Hyperflax: new applications by high value added flax functionalities

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Mankind has consumed in 2007 around 72 Mill tons fibres, this is 11 Kg a head. Developed countries consume around 25 Mill tons with 30 kg a head, emerging countries a similar figure at a rate of 8 kg a head and the poorest countries consume around 15 Mill Tons or 4 kg's a head. With a global population growing to 8 bill a people and a growth per head of 5% per year, fibre consumption is likely to increase to 90 Mill tons. This does not even account for a substitution of plastics/metals by technical textiles.

Earth does not have the capacity to cater for this quantity. Cotton has to compete with food crops, that usually offer higher revenue for farmers. The limit to natural fibres shall be increasingly limited by its demand on water, which to a ratio of 8000 lítres freshwater to one net kg of fibre is a major break on further growth of cotton. Bulk polymers have to compete with uses for which oil has more strategic relevance such as kerosene or fine chemistry for pharmaceutical use. Moreover processing of synthetic (bio-) polymers requires substantial energy inputs. We are hitting the wall around 2020-2025 (this is as we would say 2009 in 1995), and textile is no marginal subject: it represents between 5 and 10% of global materials consumption – most of it not being recycled. Unless the clothing and textile industries volunteer to be the next Chrysler of General Motors, and become overtaken by trends it could see arriving but not pre-empt, a comprehensive shift in fibres is required. Indeed it is not unlikely that textiles and clothing would experience in developed countries a demand drop of 30-40% (double than the current one) if its products are faced with a material price hike or a sudden greening of demand.

A fibre shift may entail a set of shifts that can be complementary. It may entail a "less is more" approach to consumption. A consumption of 20 Kilo's also enable a comfortable life style. It may also entail products with a longer technical life span. This would require an attack on pilling and on stains on textiles. It may also entail garments with more ecological responsible design (e.g. no ammonia finish). It should involve improvement of technologies in the supply chain, e.g. low temperature scouring and bleaching of textiles. It may entail organic cultivation yet also a agricultural management providing higher yields. Finally it may involve a higher rate of recycling. However, besides a more efficient use of current resources and recycling, a substantial part of the fibre gap should be covered by alternative natural fibres and biosynthetic fibres.

All of these challenges require change in consumption patterns, and possibly temporary acceptance of lower colour deepness and more ironing. It also requires a comprehensive technology and innovation program more around mainstream technologies, and while using progress derived from biochemistry and macro-molecular chemistry, it is far removed from the gimmicks of nanotechnology and intelligent textiles. However a fibre shift shall not occur without an enciting environment in terms of regulation, technology policies, regional and rural prices. It should also entail price levels substantially higher than the € 1,50 average for most dominant fibres, as well as price premiums for recycling. The ecological agenda of the industry, which is now becoming urgent, has long escaped the self organizing capacities of the industry. Now that neo-liberalism has lost its lustre it would be time for a new Multi Fibre Agreement covering a global alliance of countries to prepare for a new fibre basis for mankind.

One of the likely candidates are the bast fibres that have long lost the preeminence they had in the 19th century. In 1910 bast fibres represented 20% of world fibre consumption with a volume of 1 mill Tons. Now its volume is half that and its share is below 1%. Flax is best placed for a revival since it still supports an industry, while hemp and nettle are at an experimental stage. In addition linen has a proven track record with the consumer, while other bast fibres have a marginal existence and little spontaneous recognition of properties. Nevertheless while re-education of consumers is required with regard to hemp and nettle; linen has a confusing image that we shall address later. Moreover the flax chain is not be overestimated in financial, commercial and political power since the largest player in flax reach a turnover between 50 and 100 Mln Euro. Finally while the flax sector has itself a embryonic vision of the future it has not been to mobilize internally and externally the required resources.

However on the basis of agricultural economics, based on their high yield and their complementarity in a crop rotation system, substantial expansion of flax and hemp is possible, not only in Western Europe but also in North and South Eastern Europe. It is important to mention that the ecological balance of bast fibres is far superior to cotton: the fibre yield is even under average conditions higher than cotton, its water efficiency is far higher and they do require little additional input. They do however require intelligent agricultural management, more labour input and an extraction process near to growing. Neither of these conditions are unsurmountable and fully compatible with the knowledge basis, standards and organization of agriculture in developed countries.

A revival of flax shall however require the right inciting environment in terms of agricultural policies and rural management but also a technology road map towards better plants and fibre. Last but not least the fibres should have a better balance between cost and performance since currently, they are considered too expensive in relation to their perceived performance.

A weakness of flax and hemp is that both have not chosen a clear position towards the consumer. A shall set aside hemp which is too small a fibre to assess expections. However for flax the confusing position of flax is embedded in my shirt bought at Brooks Brothers for 89 USD which is “Made from the finest Irish linens”, but is also simultaneously “Made in China”. Linen tries on one hand to sell an exclusive luxurious image, an organic and ecological image, both embedded in 700 years of European Culture, on the other hand the European flax growers majoritarily export the fibre to China from which it returns in the form of 59 Euro shirts. This has led to democratization of linen, and wider reconnaissance of its potential but also to confusion and disregard to quality differences. As insiders mention, the flax growers have not chosen between Bourgogne and Languedoc: either a small volume of quality flax or a volume production. This is also visible in the breeding strategies of flax seeds: the strategy is merely based on agricultural economics not on desired and expected end-performance in the supply chain. The grading of flax is mainly carried out after breaking and scotching. The number of grades is limited (if compared to cotton and wool) and the price differential between low and high grade is much smaller than with cotton and wool.

We would like argue that flax requires a double strategy. A volume strategy is required in order to achieve a sizeable ecological impact. In countries like Lithuania, Ukraine or Romania such a strategy can be sustained as long as yields per hectare are satisfactory and robust and reliable processing methods can be implemented. A quality strategy is required in order to attract consumer appeal and is required for high cost production regions such as Western Europe. In order to realise an economical and ecological impact, revival of flax should focus on an application area where bast fibres can make a real impact in volume, performance and functionality: bed textiles. The strategy below is an example of re-establishing flax as a material of choice. It is an example – that could be one of out of many and beyond the merits of the project below it is embedding in a broader vision that matters most.

Bed textiles represent 23% of flax fibre use. Bed textiles represent with 8% of total textile use a market of some € 50 Bln worldwide. Everyone sleeps, hence it is far from a marginal activity. Comfort requirements are crucial as sleeping takes up more than 30% of human life-time. A large number of factors influence sleeping performance. Linen contributes to **sleep comfort** through creating an excellent thermic, hydrologic and hygienic microclimate[1]. Linen permits to design a functionalised sleep system that enable **sleep care** by reduction of sleep problems. Interaction between textiles and skin gives the opportunity to dispend low intensity skin care. Both comfort and care are obtained by expressing mechanical properties of textiles, often intrinsic to the fibre. Chemical functionalities, now often exogenic to the fibre are often added.

We shall present some elements of a technological strategy that has been worked out by a consortium that entails the Universities of Lille and Gent and a number of companies in each sequence of the supply chain. The objective of this strategy is to obtain fibres of a fineness and a length enabling volume production of linen yarns in the range of 50-100 NM. These grades are currently existing but are in terms of volume and price limited to high end niches (such as for the bedlinen of the pope). The second element is to improve comfort qualities of linen by adding functionalities derived from the plant itself.

It is based on four building blocs:

- Development of new plant varieties based upon increased knowledge of the biological processes underlying fibre length and fineness and optimized lignine profileDevelopment of a two step (partly enzymatic) extraction process using the fundamental understanding of lignin catalysis occurring in the plant growth
- Optimize mechanical properties of flax during the entire manufacturing process
- Strengthen bio-medical properties of flax by grafting flax extracts, in particular lignans.

The building blocs should be obtained from a structural approach that does not accept the plant or even less so the fibre as a given. We live in an era that the genome of flax has been covered and in an era in which the pathway of cellulose formation at molecular level is understood. Hence natural variety of flax should not been considered as a unchangeable fact. We live in an age of high control over processes, and do not longer need to rely on field retting and the quality of French weather forecasting.

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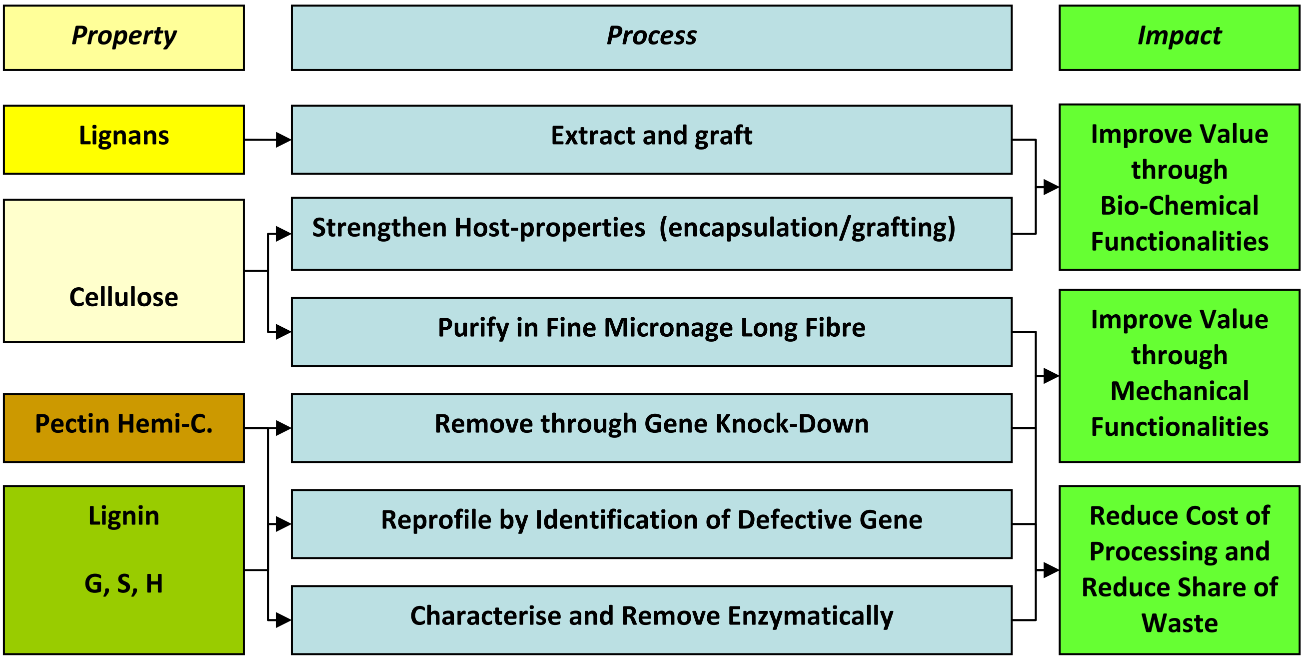
[1] M. Zimniewska, R. Kozłowski, (2004) Natural and Man-Made Fibres and their Role in Creation of Physiological State of Human Body, Molecular Crystals and Liquid Crystals, Publisher: Taylor & Francis, Volume 418 / 2004, p.113 – 130.

Figure 1 Key Properties, Processes and Impact



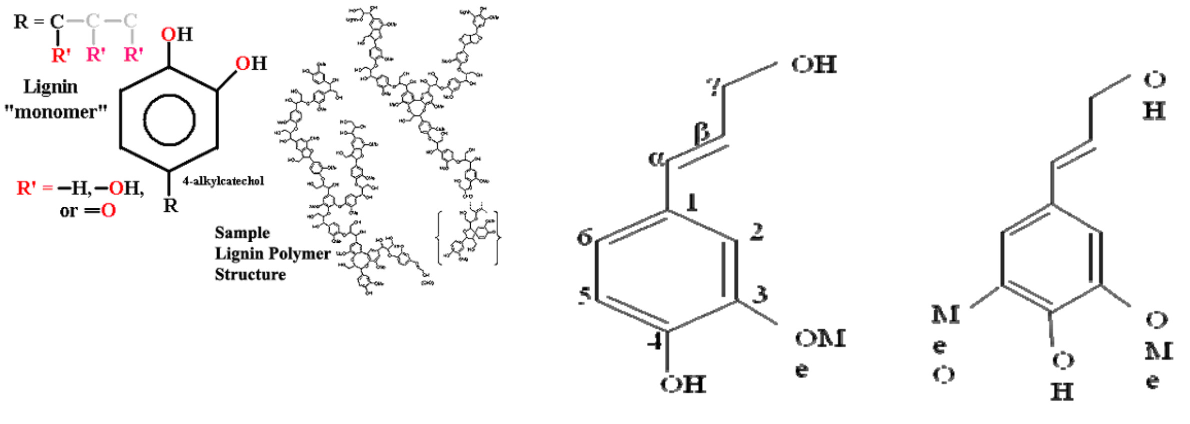
The objectives are translated in a set of bench marks:

Yarn Properties:	Substantial finer yarns derived from 12 Tex in pure long fibres, 16 Tex in blends of short fibres. Higher hydrophilicity and moisture transport (+30%), increased heat absorption (+20%), higher tensile strength (+10%) at lower weights (-30%) lower creasing by lignin reduction, faster drying time after washing (-20%).
Lignan Grafting:	Three working functionalities (cooling fabric, anti-skin-rash and sunburns, regulation of sebum secretion) with controlled release and control of mechanisms of reloading functionality after wash and wear.
Plant:	Create a family of high value plants (fibre price € 2,00-2,20) and strengthen the EU agriculture as supplier of bast fibre material of choice.
Process:	Reduction of Yarn Price at € 5-7 Kg (Comp. € 6-9 kg now -15%) Reduction of energy (-30%) and water consumption and chemistry use.

From a technological point of view the strategy for flax is based on engineering a plant dedicated to a specific end use and on developing a plant extracting process and functional graft mimicking the In this presentation we will focus on the added value to be achieved by adding functional compounds. The better understanding of lignin genesis is subject of research by Simon Hawkins in the Arcir funded project. This will lead to a better understanding of retting and enzymatic catalysis at nano-level.

Lignins (see figure below) are needed for the growth of the plant, but their presence hinders the efficient extraction and separation of bast fibres, thereby leading to a lower quality product. Work by the University of Lille and INRA Reims. has shown that the lignin associated with bast fibres presents an unusual structure (condensed, rich in lignin G and H units, and poor in lignin S units). Such a lignin type is more resistant to chemical and enzymatic degradation than typical higher plant lignins and therefore prevents efficient retting and subsequent processing. In this project, optimisation of lignin content means modifying lignin synthesis in order to reduce overall lignin levels and/or increase the proportion of S units and decrease the proportion of G and H units, thereby facilitating efficient fibre extraction and separation.

Figure 2 Lignin Pathways and Types



Coniferyl alcohol (G) Sinapyl alcohol (S)

Recent work by Lille University and INRA Reims has shown that the lignin associated with flax bast fibres and inner tissues (xylem) presents an atypical structure in comparison with other Angiosperm plants (*Arabidopsis*, willow, poplar). In particular, bast fibre lignin is highly resistant to chemical and enzymatic degradation and is therefore responsible for poor fibre extraction and separation during processing. In order to select and/or modify plants containing optimised lignin levels it is necessary to master the molecular regulation (gene and protein level) of the lignification process in flax. For the last couple of years, Lille University has been developing a global genomic approach (ESTs, Microarrays) and functional genomics[2] to identify and validate the implication of key flax genes in the biosynthesis of cell wall polymers including lignins. A similar approach was also reported by the University of Wroclaw (2004) who showed that development of genetically modified flax with increased resistance to fungi[3], also had a side effect on the reduced lignin content that resulted in facilitated retting. The expertise of this team will allow progress beyond the state of the art by providing sequence data, gene expression profiles and fundamental biological knowledge of the lignin gene/protein network in flax. Since the lignin metabolic

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[2] Day, A., Addi, M., Kim, W., David, H., Bert, F., Mesnage, P., Rolando, C., Chabbert, B., Neutelings, G. and Hawkins, S. 2005. ESTs from the fibre-bearing stem tissues of flax (Linum usitatissimum) : Expression analyses of sequences related to cell-wall development. Plant Biol. 7 : 23-32.

[3] Wróbel-Kwiatkowska, M., et al. (2004), Expression of β-1,3-glucanase in flax causes increased resistance to fungi. Physiological and Molecular Plant Pathology, 65, 245-256.

pathway is intimately associated with that of lignans, this project will also allow significant progress in our knowledge of the biosynthesis of these biologically-active molecules.

A thorough understanding of lignin/lignan metabolism in flax (non-modified and modified plants) also requires a complete and highly detailed characterisation of the structure of flax 'phenolics' (lignin/lignan and related compounds). In this context, the expertise of the world-famous VIB institute[4] enables the use of extremely sophisticated techniques for metabolite profiling. The combination of molecular studies and chemical characterisation will permit, an in-depth understanding of the unusual lignification, and lignan formation processes in flax and the natural variability in lignin/lignan metabolism between different flax varieties, but also the effects of environmental conditions on lignin/lignan gene expression and fibre quality. Such studies should provide the first information necessary for the implementation of a knowledge-based 'environmental engineering' (modulation strategy towards improving fibre structure). The combination of molecular, chemical and environmental approaches will lead to the production and cultivation of 'customised' (as a function of end-uses) fibre plants, thereby representing a technological rupture with previous practices.

Lignans

Adding functionalities to materials is a long standing practice in order to improve the properties of materials. The objective is to add functional compounds to a basic polymers mainly to improve protection and/or comfort. Most recent evolutions, mainly in the last ten years involve added functions with "anti-" properties such as anti-bacterial (more precisely bacteriostatic or protecting the material against degradation by bacteria) or by adding functionalities that compensate for negative impacts (e.g. fragrances to compensate for odour generated by bacterial activity). While the adoption of these functions has benefited from cosmetic innovations, in particular encapsulation techniques, the range of functions created is narrow, the effect often cosmetic and the durability limited to several wearings or washings. Moreover many products do claim a scientific foundation but lack a transparent justification of their claims. Finally for some functionalities negative impacts start to be assessed as is the case with silver dioxides or other non-organic nano-compounds.

Lignans are a group of chemical compounds found in plants, especially in flax seed. The lignans are often used to lay claim of beneficial properties of flax. However lignans as well as other oleogenous compounds are hardly present in the stem of the plant, and if present they are thoroughly removed in the mechanical extraction and further textile processing. Hence any claim of medical properties of linen are largely homeopathic in nature. The concept of hyperflax is based on extraction of lignans from the seeds and grafting to the fabric.

Lignans are structurally characterised by the coupling of 2 phenylpropanoid units by a bond between the β-positions in the propane side chains. Several hundreds of lignans have been identified. Lignans have been found in wooden parts, leaves, roots, flowers, fruits and seeds. The biological role of lignans in plants is still the topic of scientific discussions, but in general it is assumed that lignans play an important role in plant defence and may play a role in growth regulation.

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[4] Dauwe, R, Morreel, K, Goeminne, G, et al.2007; Molecular phenotyping of lignin-modified tobacco reveals associated changes in cell-wall metabolism, primary metabolism, stress metabolism and photorespiration PLANT J, *eFIRST* date: 31 AUG 2007 and Morreel, K, Goeminne, G, et al. 2006 Genetical metabolomics of flavonoid biosynthesis in Populus: a case study. In: PLANT J 47 (2): 224-237 Jul 2006.

Lignans are one of the major classes of phytoestrogens. Phytoestrogens can act as estrogens and antioxidants, some phytoestrogens are able to extend the life span of micro-organisms and promote survival of human cells. Lignans are host to a range of substances with care properties in oral and transdermal use (lignans are claimed to posses e.g. anti-allergenic, anti-inflammatory, bacteriostatic/anti-bacterial, anti-viral, anti-fungal, insect inhibiting properties, and to be beneficial in the treatment of some types of cancer or possibly in the prevention of skin cancer).

Flaxseed and sesame seed are among the richest known sources of lignans, though softwoods knots can contain very high concentrations of lignans. Flaxseed contains typically 0.3 g/100g fresh edible weight (3041 µg/100 g lariciresinol, 3324 µg/100 g pinoresinol, 553 µg/100 g matairesinol en 294210 µg/100 g secoisolariciresinol) and sesame seed typically contains 0.039 g/100g fresh edible weight (9470 µg/100 g lariciresinol, 29331 µg/100 g pinoresinol, 481 µg/100 g matairesinol en 66 µg/100 g secoisolariciresinol).

Secoisolariciresinol (SECO, Fig. 2) is the major alkali releasable lignan found in flaxseed and is present in flaxseed as the diglucoside (SDG), which is incorporated into a (hydroxymethyl)glutarate-linked polymer. Depending on the cultivar SDG can be isolated in overall yields of up to >3% of the seed , followed by base hydrolysis of the aqueous soluble polymer-linked complex. The extraction and refining methods

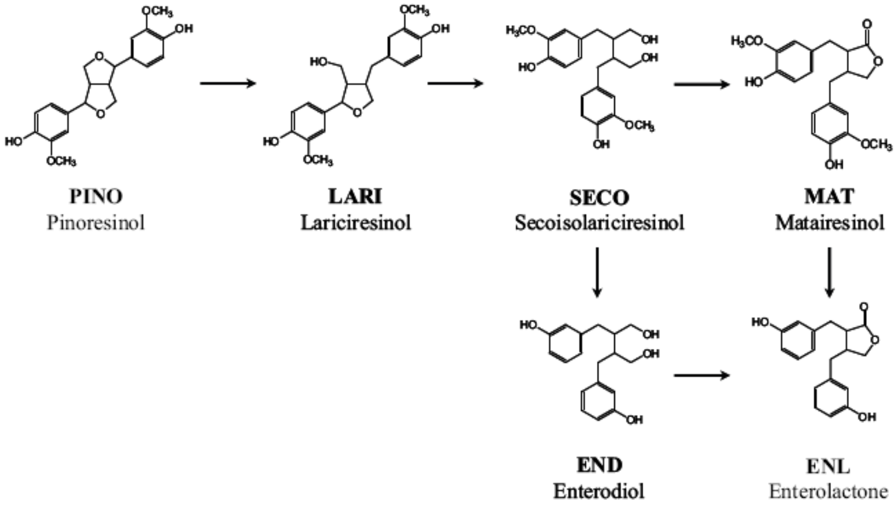

Figure 2. Biosynthetic pathway of plant lignans in flax, and the metabolic pathway for transformation of plant lignans to mammalian enterolignans by the colonic microflora.

The beneficial effect of lignans is mainly studied as food additive or as medicament. The focus of this proposal is on antioxidant, anti-ageing and ant-fungal properties of lignans. Lignans are thought to have wellness properties and are reported to reduce skin ageing. This referenced study suggests a combination of systemic and topical natural antioxidants may help to improve appearance of photo aging and also provide added benefits. In this study lignans were supplied as food additive. Significant improvement in photo damage, skin roughness, infraorbital wrinkles, facial wrinkles, and skin attributes was evident after 4 weeks. The anti-oxidant reactions for SECO and SDG (AAPH mediated oxidation) and the activities of several flax lignans and isoflavones were studied in vitro.

Anti-fungal and anti-microbial activity of lignans and neolignans and was assessed in vitro by several research groups. Minimal inhibitory concentration against dermatophytes such as of several neolignans is typically in the range of 0,5 and > 50 µg/ml.. Secoiresinol was most effective against fungi that are rooting and staining wood (45% inhibition of *Trametes Versicolor* at 100 µg/ml per disc) while pinoresinol showed moderate activity. Different lignans or combination of lignans do affect more effectively bacteries thriving in an acid or a basic environment.

Topical delivery of lignans involves percutaneous absorption. Topical application of lignans often involves emulsions (creams). Scientific research on topical application of lignans is fairly limited and of most often of qualitative nature. Various lignan formulations for dermatological application containing lignans or lignan esters in a water-in-oil or oil-in-water emulsion, gel, ointment, liposome, polymeric vesicles or cyclodextrins have been developed. The skin provides a principle barrier to topical delivery of lignans. The solubility of lignans in aqueous solutions is fairly low; simply increasing the concentration is therefore not an option. Lignan or lignan ester complexes with cyclodextrins are developed (and patented) to increase the concentration in aqueous solutions when applied as food additive or pharmaceuticals.

Limited knowledge is available regarding skin permeation and moisterising effect of oils. Using in vivo Raman microspectroscopy, the potential of different oils in skin moisterisation have been demonstrated. Oil (paraffin oil and vegetable oils) is actually absorbed by the upper skin, but only in the outer layers. The absorption of petrolatum is significantly higher, as well as the depth of absorption. In vitro skin permeation is often studied using a Franz diffusion cell, containing human or mammal skin or a model substrate. It was demonstrated that genistein absorption is increased when applied to the skin as suspension of elastic liposomes. Absorption was via the hair follicles.

Regarding extraction and application of lignans specific technologies have been selected and tested. For patenting reasons we can not be to specific, the application of a patent prohibits us of a detailed description of the process. In general terms the manufacturing process is composed of a primary extraction of lignans out of plant material, a secondary extraction on order to increase the concentration of lignans in a phenolic environment. The lignans should be reintroduced in any stable oily substance required to enable transport into the skin. This can be a purified flax oil but as demonstrated above any oil currently used in cosmetics. The hydrophobic character of the guest substance including the lignin also enables to develop an encapsulation and controlled release strategy.

The inclusion of lignin in a controlled release host is studied, as well as grafting of the hast to the substrate. Controlled and triggered release patterns have been examined and since the skin has many triggers (heat and acidity/salinity when sweating) various options are possible. Finally the host system can be applied through a classic foulard process or through more modern methods such as digital finishing, enabling single side coating. The guest molecule can be introduced with the host or in a two step process in a later manufac turing stage or in laundry process. While the stability of the host is known, there is no knowledge available on maintaining a sufficiently high and stable concentration for a defined period of time, and the delivery kinetics in dermatological applications of lignans. This is a major objective of research still to be carried out. However the lignan route enables higher concentration of active elements than with current “medical textiles” hence their is more room to play with the cocktail of lignans to be selected as well as with their concentration. We have also made pre-emptive calculations of possible costs and while lignans come at a price, the extra consumer price is within the 15-20% premium that proven added functionalities can command in the market.

Conclusion

The hyperflax route is one of many elements of a route that form the palet of a strategy to re-establish linen as the material of choice where it semantically at least belongs: bedlinen. If the improvement of mechanical properties is obtained through alignment of plant and process (lignin re-profiling and enzymatic process), as well as the lignin grafting assures a reasonable functionality over a product life cycle, than linen offers real value added to a market that since 1930 has gone to the cotton standard.

This example is not to highlight the specific merits of this mobilization of knowledge and technologies. Its aim is to guide us to look for benefits where there is critical mass, and a real economical and ecological impact. In doing so it also points the attention to an area of application that is often forgotten. Between smartwear and technical textiles it is often overlooked that there is much work that can be done in home – textiles.

We have made at the beginning some remarks of the necessary fibre shift to make the textile industry proof for the 21st century. The challenge to meet is only partly technologic. The project above should require less than 1 Mln to become commercially available. The challenge is rather political, to have a debate at the global level on the future fibre mix and to create an alliance possible. The bench mark that we would like to set is a strategy that enables bast fibres to cater for 3% of global world fibre consumption by 2020. That is only 2,7 Mln Tons but it represents a substantial multiplier above current levels. From a global welfare point of view it does not matter whereas this output comes from China or France.

We would invite the audience to reflect not only on technology but also on the strategy, organization and politics to re-establish flax as a material of choice. This is not a open invitation since we are planning a reflection process to that aim starting after this conference with those forces of progress that desire to be part of the 21th century.