Fatliquoring from a Viewpoint of Sustainability

Ivo Reetz[1], Francina Izquierdo[2], Christine Fischer[1], Ramon Segura[2], Peter Mähner[1], Josef Drexler[1],
[1]Pulcra Chemicals GmbH, Isardamm 79-83, Geretsried, Germany, Phone: 49-8171 628-218
e-mail: ivo.reetz@pulcrachem.com
[2]Pulcra Chemicals S.L. Polig. Ind. Sant Vicente, Castellbisbal, Spain, Phone: 34-93 81-71-69,
e-mail: francina.izquierdo@pulcrachem.com

Introduction

Fatliquors for leather are usually very complex products. Typically, the major part of a leather fatliquor consists 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. Due to the high amount of long, highly unsaturated carbon chains fish oil gives superior softness to the leather. By means of sulfitation or sulfation, fish oil can easily be processed 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] 30% are 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 annual world output of fish oil has, except for El Niño years, been pretty stable over the last decades oscillating at about 1 million ton/year. However, 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]. Due to declining global fish stocks bottom fisheries expand into deeper waters, what itself represents a serious impact on biodiversity [3]. It has also to be taken into account that the small pelagic fish used for the production of fish oil is the nutritional bases for larger, predatory fish, such as salmon or cod, what additionally affects marine biodiversity [4].

Regarding the use of fish oil, nowadays nearly 90% of the yearly output are used for aquafeed, and only 7% for industrial applications, including also the production of leather fatliquors [5]. 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 [6].

In comparison to 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 versus 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.

A sophisticated method for the evaluation of sustainability is Life Circle Assessment (LCA). LCA is an 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, in cases, its consumption. In LCA, the biophysical impact of a material is expressed by adequate impact categories providing information on the overall environmental impact the product, or a production has.

The results of LCA for fish oil vs. vegetable oil are given in Fig. 1. The results are adapted from a study [8,9] done with the background of using both oils for aquafeed, In the mentioned study, calculations have been done for canola (rapeseed oil) of local production 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. In Fig. 1, the results for the different impact categories are related to the greatest impact, respectively. Consequently, the smaller the impact, the closer is the line to the origin of the radar chart.

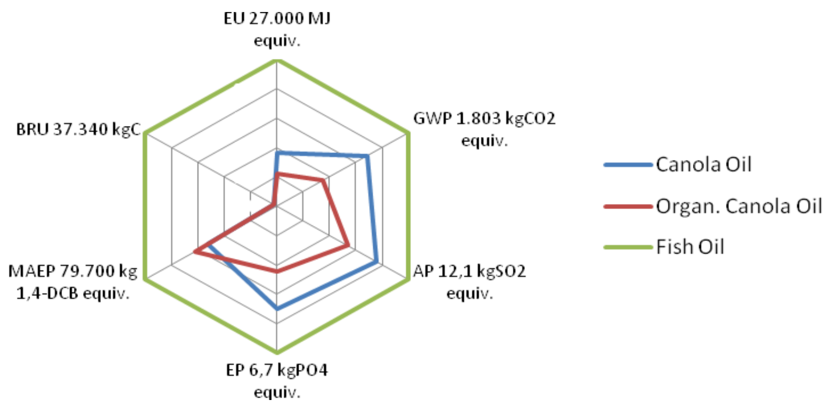

Fig. 1. Results for LCA for rape seed oil, organic rape seed oil and fish oil (Peruvian) [8]. EU = energy use, GWP = global warming potential, AP = acidification potential, EP = eutrophication potential, MAEP = marine aquatic ecotoxicity potential, BRU = biotic resource use.

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%. For the rape seed plant, the oil/plant yield is about 40%. The energy required for the generation and delivery of the oil is of course related to very yield of oil from the oil source. Notably, in this calculation all possible side products and are taken into consideration using adequate allocation criteria. When the rape seed oil is from an organic production, the energy consumption is even lower, only ca. 60% as compared with standard rape seed oil.

Not very different are the results 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 for example 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. Fish, on the other hand, is at least one trophic level higher, and has, due to a far more energy-consuming metabolism a lower net production efficiency. Therefore, in this case only an infinite fraction of the originally produced organic matter is actually used for the generation of the oil.

All together, there is solid 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 based fatliquors to high-quality vegetable fatliquoring agents.

But can one achieve the same leather performance with fish oil as with vegetable oil based fatliquors?

Leather properties and how they can be influenced

Due to the long carbon chains and the high number of double bonds, fish oil is known to give good softness to leather. However, in our work we have found that, by optimizating the formulation and reaction conditions, with vegetable oils virtually the same degree of softness can be obtained. In sulfation, reaction temperature, the ratio of oil to sulfating agent, and the very oil mix have to be optimized in order to reach the same softness. For oxo-sulfited fatliquors, along with the blend of oils and other raw materials used, blowing conditions and the amount of bisulfite have to be optimized in order to obtain a maximum softening effect. Finally, changes in product composition help to get the desired result in softness. The addition of humidity retaining components may help do improve softness. Also aspects, such as salt formation in the product (by using more sulfating or sulfiting agents), or the change in 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 an optimized version, is demonstrated in Fig. 2.

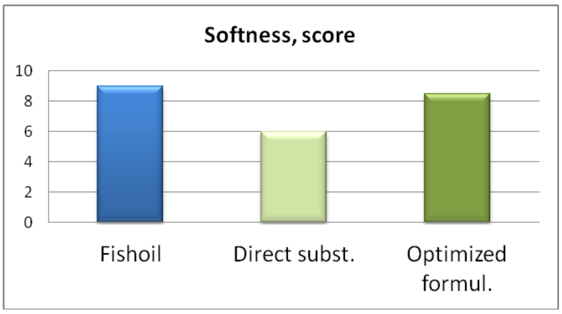

Fig. 2. Comparison softness fish oil based vs. vegetable fatliquors. Scores from 1(low)-10 (high)

A very important aspect of a fatliquor is the fact that it can be 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 deterioration of de-naturation temperature [11,12]. Since fish oil has a higher number of highly reactive double bonds, the chance of autoxidation is much higher than in vegetable oils. This circumstance is demonstrated in Fig. 3 on the example of a wet blue, fatliquored with a sulfited fatliquor based on either vegetable or fish oil. Notably, by using suitable radical-scavengers, following basic principles of processing, and of foremost importance, by using high-quality, purified raw materials, the rate of oxidation can be drastically reduced.

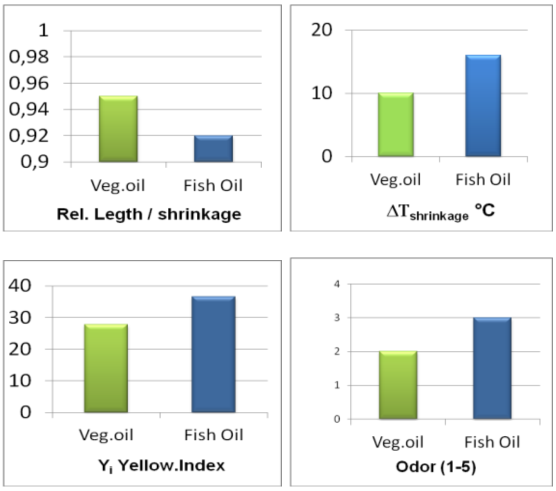

Fig. 3. Ageing phenomena for an ageing 144h at 100ºC for two wet-blues fatliquored with a sulfited fatliquor based on vegetable and fish oil, respectively

It is also worth mentioning 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 [13,14]. As has been intensively studied in the past decade, Cr(VI) is not chemically stable in the leather matrix. Cr(VI) is mostly generated 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 found in leathers.

A circumstance which has not been investigated much so far is the difference in leather emission between fish oil and vegetable oil based fatliquors. Emission measurements and fogging behavior is of crucial importance for the use of a fatliquor in car upholstery leathers [15]. Already the differences in odor, of the fatliquor itself and of the leather after ageing implies that there must be a difference in emission between both types of fatliquor.

In order to have consistent conditions, we synthesized two fatliquors based on oxo-sulfitation, and blended them with emission-proof anionic emulsifiers, which help 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 on wet blue, in a typical recipe for car-upholstery leathers. Product formulation, leather application and leather analysis have been repeated various times in order to have reliable results.

		Fog-Grav DIN 75201B		Fog Refl.	
		16h/100°C	16h/120°C	3h/100°C DIN 75201A	6h/75°C
		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

Tab. 1. Emission testing for chrome free leather (FOC) and chrome leathers, car upholstery recipe, with sulfited oil.

Most interestingly, the fatliquor based on vegetable oil gives generally less emission than the one based on fish oil (see Tab. 1). This has been found both in fogging tests, as well as with dynamic and static headspace techniques.

Surprisingly, it seems that in chrome-free leathers, the difference between the emissions of vegetable and fish oil based fatliquoring is more pronounced than for chrome leathers. This can be explained in terms of the fact that fish oil, having a higher number of double bonds, can bind more SO_3-groups and is therefore more anionic. As a consequence, the processed triglyceride in this case binds better to the cationic matrix of chrome leather, what eventually leads to lower fogging. In the case of chrome-free leather, the stronger anionic charge would not give rise to better binding.

A band which is frequently found in the VOC chromatogram of fish oil based fatliquors is the one of pristane (2, 6, 10, 14-tetramethylpentadecane). Oil of many marine fish contain very small quantities of this branched alkane. Not having any functionality which would allow pristane to bind to the leather matrix, it easily emits and is detected in VOC tests when fish oil based fatliquors have been used.

Often, the emission caused by pristane is in the double-digit percent region of the overall VOC emission. Vegetable oil, on the other hand, does practically not contain any pristane.

In Fig. 4, a typical VOC chromatogram obtained with fish oil and vegetable oil based fatliquoring is depicted.

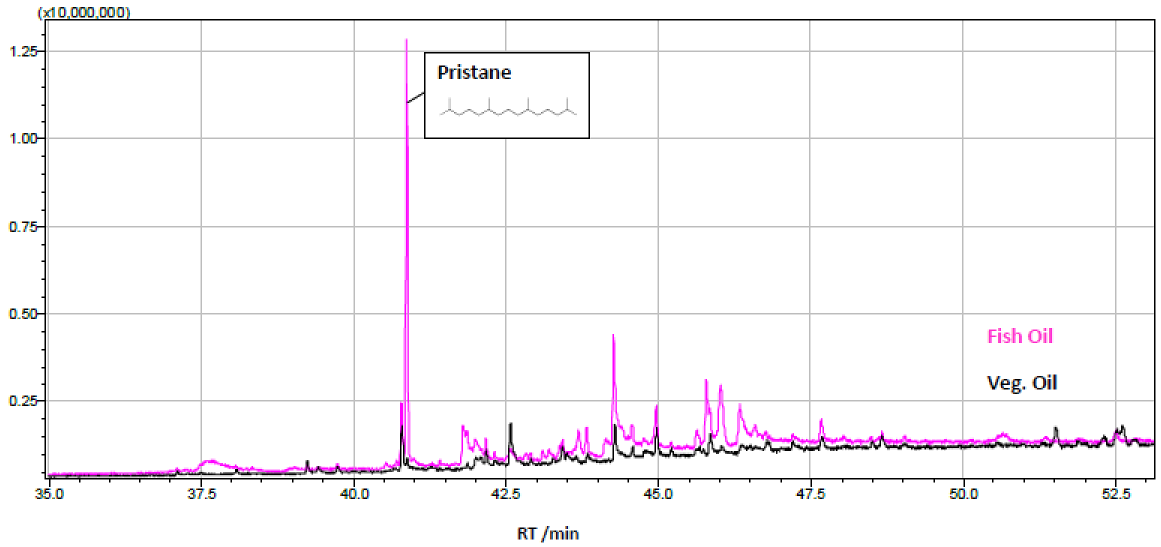

Fig. 4. VOC according to VDA278. Chrome-free leather fatliquored with oxosulfited fish oil vs. vegetable oil.

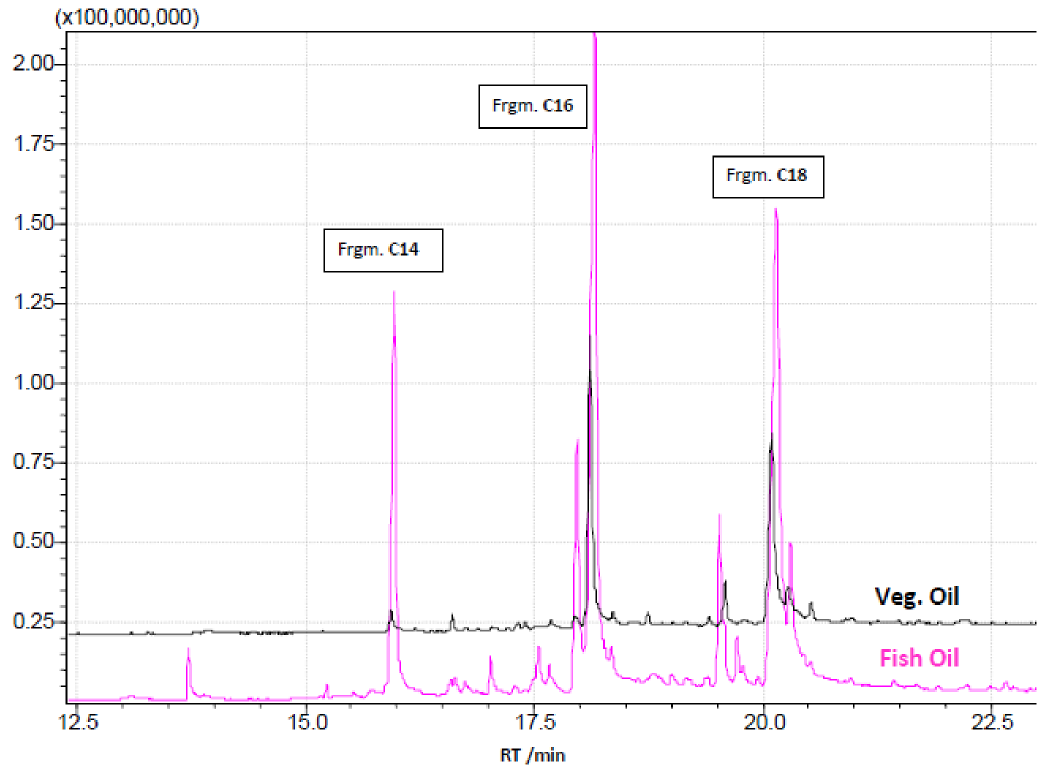

Fig. 5. FOG accord. VDA278). Chrome-free leather fatliquored with oxosulfited fish oil vs. vegetable oil.

In the FOG chromatogram, especially the higher number of decomposition products in fish oil give rise to a higher general emission. As explained above, decomposition reactions of the triglyceride are more likely in fish oil than in vegetable oil, and many of the fragments formed in this process are detected in a FOG test. In Fig. 5, a typical FOG is displayed.

In general it has to be pointed out that lower quality, less purified oils, not regarding whether it is fish oil or vegetable oil, give significantly more fogging and emissions than high-quality oils. This can be explained by the fact that the impurities of low quality oils, such as fatty acids and non-triglyceridic components, are possible direct emittents.

Conclusion

There is scientific evidence that, as far as sustainability is concerned, vegetable oil based fatliquors perform better than fish oil based fatliquors. Therefore, vegetable oil based fatliquors should be given preference for the production of sustainable and environmentally friendly leather articles..

Fish oil has advantages in application, since it gives very good softness. However, by appropriate processing and formulation, the same degree of softness may be obtained also with vegetable oil based fatliquors.

Vegetable oils retard the ageing of leather as well as CrVI formation, and, most interestingly, due to their different chemical composition, performance better in emission testing. 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.

References

[1] The state of World Fisheries. 2010 FAO Fisheries and Aquaculture Department. Food and Agriculture Organization of the United Nations. Annual report, Rome, 2010

[2] A. Chamberlain, *"Fishmeal and Fish Oil –The Facts, Figures, Trends, and IFFO's Responsible Supply Standard*", International Fishmeal & Fish Oil Organization, 2011

[3] D. Pauly, J. Alder, El. Bennett, V. Chrstensen, P. Tyedmers, R. Watson, "*The Future for Fisheries", *Science, 302 (2003) 1359-1361

[4] C. Clover, "*End of the Line: How overfishing is changing the world and what we eat*", Ebury Press, London (2004)

[5] A. Jackson, " *The continuing demand for Sustainable Fish Meal and Fish Oil in Aquaculture Diets*", International Aquafeed, (6) (2009) 32-36

[6] G. Bell., B. Torstensen. and J. Sargent, "*Replacement of marine fish oils with vegetable oils in feeds for farmed salmon*", Lipid Technology, **17** (2005) 7-11

[7] P.F. Almaida-Pagán, M.D. Hernández, B. García García, J.A. Madrid, J. de Costa, P. Mendiola, "*Effects of total replacement of fish oils by vegetable oils on n-3 and n-6 polyunsaturated fatty acid desaturation and elongation in sharpsnout seabream (*Diplodus puntazzo*) hepatocytes and enterocytes*", Aquaculture **272** (2007) 589-598

[8] N. L. Pelletier, P. Tyedmers "*Feeding farmed salmon: Is organic better*?", Aquaculture **272** (2007) 399-416

[9] N. Pelletier, P. Tyedmers, "*Life Cycle Considerations for Improving Sustainability Asessments in Seafood Awareness Campaigns*", Environmental Management, (5) **42** (2008) 918-931

[10] N. L. Pelletier, N.W. Ayer, P.H. Tyedmers, S.A. Kruse, A. Flysjo, G. Robillard, F. Ziegler, A. J. Scholz and U. Sonesson, "I*mpact Categories for Life Cycle Assessment Research of Seafood Production Systems: Review and Prospectus*", International Journal of Life Cycle Assessment **12** (6) (2007) 414 – 421

[11] V. Candar, J.J. Palma, Y. Zorluoglu, I. Reetz, "*The many faces of aging*", paper presented at the 26 IULTCS Congress, Cape Town (2001)

[12] A.M. Manich, S. Cuadros, J. Cot, J. Carilla, A. Marsal, "*Determination of oxidation parameters of fatliquored leather by DSC*", Thermochimica Acta, **429** (2005) 205-211

[13] V. Candar, I. Reetz, M. Ferranti, "*How to avoid the formation of Cr(VI) in Leathers*", Leather International, (2001) 18-24

[14] D. Graf "*Formation of Cr (VI) traces in chrome-tanned leather: causes, prevention and latest findings".* Journal of the American Leather Chemists Association, 96 (2001) 169-179

[15] M. Breitsamer, O. Götz; "*Emission from automotive leather: State of the art and a critical foresight*"; The Journal of the American Leather Chemists Association, **99** (2004) 416-423

Acknowledgements

We would like to thank Nathan Pelletier of Dalhousie University Halifax, Canada, for providing helpful material on LCA related issues.


dry feet love unexpected rain
When you're out on the road and met with unexpected rain, you can count on Densodrin® DP, the latest innovative water-repellent chemical. It keeps your leather boots water resistant and your feet dry. Our relentless pursuit to set new benchmarks also enabled us to improve other properties in process reliability, leather quality and environmental sustainability. When leather footwear is kept dry even with unexpected rain, it's because at BASF, we create chemistry.
www.basf.com/leather
BASF
The Chemical Company