Deliverable 3.2

Delivery of 3D printed automotive interior components

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LIST OF ACRONYMS

PL	Pilot Line
AM	Additive Manufacturing
BDO	Butanediol
BIOMAC	European Sustainable Biobased Nanomaterials Community
CAD	Computer Aided Design
GLY	Glycerol
HPLC-RID	High Performance Liquid Chromatography - Refractive Index Detection
LA	Lactic Acid
NFC	Natural Fiber Composite
NMR	Nuclear Magnetic Resonance
PDO	Propanediol
PE	Polyethilene
PL	Pilot Line
PP	Polypropylene
RT	Room Temperature
SA	Succinic Acid
SLA	Stereolitography
TeC1	Test Case 1
TGA	Thermal Gravimetric Analysis
2PP	Two Photon Polymerization

1. Executive Summary

Test case 1 is related to the Automotive Pilot, whose activities were developed in the framework of WP3 - Task 3.2. This task started at M18 and ended at M36 and it was supported by LTU, AUTH, BBEPP, ATB, LIST, FH-WKI, AIMEN and DIAD, end user of the proposed application.

The main goal of Task 3.2 has been to redesign the automotive component proposed by DIAD (a sun visor) with a bio - based polymer produced using BIOMAC precursors.

PL3-AUTH, PL7-ATB and PL6-BBEPP provided FH - WKI with the raw materials obtained and new formulations of bio - based PE resins were formulated and printed by AIMEN, who fabricated a series of prototypes that will be submitted to further characterisation in the last year of the project.

DIAD, as end user, coordinated the activities and provided the technical specification of the component, the CAD, the description of the process chain and of the expected performance using as a reference the commercial component at present produced in PP by injection moulding.

At the end of the period, as planned and with no deviation with respect to the Work Programme, a new category of components was obtained thanks to the joint efforts of the partners involved.

Periodical bi - weekly meetings has been held for the whole duration of the task among DIAD, FH - WKI and AIMEN to coordinate the activities, alternated by meetings with all the partners involved in the task. The following paragraphs summarise the work carried out.

2. Test Case 1 Process Flow and Contributors

TeC1 involved the use of the following pilots: PL1, PL3, PL6, PL7, PL10, PL12 and PL15, as illustrated in Figure 1.

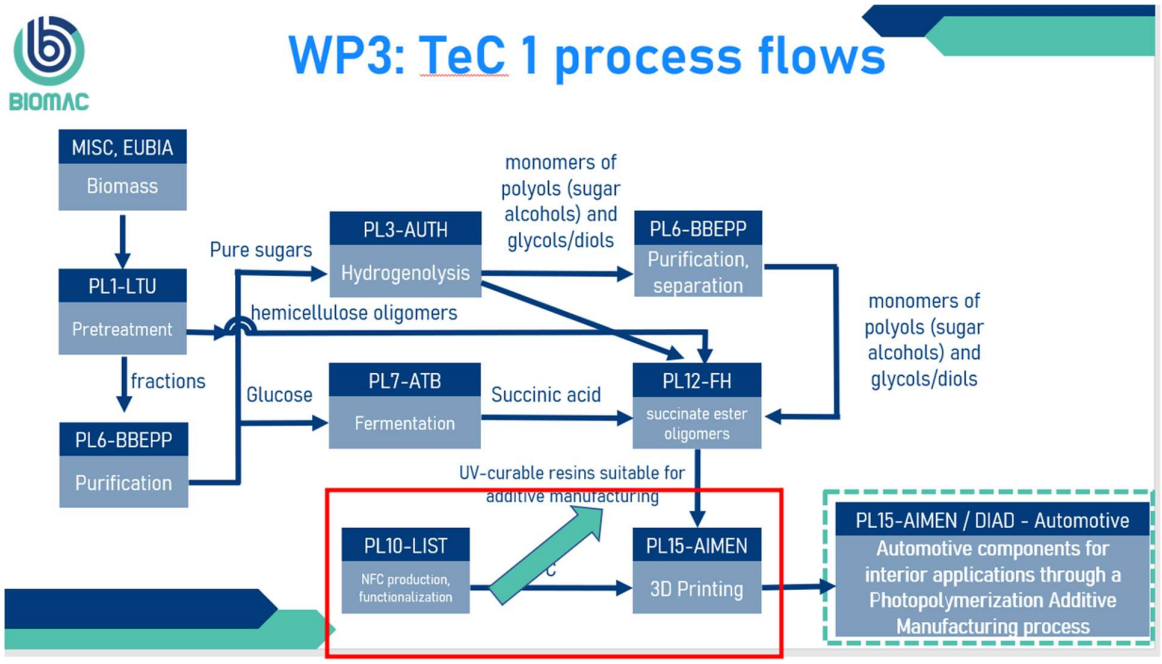


Figure 1. TeC1 Process Flow and Pilots involved

PL1 of LTU is an organosolv pre-treatment unit that is capable of fractionating lignocellulosic biomass (such as agricultural and forest residues) to its three main polymer components, i.e. cellulose, hemicellulose, and lignin. The reactor treats lignocellulosic biomass in mixture of water with organic solvents, with the most commonly used being ethanol due to its low cost, low toxicity and easiness to recover. Typically, temperatures up to 200 °C are being used and the treatment time normally is in the range of 30-60 minutes. To further assist the fractionation process, mineral acid or alkali at low concentrations can be used as catalyst. Within the BIOMAC project the PL1 has undergone a major upgrade to make the process fully continuous (as illustrated in Figure 2). By implementing a new system that continuously feed biomass and solvent from atmospheric pressure into the pressurized reactor and extracting the process liquor to atmospheric pressure the process does no longer depend on pre-prepared batches. This new system consists of three subsystems: Biomass, solvent and process liquor.

Figure 2. The PL1 located at LTU

PL3 of AUTH, is related to the production of sorbitol, as well as the production of smaller glycols and diols, i.e. glycerol, ethylene glycol and 1,2-propanediol. For this purpose, PL3 utilized glucose rich streams provided by other partners (i.e. PL1/PL6), as well as commercial glucose to perform optimization tests at lab scale and provide larger amounts of products at pilot scale. Lab scale experiments were performed to optimize the process parameters, i.e. catalyst type, temperature, time, H_2 pressure, feed concentration. The pilot scale experiment took place in order to first verify the results obtained from the lab tests and then produce larger amounts of polyols, which were sent to FH-WKI (PL12) to produce the relevant resins and to BBEPP (PL6) to perform separation/purification tests. Also, succinic acid provided by ATB's PL7, was characterized and used as feedstock for the production of 1,4-BDO for TeC5.

The PL6 of BBEPP comprises of a manifold equipment portfolio (microfiltration, ultrafiltration, nanofiltration and reversed osmosis), ion exchange equipment, solvent extraction technology and crystallization to obtain monomeric fractions. Cellulose and hemicellulose streams (different liquid fractions from PL1) were hydrolysed towards monomers (i.e. glucose, xylose, etc.) sugar rich streams and purified within PL6 of BBEPP.

The pure monomer sugar streams (i.e., glucose or xylose) were purified for PL3 and PL7. The pure sugars stream from PL6 (i.e., glucose or xylose) are subject to catalytic hydrogenation/hydrogenolysis in PL3 of AUTH towards monomers of polyols (sugars alcohols) and glycols/diols. Purification/separation mixed polyols/diols. product streams were also looked into during process optimisation in PL6. In addition, sugar alcohols (i.e.,

sorbitol) were separated and recovered from smaller glycols from the liquid products of PL3.

PL7 of ATB is responsible for monomers production: lactic acid (LA) and succinic acid (SA). PL 7 has developed tools to firstly optimize the process on small scale (even µL scale), that can be further transferred to the technical and pilot scale. ATB has a long experience in fermentation of waste streams, including lignocellulosic substrates, to organic acids, such as, succinic acid. ATB's pilot line is also experienced in the downstream processing, which means that ATB can provide other partners a pure monomer, which can be further investigated. ATB works strongly with biomass provider, such as, RISE PROCESSUM, BBEPP, LTU but at the same time ATB defines the goals together with PL-3 AUTH and PL-12 FH concerning the purity of monomers and quantities.

PL10 of LIST has upgraded NFC production using the Masuko Super Mass Colloider, shifting from batch to continuous circulation. The redesigned system, with a pump-controlled setup, inline viscometer, and power meter, addresses scalability issues. The set up is capable of producing dispersions of NFC in water with concentrations of 0.5 – 4 wt% of NFC. Using the continuous system, up to 100 litres of dispersion can be produced per day. By varying grinding gap sizes, grinding times, diverse feedstocks feedstocks can be processed into NFC. Analytical techniques precisely control size distribution, crystallinity, specific area, and morphological structure of NFC.

In PL12 of FH-WKI, the synthesis of the UV-curing polyester resin and formulation of these resins with reactive monomers and photo-initiators was performed. The synthesis of the resins can be performed up to 500 g in lab, in standard chemical glass ware. In addition, a 5 L-steel reactor was available at the Fraunhofer WKI. To further enhance the research and production of polyester resins, a 30 L-reactor was acquired. This allows for the synthesis of up to 20 kg of polyester resins. In addition, the synthesis of polyurethane dispersions on 20 kg scale is possible, which is needed in TeC5.

The fabrication of the demonstrators was carried out by **AIMEN in PL15**, available for 3D printing with photo-curable resins. In this way, two different setups for 3D fabrication were used, based on two different absorption processes: linear (Stereolithography, SLA) and non-linear (Two Photon Polymerization, 2PP), with two main advantages each of them: fabrication speed in the case of SLA and resolution in the case of 2PP. The SLA pilot line is based on a commercial 3D printer from Formlabs, that has been tuned to use the resins developed in the BIOMAC Project. The 2PP pilot line has been upgraded thanks to the installation of a resin tank, with a dispenser, in a commercial femtosecond laser micro-processing workstation (comprising high precision linear stages for a fast and precise positioning), allowing faster fabrication rates and thus the full fabrication of 3D pieces with submicron resolution. The system has been modified to be used with different resists, including those experimental provided by Fraunhofer WKI for test case 1.

3. Delivery of 3D printed sun visor for the automotive sector

3.1 Component specifications and design

The component selected by DIAD to be redesigned and reengineered using BIOMAC bio - based material is a sun visor traditionally produced via injection moulding using fossil - based polypropylene.

In D3.1 submitted at M18 there is a full description of the specifications of the component selected and it´s also visible in Figure 3 together with its main mechanical characteristics.

USE CASE	AUTOMOTIVE PILOT
BUSINESS CASE	cover of the sun car visor mirror
APPLICATION	Interior of the vehicle
FUNCTION	Mirror protection/Esthetical
PROPERTIES REQUIRED	- Fire resistance: 100 mm/min (AIS-093 Revision 1 07/18) - UV resistance: 40 hours with no color change (ISO 4892-3:2016 - Temperature resistance: TGA test for comparison with PU - Product life time: vehicle life
STANDARD MATERIAL	PU
GEOMETRY	Rectagular size: 14 cm x 8 cm x 0,3 cm
STANDARD PROCESS	Injection Moulding
CHALLENGE	Transition from PU to biobased material
END USER	DIAD
PILOT INVOLVED	PL1, PL6, PL3, PL7, PL12, PL10, PL15
HUBS INVOLVED	BFPC, IMNC and FPFC
NEW BIO - BASED MATERIAL	UV-curable Polyurethane (PU) reinforced with 3-5% wt NFC
MANUFACTURING PROCESS	Photopolymerization Additive Manufacturing process

Figure 3. TEC1 Automotive Pilot

In the first period of the task, DIAD collaborated with AIMEN and FH - WKI in order to identify the best printing conditions and offer continuous feedback to the quality of the samples produced. Once a common strategy was agreed and the 2PP process was selected for the first printing trials, it was agreed to collaborate through scheduled progress meeting, to be eventually enlarged to all the partners of the test case when required. The work carried out by DIAD is summarised in the following points:

<u>DIAD TeC1 coordination</u>

DIAD has coordinated the activities of TeC1 through bi - weekly meetings with PL12-WKI-FH and PL15 AIMEN, in which it has been followed the material flows from MISC - EUBIA, BBEPP, ATB and LTU towards WKI. This coordination activities required also extended meetings/discussions with all the partners involved in TeC1 in which were discussed the possible contingency plans due to delay in the provision of the raw materials. It was

developed a strategy in agreement with all the partners and under the leadership of PL12 - WKI, based on increasing as more as possible the content of bio - based materials using commercial bio - based monomers and additives.

A general meeting was also held in November 2022 to redefine the KPI of the test case and align it with the new needs of the project related to material flaw. DIAD analysed printability test presented by AIMEN and gave preliminary feedback about the end user needs in terms of performance and geometry. It was suggested also to prepare pre - samples with standard AM techniques with the developed bio - based resins in order to start a pre - characterisation of the obtained components.

The second experimentation trials allowed FH - WKI to develop compositions that performed in very good way in printability test. Additional supplies of materials provided by TEC1 partners in 2023 allowed to optimise the final composition with the desired bio - based content and to successfully close the experimentation printing new prototypes, that are aligned with DIAD requirements in terms of accuracy and aesthetic.

DIAD TeC 1 Mechanical and physical characterisation strategy

According to the specifications agreed in D3.1, in the considered period DIAD analysed the available standards at national and international level in order to select/identifiy the most suitable procedures to be used for the advanced characterisation planned in the Validation Services Hub of BIOMAC, WP4. The results of these analysis are summarised in Table 1.

Table 1. Expected mechanical/physical properties

TeC1 Specifications/Targeted properties	
Hardness Test (ISO 2439)	55 shore A to 75 shore D
Flexural Yield Strength and Flexural Modulus (ISO 178:2019)	50 - 70 MPa
Deflection Temperature at 0.46 MPa (ISO 75-1:2020)	130 - 150 centigrades
Fire resistance (AIS-093 Revision 1 07/18 + ISO 3795:1989)	100 mm/min
UV resistance (ISO 4892-3:2016)	40 hours with no color change
Temperature resistance	No phase changes up to 93 centigrades (TGA analysis)

DIAD evaluated which approach/procedure adopt for each standard in order to simulate as more as possible the behaviour of the final component and carry out the product characterization as planned in WP4.

As far as Hardness Test is concerned, the related standard for the determination of the load bearing properties ISO2439 specifies five methodologies. After an analysis of the test case needs and timing constraint it was selected as the most suitable method the one

associated with the code C - Determination of the indentation hardness response for quality control testing purpose.

Flexural strength and flexural modulus at room temperature will be measured following ISO 178:2019 in which different size for specimens can be applied. After analysing the standard and the project needs it was concluded that at this stage it is not possible to freeze a geometry for the sample and that further experimentation trials to check the potential of the 2R2 process will be needed. 3 points loading test was selected as a trial, that can offer a reliable measurement of the flexural yield strength and flexural modulus for thermosetting materials, sufficient to give an indication of the elastic behaviour of the material. Being the material tested a completely new composition and of bio origins it is expected that a further adaptation of the test with respect to the standard will be needed.

Concerning the deflection temperature under load, a preliminary analysis of the standard ISO75-1:2020 showed that the result that will be obtained won't be a reliable indicator of the final behaviour during exercise conditions of the component. A temperature in the car exposed to the sun can easily reach 70 - 80 degrees after one hour (especially in car with a dark external painting) and in this sense PP it´s widely used for the interior for its thermal stability. The standard also specifies that comparable results can be obtained only for materials having at room temperature the same flexural modulus. as consequence, it was concluded that this test will be used as a go/no go criteria only if the material developed in BIOMAC will show a flexural modulus comparable to PP. For this reason, it was decided that ISO178:2019 will be used also to determine this property for the new material.

Fire resistance of materials in vehicle cabs is a safety issue and strict parameters must be encountered before accepting and certifying a material for this use. According to the selected standard AIS-093 Revision 1 07/18, only materials with a burn rate not exceeding 100 mm / min can be adopted, where this parameter has to be measured according to the standard ISO 3795:1989. As a consequence, fire resistance will represent a strict go/no go criteria without which the component won´t be accepted for its final use even if all the other required specifications are met.

UV resistance determination according to the standard ISO 4892-3:2016 did not present any specific concern, as it offers a well-established and detailed technique to simulate in very reliable way material behaviour under weathering effects, giving an indicator that can be used to evaluate the performance under real conditions.

Temperature resistance will be evaluated through TGA analysis available in the partners facilities.

<u>DIAD TeC1 Prototypes validation for further advanced characterization</u>

Prototypes produced by AIMEN by SLA have been validated in terms of quality and geometrical accuracy and considered suitable to undergo the advanced mechanical and

physical characterisation foreseen in WP4. DIAD verified with AIMEN also the possibility to obtain prototypes samples of specific geometry as required by protocol standards.

3.2 Synthesis of precursors

3.2.1 Pre-treatment

The purpose of the PL1 was to efficiently pre-treat/fractionate representative residues from the forest industry in order to produce cellulose, hemicellulose and lignin fractions (Figure 4). In brief, lignocellulosic biomass (hardwood sawdust) was treated in a solution of 60% v/v ethanol to water at a solid to liquid ratio of 1:10 (w/v) for 1h at 180 °C with the presence of low concentration of sulfuric acid as an acidic catalyst. For this purpose, we initially tested a concentration of 20 mM sulfuric acid, which was later reduced to 10 mM in order to reduce the consumption of the mineral acid concentration in the process (and in turn make the conditions less harsh). After the process time elapsed, the pre-treated solids (pulp enriched in cellulose) were separated from the process liquor that contained the solubilized hemicellulose and lignin. The ethanol was recovered from the process liquor via evaporation in a rotary evaporator which allows its re-use in subsequent organosolv fractionations. Removal of ethanol, renders lignin insoluble to the water solution which is then isolated via centrifugation, leaving behind an aqueous solution containing the solubilized hemicellulose together with degradation compounds such as HMF, furfural, levulinic acid, etc. Those compounds, although not part of the BIOMAC project, could be isolated and used as platform chemicals. Pulp and hemicellulose were delivered to PL6 for purification, whereas hemicellulose was delivered to PL12. Pulp was also delivered to PL7 that was hydrolysed and used as substrate for fermentation, where hemicellulose was also tested. Finally, cellulosic pulp was also hydrolysed at LTU with the use cellulolytic enzymes (Cellic Ctec 2, Novozymes) followed by concentration of the solution, resulting to a cellulose hydrolysate of ~220 g/L glucose concentration that was delivered to PL3.

The different samples delivered by LTU have been listed in Table 9 in paragraph 3.2.5.

Figure 4. Cellulosic pulp, hemicellulose and lignin isolated from hardwood sawdust.

3.2.2 Purification

BBEPP received for PL6 input material from 2 different pilot lines. On one hand from PL1-LTU (hemicellulose and cellulose fractions), and on the other hand from PL3-AUTH (sugar stream). For each of the purification process a technical report has been prepared and shared with the partners. This technical report contains the process parameters and a mass-balance sheet which was sent also to WP7 partners for their LCA. The product mass balance considers the desired end products from each process. For process 1 and 2 these are glucose and xylose and for process 3 this is sorbitol. In the following paragraphs the approach on PL1 and PL3 sample material purification is explained in more detail.

3.2.2.1 Purification of material from PL1

PL6-BBEPP received sample material from PL1-LTU during 2023 to establish a purification protocol. There were 2 material types received: Hemicellulose and Cellulose. BBEPP developed 2 different purification processes according to the type of material.

Hemicellulose Purification

The first one is called BBEPP 'process 1' and means Hemicellulose Purification with BBEPP process developed. Table 2 below shows an overview on the starting material as received from LTU.

Table 2. Hemicellulose solution, starting material for BBEPP internal process 1

	Name	*Hemicellulose*
	Origin	LTU
	Appearance	Dark brown, very viscous liquid.
	Packaging	Two 250 mL bottles, second bottle half full

BBEPP worked on establishing the purification process and the final process is shown in the process flow diagram in Figure 5. This process has been performed on the sample material.

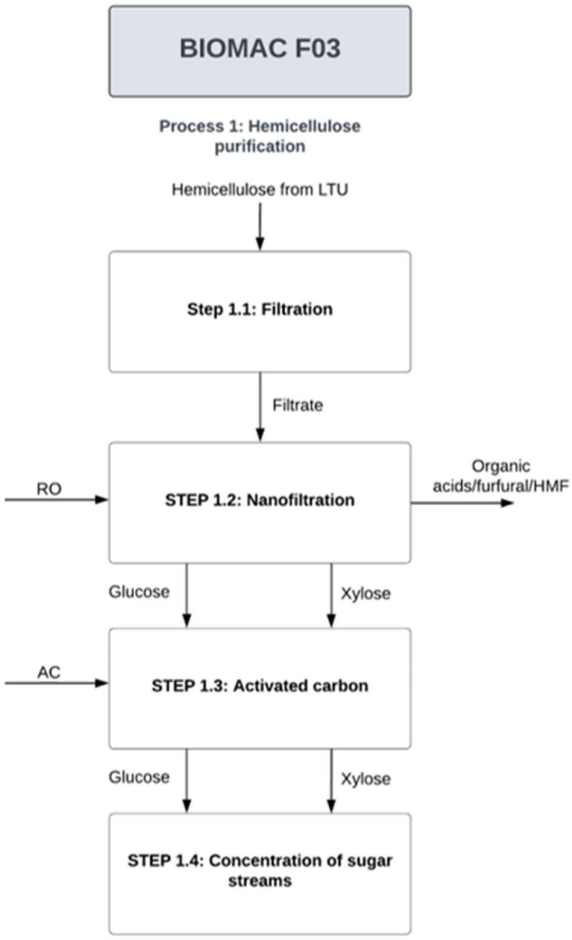


Figure 5. Process flow chart of BBEPP process 1

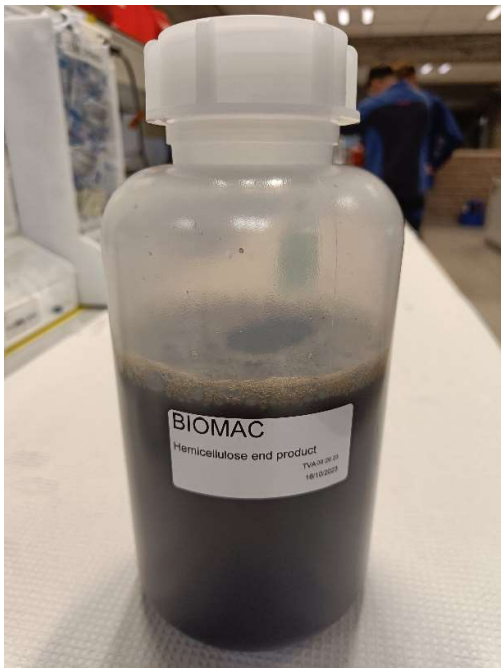
After the purification trials performed it can be concluded that an initial filtration of the stream was required due to the presence of solids. If this stream would be used for future tests, it could be beneficial to perform an additional ultrafiltration step to remove the residual lignin from the stream. The presence of the lignin does not appear to hinder the purification process but could be a problem for further use in follow-up tests by the BIOMAC partners. The removal of organic acids using nanofiltration went well and seems to be a viable option. Further testing of the use of nanofiltration as a way to separate glucose and xylose was unsuccessful. The concentration by evaporation was not performed before the hemicellulose was shipped. The reason for this is that the lignin may have an inhibiting role in further processes performed by the partners. If the lignin needs to be removed first it does not make sense to concentrate the stream.

Also, the hemicellulose stream is difficult to analyse on the HPLC using the in-house method at BBEPP, due to quite some interferences. This makes precise analysis and

quantifications of the different components in the process streams difficult. Nevertheless, based on the lab trials, some conclusions could be made as described above.

The detailed process steps have been summarized in a technical report and being made available to AUTH per email, but they are not shared in this deliverable due to its sensitive nature. The purified streams have been shipped to AUTH for further analysis. Below is the material shown after the purification (see Table 3).

Table 3. Picture and important parameters of the final material from BBEPP process 1

Hemicellulose solution		
	Production date	Summer 2023
	Amount	1387 g
	Packaging	LDPE bottle
	Storage conditions/location	-20°C freezer
	Appearance	Brown liquid, not clear due to presence of lignin.
	Glucose concentration	23,19 g/L
	Xylose concentration	23,51 g/L
	Arabinose concentration	17,81 g/L
	Lactic acid concentration	1,96 g/L
	Glycerol concentration	7,90 g/L
	Acetic acid concentration	3,48 g/L

Cellulose purification

The second one is called BBEPP 'process 2' and means Cellulose Purification with BBEPP process developed. The Table 4 below shows an overview on the starting material as received by LTU.

Table 4. Beech sawdust cellulose, starting material for BBEPP internal process 2

	Name	*Beech sawdust cellulose*
	Origin	LTU
	Appearance	Fine brown 'dust'
	Packaging	Clear plastic bag

BBEPP worked on establishing the purification process and the final process is shown in the process flow diagram in Figure 6, that is used on the material.

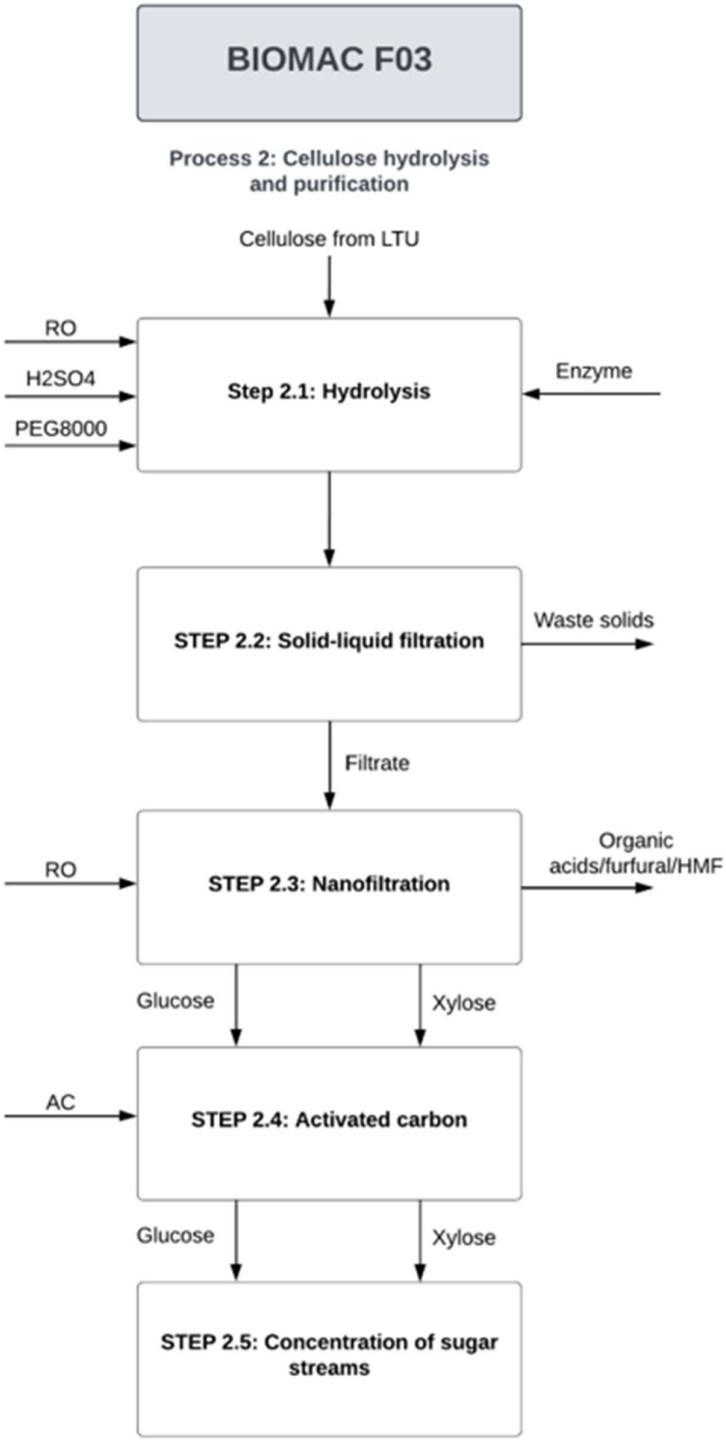


Figure 6. Process flow chart of BBEPP process 2

After the purification trials performed it can be concluded that the enzymatic hydrolysis and solid-liquid separation went well and yielded results like the BBEPPs pilot trials. The subsequent nanofiltration step to remove the organic acids from the stream also showed promising results. The crucial step of separating glucose and xylose, however, seems to be unviable using nanofiltration. Both molecules are very close in size and do not have large differences (such as electrical charge) that make separation easy with nanofiltration. More traditional methods such as chromatography could have been used for the separation, but these are of course more expensive and less sustainable.

The activated carbon treatment completely removed all colour components from the stream, with little to no loss of glucose or xylose. Final concentration of the stream using evaporation also went well. Starting from 407 g of beech sawdust cellulose, 220 g of a concentrated sugar stream was produced containing 387 g/L glucose and 48 g/L xylose. The detailed process steps have been summarized in a technical report and being made available to AUTH per email, but are not shared in this deliverable due to the its sensitive nature.

The purified streams have been shipped to AUTH for further analysis. Below is the material shown after the purification (see Table 5).

Table 5. Picture and important parameters of the final material from BBEPP process 2

Glucose concentrate from enzymatic hydrolysis		
	Production date	Summer 2023
	Amount	220 g
	Packaging	HDPE bottle
	Storage conditions/location	-20°C freezer
	Appearance	White, cloudy solution containing crystals
	Glucose concentration	378,78 g/L
	Xylose concentration	48,13 g/L
	Glycerol	1,18 g/L
	Acetic acid	0,07 g/L
	Ethanol	0,15 g/L

3.2.2.2 Purification of material from PL3

PL6-BBEPP received sample material from PL3-AUTH during 2023 to establish a purification process. The material type received: Sorbitol stream (see Table 6)

Table 6. Sorbitol, starting material for BBEPP process 3

No picture available	Name	*Sorbitol stream*
	Origin	AUTH
	Appearance	Clear viscous liquid
	Packaging	Clear plastic bottle

BBEPP worked on establishing the purification process and the final process is shown in the process flow diagram in Figure 7, that is used on the material.

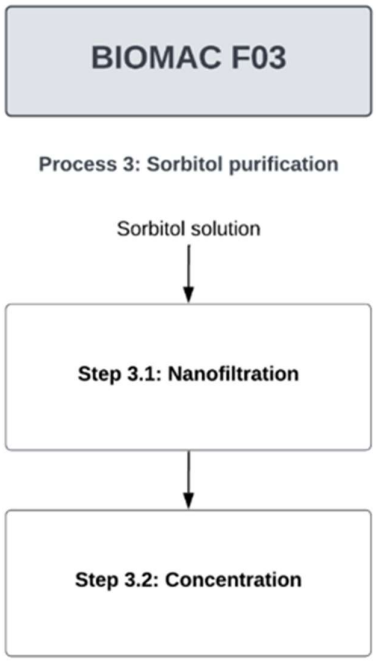


Figure 7. Process flow chart of BBEPP process 3

After the purification trials performed it can be concluded that the purification of the sorbitol stream using nanofiltration yielded good results. Fluxes during filtration were decent and the loss of sorbitol to the filtrate was also acceptable. It did take 4 diafiltrations to reach the desired 92 % sorbitol purity, so there is some water usage which has economic implications. A total sorbitol loss of 30% was measured, but this loss could maybe be mitigated by processing at a temperature lower than 25°C as losses went down as the temperature decreased.

Concentration of the stream went well but did cause a discoloration of the end concentrate. Using activated carbon, it would probably be possible to remove these colour compounds, but it may take a longer reaction time due to the viscosity of the concentrate after evaporation. Also, the removal of the AC might be difficult with a highly viscous stream. The detailed process steps have been summarized in a technical report and being made available to AUTH per email but are not shared in this deliverable due to the its sensitive nature.

The sample material has been shipped to AUTH for further analysis. Below is the material shown after the purification (see Table 7)

Table 7. Picture and important parameters of the final material from BBEPP process 3

Sorbitol concentrate		
	Production date	Summer 2023
	Amount	200 g
	Packaging	HDPE bottle
	Storage conditions/location	-20°C freezer
	Appearance	Clear brownish liquid
	Sorbitol concentration	441,06 g/L
	Glycerol concentration	15,80 g/L
	Ethyleneglycol + acetic acid concentration	5,47 g/L
	1,2-PDO concentration	14,02 g/L

3.2.3 Hydrogenolysis

The main objective of the PL3 in TeC1 is to produce polyols, such as sorbitol or smaller gycols/diols, to be used by FH-WKI (PL12) to produce bio-based, UV-curable succinate ester resins. Sorbitol is one of the top 12 high value-added building block intermediate

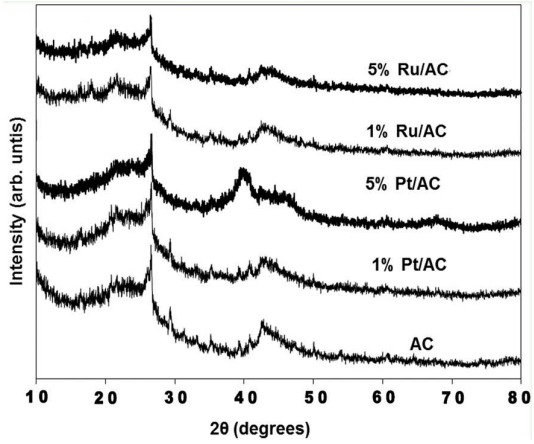
chemicals and carries immense importance for the industrial sector, particularly the bio-based polymers industry. Its low volatility, high water-solubility, and excellent stability make it an ideal ingredient in polymeric formulations, enhancing their flexibility, durability, and moisture retention. Sorbitol also plays a crucial role in the synthesis of polyesters, polyurethanes, and other polymeric materials, contributing to improved mechanical properties and desired processing characteristics.

One important element of PL3 is the catalysts that are required to induce the hydrogenation and/or hydrogenolysis reactions of sugars, i.e. glucose, towards the corresponding sugar alcohols. To this end, within the frame of BIOMAC project, the AUTH team (PL3) have optimized the preparation of in-house supported metal catalysts, utilizing previous knowledge and expertise. The method is based on tailored wet impregnation of metal salts solutions on the porous support, followed by reduction with sodium borohydride, to obtain the supported active metallic phase. More specifically, representative catalysts that have been prepared are:

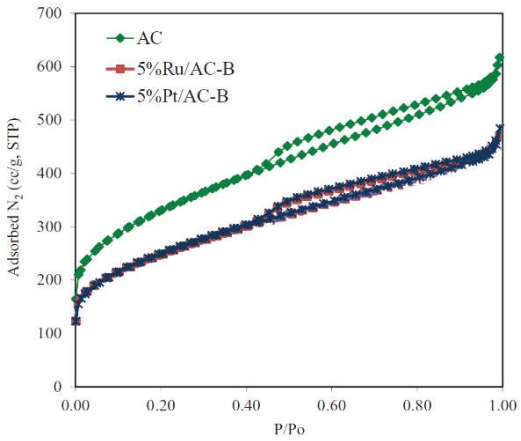
- Ruthenium and Platinium supported on porous activated carbon (AC), i.e. Ru/C, Pt/C,
- Nickel supported on tungsten modified activated carbon, i.e., Ni/W-AC
- Nickel supported on nickel aluminate spinel, i.e. $Ni/NiAl_2O_4$

The various catalysts were initially prepared at small amounts suitable for the small-scale optimization catalytic tests, while the optimum catalyst, at least for the selective production of sorbitol at pilot scale, was prepared at larger amounts of 200-300 grams. A picture is shown in Figure 8, while representative characterization results the catalysts (i.e. XRD patterns and N_2 adsorption/desorption isotherms) are shown in Figure 9. Furthermore, the developed methods can be also applied to biochar/activated biochar, that other BIOMAC partners are producing (i.e.PL8, Uedin), thus giving further potential value to this biomass derived material.

Figure 8. Picture of the 5% Ru/AC catalyst produced at AUTH (PL3)



(a) XRD patterns of the parent activated carbon (AC) and representative supported Ru and Pt catalyst samples.



(b)N_2 adsorption-desorption isotherms of the parent activated carbon (AC) and representative supported Ru and Pt catalyst samples.

Figure 9. (a) XRD patterns (b) N2 adsorption/desorption isotherms

The optimization of process parameters was performed via small/lab scale reactor experiments. The parameters that were taken into account were the type of catalyst (i.e. Ru, Pt or Ni on activated carbon and Ni based on reduced $NiAl_2O_4$ spinels), reaction temperature and reaction time, i.e. 120-220°C and 1-5h, H_2 pressure, i.e. 15-60 bar, and feed/sugar concentration, i.e. 2.5 – 20 wt.%. Two series of Ru and Pt catalysts supported on activated carbon where tested, ca. 1, 3, 5% Ru/AC and 1, 3, 5% Pt/AC and also two additional catalysts, i.e. 5% Ni/15% W-AC and $Ni/NiAl_2O_4$, as seen in the Figure 10 and 11, below.

As it can be seen, the most selective and efficient catalyst for sorbitol production is the one based on Ru, i.e. the 5%Ru@AC. This catalyst gives very high conversion of glucose (>98%) and an excellent selectivity to sorbitol, resulting a sorbitol yield over 85 wt.%, at optimized reaction conditions, i.e. 150°C, 30 bar H_2, 3 hrs, 15 wt.% glucose in water. The Pt catalysts showed also high conversions, but they were more selective towards smaller glycols and diols, such as ethylene glycol, glycerol and 1,2-PDO. For this reason, the Pt catalysts, were used to produce the smaller glycol/diols rich hydrogenolysis products. The last two catalysts (i.e. 5% Ni/15% W-AC and $NiAl_2O_4$) were completely different, as they provided very high conversion (>95%), but low selectivity/yield towards the targeted sorbitol or small sugar alcohols (further investigation is underway).

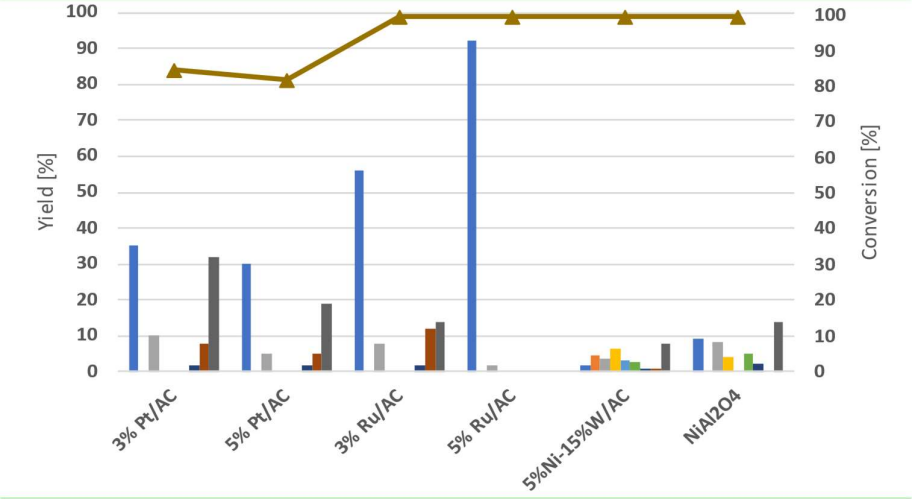


Figure 10. Screening of 6 different prepared catalysts (10wt.% Glucose feed, 150°C, 3hrs, 30 bar H_2)

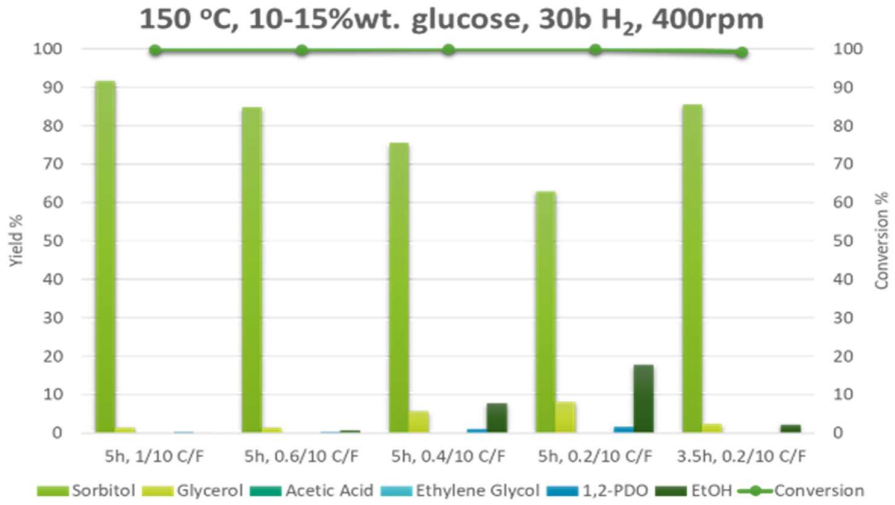


Figure 11. Optimization of reaction conditions using the sorbitol selective catalyst, i.e. 5%Ru/AC.

Based on the lab/small scale optimization experiments, the optimum catalysts/conditions were also verified on the pilot reactor (PL3) (Figure 12).

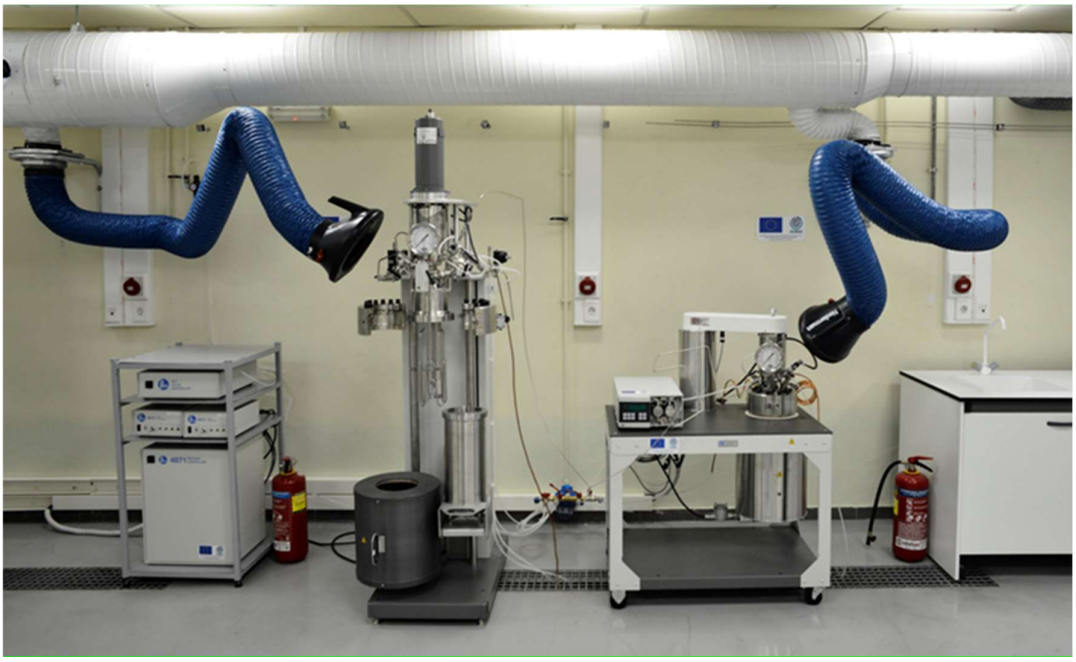


Figure 12. (Micro)Pilot reactor designed and constructed within BIOMAC project (Reactors capacity: Left 5L and Right 8L).

The experiments at the pilot scale reactor where initially performed at CSTR continuous mode in order to achieve larger scale production of sorbitol. However, the obtained conversion of the glucose and yield of the sugar alcohols was relatively low (ca. 20-30 wt.%). As this type of sugar hydrogenation reactions require relatively low temperature (i.e. 150 °C) and larger contact times to allow hydrogenation (or hydrogenolysis), a recirculation mode was necessary to achieve higher sugar conversion and polyols yield, as those obtained when the reaction performed at batch mode. To this end, the batch mode operation of the PL3 was selected, under the optimized conditions, to minimize reaction time and increase feed concentration for maximum productivity. Indicatively, an optimum set of conditions/output per run, comprise of:

Feed per run: 0.50 kg glucose, 3.2 L water, 9.6 gr of 5%Ru/C catalyst, 150°C, 3h, 30 bar H_2 R.T.

Product per run: all sugar alcohols 0.485 gr (yield 97%), sorbitol 0.480 gr (yield 96%, and purity 98%), the rest 0.005 gr (yield 1%) being smaller glycols and diols, i.e. ethylene glycol (EG), glycerol (GLY) and 1,2-propylene glycol (1,2-PDO).

This high purity sorbitol product was successful used by FH-WKI (PL12) to synthesize polyester resins, without the need of further purification. Figure 13 shows the lab and pilot scale sorbitol (>98% purity) products sent to FH-WKI for resin production and the product mixture of sorbitol (41.2%)/EG (11.9%)/GLY (13.7%)/1,2-PDO (16.5%)/acetic acid

(3.6%) produced by the Pt/C catalyst under hydrogemolysis conditions, that was sent to BBEPP (PL6) for separation/purification investigation.

Figure 13. Pilot scale (left) and small scale (middle) sorbitol product from glucose hydrogenation and the sorbitol/EG/GLY/1,2-PDO product mixture produced from glucose hydrogenolysis (right).

Succinic acid utilization

Another stream that was received by ATB (PL7) within the TeC1 was succinic acid. SA produced from ATB's PL7 and is a very useful chemical. The hydrogenation of SA will produce 1,4-BDO, that is more suitable for the synthesis of polysuccinate/PU resins at TeC5. The AUTh team performed detailed characterization of the SA samples received by ATB. In Figure 14, the HPLC-RID chromatograph is shown, while in Figure 15a and 15b the ^{1}H-NMR and ^{13}C-NMR spectra, respectively, are presented. Based on both the HPLC and NMR analysis, it is clear that the SA has an over 98% purity, with non-identified or very small number of other compounds.

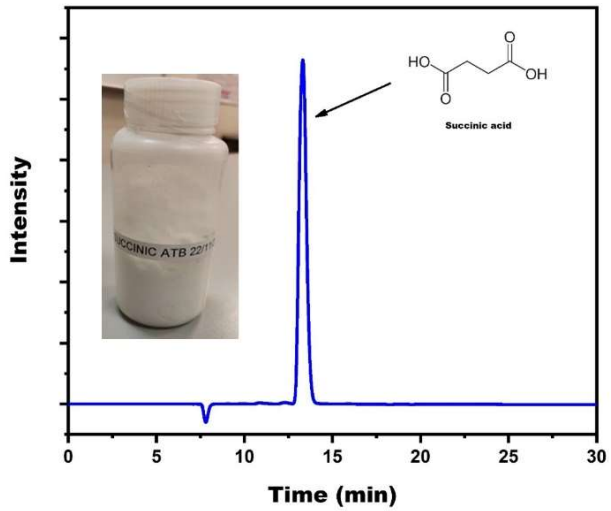


Figure 14. HPLC-RID chromatograph of the SA provided from ATB

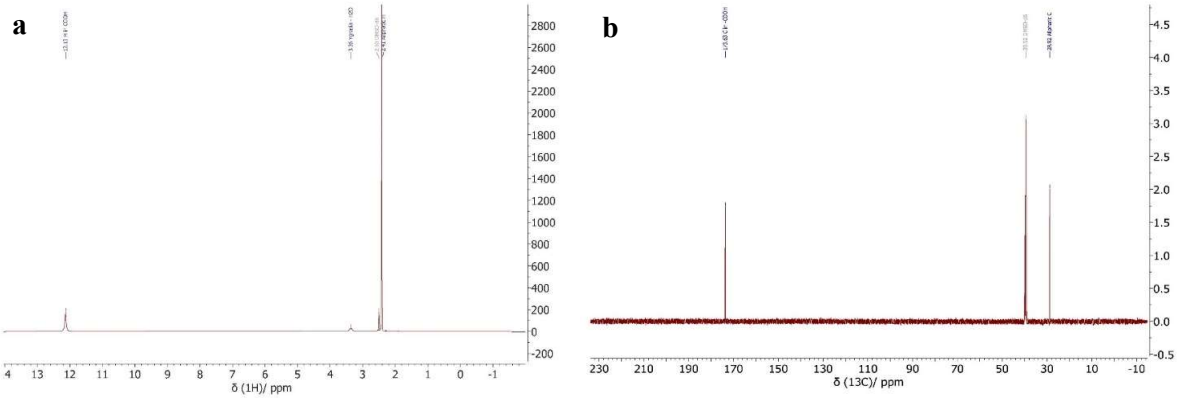


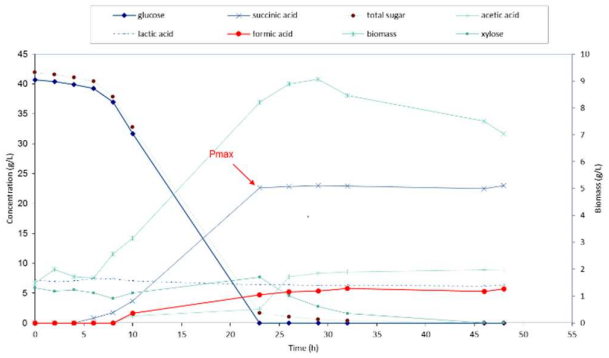
Figure 15. a) H-NMR spectrum and b) C-NMR spectrum of the SA provided from ATB

3.2.4 Fermentation

Succinic acid is a platform chemical broadly used as a precursor of chemicals and serve as an alternative for chemicals produced from fossil fuels. It's biotechnological production occurs by utilizing feedstock reach in simple sugars, mainly glucose and xylose, employing *Actinobacillus succinogenes* and *Basfia succiniciproducens* strains. Succinic acid process optimization was successfully published, and the results can be seen in the publication entitled *Bioprocess optimization for lactic and succinic acid production from a pulp and paper industry side stream*. Based on the process optimization study, ATB was able to test fibre sludge hydrolysate (SFS) at the technical scale.

ATB received the biomass mainly from **RISE Processum**, so that the succinic acid production on technical scale was possible (see the newest version of the process flow). Within TeC1, ATB sent succinic acid crystals to two partners: PL3-AUTH and PL12-FH-WKI. Technical scale fermentation was done in 72 L BIOSTAT UD bioreactor with 50 L working volume. SFS was autoclaved at 121 °C, 15 min. Additional nutrients, such as 10 g/L yeast extract, and 1 g/L of $NaHCO_3$ were dissolved in MilliQ-water and sterilized for 15 min, at 121 °C in a stainless steel vessel. Hydrolysate and nutrient solution after sterilization were transferred to the sterilized bioreactor, the fermentation parameters were set and then the preculture was pumped from 10 L vessel. The concentration of reducing sugars, succinic acid, by-products was done by liquid chromatography (HPLC). In Figure 16 succinic acid production is shown vs sugars consumption. Additionally, we may observe by-product formation, such as formic or acetic acid. Biomass formation is also shown, indicating constant growth of microbial cells. The yield of succinic acid production reached 0.65 g of succinic acid/g of total sugars. The maximum productivity (Pmax) reached 1.46 g/L*h.

(A)



(B)

Figure 16. Succinic acid production at the technical scale utilizing SFS hydrolysate and Actinobacillus succinogenes strain (A). A picture of technical scale bioreactor Biostat UD (50L).

Fermentation is the main part of SA production process, but in order to get pure crystals, the purification part needs to be implemented as well. The purification part was divided to 9 steps, including: microfiltration, softening, monopolar electrodialysis, bipolar electrodialysis, decolorization, cation and anion exchange, vacuum distillation and crystallization. These steps are also shown in Figure 17. Microfiltration is necessary for cell biomass removal without succinic acid loses. The filtrated medium could be further subjected to e.g., softening, monopolar and bipolar electrodialysis membranes, for achieving polymer-grade purity values.

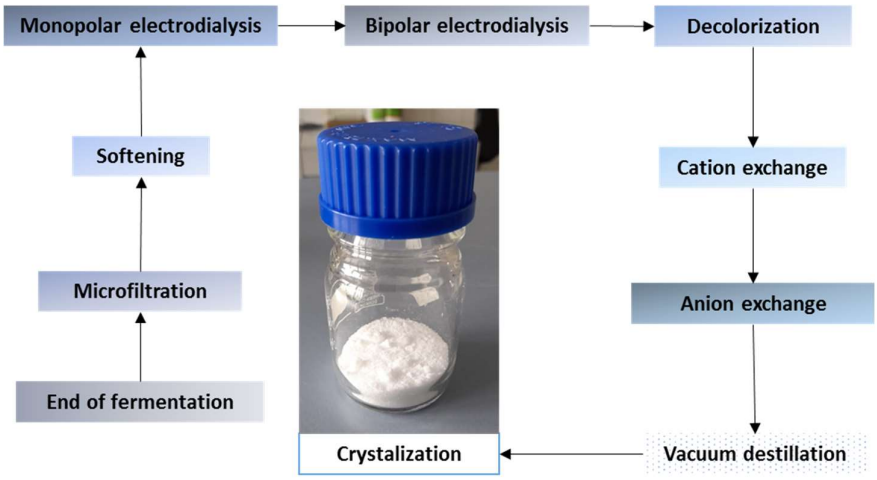
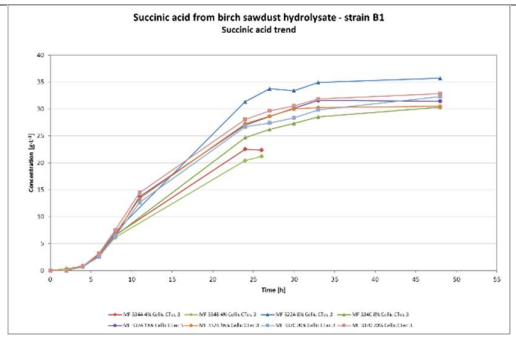


Figure 17. Schematic description of the downstream process applied for succinic acid purification and a picture of succinic acid crystals

Other partners, such as LTU or BBEPP also provided both solid and liquid fractions, that are being investigated in terms of process optimization for succinic acid production. Firstly, birch sawdust, provided by LTU, was used for microbial screening, hydrolysis optimization and small-scale SA fermentations, including batch fermentation, and simultaneous saccharification and fermentation (SSF). Some of the results are shown in Table 8.

Table 8. Other substrates received and used for succinic acid fermentation

Birch sawdust substrate from LTU



Hemicellulose and glucose filtrate from BBEPP

Component	Glucose concentrate	Hemicellulose concentrate
Glucose ($g \cdot L^{-1}$)	410	1.47
Cellobiose ($g \cdot L^{-1}$)	10.62	8.20
Xylose ($g \cdot L^{-1}$)	49.23	26.77
Arabinose ($g \cdot L^{-1}$)	0.00	6.41
Lactic acid ($g \cdot L^{-1}$)	0.00	0.00
Total nitrogen ($mg \cdot L^{-1}$)	499.9	132.4
Total phosphorus ($mg \cdot L^{-1}$)	161.8	34.3
Cl^- ($mg \cdot L^{-1}$)	92.9	290.2
SO_4^{2+} ($mg \cdot L^{-1}$)	23067	23310
Na^+ ($mg \cdot L^{-1}$)	16863	17970

	K^+ (mg·L^{-1})	178.3	591.1
	Mg^{2+} (mg·L^{-1})	104.1	203.8
	Ca^{2+} (mg·L^{-1})	281.7	418.6
	HMF (mg·L^{-1})	5.62	6.46
	Furfural (mg·L^{-1})	1.73	5.21
	Phenol (mg·L^{-1})	n.a.	13.67
	Catechol (mg·L^{-1})	34.78	305.77
	Guajacol (mg·L^{-1})	n.a.	6.47

Birch sawdust provided by LTU was used for the enzymatic hydrolysis study, as well as for batch and SSF study. Succinic acid production from sawdust can be seen in Table 8. Depending on the concentration of sugars released during enzymatic hydrolysis, different amounts of succinic acid were produced. Glucose filtrate provided by BBEPP is now used for continuous SA fermentation, whereas hemicellulose concentrate is investigated in terms of microbial screening to find the best performing microbial strain. Hemicellulose concentrate contains high amounts of inhibitors, that is why adsorption techniques utilizing biochar are implemented to test the availability of the strain to ferment mostly xylose in the presence of inhibitors. The chemical composition of both substrates is shown in Table 7. The final conclusions and remarks refer to the fact that SA producing strains used at ATB were able to utilize all above mentioned feedstocks and produce succinic acid at lab and technical scale. Different fermentation strategies were implemented to compare which process parameters (batch, fed-batch, continuous) are the most suitable for the production of SA. Additionally, the downstream process proposed is still being improved by adding biochar adsorption to reduce cost of the purification part, which is going to be shown in the next report. (Reference: Front. Bioeng. Biotechnol., 18 May 2023; Sec.Industrial Biotechnology Volume 11 - 2023 | https://doi.org/10.3389/fbioe.2023.1176043)

3.2.5 Test Case 1 Overall Matrix of samples for precursors production

In Table 9 it´s summarised the list of samples delivered by PL1-LTU, PL3 - AUTH, PL6 - BBEPP. PL7 - ATB and PL10 - LIST to PL12 FH - WKI for the formulation of the BIOMAC bio - based resins that will be used by PL16 - AIMEN for 3D printing the prototypes of the sun - visor.

Table 9. Sample matrix raw material production

PARTNER	PROJECT CODE	QUANTITY (g)	Samples description	Delivered to	Date of delivery
PL1- LTU	Cellulosic pulp	750	Solid pulp	BBEPP	June 23

PL1- LTU	Hemicellulose	1000	Liquid concentrated to syrup	BBEPP	June 23
PL1- LTU	Glucose hydrolysate from ulp	700g (~220 g/L glucose)	Liquid	AUTH	May 23
PL1- LTU	Cellulosic pulp	4700	Solid pulp	ATB	July 21, September 22, November 22
PL1- LTU	Hemicellulose	1150	Liquid concentrated to syrup	ATB	September 22
PL1- LTU	Hemicellulose	100	Liquid concentrated to syrup	FH	October 23
PL3 - AUTH	BIOMAC	50 g	Glucose hydrogenation towards almost pure (98%) sorbitol syrup produced from the small scale reactor	**Tobias Robert** Fraunhofer-Institut für Holzforschung Wilhelm-Klauditz-Institut	13.12.2022
PL3 - AUTH	BIOMAC	300 g	Glucose hydrogenolysis product mixture of sorbitol (41.2%)/EG (11.9%)/GLY (13.7%)/1,2-PDO (16.5%)/acetic acid (3.6%)	**Tim Valentin** Bio Base Europe Pilot Plant, Gent, Belgium	17.08.2023
PL3 - AUTH	BIOMAC	500 g	Glucose hydrogenation towards almost pure (98%) sorbitol syrup produced from	**Tobias Robert** Fraunhofer-Institut für Holzforschung Wilhelm-Klauditz-Institut	25.10.2023

			the pilot scale reactor		
PL6 - BBEPP	BIOMAC F03	100g	Sugar stream from EH (F03) - liquid	ATB	Nov-23
PL6 - BBEPP	BIOMAC F03	100g	Sugar stream from EH (F03) - liquid	AUTH	Nov-23
PL6 - BBEPP	BIOMAC F03	2kg	Hemicellulose - liquid	AUTH	Nov-23
PL6 - BBEPP	BIOMAC F03	200g	Purified sorbitol - liquid	AUTH	Nov-23
PL7 - ATB	BIOMAC	60 g	Purified succinic acid crystals produced from fermentation SFK 3663, C1 – crystalization 1	**Tobias Robert** Fraunhofer-Institut für Holzforschung Wilhelm-Klauditz-Institut	13.09.2022
PL7 - ATB	BIOMAC	80 g	Purified succinic acid crystals purified from fermentation SFK 3663, C2 – crystalization 2	**Tobias Robert** Fraunhofer-Institut für Holzforschung Wilhelm-Klauditz-Institut	13.09.2022
PL7 - ATB	BIOMAC	200 g	Purified succinic acid crystals produced from fermentation SFT 3720, C1-crystalization 1	**Dr. Konstantinos S. Triantafyllidis** Department of Chemistry Aristotle University of Thessaloniki	12.11.2023
PL7 - ATB	BIOMAC	200 g	Purified succinic acid crystals produced from fermentation SFT 3720, C1-crystalization 1	**Tobias Robert** Fraunhofer-Institut für Holzforschung Wilhelm-Klauditz-Institut	02.06.2023

PL7 - ATB	BIOMAC	200 g	Purified succinic acid crystals produced from fermentation SFT 3720, C1-crystalization 1	**Dr. Konstantinos S. Triantafyllidis** Department of Chemistry Aristotle University of Thessaloniki	02.06.2023
PL10 - LIST	BIOMAC	250	NFC from MFC in PDO	WKI	15/12/2022
PL10 - LIST	BIOMAC	250	NFC from Pulp in PDO	WKI	15/12/2022

3.3 Synthesis of bio - based resins for 3D Printing

3.3.1 First experimentation trials with bio - based commercial precursors

At the beginning of the project, bio-based resins derived from biotechnologically produced itaconic acid. This dicarboxylic acid is a bio-based alternative to acrylic acid or methacrylic acid, which are usually used in UV-curing binder resins for additive manufacturing. In addition to itaconic acid other bio-based monomers that will be made available from the other pilot lines, such as sorbitol, succinic acid, 1,4-butanediol, 1,2-propanediol. But also other bio-based monomers, such as 1,3-propanediol, sebacic acid were used to synthesize polyester resins with a bio-based content up to 100%. Different compositions of monomers were used to synthesize polyester resins with different properties and varying amounts of renewable content via azeotropic polycondensation. These resins were obtained as colorless to yellowish resins with viscosities to high be directly printed on a UV-curing 3D-printer. Therefore, formulations with monomeric reactive diluents were made by using either bio-based IBOA or petrochemical-derived ACMO. Furthermore, different variations of photo-initiator were used. A large variety of formulation was sent to AIMEN to examine the printability in the 2-photon polymerization process, as indicated in Table 10 and Table 11. After the first feedback from AIMEN it became clear that 1% of photo-initiator is enough for this printing process. In addition, IBOA or a mix of ACMO and IBOA seemed to be the most suitable. Therefore, a second round of formulations were prepared and sent to AIMEN. With these formulations we were able to obtain a bio-based content of up 85%.

Table 10. Samples Matrix - First Experimentation Trial in FH - WKI

PARTNER	PROJECT CODE	QUANTITY (g)	Samples description	Delivered to	Date of delivery
WKI	BIOMAC-AM-001-A	50 g	Formulation for 2-PP-printing	AIMEN	21.10.2021
WKI	BIOMAC-AM-001-B	50 g	Formulation for 2-PP-printing	AIMEN	21.10.2021
WKI	BIOMAC-AM-001-C	50 g	Formulation for 2-PP-printing	AIMEN	21.10.2021
WKI	BIOMAC-AM-001-D	50 g	Formulation for 2-PP-printing	AIMEN	21.10.2021
WKI	BIOMAC-AM-001-E	50 g	Formulation for 2-PP-printing	AIMEN	21.10.2021
WKI	BIOMAC-AM-001-F	50 g	Formulation for 2-PP-printing	AIMEN	21.10.2021
WKI	BIOMAC-AM-002-A	50 g	Formulation for 2-PP-printing	AIMEN	23.02.2022
WKI	BIOMAC-AM-003-A	50 g	Formulation for 2-PP-printing	AIMEN	23.02.2022
WKI	BIOMAC-AM-003-B	50 g	Formulation for 2-PP-printing	AIMEN	23.02.2022
WKI	BIOMAC-AM-004-A	50 g	Formulation for 2-PP-printing	AIMEN	23.02.2022
WKI	BIOMAC-AM-005-A	50 g	Formulation for 2-PP-printing	AIMEN	23.02.2022
WKI	BIOMAC-AM-006-A	50 g	Formulation for 2-PP-printing	AIMEN	23.02.2022

Table 11. Optimized formulations for 2-PP printing with high bio-based content.

	Formulation composition												Biobased Content		
Name	Oligomer/Resin			Reactive diluent			Photoinitiator			Inhibitor			Oligomer	Diluent	Overall
BIOMAC-AM-002-A	BM-UV-004-A	50,00	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	100	71	84,8
BIOMAC-AM-003-A	UV-3D-10-B13	50,00	%	IBOA+ACMO	48,95	%	TPO	1,00	%	MeHQ	0,05	%	37	35,5	35,9
BIOMAC-AM-003-B	UV-3D-10-B13	50,00	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	37	71	53,3
BIOMAC-AM-004-A	BM-UV-005-A	50,00	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	100	71	84,8
BIOMAC-AM-005-A	AF-Form-022-A	50,00	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	74,6	71	72,1
BIOMAC-AM-006-A	AF-Form-024-A	50,00	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	100	71	84,8

3.3.2 Second experimentation trials with BIOMAC precursors

Building on the results from 3.3.1, polyester resins, as well as formulations were optimized with a focus on using the monomers from PL 3 and 7. Furthermore, nanocellulose was incorporated into the formulations to examine the influence of these on the printing and the final properties of the resins. In the beginning, sorbitol from PL3 and succinic acid (PL7) were incorporated in the resins. In addition, reference resins with monomers from commercial sources were synthesized to see if any difference could be observed (see

Figure 18). In both cases, the monomers from the BIOMAC pilot lines had very good quality and could be processed without any problems. No side reactions or discolorations could be observed (20).

Figure 18. Resins derived from sorbitol (left) and succinic acid (right).

Furthermore, nanocellulose and pulp was incorporated into the resins, as shown in Figure 19. To avoid coagulation of the solids, as well as exposure to dust from these, PL 10 (LIST), used aqueous dispersion and added one of the key monomers (1,3-propanediol). Then the water was evaporated, delivering a dispersion of pulp and nanocellulose in 1,3-propanediol. This dispersion was directly used in the synthesis of the polyester resins. Again, the resins could be obtained without any discoloration or side-reactions. The only problem was that some of the 1,3-propanediol evaporated during the transport, which resulted in lower amounts of it in the resin and in turn slightly higher molecular weights, which was not a problem for the formulations in the next step.

Figure 19. Resins obtained from experiments with nanocellulose, reference left, with pulp in the middle, nanocellulose on the right.

All resins were used to prepare formulations, which were in turn send to AIMEN. Furthermore, another round of optimization was conducted after additional feedback from AIMEN, as indicated in Table 12.

Table 12. Second round of optimised compositions for AIMEN

	Formulation composition												Biobased Content		
	Oligomer/Resin			Reactive diluent			Photoinitiator			Inhibitor					
BIOMAC-AM-005-B	AF-Form-022-A	50,00%	%	ACMO	48,95	%	TPO	1,00	%	MeHQ	0,05	%	74,6	0	37,3
BIOMAC-AM-005-C	UV-3D-10-B13	50,00%	%	IBOA+ACMO	48,95	%	TPO	1,00	%	MeHQ	0,05	%	37	35,5	17,6
BIOMAC-AM-005-D	UV-3D-10-B13	50,00%	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	37	71	53,3
BIOMAC-AM-005-E	BM-UV-005-A	50,00%	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	100	71	84,8
BIOMAC-AM-005-F	AF-Form-022-A	50,00%	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	74,6	71	72,1
BIOMAC-AM-006-A	AF-Form-024-A	50,00%	%	IBOA	48,95	%	TPO	1,00	%	MeHQ	0,05	%	100	71	84,8

The best formulation turned out to be BIOMAC-AM-005-C, which had unfortunately a lower bio-based content of only 17,6%. Therefore, the resins were further optimized by replacing the 1,6-hexanediol with 1,3-propanediol, which allowed for the improvement to 55,4 % (BIOMAC-AM-007-A) indicated in Table 13.

Table 13. Optimised composition for 3D printing - final choice for printing test

	Formulation composition												Biobased Content		
	Oligomer/Resin			Reactive diluent			Photoinitiator			Inhibitor					
BIOMAC-AM-007-A	BM-UV-018-A	50,00%	%	IBOA+ACMO	48,95	%	TPO	1,00	%	MeHQ	0,05	%	75,20%	35,50%	55,4%

The materials with nanocellulose were not processable without defects, which might be a result of the light scattering of the particles, the materials with sorbitol did print, however not as good as the material BIOMAC-AM-007-A.

In Table 14 the formulations delivered to AIMEN in the second experimental trial are summarised.

Table 14. Samples Matrix - Second Experimentation Trial

PARTNER	PROJECT CODE	QUANTITY (g)	Samples description	Delivered to	Date of delivery
WKI	BIOMAC-AM-005-B	50 g	Formulation for 2-PP-printing	AIMEN	01.07.2022
WKI	BIOMAC-AM-005-C	50 g	Formulation for 2-PP-printing	AIMEN	01.07.2022
WKI	BIOMAC-AM-005-D	50 g	Formulation for 2-PP-printing	AIMEN	01.07.2022
WKI	BIOMAC-AM-005-E	50 g	Formulation for 2-PP-printing	AIMEN	01.07.2022
WKI	BIOMAC-AM-005-F	50 g	Formulation for 2-PP-printing	AIMEN	01.07.2022
WKI	BMF-CNC-001	50 g	Formulation with CNC/pulp	AIMEN	17.02.2023
WKI	BMF-CNC-002	50 g	Formulation with CNC/pulp	AIMEN	17.02.2023
WKI	BMF-CNC-003	50 g	Formulation with CNC/pulp	AIMEN	17.02.2023
WKI	BMF-CNC-004	50 g	Formulation with CNC/pulp	AIMEN	17.02.2023
WKI	BMF-CNC-005	50 g	Formulation with CNC/pulp	AIMEN	17.02.2023
WKI	BMF-CNC-006	50 g	Formulation with CNC/pulp	AIMEN	17.02.2023
WKI	BIOMAC-AM-007-A	50 g	Formulation for 2-PP-printing	AIMEN	04.04.2023
WKI	BIOMAC-AM-007-B	50 g	Formulation for 2-PP-printing	AIMEN	04.04.2023

WKI	BIOMAC-AM-005-CL	500 g	Formulation for DLP-printer	AIMEN	04.04.2023
WKI	BIOMAC-AM-007-A1	100 g	Formulation for 2-PP-printing	AIMEN	15.11.2023
WKI	BIOMAC-AM-008-A	50 g	Sorbitol-based formulation	AIMEN	15.11.2023
WKI	BIOMAC-AM-009-A	50 g	Sorbitol-based formulation	AIMEN	15.11.2023
WKI	BIOMAC-AM-005-CL2	500 g	Formulation for DLP-printer	AIMEN	15.11.2023

3.3.3 Synthesis of NC particles

PL10 successfully employed the Massuko Super Mass Colloider to produce nano-fibrillated cellulose (NFC) from two distinct feedstock sources: pulp and micro fibrillated cellulose (MFC). The size distributions of the generated NFC, falling within the range of 100 to 300 nm, were determined using the Light Intensity Sedimentation mode.

In the case of MFC, an optimal outcome was achieved with merely 5 grinding cycles at both 2% and 3% concentrations, ensuring a narrow size distribution. Conversely, for pulp, a more extensive grinding process was necessary, requiring 15 cycles at a 2% concentration and 20 cycles at a 3% concentration, as illustrated in Figure 20.

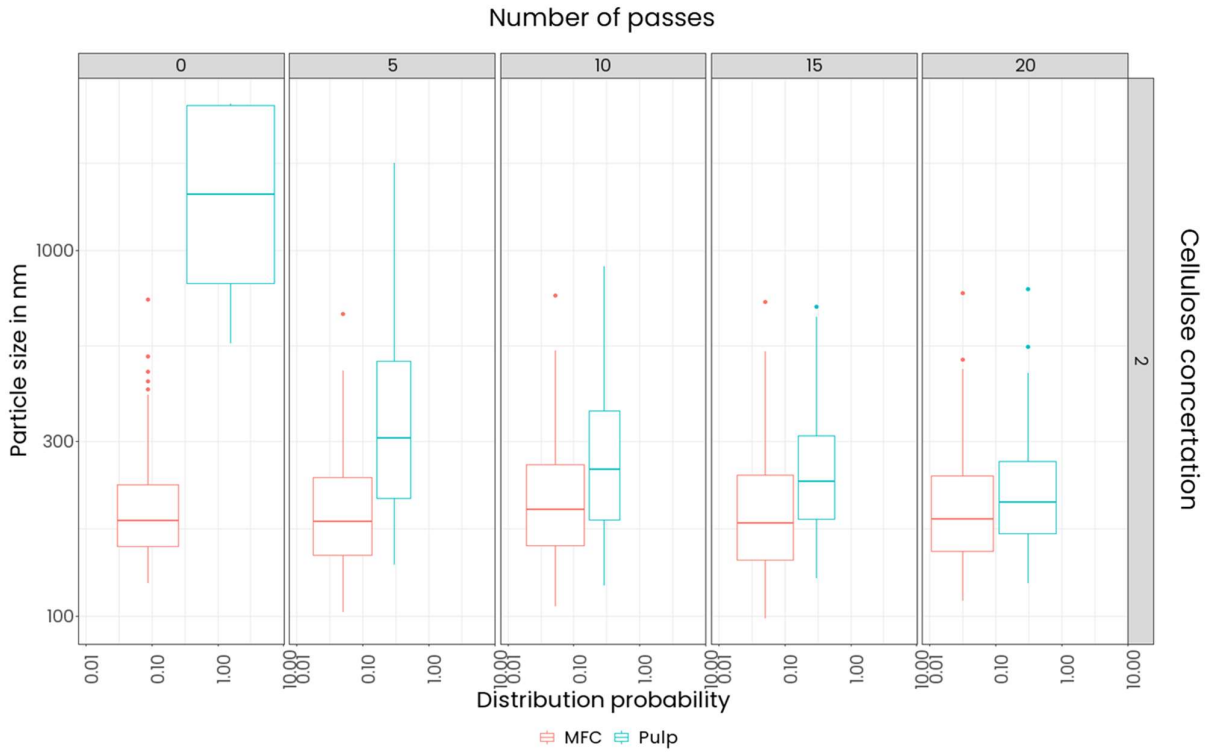


Figure 20. MFC Production

To prepare NFC for PL12-FH, water was efficiently removed from the NFC slurries through centrifugation at 10000 rpm. Subsequently, the excess water was replaced with 1,3 propane diol (PDO). This meticulous procedure was iterated six times until the slurry reached a state where no further liquid could be extracted.

The resulting NFC formulations were then appropriately diluted with 1,3 propane diol, yielding the following compositions (see also Table 15).

NFC from pulp: 1 wt.% NFC, 43 wt.% water, 56 wt.% PDO

NFC from micro fibrillated cellulose: 0.8 wt.% NFC, 48 wt.% water, 51.2 wt.% PDO

Table 15. Samples Matrix - First Experimentation Trial

PARTNER	PROJECT CODE	QUANTITY (g)	Samples description	Delivered to	Date of delivery
LIST	BIOMAC	250	NFC from MFC in PDO	WKI	15/12/2022
LIST	BIOMAC	250	NFC from Pulp in PDO	WKI	15/12/2022

3.4 Delivery of 3D Printing components

The fabrication of printed components has been carried out at AIMEN using two photopolymerization techniques based on linear SLA and non-linear light absorption,2PP.

3.4.1 First experimentation trials with R2RP techniques

The validation of the resists provided by 2PP was performed in two dedicated setups available at AIMEN, one of them built on an optical microscope form Zeiss, ideal for the fabrication of small 3D microstructures, and another using a 3 axes motion system and a cuvette with a resin dispenser.

The resins provided by Fraunhofer WKI (see Table 16) were tested in these two systems, with a simple geometric pattern (Figure 21) to check the maximum resolution that could be achieved with the resin for 2PP. A Photo Initiator (PI) was added to the resins by WKI in order to improve their sensitivity to the wavelength of the laser used at AIMEN for 2PP (515 nm).

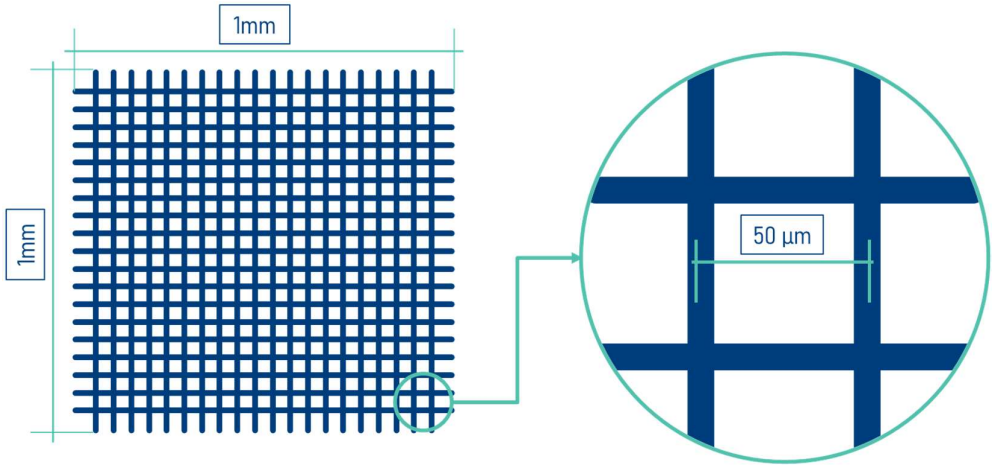


Figure 21. Geometry pattern that was used for the validation of the resins provided by Fraunhofer WKI

Table 16. Samples Matrix - First Experimentation Trial - Received in AIMEN by FH - WKI

PARTNER	PROJECT CODE	Delivered to
FH - WKI	BIOMAC-AM-001-A	AIMEN
FH - WKI	BIOMAC-AM-002-A	AIMEN
FH - WKI	BIOMAC-AM-003-A	AIMEN
FH - WKI	BIOMAC-AM-003-B	AIMEN
FH - WKI	BIOMAC-AM-004-A	AIMEN
FH - WKI	BIOMAC-AM-005-A	AIMEN
FH - WKI	BIOMAC-AM-005-B	AIMEN
FH - WKI	BIOMAC-AM-005-EF	AIMEN
FH - WKI	BIOMAC-AM-006-A	AIMEN
FH - WKI	BIOMAC-AM-007-A	AIMEN
FH - WKI	BIOMAC-AM-007-B	AIMEN
FH - WKI	BMF-CNC-005	AIMEN
FH - WKI	BMF-CNC-005	AIMEN
FH - WKI	BMF-CNC-005	AIMEN

A complete search of the best fabrication parameters was realized for each of the resists, looking for the optimal laser power and fabrication speed, as can be observed for example for the resin BIOMAC-AM-007-A in Figure 22. In this way, a wide range of laser powers and fabrication speeds was used to try to find the best resolution for the fabricated microstructures but also the fastest fabrication speed possible since this is the main limiting factor in 2PP fabrication.

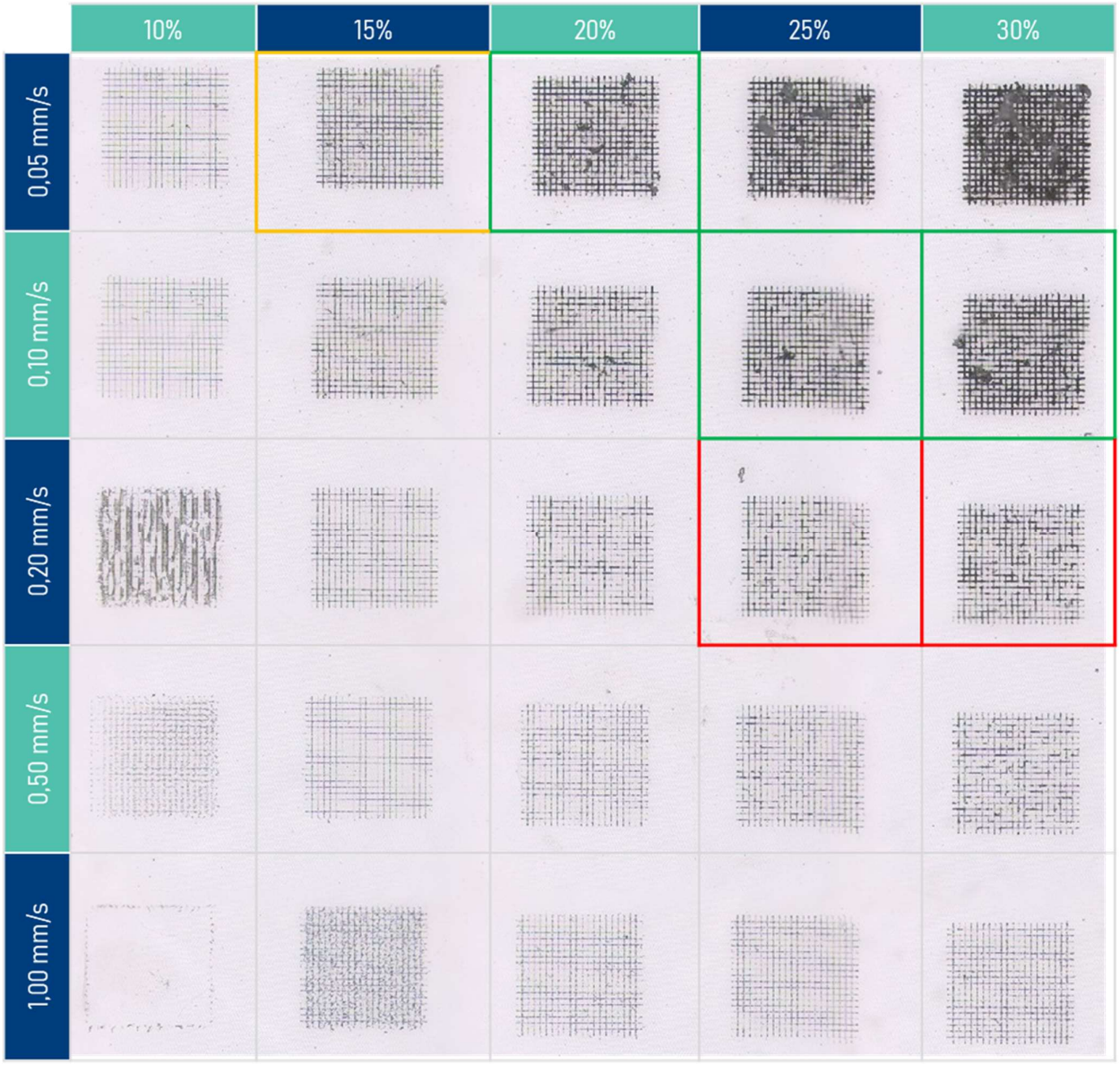


Figure 22. Fabrication parameter search for the resin BIOMAC-AM-007-A

One of the best results were found for the resin BIOMAC-AM-007-A, where a resolution around 700 nm could be found using focusing optics with a magnification of 40X and 0.95 NA.

3.4.2 Second experimentation trials with SLA techniques

The fabrication of larger structures was also tackled using SLA printers, which allow the fabrication of 3D pieces with sizes in the range of tens of cm^3 in reasonable times. The fabrication was carried out using a resin provided by WKI that did not include any PI, since

the SLA printer was using a UV light source for the fabrication of the 3D sample. The selected resin was **BIOMAC-AM-005-CL-2.**

3.4.3 Delivery of 3D printed parts

Finally, once settled the best fabrication parameters, AIMEN started the fabrication of the selected demonstrator with an SLA printer available at their facility.

Several demonstrator samples were fabricated with this technique, as shown in Figure 23, using different fabrication and postprocessing parameters to try to improve the finishing and physical properties of the fabricated demonstrator. The optical properties of the demonstrators were found to be tied to the postprocessing step used. Different coloration and transparencies were found as a function of the postprocessing procedure selected. In fact, transparency seemed to improve when the samples were submitted to an additional curing step with an UV lamp after fabrication. Moreover, their colour changed from yellowish to completely transparent.

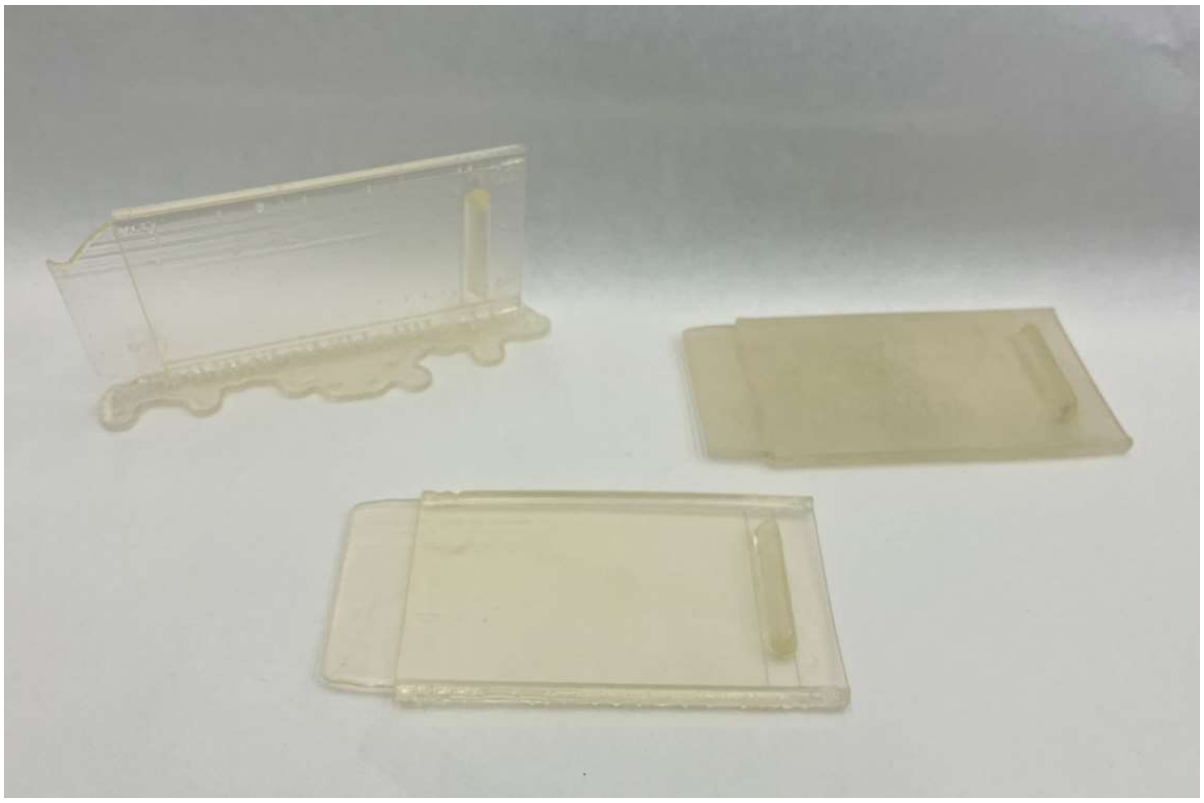


Figure 23. Demonstrator samples fabricated at AIMEN with the resin provided by Fraunhofer WKI

The prototypes samples obtained are listed with the code in Table 17.

Table 17. Samples Matrix - First Experimentation Trial

PARTNER	PROJECT CODE	Samples description
AIMEN	DEMO-1	Sun visor
AIMEN	DEMO-2	Sun visor
AIMEN	DEMO-3	Sun visor with BIOMAC logo
AIMEN	DEMO-4	Sun visor with BIOMAC and AIMEN logo

4. Conclusions

The activities in Task 3.2 allowed in the period considered to produce a set of AM printed samples by 2PP and SLA of the component selected by DIAD (sun visor for the medium - high automotive segment) with a new BIOMAC composition based on PE resins developed by FH - WKI with raw materials made by LTU, ATB, AUTH and BBEPP.

The selected composition for further characterisation and testing is **BIOMAC-AM-005-CL-2.**

The prototypes samples produced will be submitted to an extensive mechanical and physical characterisation in WP4.

All the partner collaborated in active and synergic way and at the end of the activities no deviations with respect to the planned work have been identified.