FINAL PUBLISHABLE SUMMARY REPORT

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Partners:

ASOCIACIÓN MURCIANA DE INDUSTRIAS QUÍMICAS - AMIQ
Technical Textiles Rhône-Alpes - TECHTERA
CZ Biom - Czech Biomass Association - CZBIOM
NUTRAFUR SA - NUTRA
RAIDLIGHT VERTICAL - RAIDLIGHT
Tecnicas Reunidas - TR
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Tecnologías Avanzadas Inspiralia SL -INSP
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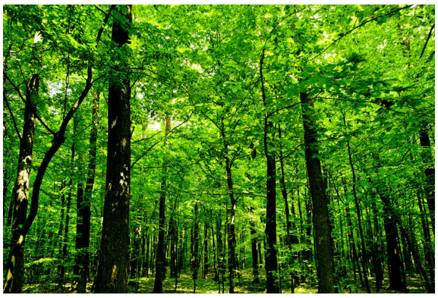
Table of contents

1 Summary description of the project context and the main objectives

1.1 Relevance and goal of the project.

ECOLASTANE has been designed to overcome the technical obstacles preventing our value chain from addressing the common needs of bio-based chemicals and bio-based synthetic fibres as a technical solution providing the whole community with strengthened competitive advantage.



Around 25% of the fibres consumed in Europe are natural (cotton, wool, silk), while man-made fibres represent 75%. Man-made fibres are basically synthetic fibres based on petrochemicals that dominate the market: polyester (72%), cellulosic, acrylics, polypropylene, polyamide, and elastane (28%). Chemicals industry needs to prepare synthetic monomers and polymers according to the chemical, physical and performance characteristics demanded by the Textile & Clothing (T/C) industry.

Bio-mass is the only source of bio-based chemical for *Bio-based synthetic textile fibres.* Nowadays there is an increasing need of bio-based chemicals such as FF (furfural) and HMF (hydroxymethyl furfural) from renewable, natural and non-edible vegetal raw materials.

The socio-economic downturn of the European T/C and Fibres Industries is due to imported finished products. The end of Trade Agreement on Textiles and Clothing in 2005 resulted in no restrictions to foreign imports into the EU. This rapid growth in cheap imports of finished product is forcing European textile SMEs to close down.

Innovations like high added value and bio-based synthetic fibres produced by eco-efficient European processes are the required solution for a regain of competitive advantage against the current economic downturn. ECOLASTANE bio-based synthetic fibres are derived from renewable resources (70% to 100% bio-based), are biodegradable and will have an increased (high & bio-based) quality as well as competitive price ratio against low-quality / cheap foreign imports from Asia.

The main limitations of current bio-based synthetic fibres are:

- Lignocellulose is difficult to transform to bio-based monomers.
- FF production from the hemicellulosic part of lignocellulose is unprofitable in Europe due to: loss of FF by deficient extraction, inefficient energy consumption, poor FF purification, inefficient solvent recovery, etc. On the other hand, the technologies used to synthesize FF are only available starting from hemicellulose pentoses (20-40% of lignocellulose); i.e. they cannot valorise cellulose (30-50 %).
- The industrial production costs of HMF are quite high.

In conclusion, there are very few bio-based synthetic polymers available in the market and they are of low quality and high price.

The ECOLASTANE solution addresses the following needs:

- Reduce the processing costs of lignocellulosic biomass. A wide range of processable biomass types will reduce dependence on the price and availability of only one feedstock. By a versatile and inexpensive drying and / or milling pre-treatment, a very small particle size is obtained to increase product yield of subsequent operations. Moreover, during the pre-treatment, ground biomass is subject to an acid-free hemicellulose hydrolysis with the subsequent isolation of *pentoses*. Lignin is removed from the remaining material in order to isolate free *glucoses* from hydrolysed cellulose. Isolation of precursors increases the yield by avoiding side-reactions with lignin.
- Furfural is produced from Pentoses by an optimised version of the current process for a broad acceptance of our ECOLASTANE technology. A quick furfural extraction prevents furfural loss by fragmentation reactions, and low energy-intensive gas-liquid absorption reduces purification costs.
- HMF is synthesized from hexoses in polar aprotic solvents in scalable conditions, and in this form ECOLASTANE can develop an industrially feasible production of HMF.

With these two compounds (FF and HMF) we have developed price-competitive 100% bio-based monomers (THF, FDCA). Finally, these bio-based monomers, resembling today's petrochemical structures, are combined into bio-based synthetic polymers of high performance and quality for textile fibres (70% bio-based commercial elastane and new polyester and elastanes with improved structures and performance industrially validated for textile uses). In the end, in ECOLASTANE we have developed price-competitive and novel bio-based fibres with improved physico-chemical performance.

In that sense, the ECOLASTANE project will provide the European SME-based biomass sector with a modern high-yield and eco-efficient process to prepare price-competitive FF, HMF and THF from valorised waste. The objective is to turn this European industry into a competitive global scenario by expanding its target market, using these chemicals as suitable monomers for synthetic textile fibres and opening a new route for the industrial production of highly valuable bio-chemicals.

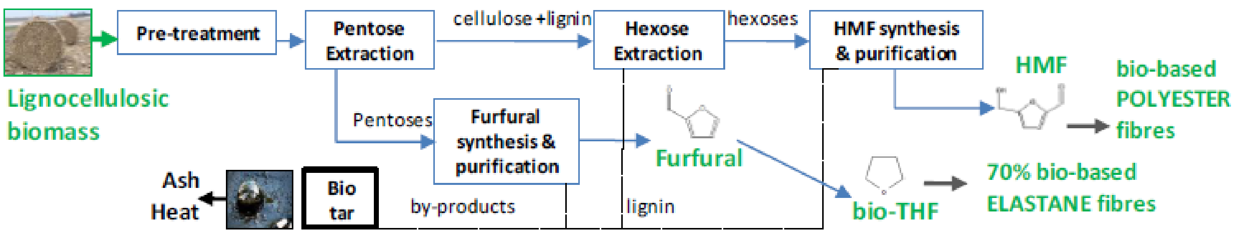


Figure 1. - ECOLASTANE industrial process.

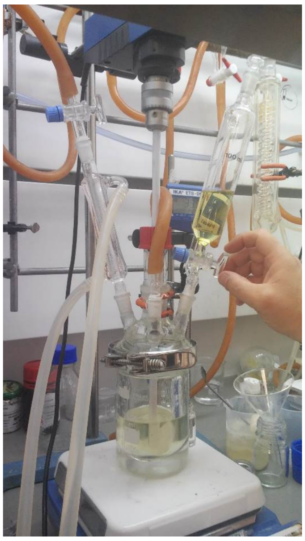
1.2 ECOLASTANE technical approach.

The industrial process of ECOLASTANE is presented in Figure 1 while the development process, from the raw materials to the finished fibres, can be summarised in the following phases:

- Selecting and characterizing the best group of raw materials based on chemical studies, testing and / or developing different pre-treatments and particle sizes and testing the rheological behaviour of the mixture in the reactor.
- Developing an improved Bio-Furfural (FF) synthesis with higher yields and lower costs.
- Developing an innovative industrial Bio-hydroxymethylfurfural (HMF) synthesis.
- Our novel ECOLASTANE fibres (Elastanes from Bio-FF, and polyesters from Bio-FF and Bio-HMF) have been designed with the necessary polymer chemical studies and trials in order to come up with the chemical structures showing the best performance, which required intensive laboratory work.

1.3 Scientific and Technical Objectives.

ECOLASTANE addressed the following scientific objectives:



1. **Lignocellulosic biomass**: to understand how seasonal quantitative availability, chemical composition, market value, transportation costs affect biomass raw materials.
2. **Pre-treatment and extraction**: to study the effects of eh mechanical, chemical and physical pre-treatments on biomass processing costs. Evaluate the efficiency of hemicellulose hydrolysis into pentoses and cellulose into hexoses.
3. **Synthetic Fibre polymers:** to understand the way in which key polymer functional groups, soft/hard segment proportion, chain length, cross-linking and additives contributes to the final performance of the material in the extruded monofilament.
4. **HMF (5-hydroxymethyl-2-furaldehyde) synthesis:** to understand how glucose isomerization to fructose; fructose to HMF; conversion mechanism, different acid catalysts, yield-loss side reactions, and reaction conditions affect HMF synthesis.
5. **Bio-tar**: to study its chemical composition, rheological behaviour, the effect of different and burning conditions on the calorific power in order to identity the most appropriate parameter for in-plant combustion for a high efficiency heat release.
6. **Synthetic fibers:** to study novel chemical structures of polyester and polyamide fibres; extrusion, drawing and texturing operations on filaments; and behaviour, applications of novel bio-based ECOLASTANE fibres for sports and leisure products.

ECOLASTANE addressed the following technical objectives:

1. **Biomass-pre-treatment**: Pre-treatment to reduce lignocellulosic waste grinding biomass from #80 to #120 mesh.

2. **Pentose and hexose extraction:** Efficient hydrolysis of hemicellulose pentoses preventing the synthesis of FF and preserving cellulose. The aim is the obtaining of solutions 95% rich in pentose and 95% hexose from selected biomass.
3. **HMF synthesis** from lignin-free cellulose/hexoses extract. Estimation of reaction kinetics. Conceptual design of HMF reactor using Computational Fluid Dynamics (CFD) models.
4. **Bio-Tetrahydrofuran (THF):** synthesis of 100% bio-based THF from furfural by catalysed oxidation, subsequent decarboxylation and followed by metal-catalysed hydrogenation.
5. **Bio-tar:** production of a sample of bio-tar from lignin and by-products from FF and HMF synthesis and purification residues with a calorific power higher than the original material.
6. **Synthetic fibre plastics polymer**: bio-based elastane and polyester will be synthetized by extension of corresponding prepolymers.
7. **FF (furfural) purification and organic solvent recovery**: 98% pure furfural for synthesis uses will be isolated by hetero-azeotropic distillation. Organic solvents recovered by absorption.
8. **HMF purification:** 99% pure HMF.
9. **Prototype**: Continuous operation prototype at approx. 4L scale for furfural synthesis. Conceptual design of HMF reactor using CFDs models. Up-dated bio-THF synthesis.
10. **Validated ECOLASTANE products**. Samples of formulated polymer chips and extruded and spun synthetic fibre monofilament of 70% bio-based elastane and 100% bio-based polyester.

2 Description of the work performed since the beginning of the project and the main results achieved.

The outcome of the ECOLASTANE project can be measured in terms of its five main methods or results:

1. Furfural production method from lignocellulose.
2. HMF production method from lignocellulose.
3. Bio-THF production method from lignocellulose.
4. Method for the production of novel bio-based polyester-like synthetic textiles fibres.
5. Method for the production of novel bio-based elastane synthetic textile fibres.

2.1 Furfural production method from lignocellulose.

The current furfural production is still based on modified processes of the original Quarker Oats process (1953). This process mostly consist of suitable reactors loaded with acid-impregnated biomass, where steam is injected through the biomass bed at an optimal pressure and temperature, while a furfural enriched vapour stream is continuously retired. The furfural-containing stream is subsequently concentrated via azeotropic distillation and rectified via vacuum distillation which demands high energy. The solid biomass residues are normally incinerated or disposed of to take benefit of the energy in the process. This whole process runs in batch mode.

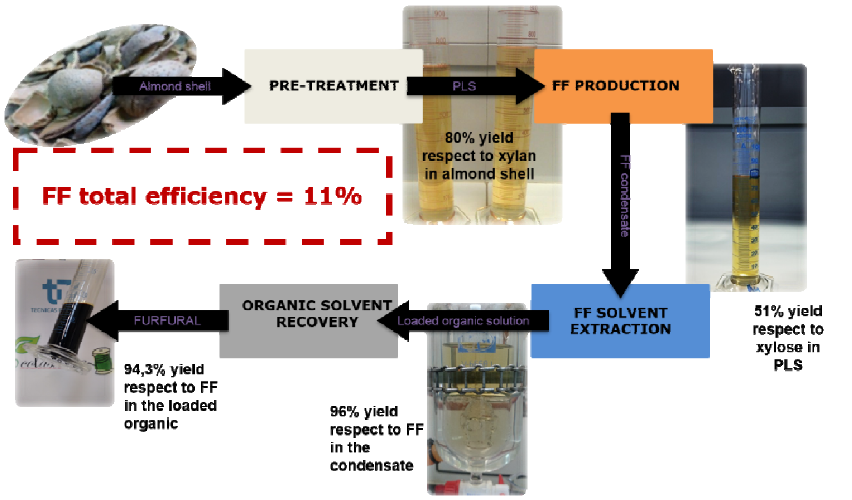


Figure 2. New furfural production process.

The disadvantages of current technology are low yields (around 50% respect to xylose content) and high energy demanding purification, which means significant economic and environmental concerns. All these reasons contributed to shrink the furfural production capacity in EU downing to an only limited presence, and hindering the expansion and modernization of the furfural industry below its actual potential. A key objective in ECOLASTANE was to improve current Furfural (FF) yield in order to give solution to existing production and economical concerns. The idea was to avoid the production of resins derivated from the formation of FF inside the reactor. ECOLASTANE provides a novel and alternative technology which is capable of enhancing the total production of Furfural into 11% that means 3% more than classical technology. The ECOLASTANE technology for Furfural production is based on 4 stages:

1. Physic-chemical pre-treatment
2. Furfural production
3. Solvent extraction
4. Organic solvent recovery

2.2 *HMF production method from lignocellulose.*

The production of bio-based furfural utilizes only a small fraction of the biomass and, in particular, only the hemicellulose. Consequently, the remaining biomass which contains glucose and lignin is discarded as a waste and / or burned. However, the increased cellulose concentration of this material makes it a good candidate for the synthesis of other bio-based chemicals such as HMF.

Within the scope of the ECOLASTANE project was the development of a process that could utilize this hemicellulose-free biomass for the synthesis of HMF, thereby creating a side-stream production process in order to increase the biomass utilization and offer additional economic benefits thus aiming to renew the interest of industry in EU for the synthesis of bio-based chemicals. Towards this end, in ECOLASTANE we studied the conditions for cellulose hydrolysis and concluded with the optimum ones for obtaining a glucose rich solution that was further used for the synthesis of HMF. In the next step, a new catalyst was synthesized and applied for the direct synthesis of HMF from the glucose rich solution. An intermediate isomerization step between glucose and fructose (in view of enhancing the HMF yield) was also investigated. Finally a four step extraction process was developed, minimizing the use of chlorinated solvents, which are the current state-of-the-art for the HMF purification. Consequently, the technology proposed for HMF synthesis could be summarized as follows:

1. Hydrolysis of cellulose from the hemicellulose-free biomass.
2. Conversion of glucose to HMF over heterogeneous catalyst.
3. Solvent extraction of HMF.
4. HMF purification.

The process has a 31% yield of HMF based on the glucose rich solution which corresponds to an overall yield of 4.8% based on hemicellulose-free biomass.

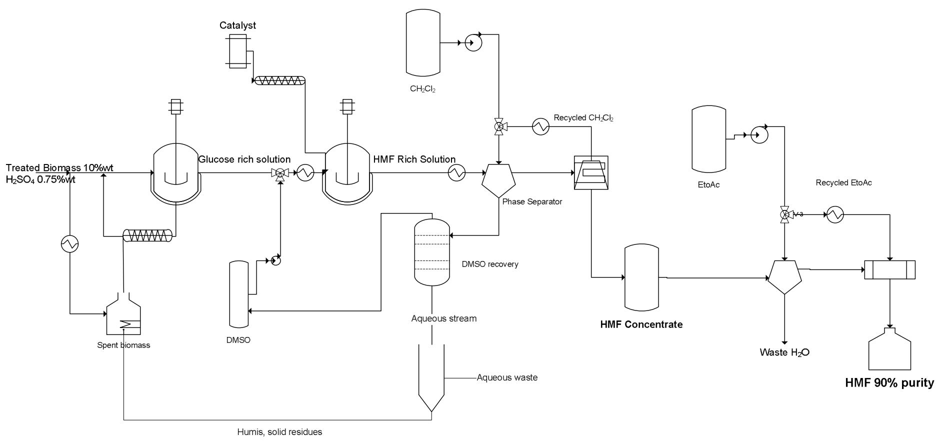


Figure 3. Flow chart of the developed HMF synthesis process.

2.3 Bio-THF from lignocellulose.

FF is converted to bio-THF by an up-dated industrial method. Our bio-THF is chemically identical to petrochemical THF and thus does not require any different technology to produce a 100% bio-based PTMEG. This elastic diol accounting for ca 70% of the mass of commercial elastane fibres. Using these bio-based diols we obtain 70% bio-based elastane fibres with unchanged chemistry and performance compared to petrochemical alternatives which is made possible thanks to our ECOLASTANE bio-THF.

2.4 Novel bio-based polyester-like synthetic textiles fiber.

New 100% bio-based polyester have been synthesized with a chemical structure resembling commercial polyester PBT. Starting from Bio-5-HMF it has been produced furan dicarboxylic acid (FDCA), a real bio-based monomer alternative to terephtalic acid (PTA) used in commercial polyester. On the other hand, a diol monomer, bio-Butanediol (BDO) has been obtained from bio-THF, prepared in a previous step from furfural (FF). Afterwards, an optimized strategic method for synthetizing polybutylene- furanoate (PBF), a 100% bio-based new polyester, has been developed using the ester derivate of the previous FDCA and the butanediol (BDO). In a later process 100 % bio-fibres with very good properties and textile sample products were also produced.

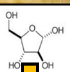
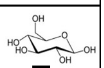
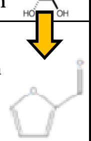
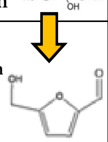
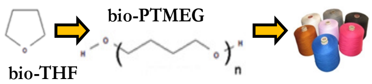
Component technology or material		Phase	Funcitionalities and derived Benefits	
ECOLASTANE TECHNOLOGY 2nd generation biomass	Wide range of processable feedstock	Lignocel. Biomass	Reduced dependence on the price and availability of only one biomass, ensuring acces to a more secure and cheaper spectrum of raw materials → **Continuos supply of low market value biomass**	
	Optimised Pre-treatment	Pretreatment	Inexpensive drying and milling for a small particle size → **Increased product yield of subsequent operations**	
Pentose extraction 	Hexose extraction 		Isolation of product precursors and lignin removal → **Reduced yield-loss side reactions for improved subsequent synthesis**	
Furfural production 	HMF production 	Monomer	Quick product extraction → **less furfural loss** Improved less energy-intensive purification → **Lower costs**	Selective conversion to HMF → **higher yield at industrial scale** Quick HMF removal → **reduced HMF loss**
Biochar burning & Solvent recovery &Eco-efficient design		Integration	By-product valorisation to save energy costs, solvent input cut and costs, efficient energy use → **Low costs, eco-efficient profile**	
ECOLASTANE BIO-BASED FIBRES 		Polymer	Price-competitive and high-quality fibres: → **70% bio-based but identical-to-commercial elastane** → **New bio-based elastane and polyester fibres with improved** structures and performance industrially validated for textile uses.	

Figure 4. Results and Benefits.

2.5 Novel bio-based elastane synthetic textile fiber.

On a basis of the highest performance / price ratio, two novel elastane structures have been developed by using ECOLASTANE monomers and derivates. 70% bio-based elastane (polyurethane polyurea polymer), with chemical structure and performance equivalent to petrochemical fibres, was produced by employing long chain diols such as polytetramethyleneglycol (PTMEG, 70% of final elastane fiber's weight). These materials were obtained from 100% renewable lignocellulose sources (bio-THF) and diphenylmethane-4.4-diisocyanate (MDI) and ethylene-diamine (EDA).

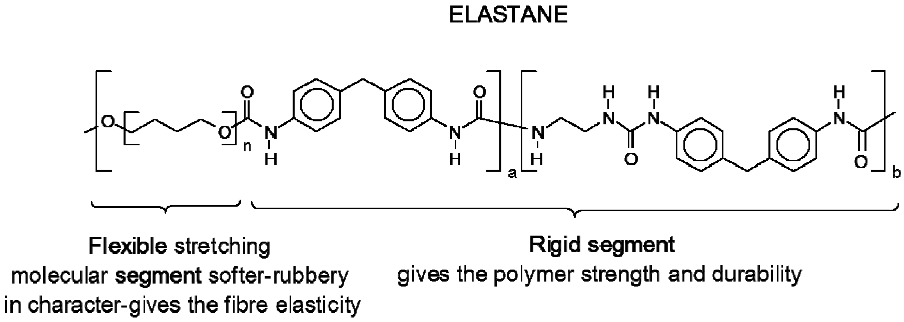
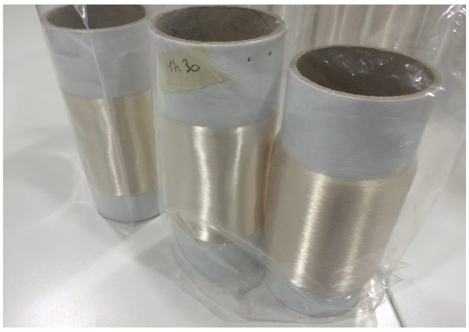


Figure 5. Elastane based fibres.

3 Description of the expected final results and their potential impacts and use.

3.1 Expected final results.

Virtually all companies of the T/C and man-made fibres could potentially benefit from our ECOLASTANE elastane and polyester. The price of our 70% bio-based elastane will successfully compete with today's petrochemical alternatives without demanding a change of current technologies. Elastane is an elastic fibre present in small amounts in almost all types of fabrics. It is a fibre that can be spun with other fibres to produce unique textiles. All downstream textile products, especially sports clothing, backpacks, hydration devices, tents, accessories and miscellaneous will have the high added value given by our high-quality ECOLASTANE fibres from renewable materials. These two features will render them more attractive for the final individual consumer against low-quality and low added-value foreign imports on the basis of a more favourable high-green quality / price ratio. Bio-based products will give European producers an advantage-novel functionality, green credentials.



On the other hand, the Chemicals industry will directly benefit from our solution by having access to secure, non-petrochemical and abundant European sources of inexpensive and 100 % bio-based THF to satisfy the demand of elastane of man-made fibres industry. The major use of THF is as a monomer in the production of PTMEG, and secondarily as a solvent for multiple uses (solvent for oil cracking furfural alcohol for furan resins in metal casting industry, plastic manufacture, laboratory solvents, coating formulation additives, vulcanization catalyst and production of pesticides). In turn, around 80% of PTMEG goes to elastane fibres. Our THF will be cheaper than similar products thanks to the use of lignocellulosic low-value raw materials and an eco-efficient technology for its production; thus saving energy and waste disposal costs as well as solvent input. Our HMF production method from lignocellulose will be used for the production of FDCA (furan dicarboxylic acid), for the synthesis of synthetic polymers for textiles fibres with a wide range of different fine chemicals; since HMF is a platform chemical for commodity chemicals. But the fact that our THF and HMF are a 100 % bio-based will translate into a more promising expansion in the market.

Biomass companies will see their technological obstacles overcome and will be provided with our ECOLASTANE technology for preparing FF and HMF from a wide variety of lignocellulosic sources with a high yield, eco-efficient process, with low environmental energy and overall economic costs. ECOLASTANE is in line with the strong wind in favour of environmental sustainability worldwide and the foreseen new legislations promoting the usage of bio-based plastics and sustainable materials. For bio-based plastics the price comparison is also favourable against conventional oil-based polymers, as crude oil prices will keep increasing.

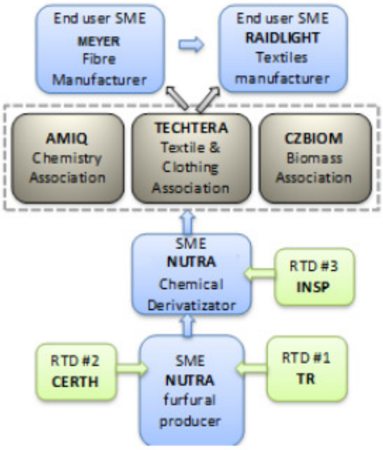


Figure 6. – The ECOLASTANE consortium.

3.2 The ECOLASTANE Consortium.

ECOLASTANE is a project put forward by three European SME Associations: **TECHTERA** (Technical Textiles Rhône-Alpes, France); **AMIQ** (Asociación Murciana de Industrias Químicas, Spain); and **CZBIOM** (CZ Biom–Czech Biomass Association, Czech Republic). We share a common value chain connecting final textile fibres (Textile and Clothing industry) with its starting bio-materials (biomass SME companies) through the intermediate transformation of bio-materials to bio-based synthetic fibres (Chemicals industry).

The Consortium also counts with the participation of NUTRAFUR; due to its 50-year experience in furfural production. The role of NUTRAFUR was to validate at industrial scale the novel technology developed for converting vegetal matter to furfural and HMF. Another important contribution comes from MEYER. MEYER assumed the vital role of validating elastane fibres (70% bio-based and identical-to-petrochemical elastane); as well as new bio-based polyester fibres. At the end of the supply chain we have RAIDLIGHT. RAIDLIGHT acted as the end-user in charge of validating the use of new textile fibres in real products. They evaluated the use of elastane and polyester fibres to produce woven textiles that can be used in the Textile and Cloth industry.

The core of the scientific and technical work was developed by three reputed research organizations: Tecnologías Avanzadas Inspiralia (INSP), Técnicas Reunidas (TR) and The Centre for Research and Technology Hellas (CERTH). TR developed the ECOLASTANE technology for bio-based monomers, particularly the development of the FF production method working on the industrial pre-treatment of biomass and on the pentose production process towards the production of furfural (furfural purification, recovery of solvents, etc.). CERTH was chosen for the key role of developing an industrially feasible technology for preparing HMF as one of ECOLASTANE bio-based monomers. CERTH did the biomass selection, hexose extraction from cellulose and bio-tar preparation and characterization. Moreover they performed the synthesis and the design of the correspondent HMF reactor. CERTH conducted a full analysis of the costs and scalability of ECOLASTANE technology. Inspiralia applied their expertise in the area of material chemistry, polymer science, formulation and mechanical analysis to lead the tasks dealing with the synthesis of ECOLASTANE elastane and polyester fibres (monomer functionalization and synthesis, prepolymers synthesis and polymer synthesis). They formulated and characterized the final plastics polymers. Inspiralia worked alongside MEYER and RAIDLIGHT in the validation of ECOLASTANE fibres and performed the simulations leading to the design of the HMF reactor.

3.3 *Project Web and Contact Details.*

Partner	Short name	Web site	Country
Asociación Murciana de Industrias Químicas	AMIQ	http://amiq.net	Spain
Technical Textiles Rhône-Alpes	TECHTERA	www.techtera.org	France
CZ Biom–Czech Biomass Association	CZBIOM	www.czbiom.cz	Czech Republic
SAS CORDERIE MEYER SANSBOEUF	MEYER	www.nutrafur.es	Spain
Nutrafur SA	NUTRAFUR	www.meyer-sansboeuf.com	France
Raidlight	Raidlight	www.raidlight.com	France
Centre for Research and Technology Hellas	CERTH	www.certh.gr	Greece
Técnicas Reunidas	TR	www.tecnicasreunidas.es	Spain
Tecnologías Avanzadas Inspiralia.	INSP	www.inspiralia.com	Spain

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