have to be optimized in order to have the same level of softness. For oxo-sulfited product components, along with the blend of oils and other raw materials used, blowing conditions and the amount of bisulfite are to be optimized in order to obtain a maximum softening effect. Finally, changes in product composition help to get the desired result in softness, whereby even aspects, which do not directly have its reflection in softness or other leather parameters, such as the salt formation in the product (by using more sulfating or sulfiting agents), or the uptake of product from the float have to be taken into account. The softness obtained on chrome leather for a sulfited product with direct substitution of fish oil by vegetable oil, and for the optimized product, is given in Fig. 1.

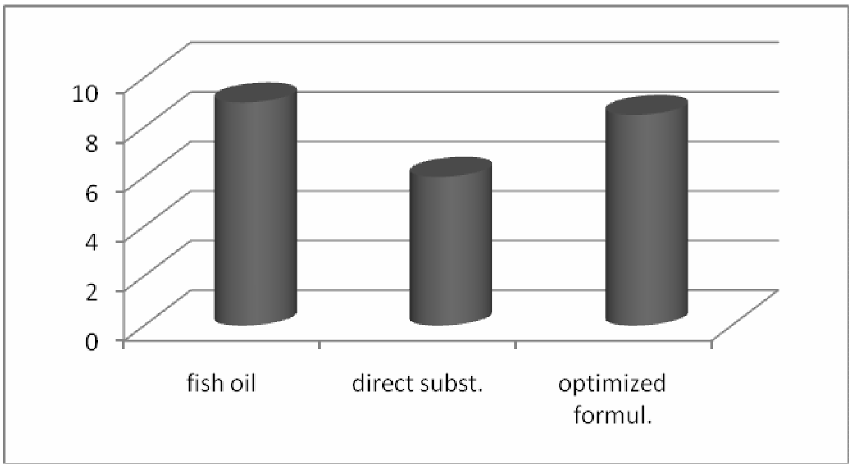

Fig. 1. Comparison softness fish oil based vs. vegetable fatliquors. Scores from 1(low)-10 (high)

A very important aspect of a fatliquor is the fact that it is the starting point for oxidation reactions and therefore ageing processes in the leather.

As a consequence of thermally or light-induced autoxidation of the fatliquor, reactive peroxides are formed, which radically attack the collagen giving rise to scissions or de-naturation reactions. Typical phenomena observable in the course of ageing are yellowing, shrinkage, odor formation or the fall in de-naturation temperature [12,13]. Hence, since fish oil has a higher number of double bonds, and the latter are more reactive, the chance of autoxidation is much higher than in vegetable oils. This is demonstrated in Fig. 2 on the example of a wet blue fatliquored with sulfited fatliquor based on vegetable and a fish oil. Notably, by using suitable radical-scavengers, following basic principles of processing, and of foremost importance, using high-quality, purified raw materials, the rate of oxidation can be drastically reduced.

It is also worth to note that the formation of Cr(VI) is more likely when fish oil based fatliquors are used. This is again due to the fact that oxidation in the leather starts with the fatliquor, and fish oil has the higher iodine values and more reactive double bonds and thus creates a higher risk [14,15]. As has been intensively studied in the past decade, Cr(VI) is not a very stable compound in the leather matrix, and formed mainly by forced oxidations in a relatively dry environment. Vegetable tanning agents and some Cr(VI)-protectors which have been developed by the industries are a very efficient means for avoiding that Cr(VI) would be formed.

A circumstance which has not been investigated much so far is the emission behavior of fish oil based fatliquors on one side and vegetable based fatliquors on the other. Emission measurements and fogging behavior is of crucial importance for the decision of a fatliquor for use in car upholstery leathers [16].

In order to have comparable conditions, we synthesized two fatliquors based on oxo-sulfitation, and blended with emission-proof anionic emulsifiers helping to penetrate the product into the leather. The two products, one based on fish oil, the other on vegetable oil, were applied on chrome-free leather and one wet blue, in a typical recipe for car-upholstery leather. Product formulation, leather application and leather analysis have been repeated various times in order to have consistent reliable results.

Most interestingly, the product based on vegetable oil gives generally a better emission performance than the product based on fish oil. This has been found both in fogging tests, as well as with dynamic and static headspace techniques.

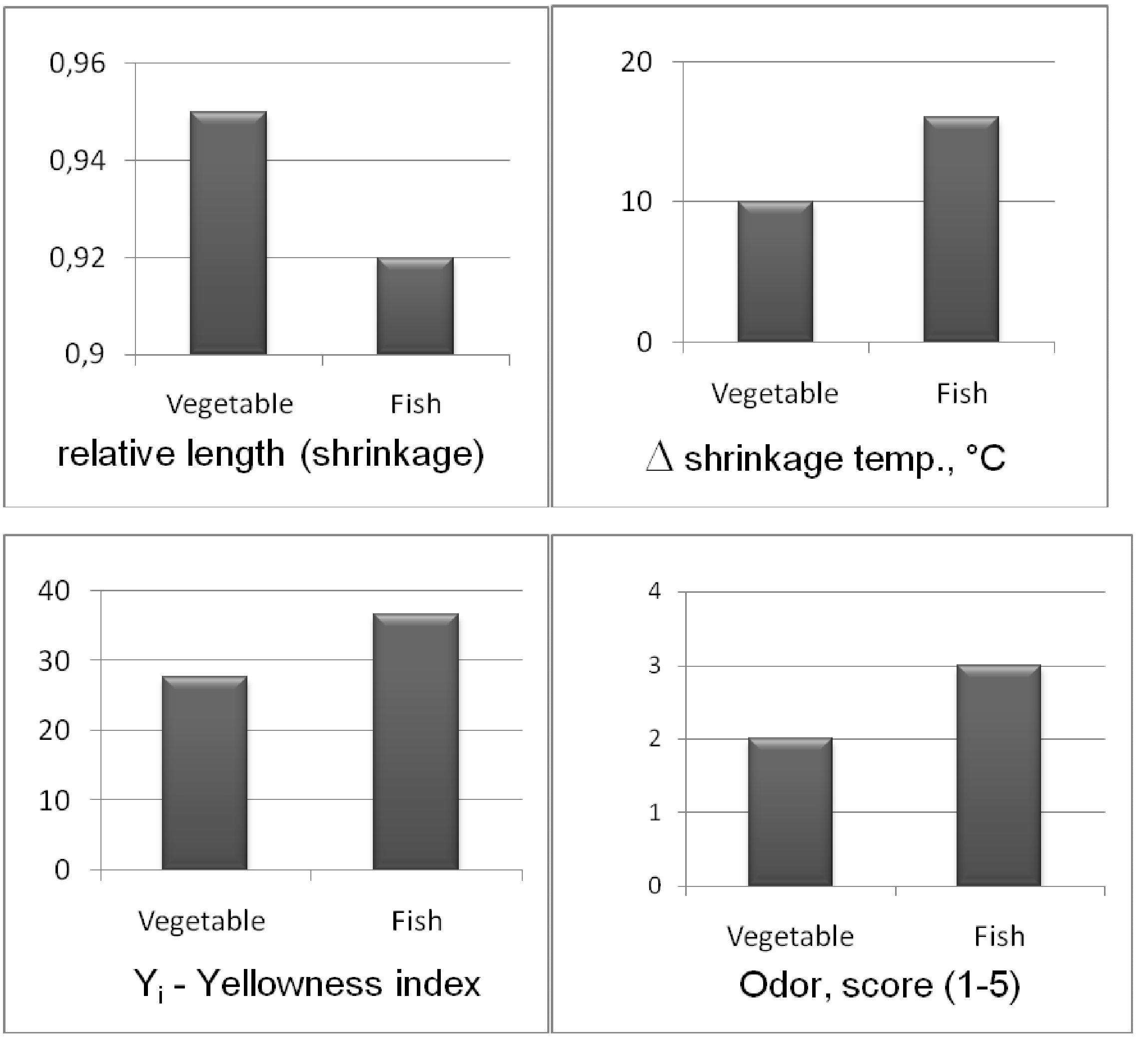

Fig. 2. Ageing phenomena for an ageing 144h at 100°C for two wet-blues fatliquored with a sulfited fatliquor based on vegetable and fish oil, respectively

Emission of leather is of course a very complex phenomenon. One possible explanation for the difference found is the partial decomposition of the oil during the test, what, for the reasons explained above, is more pronounced for fish oil than for vegetable oil. Furthermore, also substances different from the very triglyceride may be responsible for the higher emission values. For example pristane (2, 6, 10, 14-tetramethylpentadecane), which fish oil of marine origin may contain in small amounts, is frequently detected as part of the emission, especially in VOC-analysis. Oils of vegetable origin do not contain pristane. In general, lower quality, less purified fish oil gives significantly more fog and emissions than high-quality fish oils. This is also in line with the odor – high quality fish oil which is used for state of the art car upholstery fatliquors, smell much less of fish than low grade technical oils.

Surprisingly, it seems that in chrome-free leathers, the difference between the emissions of vegetable and fish oil based fatliquoring is significantly bigger than for chrome leathers. It has to be taken into account that fish oil, having a higher number of double bonds, can also bind more SO_3-groups and is therefore more anionic. This gives rise to a better binding to the more cationic matrix of chrome leather, than with vegetable based fatliquor, what would eventually leads to lower fogging.

		Fog-Grav DIN 75201B		Fog Refl.	
		16h/100ºC	16h/120ºC	3h/100ºC DIN 75201A	6h/75ºC
		g	g	%	%
FOC	fish	2,6	9,9	40	88
	vegetable	1,8	7,2	55	91
Cr-Leather	fish	1,1	4,3	50	96
	vegetable	0,8	3,8	65	98
		Dynam. Headspace VDA 278		Stat. Headsp. VDA 277	Odour VDA 270 C3
		VOC	FOG	Total C	
		ppm	ppm	mgC/g	score
FOC	fish	250	1793	26	4
	vegetable	188	1120	24	4
Cr-Leather	fish	126	475	21	3
	vegetable	109	430	21	3,5

Fig. 3. Emission testing for chrome free leather (FOC) and chrome leathers, car upholstery recipe, with sulfited oil.

Conclusion

With the idea of producing sustainable leather articles, we have discussed in this paper pros and contras of using fish or vegetable oil based fatliquors. From the point of view of sustainability, vegetable oil clearly wins over fish oil, as can be scientifically proven by life cycle analysis. Fish oil has advantages in application, since it gives very good softness. However, by appropriate processing and formulating the fatliquors, the same degree of softness may be obtained. Vegetable oils retard the ageing of leather as well as CrVI formation, and, most interestingly, also do have a generally better performance in emission behavior. In general, it has to be emphasized that for having a good overall performance of the fatliquor, the use of high-quality oils is of foremost importance.

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