

Bio *SPRINT*

Biorefining of sugars via Process Intensification

Research and Innovation action (RIA) – Horizon 2020-BBI-2019-SO2-R6

Improve biorefinery operations through process intensification and new end products

D3.1 Methodology overview report on downstream purification



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Glossary of terms and abbreviations used

Abbreviation / Terms	Description
CPME	Cyclopentyl methyl ether
DCM	Dichlormethane
DSP	Downstream Processing
2-EHOL	2-Ethyl-1-hexanol
HMC	Hemicellulose
5-HMF	5-Hydroxymethylfurfural
HTP	Hydrothermal process
Kd	Partitioning coefficients
LA	Levulinic acid
LLE	Liquid/liquid extraction
MIBK	Methyl isobutyl ketone
MTBE	Methyl tert-butyl ether
2-MTHF	2-Methyl tetrahydrofuran
NaCl	Sodium chloride
O/A	Organic to aqueous phase ratio
P	Pressure
pH	Acidity or basicity
PI	Process intensification
pKa	Dissociation constant
2-SBP	2-Sec-butyl phenol
T	Temperature
TAA	2-Methyl-2-butanol
Taz	Boiling temperature of azeotrope
THF	Tetrahydrofuran

1 Executive Summary

BioSPRINT project, Biorefining of sugars via Process Intensification, is a research and innovation action in the frame of Horizon 2020. The main goal is to valorize the hemicellulose (HMC) waste streams, stemming from different sources. The intention is to start with purification of HMC to obtain purified and concentrated C5 and C6 sugar streams that undergo catalytic conversion employing process intensification (PI) method to produce furan (mainly furfural and 5-Hydroxymethylfurfural) products or intermediates, which will further be used to produce polymers. Since sugars exhibit high solubility in water, water is the primary reaction medium for sugar conversion towards furans/furfurals products. It is known, that at the reaction conditions in aqueous phase both products, furfural and 5-Hydroxymethylfurfural undergo self-condensation and form humins, while 5-Hydroxymethylfurfural (5-HMF) can also undergo rehydration reaction to form levulinic and formic acids as side products. In order to avoid or limit the extend of the mentioned side reactions and maximize the yields of the conversion reaction, the in-situ extraction of products from the reaction medium will be applied using biphasic reaction/extraction as part of the PI action. In this process intensification step organic solvent with high affinity towards furfural and 5-HMF will be used, therefore thermodynamic equilibrium will be shifted towards products. The liquid-liquid phase separation will be enhanced using hydrocyclones to minimize the residence time and reduce the decanter size. The reaction products (mainly furfural and 5-Hydroxymethylfurfural) from both, organic and aqueous streams, are intended to be separated to a commercial chemical specification and solvent will be recycled to the reaction/extraction stage. The purified monomers will be used as a replacement for formaldehyde in polymerization process to produce novel novolac-, resole- and Mannich-type resins.

The subject of the deliverable D3.1 is to

- i) overview possible separation strategies to purify furan-based monomers or mixture thereof,
- ii) recycle solvent as well as possible unreacted sugars back to the reactor and
- iii) to remove short chain acids and humins, that might be present in the stream after the dehydration reaction of sugars and should also be considered, if possible.

From the separation techniques, mainly distillation and solvent extraction will be considered as well as ultrafiltration (membrane separation) for humins removal when necessary. Both streams from the biphasic reaction/extraction will enter the downstream purification, and finally the main products furfural and 5-HMF will be transferred to organic phase and separated in an efficient manner to achieve the desired specification. It is of great importance to remove both reaction product components as soon as possible from an aqueous phase, since both components are highly reactive and can undergo further decomposition reactions even during downstream purification steps.

With this deliverable, first objective of the WP3 on Intensification of Downstream Purification, which is to separate main, secondary and trace reaction components to a commercial chemical specification is addressed, the solvents for efficient 5-HMF extraction as well as furfural extraction are proposed and some of them selected for further use in proposed separation and purification combined approach that will follow. Various separation configurations will be calculated later in the project and presented.

The purpose of the deliverable is to prepare a strategy for efficient separation and purification of the main reaction products (furfural and 5-HMF) generated in the biphasic catalyzed conversion of C5 and C6 sugars from aqueous streams of different origin. The purified furan monomers, furfural and 5-HMF using the proposed separation scheme will be an input into the next WP4 for polymer formulation.

Deliverable Keywords: downstream purification, continuous distillation, solvent extraction, membrane filtration, furfural, 5-HMF

2 Introduction

With this report, we follow the first objective of the WP3 on Intensification of Downstream Purification, which is to separate main, secondary and trace reaction components to a commercial chemical specification. This phase is extremely important to be able to proceed with the WP4 Development of Biorenewable Resins and Polymerization Intensification. Monomers, namely, furfural and 5-HMF, purified according to the proposed separation scheme, will be used as a replacement for formaldehyde in the synthesis of novolac-type resins as well as in the development of polyols for polyurethane applications, namely novolac-type and Mannich-type polyols, used for the development of rigid foams. We have followed the approach described below. The connection of this work-package with WP2 and WP4 is shown in Figure 1.

Connection with WP2 and WP4

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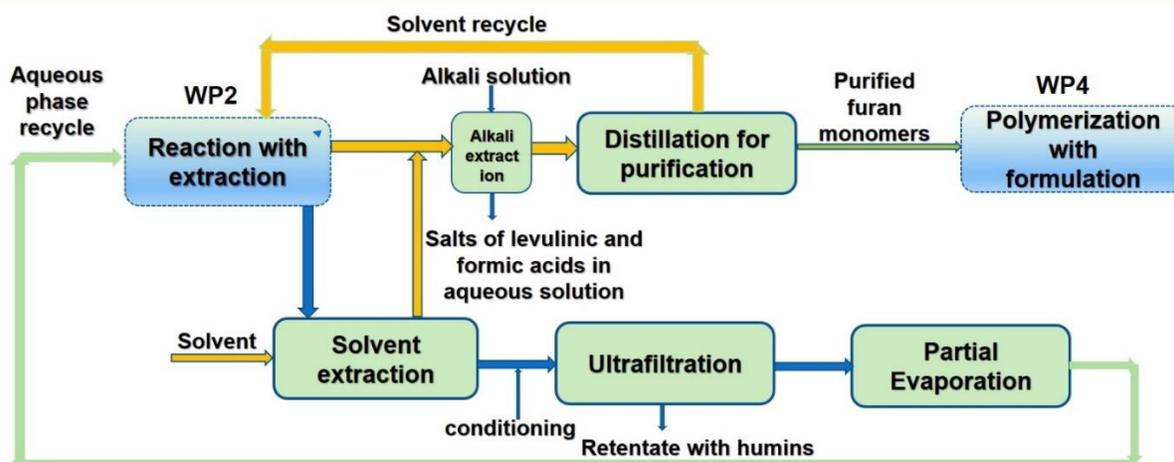


Figure 1. Connection of WP3 Intensification of Downstream Purification with WP2 and WP4, together with proposed separation and purification steps

The streams leaving the biphasic reaction/extraction, namely catalytic dehydration of C5 and C6 sugars towards furfural and 5-HMF, enter the downstream purification stage, where primarily the separation of 5-HMF/furfural from the extractive-reaction solvent by means of distillation is considered. Solvents that exhibit two-phase behavior with an aqueous phase and with high partition coefficients of furfural and 5-HMF towards organic phase will be used in the biphasic reaction/extraction. With this hybrid operation we will transfer a major amount of furfural and 5-HMF to organic phase and prevent the undesired side reactions of both main components in an aqueous phase towards humins as well as the rehydration reaction of 5-HMF towards levulinic and formic acids. We know that solvent extraction will be less efficient for 5-HMF compared to furfural, and that besides 5-HMF also a minor part of furfural will stay in the aqueous phase; therefore, the aqueous phase has to be a stream that also enters the downstream purification. For this stream, solvent extraction is proposed to remove the rest of furfural and 5-HMF from an aqueous phase. In the aqueous stream, there will be most probably acids (levulinic and formic acids) present, as mentioned above and acids are also partially extracted by solvent, therefore they have to be considered as part of the separation scheme as well. And at the end, humins that might be present in an aqueous stream should be removed by membrane separation technique (ultrafiltration) before the aqueous stream with possible unreacted sugars is recycled back (after evaporation/concentration) to the biphasic reaction/extraction. Organic stream that consists of organic outlet from the biphasic reaction/extraction and the one from solvent extraction, enter necessary separation steps towards purified furan monomers.

2.1 Mapping Project's Outputs

Purpose of this section is to map BioSPRINT's Grant Agreement commitments, both within the formal Deliverable and Task description, against the project's respective outputs and work performed.

Table 1. Adherence to BioSPRINT's GA Deliverable & Tasks Descriptions

BioSPRINT Task		Respective Document Chapter(s)	Justification
To separate main, secondary and trace reaction components to a commercial chemical specification			
Task 3.1 - Preparatory processing actions for downstream	From WP2, various material streams containing unreacted sugars, but predominantly furans/furfurals, will be provided. T3.1 will analyse, qualify and quantify the selected valorised products in solutions. Primarily, isolated 5-HMF and furfural will be targeted, while the mixtures of different furan homologues will also be considered.	<p>Section 1: Excellence</p> <p>Objective 3 (Research & Innovation): In downstream purification, to develop methods to purify the converted sugar streams into non-aqueous functionalised furan monomer bulk/solutions and to create intensification strategies minimising furans degradation</p> <p>Sub-objectives</p> <p>SO3.2: To investigate the use of advanced continuous techniques for the removal of small chain acids, humins and other by-products generated in dehydration reactions to guarantee maximum product quality downstream.</p>	This report covers the proposed separation and purification scheme towards main products furfural and 5-HMF, using continuous techniques and solvents with high separation ability for both main products.. Main components will be transferred to organic phase and purified using distillation. Solvent as well as the remained aqueous stream with unreacted sugars will be recycled to the biphasic reaction/extraction process. Products from side reactions, namely acids and humins, are intended to be removed from an aqueous phase by means of alkali extraction and ultrafiltration, respectively. Intensification, where planned, will be included in the later stage of the project.
BioSPRINT Deliverable			
D3.1 & Methodology overview report on downstream purification			
A report, covering the downstream purification of furan-based monomer mixtures, where various separation strategies are considered.			

3 Downstream separation and purification approach

A key challenge in this process section is to achieve separation of the furans (furfural, 5-HMF) from the extraction solvent used and from other by-products formed upstream in a reliable and efficient way, with the required product purity. It is anticipated that a continuous distillation processes play a central separation role as this will provide the most efficient purification, in order to attain furfural, 5-HMF or a mixture of mentioned furan monomers, mainly non-aqueous, as water would inhibit the kinetics/thermodynamics of polymerization.

Esteban et al. (1) discussed the use of biphasic systems for solely production of furfural or 5-HMF in detail, where an overview of the biphasic dehydration of sugars was given together with a guide for rational selection of solvents. Torres et al. (2) have focused on extractive-reaction processes as an alternative for the production of 5-HMF. The use of biphasic systems for the conversion of alternative carbohydrate substrates, including actual biomass sources towards 5-HMF and furfural was also mentioned by Menegazzo et al. (3). In their review, different processes and catalytic systems have been outlined with their merits, demerits and requirements for commercialization.

The individual technologies already exist, but the downstream purification processes used to convert C5/C6 sugars into combined production of both products, furfural and 5-HMF are at the moment non-existent. The current commercial furfural production processes, which give poor yields with high-energy consumption, are not economically viable (4). Here, often wood is considered as a feedstock for furfural, where under selective conditions, e.g. P, T, vapor stripping module, only HMC is decomposed and the rest of the biomass is used for energy. No side/waste streams of other origin are considered. Furfural is separated from an aqueous phase by a sequence of distillation steps or by extraction process and distillation. For solely production of 5-HMF, assorted biomass containing C6 sugars is used and downstream processing techniques for humins, unreacted sugars and water removal, extraction and crystallization are applied (AVA-Biochem's Process, (5)). However, in the industrial scale biorefineries, separation processes in downstream purification have been poorly reported.

3.1 Extraction purification

3.1.1 Solvents for extraction

In our proposed downstream processing approach, special attention is given to the solvent used in the hybrid reaction-extraction step, where both main products (furfural and 5-HMF) are generated from C5/C6 sugars. The choice of the solvent should consider different criteria, with regard to extractive reaction, solvent recovery and sustainability. From the separation point of view, solvent should exhibit immiscibility or very low miscibility with water, should not form azeotrope with the main product components, should not degrade at operating temperatures, the heat of vaporization should not be too high. However, most importantly is the selectivity of the solvent and partitioning of the main components towards the solvent. The lower water content in solvent rich phase is beneficial for extraction process, as it decreases the energy demand in the product purification and solvent recycling processes. In order to develop a process to be economically viable, also other aspects such as safety, reusability, cost and regulatory aspects should be considered.

A number of articles (6-15) is available in the literature discussing the choice of the solvent for furfural extraction, but on the other side limited information and practically no liquid-liquid-equilibrium data is available for 5-HMF, except for the solvent methyl isobutyl ketone (MIBK) (16), which was taken as a benchmark solvent. Since the structure of 5-HMF differs from the structure of furfural, we cannot expect that the solvent with high distribution coefficients for furfural will be the best solvent for 5-HMF extraction. Alcohols and ketones have been widely used in 5-HMF production as extraction solvents (17-20). Different solvents are proposed in this WP for 5-HMF extraction, such as 2-MTHF (2-methyl tetrahydrofuran), CPME (cyclopentyl methyl ether), 2-EHOL (2-ethyl-1-hexanol), 2-SBP (2-sec-butyl phenol), and THF (tetrahydrofuran) with an addition of sodium chloride salt (NaCl) to aqueous phase, and liquid-liquid equilibria for 5-HMF between aqueous and organic phase is determined in order to be able to start with downstream processing. Since solvents 2-EHOL and CPME are

shown not to be efficient for 5-HMF extraction, solvent screening is done and two other potential extraction solvents are identified, namely isophorone and benzyl alcohol.

At the beginning, the initial separation and purification scheme is proposed and it will be further optimized with respect to solvent and furfural as well as 5-HMF extraction and with respect to energy efficiency.

Table 1 presents solvents for physical extraction of furfural from an aqueous stream, together with solvents' boiling points, literature available partitioning coefficients (K_d) data at given temperatures, mutual solubility with water, azeotropic information e.g. boiling temperature (T_{az}) of the azeotrope (solvent + water, solvent + furfural) as well as a type of the azeotrope. Due to differences in thermophysical properties of solvents, various configurations of downstream processing are expected.

It is anticipated that solvent of our choice will be efficient for furfural as well as for 5-HMF extraction from a reaction aqueous mixture, but also acids (formic acid and levulinic acid) will enter the organic phase to some extent, although the partitioning coefficients are low. These acids, formic and levulinic, are weak acids with dissociation constants (pK_a) of 3,745 (25 °C) and 4,64 (18 °C), respectively. The distribution coefficients to organic phase vary strongly with the pH values of an aqueous phase. At $pH \leq pK_a$, the major part of an acid distributes to organic phase; at $pH \geq pK_a$, higher amount of acid will be in ionization state and therefore it will stay in an aqueous phase. Since the reaction with extraction will be carried out at certain operating conditions (pressure P , temperature T , pH (acidity), O/A (organic to aqueous phase ratio), catalyst concentration), pH cannot be altered at this stage. To remove acids from organic phase, organic stream has to be cooled down and alkali rinsing (alkali extraction) can be performed. The lean organic stream on acids is led further to distillation train (e.g. removal of an azeotrope solvent-water, vacuum distillation for solvent removal and finally the separation of furfural and 5-HMF under vacuum). At the last step, namely the separation of furfural and 5-HMF, crystallization may be used, due to a very large difference in freezing points between the two main components to avoid very high temperature in the vacuum distillation column and as a consequence the decomposition of 5-HMF.

In aqueous phase that will leave the reaction/extraction step, there will still be some products (furfural and 5-HMF) present, but also some acids and humins, both as products of side reactions as well as unreacted sugars. Humins are polymers with complex composition and behavior. The aqueous stream has to be cooled down and further led to solvent extraction carried out counter-currently. Organic stream leaving the extraction column will merge with an organic stream from reaction/extraction, which is further subjected to alkali rinsing to remove acids. The (A/O) ratio and the type and concentration of alkali solution should be determined by experimentation due to modelling limitations. An aqueous stream leaving the solvent extraction column will enter the ultrafiltration module (membrane separation) after aqueous stream conditioning to remove humins (retentate) that can be further valorized (biorefinery side product). Permeate with unreacted sugars can be concentrated by means of evaporation and recycled back to the reactor.

Table 2. Possible solvent candidates (physical extraction)

Solvent	Formula	Tb(°C)	Kd(F); T(°C); (ref)	Solubility (wt%)		S+W	S+F
				S in W	W in S	Taz (°C); type	Taz (°C)
2-methyl-2-butanol (TAA)	C5H12O	102,4	4-9,7 (w/w); 25; (6)	11,01	23,46	87;hetPmax	no
			3-4,8 (w/w); 98,3; (7)				
			4-4,2 (w/w); 128; (7)				
2-ethyl-1-hexanol	C8H18O	184,6	3,9-10,4 (w/w); 25 (6)	0,088	2	yes;hetPmax	n.a.
4-methyl-2-pentanone (MIBK)	C6H12O	116	7 ((mole/L)/(mole/L)); 25; (8)	1,25	2,6	87,8;hetPmax	no
			11,7(w/w); 29,4; (7)				
			10,9 (w/w); 48,7; (7)				
			9,3 (w/w); 67,8; (7)				
			5,6-7,6 (w/w); 98,5; (7)				
			5,9(w/w); 128; (7)				
toluene*	C7H8	110,65	3,1 ((mole/L)/(mole/L)); 25; (9)	0,0682	0,0532	84,5; hetPmax	no
isophorone	C9H14O	215,32	10-12,5 (w/w); 30; (10)	1	4,5-6	n.a.	no
2-methyl tetrahydrofuran (2-MTHF)	C5H10O	78,85	8-12,5 (w/w); 25,85; (11)	11,5	3,7	89;	no
			8,2-10,6 (w/w); 48,85; (11)	11,6	3,5		
			7,7-8,5 (w/w); 67,85; (11)	5,6	3,8		
cyclopentyl-methyl-ether (CPME)	C6H10O	106	5,9-11,9 (w/w); 25, (11)	1,12	0,55	85;	no
			5,8-10,2 (w/w); 49,85; (11)	0,75	0,66		
			5,5-8,1 (w/w); 69,85; (11)	0,72	0,65		
methyl tert-butyl ether (MTBE)	C5H12O	55,05	6,1-11,84 (w/w), 24,85; (12)	4,1	1,4	52,9	no
			6,5-11,15 (w/w), 34,75 (12)	3,2	1,6		
2-sec-butyl phenol (2-SBP)	C10H14O	226,85	19,78 /w/w); 30 at 25 bar; (13)	0,1478 (30)	0,3056 (30)	n.a.	n.a.

*- not a green solvent, only for comparison; S-solvent, W-water, F-furfural; n.a.- information not available; Taz- azeotrope temperature at 101.32 kPa

3.1.2 Example of separation scheme using benchmark solvent MIBK

In Figure 2, the separation and purification scheme are presented for furfural and 5-HMF production from C5/C6 sugars from reaction/extraction using MIBK as solvent. Acids were not intended to be removed from organic stream in this scheme; therefore, they are present in small amounts in both products, furfural and 5-HMF. Aqueous stream leaving an extraction column, which is lean on furfural and 5-HMF but contains humins and unreacted sugars, enters ultrafiltration after conditioning to remove humins and is led further to evaporator, where a part of water is evaporated, and concentrated aqueous stream is recycled to the reactor.

T3.2 Development of distillation with w/o extraction

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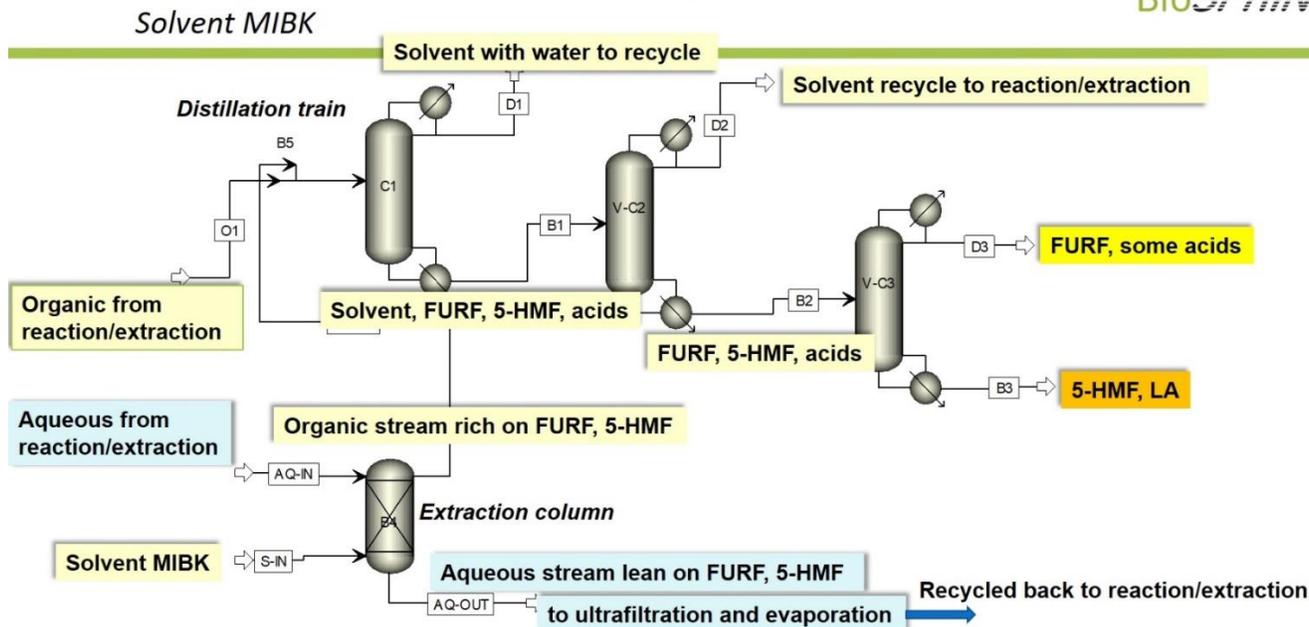


Figure 2. First proposed separation and purification scheme using benchmark solvent MIBK for furfural and 5-HMF without acids removal.

3.1.3 Lab scale extraction experiment

In previous experiments in the SteamBio project (636865) and in the BBChem project (033RK031C), acidic aqueous feed solutions have already been investigated using extraction. The selected solvents were selected according to the following criteria: solubility of the target products, boiling point, density difference to target product, azeotrope formation with feed material. The experimentally generated data should provide initial points of reference as to how the later HMC solution from WP2 and in the DSP (downstream processing) in WP3 could behave.

The slightly acidic aqueous feed solution (> 90 wt% water) used in SteamBio contained 5-HMF (2 g/L), furfural (5 g/L) and carboxylic acids (6 to 25 g/L) as value components. The feed solution was created through a torrefaction process of biomass such as wood. The results shown in Table 3 could be achieved through an LLE (liquid-liquid extraction) using 2-SBP, MIBK and chloroform. A sufficiently good separation of furfural by all three solvents was found. In contrast, only chloroform showed a sufficiently good separation for 5-HMF.

A sugary aqueous HTP (hydrothermal process) feed solution was used in the BBChem project. 2-SBP, MIBK, chloroform and DCM were used for the LLE. The feed solution (model solution + real solution) consisted mostly of water (> 90 wt%). The concentration of the value components was as follows: 5-HMF (1 to 18 g/L), furfural (1 to 14 g/L), carboxylic acids (3 to 19 g/L), xylose (<150 g/L), glucose (<150 g/L). A sufficiently good separation of furfural from the aqueous phase by means of 2-SBP, chloroform and DCM was possible in this matrix. 5-HMF could be extracted by 2-SBP with a high yield.

The LLE plays a major role in BioSPRINT, as it can selectively release the target products, furfural and 5-HMF, from the feed matrix.

Table 3. Overview of LLE with different solvents in other projects

DSP	Scale	Feed	Solvent	Results	Source
LLE	lab	torrefication stream from wood/bushes	2-SBP MIBK Chloroform	<p><u>2-SBP:</u> not suitable for 5-HMF suitable for Furfural</p> <p><u>MIBK:</u> suitable for Furfural (high extraction yield) 5-HMF insufficient extraction</p> <p><u>Chloroform:</u> suitable for 5-HMF (high extraction yield) suitable for Furfural (high extraction yield)</p>	SteamBio project
LLE	lab	HTP with C5/C6	2-SBP MIBK Chloroform DCM	<p><u>2-SBP:</u> suitable for 5-HMF (high extraction yield) suitable for Furfural</p> <p><u>MIBK:</u> Furfural insufficient extraction 5-HMF insufficient extraction</p> <p><u>Chloroform/DCM:</u> suitable for Furfural 5-HMF insufficient extraction</p>	BBCHEM project

3.2 Distillation purification

In the past, Fraunhofer has separated furfural by distillation in laboratory and in pilot scale. A sufficiently larger number of separation stages (> 6) in the distillation column is necessary to separate the heterogeneous furfural/water azeotrope from the feed solution. After the distillate has cooled down, the heterogeneous azeotrope breaks down into two phases. The heavier organic phase consists of a high concentration of furfural with a low water content. This phase would have to be thermally purified again to reach a higher concentration of furfural. The lighter aqueous phase, on the other hand, has a low proportion of furfural and could therefore be fed back as a recycling stream to reach the recovery of at least 90 % of the weight of 5-HMF and furfural.

To obtain 5-HMF by distillation directly out of the feed solution, the lower boiling components (water, carboxylic acids etc.) must be removed from the mixture as completely as possible. The result is a highly viscous mixture of different high boiling substances, which has to be treated further in order to produce industrially usable 5-HMF. In the previous projects, a concentration factor of 87 could be achieved by means of thermal treatment. The simultaneous production of furfural and 5-HMF in just one process step is difficult because the furfural yield is

avored at high pressure, but the increased boiling temperature promotes the decomposition of the 5-HMF in an acidic environment.

3.3 Membrane filtration purification

Membrane filtration experiments were carried out in the SteamBio project with a bench-scale crossflow membrane filtration plant (LSTa60-LM from SIMA-tec GmbH) at the Fraunhofer CBP. The sample was pre filtered via a laboratory suction filter with a pore size of 1 to 2 μm . The upstream microfiltration serves to prevent fouling. The next step was testing of a reverse osmosis membrane (DOW FILMTEC BW30) with a salt retention of >90 % NaCl for the separation of furan derivatives from water and carboxylic acids. The membrane used, showed a very good support for furfural and 5-HMF but also the retention of formic acid and acetic acid was in a very high range between 96 – 99 %. In another experiment, the membrane NF90 also from DOW FILMTEC with a salt retention of >97 % was tested. As expected, the retention was not so pronounced. 5-HMF was found at 15 %, furfural at 39 %, acetic acid at 35 % and formic acid at 59 % in the permeate.

In conclusion for BioSPRINT it can be said from findings that membrane technology can be used to concentrate the feed solution or separate water. For the preparation of the furan derivatives in WP3, membrane technology could play a key role in reduction of energy demand.

4 Conclusions and Next Actions

The deliverable 3.1. Methodology overview report on downstream purification, with the suggested separation and purification approach will contribute to the following project goals or objectives:

- i) KPI 5 - The reduction of waste with Target < 10% remaining C5,
- ii) KPI 7 - Reduction of energy demand (removal of water),
- iii) KPI 8 - Reuse of solvents with Target > 20 times and
- iv) KPI 9 - Purity of furans (Target >90% (extraction/distillation)).

By applying the proposed separation and purification approach, furfural and 5-HMF separately or as a mixture in different purities will be obtained and handed over to the next stage WP4 for further polymerization activities towards the final products.

As shown on the proposed separation and purification scheme, the solvent will be recycled to the reaction/extraction step therefore only minor amount of 'make-up' solvent will be needed in the process. Since different solvents will be applied for extraction purposes, various separation configurations will be proposed and calculated later and the comparison in terms of the energy costs per mass balance and in terms of purity of the main products, furfural and 5-HMF, will be presented. Results will be used further for life cycle analysis and operation cost studies in WP5 and WP6.

Experiments from previous studies have shown that membrane technology can be effectively used to concentrate the feed solution or separate water, and membrane technology can be seen as a key technology in reduction of energy demand. Unreacted sugars still present in the aqueous stream leaving an extraction column are intended to be partly concentrated and recycled back to the reaction/extraction step as well. With this the whole process will be closed and the waste will be minimized.

5 References

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