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Biomass based energy intermediates boosting biofuel production

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Publishable Summary

In BioBoost, there is a strong focus on the economics of the processes. To improve the economics of the overall value chains the extraction of chemical byproducts from the pyrolysis products and the HTC process were investigated. Focus was set on:

- Recovery of phenol and phenolic compounds from fast and catalytic pyrolysis
- Recovery of furanoics and organic acids from HTC process water and aqueous phases from pyrolysis
- Recovery of primary and secondary nutrients from HTC process water

For the isolation of mixtures of phenol derivatives CERTH developed several different extraction schemes depending on the source of starting material KIT fast pyrolysis oil or CERTH catalytic pyrolysis oils. When starting with fast pyrolysis bio-oil an extraction with an organic solvent yields a final fraction consisting of 14.6 wt.% phenolics with 80 % extraction efficiency. The enrichment achieved is satisfying, especially considering the low concentrations of phenolics in the bio-oil used as feed. Catalytic pyrolysis bio-oil has a far higher concentration of phenolic compounds and a multi-stage processes has been developed for their efficient extraction. Experiments at CHIMAR showed that phenolic fractions from pyrolysis oil could be successfully used in the synthesis of phenol-formaldehyde resins suitable for the production of plywood panels.

For the isolation of furfurals (HMF, hydroxymethyl furfural, one of the most important chemical platform molecules from biomass, from the aqueous effluent stream of the HTC process two methods were investigated. Solvent extraction with chloroform performed best making use of an 8-stage mixer settler battery. Also, the adsorption of HMF to activated charcoal and the following desorption was tested. However, when optimised towards the production of bio-coal, the amount of furfural in the HTC process water is insufficiently low for extraction. A staged or combined process has been suggested to integrate HMF and biocoal production to make use of the added value. CHIMAR tested the use of 5-HMF as formaldehyde substitute in the synthesis of PF resins for plywood panels.

Separation and recovery of nutrients also may contribute to higher process efficiency, at the same time meeting the demand for closed nutrient cycles in view to optimum life cycle performance.

Table of Content

Report

1 Recovery of pure phenol, phenolics and high value compounds from fast pyrolysis oil, catalytic pyrolysis oil and treated pyrolysis oil

1.1 Recovery of phenols from pyrolysis oil

Thermal or catalytic pyrolysis biooils could potentially be used as sources of chemicals production, since they consist of hundreds of different compounds. One of the main classes of compounds detected in considerable amounts in the biooils is phenol and phenolic derivatives (phenolics). They form mainly during the de-polymerization of lignin. The main compounds formed are guaiacol and syringol, which are the main building blocks of lignin and their concentration is depended on the prevailing type of lignin in the original biomass. Other phenolic derivatives produced at considerable quantities during the pyrolysis are catechols, cresols and anisoles as well as phenol itself. The content of the phenolic compounds depends largely on the biomass used and on the pyrolysis conditions employed. The separation of these compounds individually or as a group would be of economic importance for the valorization of pyrolysis oil.

However, the inherent complexity of the biooil synthesis renders difficult the direct extraction of a single compound, with satisfactory recovery rate and naturally multiple extraction steps are needed. An alternative possible approach is the separation of an enriched phenol extract since this can be the starting point for the separation of individual compounds or the development of a chemical modification process towards the production of phenol. Moreover, such an enriched phenolic extract can be used for partial substitution of petrochemically derived phenol in various applications among which is the production of binders and resins for the wood industry, as proposed in this project.

This is report includes the final findings regarding the development of extraction schemes for the recovery of the phenolic fraction of from either thermal or catalytic pyrolysis oils.

1.1.1 Experimental part

All the extractions described are liquid-liquid extractions with organic solvents of analytical purity or higher, performed at room temperature unless mentioned otherwise, in batch mode and in common glassware at CERTH. The mixing of the solutions was performed either on a stirring plate or in an ultrasonic bath. The gas chromatographic methods employed are described in detail below.

GC-FID

Pyrolysis oil is a polar mixture rich in acids and phenols. Some of the main compounds can be identified and quantified by means of a developed GC-FID method, employing external calibration. The described method was employed in this work mainly for the quantification of acetic acid and the primary evaluation of the extracts received during the different extraction protocols examined. This method has

been previously developed in our lab for the efficient separation and quantification of 34 compounds, including phenols, furans and cyclic aldehydes and ketones.

The gas chromatographic unit used was a HP5890 II GC, equipped with an FID. The column used was a DB-WAX 30m x 0.53 mm x 1 μm. The carrier gas was Helium at a flow rate of 2 mL/min. Injections (0.4 μL) were made in the splitless mode at an injector temperature of 200 ^{o}C. The detector temperature was set at 235 ^{o}C. The temperature program employed was: initial oven temperature at 80 ^{o}C increasing at 4^{o} C/min up to 140 ^{o}C, stable at 140 ^{o}C for 2 min, then at 4 ^{o}C/min up to 225 ^{o}C and kept constant until the end of program. The total run time was 48.25 min.

GCxGC-TOFMS

Two-dimensional gas chromatography is an advanced separation technique that uses two columns of different polarity, connected sequentially, thereby allowing separation of the compounds both due to their boiling point and polarity. The increased separation achieved by this technique is essential for complex mixtures such as bio-oils that contain numerous compounds of similar structures and properties. This technique is available at CERTH, and is connected to a time-of-flight mass spectrometer that allows the positive identification of many unknown compounds at a wide range of molecular weights.

The analytical system at CERTH consists of an Agilent 7890A GC with an injector Agilent 7683 B series (Agilent Technologies, Palo Alto, CA, USA) connected to a Pegasus 4D time-of-flight mass spectrometer from Leco Instruments (St. Joseph, MI, USA). The first dimensional chromatographic separation is performed by an apolar column BPX-5 (5 % phenyl polysilphenylenesiloxane); 30m, I. D. 0.25 mm, d. f. 0.25 μm. The second dimensional column is situated in a dual internal oven and is a BPX-50 (50% phenyl polysilphenylenesiloxane); 1.5 m, I.D. 0.1 mm, d. f. 0.1 μm. Both columns were purchased from SGE Analytical Science Pty Ltd (Australia). Cryofocusing was achieved by liquid nitrogen and a quad jet dual stage modulator (Zoex, Houston, TX, USA) and the modulation period was 5s. The ToF-MS operated at 70eV, at an acquisition rate of 100 spectra/s and a mass range of m/z 45 – 400 mu. The identification of the compounds was based on the NIST05 library while the quantitative analysis was performed via a developed internal standard calibration method. The samples were properly diluted in acetone and injected into the chromatographic system at a volume of 0.5 μL, employing split injection at a split ratio of 1:20, while the injector temperature was 250 ^{o}C. Total run time was 102 min.

Thermal and Catalytic pyrolysis oils studied

Thermal Fast Pyrolysis oils (FPoils)

The following thermal pyrolysis oils have been used in this work:

1. Q12-3792: Aqueous phase of an FPoil from KIT
2. Q11-3793: Organic phase of an FPoil from KIT
3. FPoil from KIT: FPoil produced from campaign KW29/2011
4. FPoil from CPERI: wheat straw based FPoil.

Catalytic Pyrolysis oils (CPoils)

The catalytic pyrolysis oil used during the method development was produced in CPERI using a woody biomass and a ZSM-5 catalyst.

1.1.2 Results and discussion

1.1.2.1 Development of separation schemes for the extraction of the phenolic fraction from FPoil

Several extraction schemes have been developed for the recovery of the phenolic fraction from FP oil employing either H_2O at different pH levels or organic solvents such as methanol, ethanol, ethyl acetate, diethyl ether, dichloromethane pentane, hexane, cyclohexane, or petroleum. Out of the schemes developed, the three that resulted in the highest concentration phenolic extracts were the following:

- Scheme 1: FPoil+0.6M $NaHSO_3$.
  Extract yield less than 2 %, with 27 %wt phenolics
- Scheme 2: FPoil+CH_2Cl_2.
  One step process, extract yield 30 % with 5.7 %wt phenolics
- Scheme 3: FPoil+CH_2Cl_2.
  5-step process, extract yield 13 % with 14.6 %wt phenolics

The details regarding the schemes and the method development were reported in D3.1. Following scheme 2, an extract was obtained that was supplied to CHIMAR for resins synthesis (KITFP-phenolic extract Chimar 2). Extraction scheme 3 offers a phenolic extract with increased concentration and acceptable yield, however since CH_2Cl_2 is not an environmentally friendly solvent and its use in large scale is avoided, attempts were made to find an alternative. The results are presented in the next paragraph.

1.1.2.2 Development of optimized extraction of phenolics from thermal pyrolysis oil (FPoil)

During the method development the FPoil KIT (KW29/2011) and its chromatographic analysis results are presented in Figure 1.1 and Table 1.1.

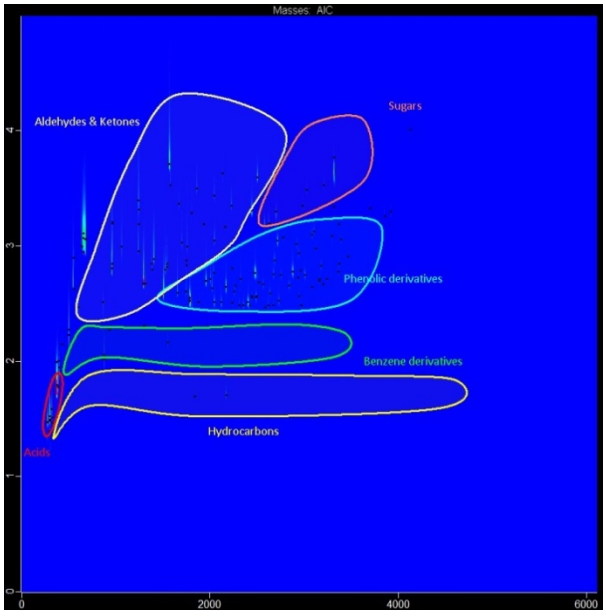


Figure 1.1: GCxGC-ToFMS analysis of FPoil

Table 1.1: GCxGC-ToFMS quantification of FPoil

FPoil KIT (KW29/2011)			
Biomass: WOOD			
Compound	*% w/w*	*Group*	*Total % w/w*
1,2-Benzenediol	0.66	AR	0.00
2(5H)-Furanone	0.24	ALI	0.05
Phenol, 2,6-dimethoxy-	0.23	PH	2.51
Hydroquinone	0.20	FUR	0.07
Guaiacol	0.17	AC	0.00
Phenol	0.12	EST	0.02
2-Cyclopenten-1-one	0.12	AL	0.00
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.11	ETH	0.00
1,2-Benzenediol, 3-methoxy-	0.11	ALD	0.12
2-Cyclopenten-1-one, 3-methyl-	0.10	KET	1.05
		PAH	0.00
Total $_{\text{Top 10 compounds}}$ (% w/w)	2.05		
Total (% w/w)	3.85		

Biooil is a polar mixture of components and therefore miscible with polar solvents such as ethanol, methanol acetone etc. However, it is not miscible with these solvents at any ratio as proven by the fact that ethanol is used to determine the total suspended solids in bio-oils. Based on this observation, FPoil was mixed with acetone and it was observed that after a certain ratio some precipitate was formed. The precipitate formed is probably due to lignin macromolecules that could not remain in solution due to the polarity of their environment. The precipitate was filtered off, and the acetone extract was evaporated under reduced pressure in order to collect the FPoil extract while the solvent was retrieved and recycled. It was concluded that at a 1:25 FPoil: acetone ratio, 8.2 %wt of the sample was removed as a solid, 67.8 %wt of the FPoil was retrieved as an extract and the rest 24 %wt was removed as volatiles during the evaporation of acetone. This extract had a 3.7 %wt concentration in phenolics so it was slightly concentrated compare to the initial FPoil. This extract was used as starting material for the further extraction of phenolics. The solvents used in the second extraction step were ethyl acetate, cyclohexane and H_2O and their mixtures based on the initial work presented in D3.1, while n-butanol was also tested. The purpose was the fine-tuning of the polarity of the extraction solvents mixture, in order to achieve the best possible selectivity for phenolics. The solvents tested, the extract received and the phenolics concentration in the extracts obtained are presented in Table 1.2.

Table 1.2: Extraction solvents employed on acetone-extracted FPoil

Extractant	Bio-oil based extract (%)	Phenolics content (%wt GC-FID)
100 % Ethyl acetate	44.7	1.7
80 % Ethyl acetate + 20% C_6H_{12}	37.6	3.4
50 % Ethyl acetate + 50% C_6H_{12}	19.6	5.1
10 % n-butanol + 90% C_6H_{12}	11.9	6.9

As is evident from the results, the 50 % Ethyl acetate + 50 % C_6H_{12} and 10 % n-butanol + 90 % C_6H_{12} mixtures present the highest phenolics extractability, however the mixture containing n-butanol has a higher boiling point and therefore it is more difficult to evaporate.

The acetone extracted FPoil was also further extracted with H_2O at pH3, and the aqueous phase collected was further extracted with 50 % Ethyl acetate + 50 % C_6H_{12}. As a result a phenolic extract containing 15.8%wt phenolics was obtained, with the phenolics recovery being 83.5 % and the overall recovery based on the FPoil was 12.8 %. Compared to the CH_2Cl_2-based extraction presented in D3.1 this scheme is improved in terms of phenolics concentration in the final extract and requires the use of non-toxic solvents that can be recycled. The extraction scheme is presented in Fig. 1.2.

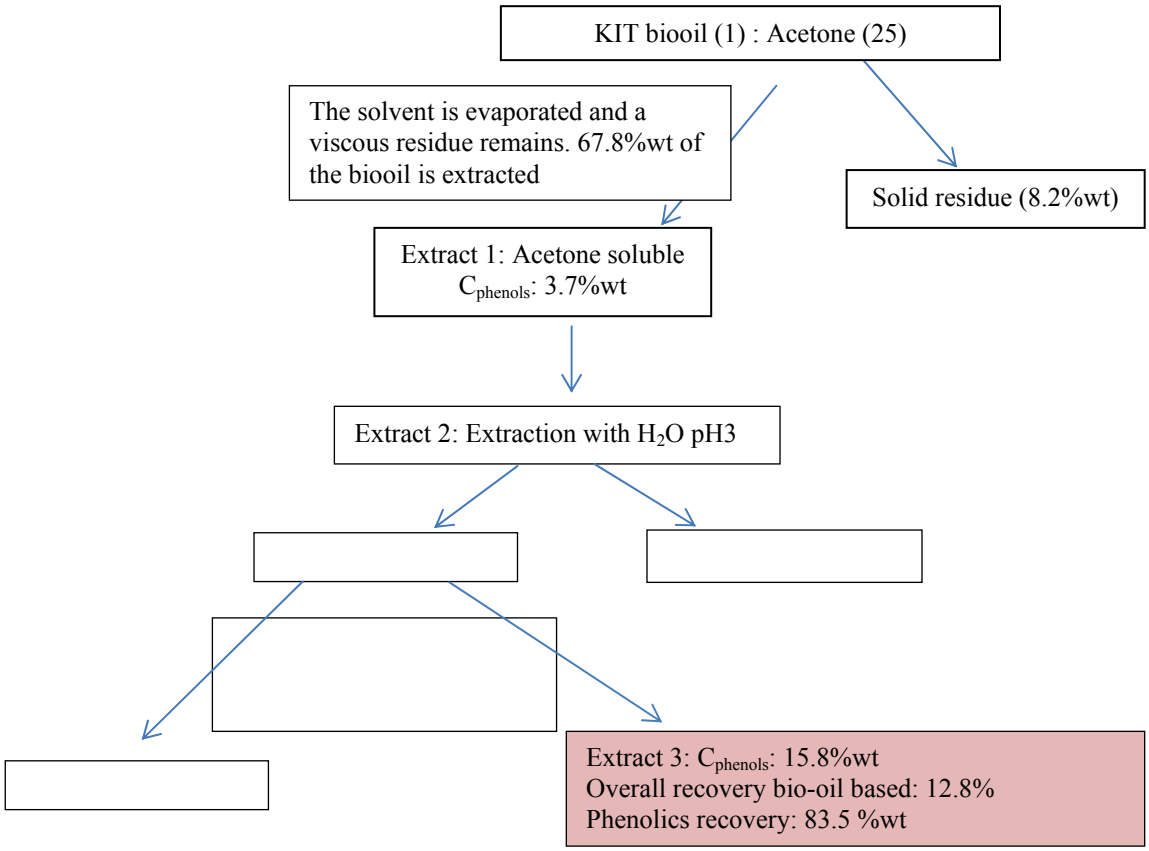


Figure 1.2: Proposed extraction scheme for the isolation of the phenolic fraction of FPoils

The above scheme (Fig. 1.2) represents a simple process, were the solvents can be recycled at each step and the final extract has 12.8 %wt phenolics. Nonetheless, in view of developing a one-step procedure for the phenolics recovery, the different combinations of ethyl acetate, acetone and cyclohexane were applied directly to the FPoil. The results are presented in Table 1.3

Table 1.3: Extraction solvents employed directly on FPoil

Extractant	Bio-oil based extract (%)	Phenolics content (%wt GCxGC-ToFMS)
100 % Ethyl acetate	55.1	4.6
90 % Ethyl acetate + 10 % acetone	59.3	3.5
70 % Ethyl acetate + 30 % C_6H_{12}	33.6	5.9
50 % Ethyl acetate + 50 % C_6H_{12}	18.0	9.5

As is evident from Table 1.3, the solvent mixture of **50 % Ethyl acetate + 50 % C_6H_{12}** is suitable for the direct extraction of phenolic compounds from FPoil, in one step. Compared to the above described 5-step process, the phenolic concentration of this final extract is lower, however the simplicity of one simple extraction instead of

five suggests this process as optimum. This optimized one-step process was applied to two FPoils provided by KIT in order to obtain phenolic extracts to deliver to CHIMAR for resins synthesis.

1.1.2.3 Application of the optimized phenolics extraction scheme to KIT-FPoil (KW29/2011)

The KIT FPoil was subjected to multiple extractions with 50 % Ethyl acetate + 50 % C_6H_{12} until obtaining 350 g of extract. This extract named KITFP-phenolic extract Chimar 3 was delivered to CHIMAR. The chromatographic analyses of these extracts are presented in Figure 1.3 and Tables 1.4 and 1.5, in comparison to the initial FPoil and KITFP-phenolic extract Chimar 2.

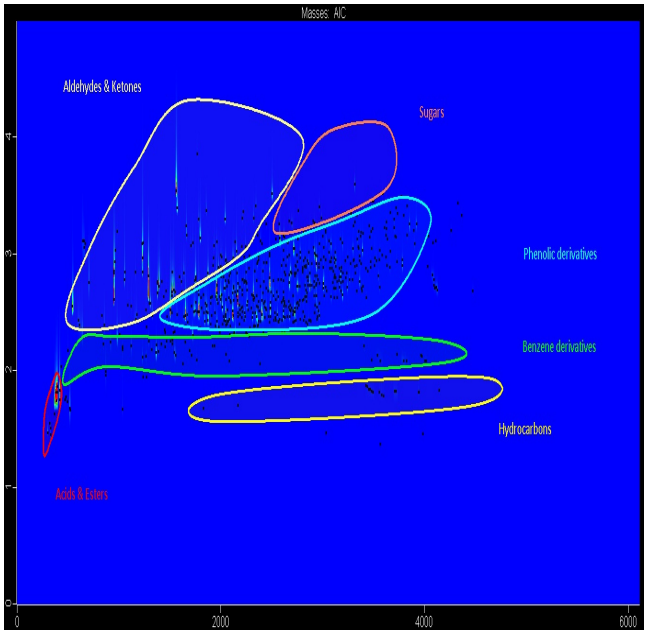


Figure 1.3: GCxGC-ToFMS analysis of KITFP-phenolic extract Chimar3

Table 1.4: Distribution of quantified (GCxGC-ToFMS) compound group in KIT FPoil

	KITFP-phenolic extract Chimar 3	KITFP-phenolic extract Chimar 2	KITFP-oil
Average Yield (%)	**23**	**30**	**-**
Group	**Total %wt**	**Total %wt**	**Total %wt**
AC	6.07	8.83	4.28
AR	0.02	0.02	0.00
ALI	0.04	0.00	0.05
PH	**13.13**	**5.73**	**2.51**
FUR	0.32	0.20	0.07
EST	0.04	0.01	0.02
AL	0.30	0.18	0.00
ETH	0.00	0.00	0.00
ALD	0.22	0.15	0.12
KET	7.18	3.09	3.17

Table 1.5: Top 10 compounds of highest concentration determined by GCxGC-ToFMS

	KITFP-phenolic extract Chimar 3	KITFP-phenolic extract Chimar 2	KITFP-oil
Compound	% wt	% wt	%wt
1. Acetic acid	6.07	8.83	4.28
2. Hydroxyacetone	3.08	3.83	2.12
3. 1,2-Benzenediol	2.84	0.58	0.66
4. Phenol, 2,6-dimethoxy-	1.48	0.83	0.23
5. Phenol, 2-methoxy-	1.04	0.61	0.17
6. Phenol	0.74	0.34	0.12
7. 2(5H)-Furanone	0.58	0.56	0.24
8. 1,2-Benzenediol, 3-methoxy-	0.55	0.27	0.11
9. Hydroquinone	0.47	0.06	0.20
10. Phenol, 3-methyl-	0.46	0.23	0.08

The physicochemical properties of KITFP-phenolic extract Chimar 3 were also determined and are presented in Table 1.6.

Table 1.6: Comparison of the physicochemical analysis of the phenolic extracts

	KITFP-phenolic extract Chimar 3	KITFP-phenolic extract Chimar 2
TAN	89.63 mgKOH/g	60.97 mgKOH/g
Density (15 ^{o}C)	1.14 g/mL	1.19 g/mL
Water	0.29 %	0.52 %
Viscosity (50 ^{o}C)	12.42 cSt	6.32 cSt
Elemental analysis	C: 59.03 % H: 8.20 % O: 32.77%	C: 50.32 % H: 5.66 % O: 44.02%
Calorific Value	25.1 MJ/kg	22.9 MJ/kg

1.1.2.4 Application of the optimized phenolics extraction scheme to KIT-FPoil Q11-3793

The same extraction method was applied to the FPoil sample Q11-3793 delivered to CERTH from KIT. Initially a chromatographic analysis was performed on both Q11-3793 and Q12-3792, in order to determine their phenolic content and decide which one is suitable of phenolics extraction. The corresponding chromatograms are presented in Figures 1.4 and 1.5, while the detailed quantification results are presented in Table 1.7.

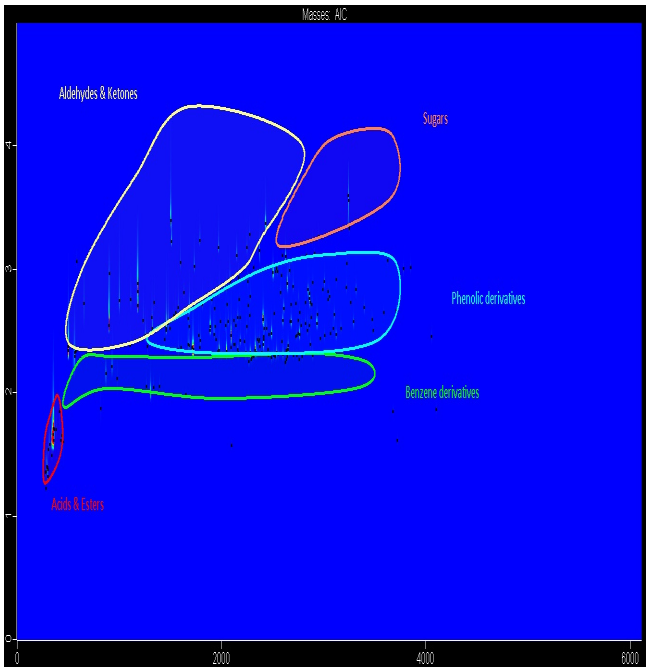


Figure 1.4: GCxGC-ToFMS analysis of Q12-3792

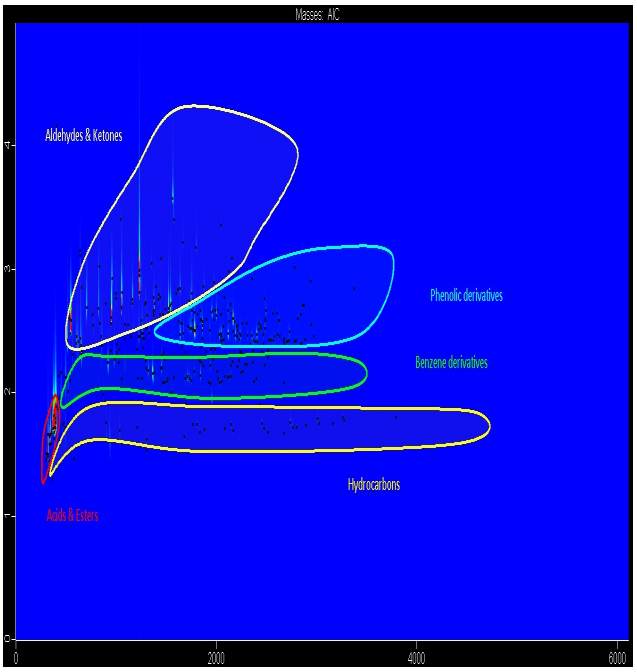


Figure 1.5: GCxGC-ToFMS analysis Q11-3793

Table 1.7: GCxGC-ToFMS quantification of Q12-3792 and Q11-3793

Q12-3792 aqueous phase				**Q11-3793 organic phase**			
Compound	%wt	Group	Total wt	Compound	%wt	Group	Total wt
1. Acetic acid	5.58	AR	0.01	1. Acetic acid	4.51	AR	0.02
2. Hydroxyacetone	2.91	ALI	0.03	2. Hydroxyacetone	2.78	ALI	0.06
3. Furfural	0.36	PH	0.32	3. 1,2-Benzenediol	1.67	PH	6.81
4. 2-Cyclopenten-1-one	0.24	FUR	0.12	4. Hydroquinone	0.44	FUR	0.06
5. 1-Hydroxy-2-butanone	0.13	AC	5.58	5. Phenol, 2-methoxy-	0.44	AC	4.51
6. 2-Butanone	0.11	EST	0.02	6. 4-Ethylcatechol	0.30	EST	0.08
7. Phenol, 2-methoxy-	0.10	AL	n.d.	7. 1,2-Benzenediol, 3-methoxy-	0.29	AL	n.d.
8. Cyclopentanone	0.09	ETH	n.d.	8. Phenol	0.27	ETH	n.d.
9. 2-Cyclopenten-1-one, 2-methyl-	0.08	ALD	0,57	9. Phenol, 4-ethyl-	0.27	ALD	0.37
10. Benzaldehyde	0.07	KET	4,19	10. 2-Cyclopenten-1-one	0.27	KET	4.69
Total $_{\text{Top 10 compounds}}$ (%wt)	9.67			Total $_{\text{Top 10 compounds}}$ (%wt)	11.24		
Total (%wt)	10.90			Total (%wt)	16.70		

Based on the analysis results it appears that the phenolic compounds have partitioned preferentially to the organic phase. The optimized extraction scheme developed was applied to KIT-FPoil Q11-3793, in order to obtain a phenolic extract to deliver to CHIMAR for resin synthesis. The sample was analysed chromatographically and its phenolic content was determined, along with its physicochemical properties. The results are presented in Tables 1.8 and 1.9.

Table 1.8: GCxGC-ToFMS quantification of KIT-FP-phenolic extract Chimar4

Compound	% w/w	Group	Total %wt
1. Vanillin	3.28	AR	<0.01
2. 1,2-Cyclopentanedione, 3-methyl-	2.55	ALI	<0.01
3. 1,2-Benzenediol	1.69	**PH**	**18.55**
4. Phenol, 2,6-dimethoxy-	1.32	FUR	0.09
5. Phenol, 2-methoxy-	1.24	AC	0.63
6. Phenol	1.05	EST	0.11
7. Phenol, 4-ethyl-	0.81	AL	0.18
8. Phenol, 3-methyl-	0.77	ETH	<0.01
9. Phenol, 2-methoxy-4-(1-propenyl)-	0.74	ALD	0.28
10. Hydroquinone	0.51	KET	6.72
Total $_{\text{Top 10 compounds}}$ (%wt)	13.95		
Total (%wt)	26.78		

Table 1.9: Physicochemical analysis of the KIT-FP-phenolic extract Chimar4

TAN	61.9007 mgKOH/g
Density (15°C)	1.1052 g/mL
Water	2.618 %
Viscosity (50°C)	27.5805 cSt
Elemental analysis	C: 66.00 % H: 5.97 % O: 28.03 %
Calorific Value	29.708 MJ/kg

1.1.2.5 Development of separation schemes for the extraction of the phenolic fraction from CPoil

CPoil has higher initial phenolics concentration, depending on the catalyst used, as was demonstrated in WP2 of this project. A CPoil sample, enriched in phenolics, was delivered to CHIMAR in order to be used for resins synthesis. This sample name CPoil-chimar 1 had phenolics concentration 14.5 %wt as determined by GCxGC-ToFMS analysis. The complete analysis of this sample is presented in Table 1.10.

Table 1.10: Analysis of CPoil-chimar 1

Compound	%wt	Group	Total wt
1. p-Xylene	2.99	AR	12.69
2. 1,2-Benzenediol	2.18	ALI	2.38
3. 2-Cyclopenten-1-one	2.06	PH	14.56
4. Phenol	1.84	FUR	3.18
5. Phenol, 3-methyl-	1.64	EST	0.24
6. Phenol, 2,5-dimethyl-	1.12	AL	0.14
7. Toluene	1.10	ETH	0.16
8. Benzene, 1,2,3-trimethyl-	1.03	ALD	3.97
9. Benzofuran, 2-methyl-	1.03	KET	8.62
10. Phenol, 3-methyl-	1.00	PAH	2.27
Total $_{\text{Top 10 compounds}}$ (%wt)	15.98		
Total (%wt)	48.24		

CPoil presents higher solubility, compared to FPoil, in most of the organic solvents rendering its fractionation challenging. Therefore, several extraction schemes have been attempted and those that presented the best results were the following:

- Scheme 1: CPoil + $NaHSO_3$ 0.6M. Resulted in 2 phenolic rich extracts, extract 1 with 29.6 %wt phenolics at 0.8 % yield and extract 3 with 30.4%wt phenolics at 17.2% yield
- Scheme 2: CPoil + H_2O pH13: Extract 1 with 58.93 %wt phenolics and 6.8 % yield
- Scheme 3: CPoil + petroleum ether: Resulted in 2 phenolic rich extracts, extract 1 with 16.0 %wt phenolics at 30.9 % yield and extract 2 with 30.5 %wt phenolics at 3.1 % yield
- Scheme 4: CPoil + cyclohexane extract 1 with 17.0 %wt phenolics at 30.0 % yield
- Scheme 3: CPoil + acetonitrile + hexane: Extract 2 with 14.07%wt phenolics and 20.09% yield

These extraction schemes are presented in detail in D3.1. Considering that the initial CPoil had 15.4 %wt phenolics concentration, the only extraction scheme that managed substantial preconcentration of the phenolic fraction was scheme 2 with alkaline H_2O. This option was pursued further using the aqueous phase of the catalytic bio-oil instead of H_2O. Another approach investigated was the use of a refining stream for extracting the non- and less polar components of CPoil. The results are presented below.

1.1.2.6 Development of optimized extraction of phenolics from CPoil

A CPoil, named C-CPoil, produced in CPERI from a woody biomass was used for the development of the extraction schemes. Its GCxGC-ToFMS quantitative chromatographic analysis is presented Table 1.11.

Table 1.11: GCxGC-ToFMS quantification sample C-CPoil

Compound	%wt	Group	Total wt
1. p-Xylene	3.44	AR	12.96
2. Phenol, 3-methyl-	2.79	ALI	1.01
3. Phenol	2.74	PH	15.44
4. Naphthalene, 2-methyl-	1.83	FUR	2.56
5. 1,2-Benzenediol	1.75	EST	0.18
6. Phenol, 2,5-dimethyl-	1.56	AL	0.16
7. Phenol, 3-methyl-	1.37	ETH	0.14
8. Benzofuran, 2-methyl-	1.29	ALD	1.83
9. 2-Cyclopenten-1-one	1.26	KET	4.58
10. Toluene	1.03	PAH	3.76
Total $_{\text{Top 10 compounds}}$ (%wt)	19.09		
Total (% wt)	42.63		

As presented in D3.1, the optimum method for extracting phenolics from the C-CPoil involved the use of alkaline H_2O which resulted in an extract of 58.9 %wt phenolic concentration, but with a low phenolic-based recovery of 25.8 %. Despite the low recovery, this method was considered further due to the possibility of using the aqueous fraction produced along with the CPoil as an extraction media. Therefore, the aqueous phase of the C- CPoil was used, which had phenolics content of 1.03 wt.%, H_2O 79.7 %wt and pH2.3. This aqueous phase was extracted with ethyl acetate or 50 % Ethyl acetate + 50 % C_6H_{12} without affecting the pH, and was also extracted with ethyl acetate after changing the pH to 5. The change in the pH and the subsequent extraction with 100 % ethyl acetate facilitated the removal of the less polar organic compounds from the aqueous phase, including the phenolic components. This 'purified' aqueous phase was brought to pH13 and was used for the extraction of the phenolic fraction of C-CPoil, with similar results as those obtained when using H_2O.

Another approach for obtaining a phenolic rich fraction from the C-CPoil, involved the removal of the non-polar compounds with a stream encountered in refineries, such as naphtha. Three different samples of naphtha with varying aromatics content were mixed with the C-CPoil. The results are presented in Table 1.12

Table 1.12: Analysis results of the extraction of C-CPoil with naphtha

% aromatics in naphtha	**CP-oil extracted (%wt)**	**Naphtha extract**		
		TAN (mg KOH/g)	H_2O (%wt)	Phenolics content (%)
0	32.2	0.25	0.015	0.98
10	44.1	0.48	0.027	1.53
21	48.9	0.01	0.060	1.59

It was concluded that the naphtha with the highest aromatic content was able to retrieve 48.9 % of the CPoil. The remaining CPoil was subjected to GCxGC-ToFMS analysis and the results are presented in Table 1.13.

Table 1.13: Distribution of quantified compounds per group in the C-CPoil extract

Group	CPoil after naphtha extraction (%wt)	CPoil before extraction (%wt)
AR	5.57	12.96
PH	21.93	15.44
FUR	0.76	2.56
ALD	1.55	1.83
KET	4.46	4.58
PAH	0.37	3.76

Naphtha was able to retrieve the less polar compounds from the CPoil, along with the majority of the aromatic hydrocarbons leading to an enrichment of the remaining CPoil in phenolics. In fact the phenolic content, as determined quantitatively by GCxGC-ToFMS, increased from 15.44 wt.% to 21.93 wt.%. This sample can be used as is for the synthesis of resins, or could be submitted to further processing for the purification of the phenolics. Such a sample has been delivered to CHIMAR for resins testing

1.1.3 Conclusions

Bio-oil, either thermal or catalytic, is complex mixture of compounds whose extraction requires the use of large solvent volumes and multistep-procedures. However, in order to use bio-oils as a source of chemicals the development of a simple extraction procedure is required. In this context, CPERI has developed two simple schemes for the extraction of the phenolic fraction of FPoils. The 1st scheme consists of 4 steps and requires the use of solvents such as acetone, ethyl acetate, cyclohexane and H_2O at pH 3. The result is a phenolic extract with 15.8 %wt concentration in phenolics (quantified by GCxGC-ToFMS). During the development of this scheme it was found that a solvent mixture consisting of 50 % Ethyl acetate and 50 % cyclohexane presents selectivity for the extraction of phenolics, therefore as 2nd scheme it is proposed to extract the FP oil directly with this mixture. From this one-step scheme results an extract with 13.1 to 18.6 %wt concentration in phenolics, depending on the initial phenolic content of the bio-oil. Based on the results obtained and the methods described it is concluded that the extraction of a phenolic fraction from FPoil, is possible and can be achieved in a few steps and by using benign solvents that can be recycled.

Regarding CPoils, they have a higher initial phenolics concentration but their solubility in most organic solvents poses a problem for their extraction. Therefore it is proposed to use a refinery stream in order to extract the less polar components and use the residue as a phenolics concentrate. For this reason, when naphtha containing 20 % aromatics was used as an extraction solvent almost 49 %wt of the CPoil was diluted in naphtha leaving behind a CPoil residue with 21.9 %wt phenolics concentration. This extract can either be further purified or can be used directly for resins synthesis.

1.2 Extraction of pyrolysis oil: phenol and organic acids – an industrial approach

Phenol is an important raw material for the chemical industry. The worldwide production capacity exceeds 11.000 kt/a (Funada & Greiner, 2011) of which 8 % is used for the production of caprolactam. DSM is one of the world leaders in caprolactam production whereby phenol is a starting material for this product. The interest in renewable starting materials for caprolactam is DSM's prime objective to participate in BioBoost.

The relevance of phenol as feedstock for the chemical industry and the potential impact a biobased phenol are further discussed in Del.3.1. In the same report the economy of scale factors for a bulk chemical production are mentioned. The choice of CPoil as starting material for an economic extraction is also explained.

In the previous report several process schemes were introduced. Figures 1.5 and 1.6 show the two most relevant once. In the process to isolate phenol from catalytic bio-oils an extraction step to remove small organic acids is necessary otherwise a selective phenol extraction with water or aqueous base is not possible. This is achieved in the first extraction column (acid extraction). Here the bio-oil is mixed with a low viscosity diluent to ensure processability. If this measure is not taken the bio-oil viscosity increases such that a processing is very difficult. As diluents light hydrocarbons and crude oils in concentrations between 2 % and 4 % were successful. At higher concentrations an additional organic layer separates from the bio-oil. Due to the nature of the diluent it does not have to be recovered from the bio-oil since it has a fuel value by itself. It is envisioned to dilute the starting material with upgraded bio-oil from the hydroprocessing unit whereby the fuel would be completely renewable.
The acid lean bio-oil can now undergo a number of further processing steps. In ***Figure 1*** phenol is directly recovered by a hot water extraction. The phenol lean bio-oil is transferred to a refinery for upgrading to fuels.

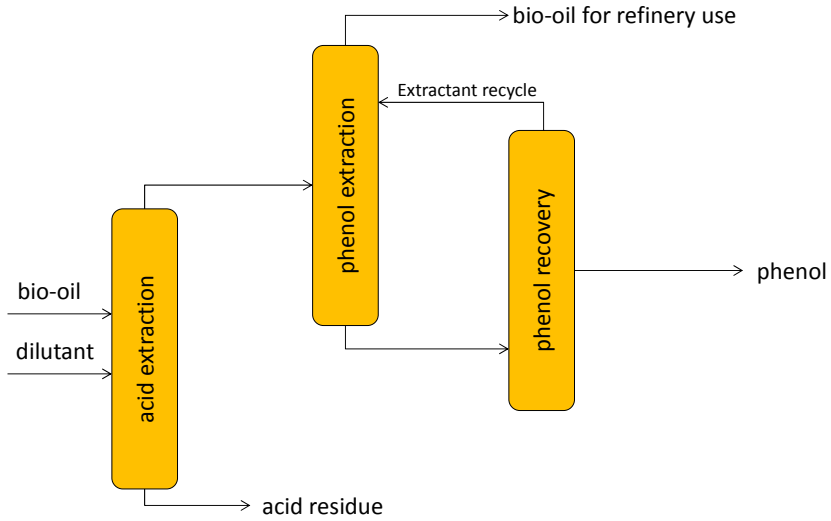


Figure 1.5: Process scheme for the isolation of phenol

In Fig. 1.5 a different route is chosen. Here the acid lean bio-oil is hydro-treated to remove aldehydes and ketons as well as residual organic acids of high molecular weight from the mixture. They are transformed into hydrocarbons. The removal of the phenolic OH requires the harshest temperature and pressure in such a process. If the

process conditions are chosen cleverly, all OH-groups will be removed except for the phenols. This gives the opportunity to have an efficient extraction of phenols via either an alkaline medium or water. Fig. 1.6 shows a process where next to the hydrotreatment also an alkaline extraction is suggested. This requires a different further processing to yield a phenol derivative rather than phenol as product.

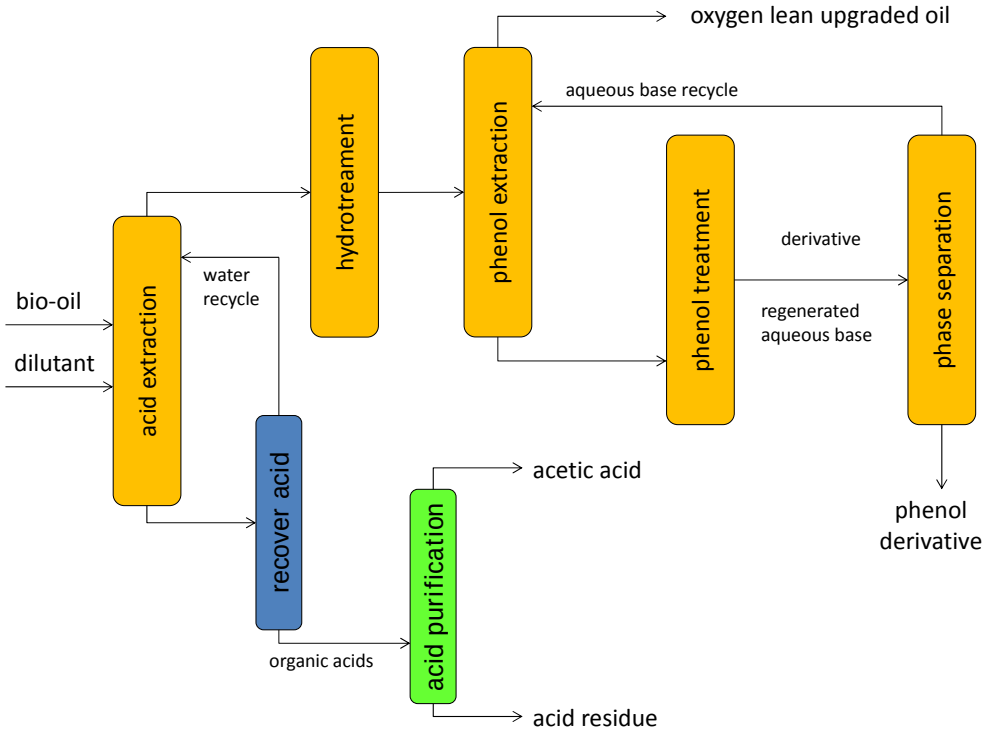


Figure 1.6: Process scheme integrating hydro-treatment and phenol extraction from biooil

The two schemes shown here are two extremes in the process design. The economic impact of several permutations of these processes will be further evaluated in WP5.

This report will now discuss experiments that were performed as a proof of principle for each of the critical steps shown in the schemes above.

1.2.1 Characterization of biooils

The factor determining the feasibility of the phenol recovery process from bio-oil is its concentration. Table 1.14 presents the concentrations of phenol and acetic acid in the bio-oil samples, obtained using different catalyst or process conditions. The other phenolic components may also be interesting for recovery yet an additional step would be required to convert them to phenol. Acetic acid is measured as the main unwanted impurity in biooil, together with other carboxylic acids present in smaller quantities. From the presented composition, we concluded that CP oil is a better source of phenols than FP oil. The fast pyrolysis is optimized to maximize the yield of transportation fuel components rather than chemicals, whereas the catalytic pyrolysis can more easily be tuned for increased concentration of chemicals through the choice of a catalyst.

Table 1.14: Concentration of relevant components in the pyrolysis oils

Type of oil	Sample	Concentration, wt.%		
		phenol	Cresol	acetic acid
Catalytic pyrolysis oil	CP1	2.8	1.5	4.0
	CP2	1.8	n.a.	8.5
	CP3	3.0	n.a.	5.5
Fast pyrolysis oil	FP1	0.49	n.a.	7.1
	FP2	0.46	n.a.	6.4

In large scale processing, it is important to know the biooil's physical characteristics, such as density and viscosity which determine the ease of operation and pose certain constrains. As can be seen from Table 1.15, biooil is rather viscous and thus difficult to process. Different CP bio-oils have different viscosities, but all are in the same range (200-300 mPas). As a comparison, the viscosity of a typical Middle East crude oil at 20 °C ranges from 0.1 to 77 mPas (Hemmati-Sarapardeh, 2014), depending on composition. Additionally, the extraction of chemicals caused a further increase in viscosity. The remaining non-aqueous biooil (raffinate) turned into a sticky solid making further processing almost impossible and is undesired for an industrial extraction process. CPoil was more processable than FPoil due to its lower viscosity. FP bio-oil proved to be extremely viscous and at lower temperatures viscosity measurements were impossible.

However, the characteristic of viscosity is that it exponentially decreases with the temperature increase. Thus the viscosities of the CPoils also decrease to processable values already at 40 °C. This is important to take into account for the overall process design and its heat integration. However, exposing bio-oil to temperatures higher than 40 °C is less desirable as at higher temperatures the risk of oil degradation, due to for instance polymerization of smaller molecules, is increased. The viscosity of FPoil at 60 °C is still rather high.

Table 1.15: Densities and viscosities of the various pyrolysis oils before and after extraction with water

Sample	Temperature (°C)	Before extraction		After extraction	
		Density (g/cm^3)	Viscosity (mPas)	Density (g/cm^3)	Viscosity (mPas)
CP1	20	1.122	294	1.125	743
	40	1.105	56.4	1.109	108
	60	1.090	19.0	1.092	28.7
CP2	20	1.155	326	1.137	624
	40	1.138	65.7	1.121	92
	60	1.121	21.1	n.a.	n.a
CP3	20	1.135	217.5	n.a.	n.a.
	40	1.119	42.1	n.a.	n.a.
	60	1.102	14.7	n.a.	n.a.
FP1	40	not measurable		n.a.	n.a.
	60	1.155	240-245	n.a.	n.a.

1.2.2 Extraction of phenol and acetic acid

Biooil used in this work is a viscous and difficult to process liquid. It tends to adhere to the glass wall of the experimental vessel resulting in difficult mixing and phase separation. It was therefore very difficult to perform a reproducible experiment (Table 1.16). Nevertheless, the mass balance check between measured and calculated values shows deviations up to a maximum of 5.8 %, which we considered acceptable for the preliminary experiments. However, the quantification of acetic acid is not so accurate and the results should be taken only as indications rather than absolute values.

Two groups of experiments were performed to assess the aqueous extraction step. In the initial experiments, performed with small quantities of feed, only phenol was quantified (Table 1.16), whereas in subsequent experiments, with somewhat larger amounts of feed (to improve the reproducibility), also cresol and acetic acid were quantified (Table 1.17). The distribution ratio is defined as the concentration of the solute in the aqueous phase over its concentration in the organic phase. The obtained distribution ratios of phenol are in agreement in both sets of experiments. The low value of distribution ratio is in this case very desirable as it minimizes the losses of phenol in this step. As expected, losses are higher for higher W/O ratios. Cresol, due to the presence of a methyl group, exhibits even lower distribution towards aqueous phase, and subsequently lower losses. The obtained results are similar to those reported by Vitasari et al.[1] for guaiacol and syringol, although phenol exhibits somewhat lower distribution ratios and yields. Compared with the results reported by Fele-Žilnik and Jazbinšek[2], we obtained consistently lower values for the distribution ratios of phenol. For instance, at a W/O ratio of 0.8 they report distribution ratio of about 0.2, whereas we obtained values of about 0.07 to 0.09. In their case, however, there was no difference between phenol and guaiacol and syringol. With the decrease of W/O ratio, Fele-Žilnik and Jazbinšek2 observe the increase in distribution ratio of phenol towards water. Since the variation in our results falls within the error of the analytical method we cannot confirm this trend. It is likely that the differences between literature values as well as our own, stem from the different origin, and thus composition, of the bio-oil feedstock1.

Table 1.16: Extraction of phenol from CP1 biooil

Exp No	W/O ratio	Phenol mass			Loss	Mass balance check	Phenol concentration		Distribu-tion ratio
		initial	extracted	in raffinate			in extract	in raffi-nate	
		µg	µg	µg	%	%	wt.%	wt.%	wt.%/ wt.%
1	0.83	12.8	0.86	12.6	6.7	5.5	0.17	1.98	0.087
2	0.83	12.8	0.73	12.2	5.7	1.4	0.15	2.00	0.073
3	0.82	12.8	0.69	12.7	5.4	5.4	0.14	1.97	0.070

Acetic acid being the most polar component, as expected, distributes preferentially to the aqueous phase. In this case, the loss is desirable, as removal of acids reduces the complexity of bio-oil, enabling the efficient subsequent recovery of phenols. The distribution ratios calculated from our experiments are not very accurate, though the values obtained are rather similar to those obtained by Vitasari et al.1. They report distributions in the range of 2 to 2.7, whereas our values are in the range of 2.2 to 3.9.

[1] Vitasari, C., Meindersma, G.W. and Haan, A.B de., 2011, Biores. Techn., Vol. 102, pp. 7204-7210.
[2] Fele-Žilnik, Lj. and Jazbinšek, A., 2012, Sep. Pur. Techn., Vol. 86, pp. 157-170.

Similarly to phenols, they also observe different values of acetic acid distribution ratios for biooils of different origin.

Table 1.17: Extraction of phenol, cresol and acetic acid from CP1 bio-oil

Exp No	Compo-nent	W/O ratio	Mass initial	Mass extracted	Mass in raffi-nate	Loss	Mass balance check	Concentration in ex-tract	Concentration in raffi-nate	Distrib ution ratio
			mg	mg	mg	%	%	wt.%	wt.%	wt.%/ wt.%
1	Phenol	0.49	68.0	2.5	67.2	3.7	2.6	0.23	2.57	0.089
	Cresol		36.7	0.5	36.1	1.3	0.4	0.04	1.38	0.031
	Acetic acid		98.1	51.7	56.6	52.7	10	4.65	2.16	2.2
2	Phenol	0.47	69.5	2.8	67.2	4.1	0.8	0.23	2.57	0.089
	Cresol		37.6	0.5	36.1	1.4	2.5	0.04	1.38	0.029
	Acetic acid		100.3	54.0	56.6	53.8	10	4.47	1.33	3.4
3	Phenol	1.0	280.8	24.1	273.0	8.5	5.8	0.23	2.76	0.083
	Cresol		151.7	5.3	149.6	3.5	2.1	0.05	1.51	0.033
	Acetic acid		405.02	356.3	85.4	88.0	9.1	3.40	0.86	3.9

1.2.3 Phenol extraction

The biooil raffinate of the acid extraction column is further processed in order to recover phenol. Three different aqueous basic solutions were tested for their ability to extract phenol: sodium hydroxide, sodium bicarbonate and triethylamine (TEA).

The biooil raffinate obtained from the previous step was contacted with the equal amount of aqueous phase and equilibrated at 20 °C. Afterwards, samples of each phase were taken and analyzed. However, quantification of the aqueous phase was not straightforward as the extracted solutes for a complex (salt) with the base that is present in the aqueous phase. It is, therefore, decided to estimate the concentrations of phenol and acetic acid based on the mass balance. The mass balance was checked in the experiment with pure water as extractant and it was observed that the deviations are in line with our previous experiments (up to 2 % for phenol and up to 10 % for acetic acid).

The experimental results are presented in Table 1.18. The distribution ratio is defined as the concentration of the solute in the aqueous phase over its concentration in the organic phase. The distribution ratio measured with pure water as a solvent was somewhat lower than in our previous experiments. At this moment it is not clear why. It is possible that the changed composition of the starting biooil solution has significant influence on the distribution of phenol.

With all of the tested solvent systems the distribution ratio of phenol is rather low. However, the concentration of acetic acid in our starting solution was still rather high (0.5 wt.%) and it is also found in literature[3] that the presence of acids can influence the distribution of phenol. Our future experiments will focus on evaluating the

[3] Korenman, Y.I., Bortnikova, R.N. (1978) Russian Journal of Physical Chemistry, 52 (9) : 1341-1343

magnitude of this influence. Nevertheless, this stresses out the necessity to completely remove acids from the bio-oil prior to phenol extraction in order to design an economically feasible process.

Comparing different basis, even though the obtained values differ very little, it can be observed that the distribution ratios of phenol are higher when TEA is used. The highest capacity for the acetic acid is observed with NaOH.

Table 1.18: Extraction of phenol and acetic acid from biooil raffinate

Exp. No.	Solvent	Distribution ratio (wt.%/wt.%)			
		without hydrotreatment		with hydrotreatment	
		phenol	acetic acid	phenol	acetic acid
1	water	0.051	4.1	0.133	3.6
2	water + 0.5 % NaOH	0.082	15.5	0.095	20.5
3	water + 1 % NaOH	0.077	20.1	0.140	23.0
4	water + 2 % NaOH	0.100	8.2*	0.448	18.9
5	water + 1 % $NaCO_3$/$NaHCO_3$	0.168	1.5	-	-
6	water + 2 % $NaCO_3$/$NaHCO_3$	0.107	1.4	-	-
7	water + 3 % $NaCO_3$/$NaHCO_3$	0.096	1.1	-	-
8	water + 1 % TEA	0.168	3.2	-	-
9	water + 2 % TEA	0.161	2.7	-	-
10	water + 3 % TEA	0.173	3.3	-	-

* possible outlier

Table 1.19: Extraction of phenol and acetic acid from biooil raffinate

Exp. No.	Solvent	Distribution ratio (wt.%/wt.%)	
		Phenol	acetic acid
1	water	0.051	4.1
2	water + 0.5 % NaOH	0.082	15.5
3	water + 1 % NaOH	0.077	20.1
4	water + 2 % NaOH	0.100	8.2*
5	water + 1 % $NaCO_3$/$NaHCO_3$	0.168	1.5
6	water + 2 % $NaCO_3$/$NaHCO_3$	0.107	1.4
7	water + 3 % $NaCO_3$/$NaHCO_3$	0.096	1.1
8	water + 1 % TEA	0.168	3.2
9	water + 2 % TEA	0.161	2.7
10	water + 3 % TEA	0.173	3.3

* possible outlier

1.2.4 Acid recovery

As shown previously, the aqueous extract from the acid extraction column contains organic acids such as acetic acid and propionic acid, but also some small amount of phenol. In order to assess possibilities for further processing of this stream we performed exploratory experiments testing three different solvents for their ability to extract acetic acid. The tested solvents were 2-methyltetrahydrofuran (MTHF), nonylphenol and trioctylamine (TOA).

The aqueous extract obtained from the previous step was contacted with the equal amount of solvent and equilibrated at 20 °C. Then samples of each phase were taken and analyzed. However, for experiments with TOA, only the aqueous phase resulted in reliable analysis, as in the TOA phase solutes react with the solvent forming a complex which is then not straightforward to quantify. Therefore, the concentrations of solutes in the organic (TOA) phase were assumed from the mass balance.

The experimental results are presented in Table 1.20. The distribution ratio is here defined as the concentration of the solute in the organic phase over its concentration in the aqueous phase. It is obvious that the obtained experimental results should be treated with caution as the mass balance deviation appeared to be rather large. Nevertheless it can qualitatively be observed that none of the tested solvents is selective towards the acetic acid, but rather towards phenol. It is possible to envisage some modification of the proposed process in which first phenol is selectively extracted from the aqueous extract and then only the raffinate of that extraction process is further treated to recover acetic acid. However, one has to consider that the overall concentration of phenol in the aqueous extract is 10 times lower than that of acetic acid, thus another alternative would be to extract both acid and phenol and then separate them from the organic solvent (for example based on differences in boiling points).

Table 1.20: Extraction of phenol and acetic acid from aqueous extract

Exp. No.	Solvent	Component	Mass balance check %	Distribution ratio wt.%/ wt.%
1	2-methyl-tetra-hydrofuran (MTHF)	Phenol Acetic acid	1.2 5.0	6.7 1.8
2	nonylphenol	Phenol Acetic acid	7.6 1.8	5.5 0.25
3	trioctylamine (TOA)	Phenol Acetic acid	- -	3.1 1.4

1.2.5 Phenol treatment

One of the possibilities to isolate phenol is in the form of either cyclohexanone, cyclohexanol or a mixture thereof. In the industry this mixture is known as KA oil an intermediate used in the production of caprolactam and adipic acid both nylon intermediates.

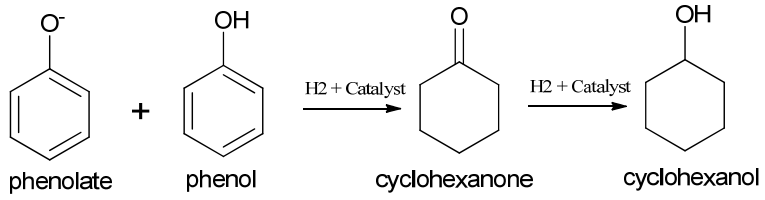


Figure 1.7: Reaction scheme from phenol or a phenolate to cyclohexanol and cyclohexanone

The challenge is to perform the hydrogenation under aqueous and alkaline conditions with high concentrations of phenol present in the feed. A first set of experiments was conducted to determine the influence of the phenol concentration in the feed (see Table 1.21). As Pd/C catalyst with a 10 % metal loading was chosen. The reaction temperature was 100 °C and the hydrogen pressure 50 bar. From these reactions we can conclude that a reaction is possible with high phenol concentration of up to 10 % in the water phase (Fig. 1.8).

Table 1.21: Hydrogenation of phenol in aqueous phase, different phenol concentrations

Exp. Nr	reaction conditions		masses			ratio of products (mole/mole)			
	Time	phenol	water	phenol	dry catalyst 10% Pd/C	anol	anone	phenol	conversion of phenol
	h	% (m/m)	g	g	mg				
005923-3	1	1.27%	150.60	1.89	35.168	31.0%	4.3%	64.7%	35.3%
005923-6	3.5	9.94%	135.00	14.93	130.6	52.1%	26.5%	21.5%	78.5%
005923-21	4	5.22%	141.24	7.79	119.7	65.7%	5.9%	28.3%	71.7%

It could be shown that the speed of the reaction increases by the use of a NaOH as base which can also be used in the extraction of phenol from a hydro-treated biooil. A Ni catalyst was also successfully tested under similar reaction conditions.

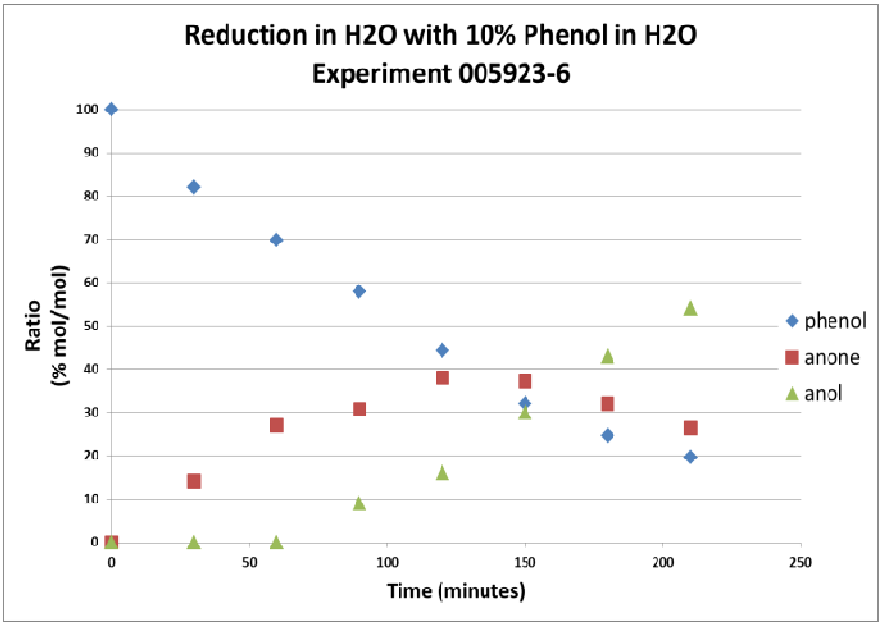


Figure 1.8: Reaction profile of the hydrogenation of phenol in aqueous phase (for conditions see Table 1.21 entry 005923-6).

The choice for conducting a hydrogenation of phenol as further processing was taken since the reaction products are neither soluble in water nor in an aqueous alkaline solution. Thus a product separation is possible without costly removal of the extraction solvent (water) via distillation. Fig. 1.9 illustrates the spontaneous phase separation nicely.

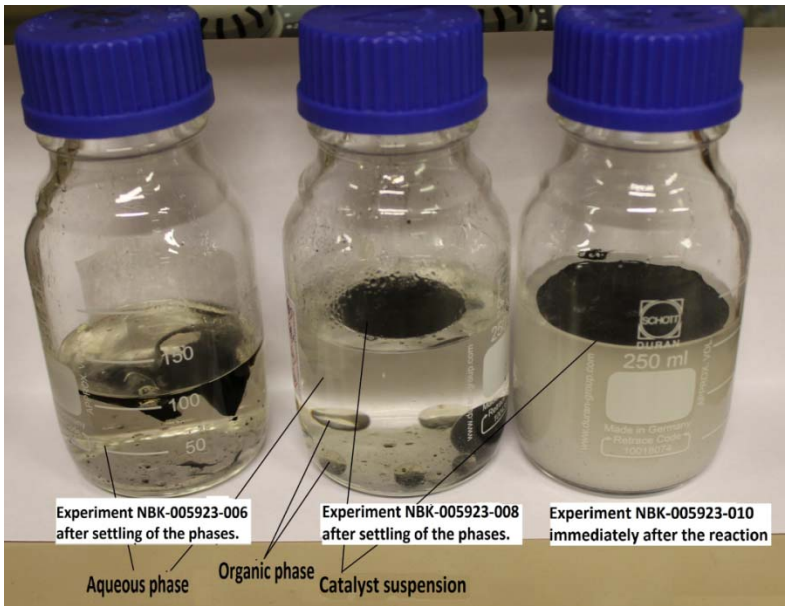


Figure 1.9: Spontaneous phase separation of organic layers after hydrogenation of phenol

2 Recovery of furanoics and organic acids from HTC process water and from FP aqueous condensates

2.1 Introduction

Hydroxymethylfurfural (HMF) and its consecutive product, the furanic dicarboxylic acid, are indicated as very interesting platform chemical and basis for the production of polymers from biomass. Some examples for consecutive products are shown in Fig. 2.1. A special focus is on the formation of the dicarboxylic acid, because this compound is able to substitute terephthalic acid in polyesters. Another interesting application is the substitution of formaldehyde in phenolic resins. On the other hand also HMF itself is an interesting product as a monomer. With the taste of caramel is may give aroma to food. Other applications are seen in the pharmaceutical sector.

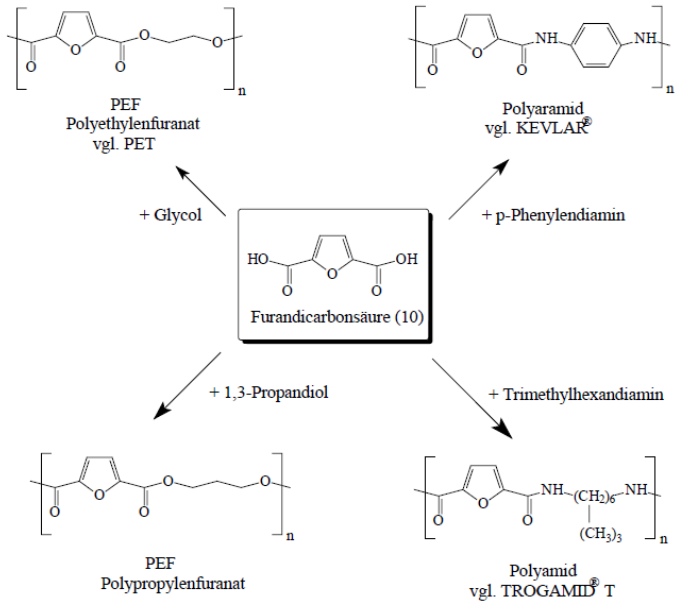


Figure 2.12: Polymers from furfuranic acid

The basic idea within BioBoost was to use the residual process water from the HTC process to recover HMF. Biomass consists mainly of carbohydrates. In the case of wood or grass/straw the main components are hemicellulose, cellulose, and lignin. By hydrothermal treatment, all types of carbohydrates are hydrolyzed to sugars especially in the presence of acids or bases. In the case of cellulose or starch the product of complete hydrolysis is glucose (Fig. 2.2). In case of hemicellulose also other sugars like pentoses are formed. Glucose partly converts to fructose, catalyzed by Lewis acids. At rather low temperatures water elimination from fructose to HMF occurs. On the other side glucose and fructose can split to smaller compounds as shown in Fig. 2.2Figure. The water elimination from glucose to levoglucosan/anhydro-glucose is shown at the left hand side of the figure, and is usually of minor importance at hydrothermal conditions compared to dry pyrolysis. In water as reaction medium, more than one water molecule is eliminated and HMF is formed.

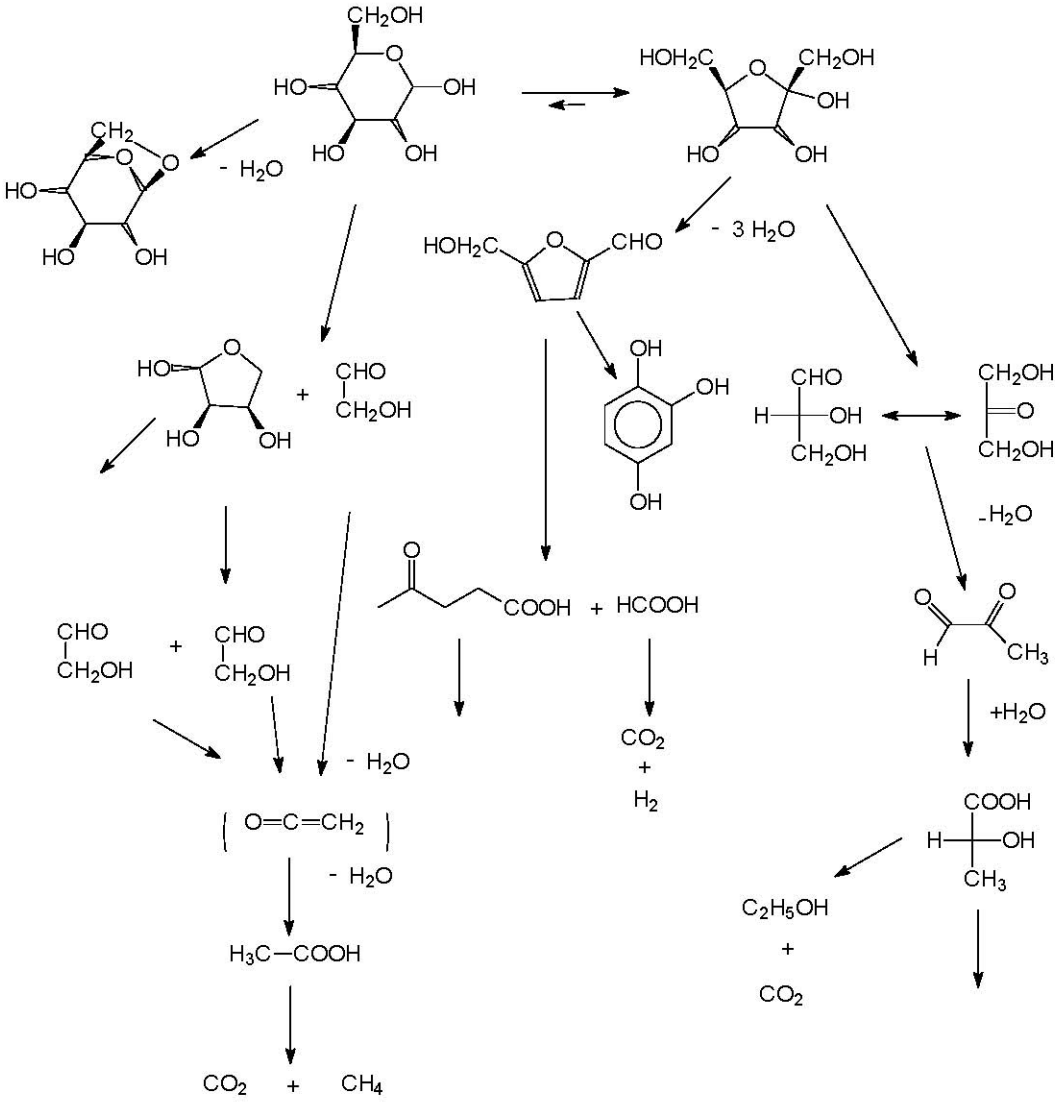


Figure 2.2: Reaction pathways of carbohydrates in water [12]

In addition to the degradation reactions HMF may polymerize to form solid products that are called “humines” or “HTC coal” depending on the composition and process conditions applied.

2.2 HMF in Process Water

The challenge to recover furfurals as the main target molecules is that the content of these products in HTC process water delivered by AVA-CO2, usually is low. Furfurals are the chemical precursors of HTC coal and, consequently in an optimized process to maximize the HTC coal yield, the furfurals yield is low. This has been investigated in more detail to identify potential optimum conditions for HTC and HMF production. For this purpose, a lab-scale plant was built up by KIT in which biomass has been hydrothermally reacted. Intermediates formed were extracted in a continuous flow of water. With this method, the time dependence of the formation and degradation can be determined. An example is shown in Fig. 2.3. Here, the intermediate character of the furfurals, namely furfural and HMF, is obvious.

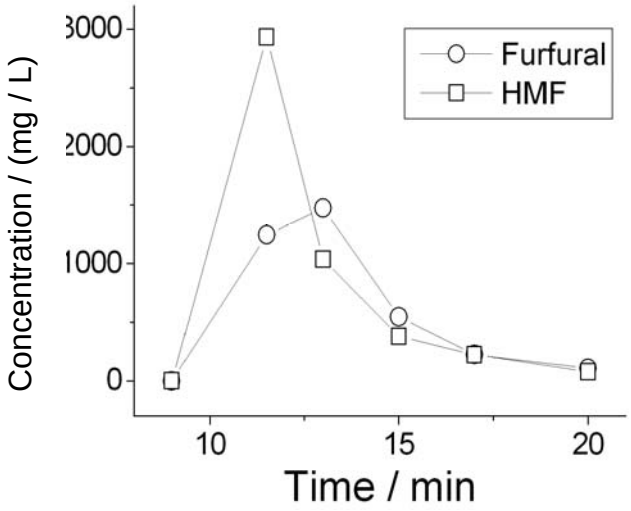


Figure 2.3: Concentration of HMF and furfural formed from wood at 200 °C with pure water and water with citric acid as function of time (semi-batch, 3 mL/ min flow)

If furfurals are the desired products, the HTC process as such has to be modified. In view of the high selling price of HMF and its important position as platform chemical in the bio-economy it is interesting to design a process for HMF production from biomass. In this case, the furfurals have to be isolated as intermediates. In order to develop such a process extraction and adsorption methods have been investigated.

2.3 Extraction process

For separation of HMF and furfural the extraction with an organic solvent is a suitable technique. For the choice of the solvent, the following criteria are important:

- The solvent should have a low boiling point, because it has to be separated from the furfurals by distillation.
- The partition coefficient should be high for the furfurals to be recovered.
- The partition coefficient should be low for undesired compounds.
- The solubility of the solvent in water should be low.
- The mixture of solvent and water should easily separate. In particular, no emulsion should be formed.

2.3.1 Screening Experiments

Different solvents tested in lab-scale experiments in KIT as shown in Fig. 2.4. Among others, toluene, diethyl ether, methyl-iso-butylketone (MIBK), ethyl acetate, and solvent mixtures e. g. of diethyl ether/ petrol ether have been used. The experiments were conducted at room temperature with an HMF concentration of 1 g/L and water-solvent ratio of 1:1, 1:2, or 1:3. The HMF concentration was measured before and after extraction by HPLC (HPLC by Merck, RP 18 column by Phenomenex, 90 vol.% H_2O + 10 vol.% acetonitrile as eluent, 20 °C, 1.4 ml/min, UV detection at 290 nm).

Figure 2.4: Phase separation during screening

Examples of the partition coefficients measured for HMF with diethyl ether, MIBK and the solvent mixture of diethyl ether/ petrol ether as organic solvent and water in a liquid-liquid extraction are shown in Fig. 2.5. Here, also the influence of the pH-value was investigated. In these experiments, the ketone was the best performing solvent in all cases.

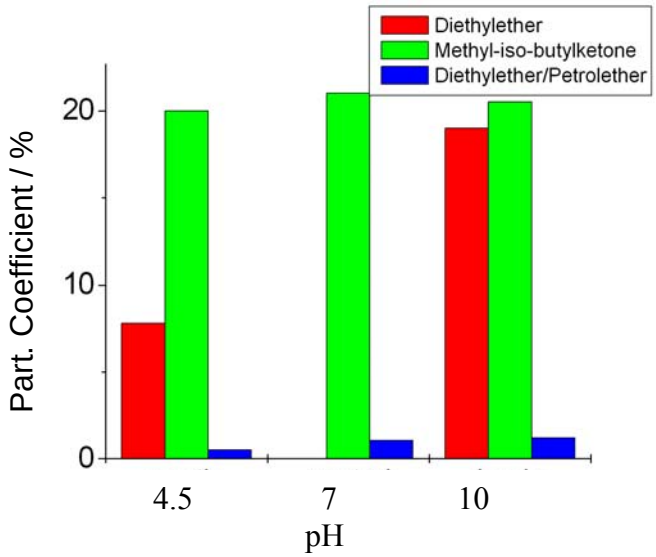


Figure 2.5: Partition coefficient (molar) of HMF from aqueous solution at pH-values of 4.5, 7 and 10 with three solvents diethylether, MIBK, and a mixture of diethylether/petrolether (ratio water:solvent = 1:1)

2.3.2 Calculations and continuous extraction

In addition to the above described studies the influence of salts and other by-products present in the water was tested. The experimentally found data have been compared to calculated data of phase behaviour, gained from using ASPEN PLUS (Fig. 2.6). MIBK is a very good extraction medium for HMF, but is has a rather high boiling point of 117 °C. This is problematic, because at the high temperatures same of the HMF most likely will be decomposed. Therefore, also chloroform as extracting agent

was tested experimentally and calculated in regard to its phase diagram. Chloroform has a boiling point of 62 °C and is also a good solvent to remove HMF as shown in Fig. 2.6. Calculations of the phase diagram predict that the two phase region of chloroform+water is larger than that with MIBK. This means that the mutual solubility of solvents is lower along with potential contamination or losses of solute.

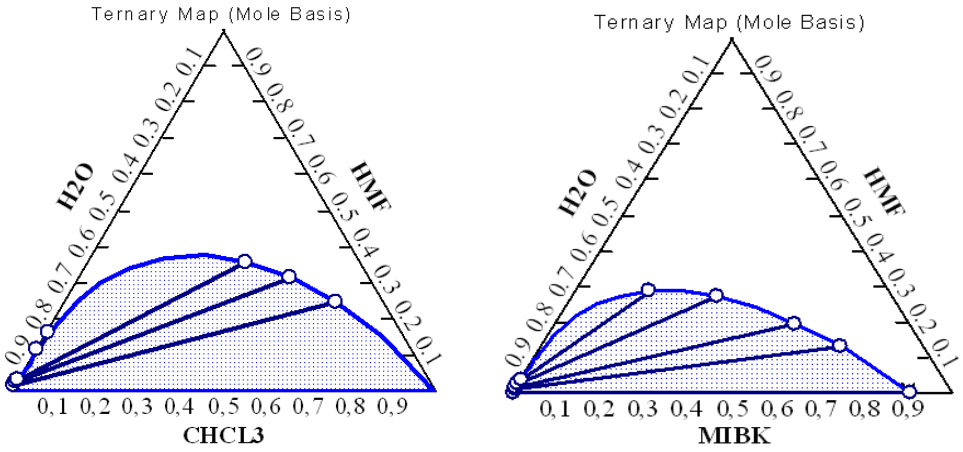


Figure 2.6: Calculated ternary phase diagram of water, HMF and an organic solvent, here chloroform (left side) or MIBK (right side)

Another important aspect is how good compounds, which are not desired for recovery, are extracted. As an example, acetic acid extraction was investigated (Fig. 2.7). In this case chloroform turned out to be the better choice, because the two-phase region is larger, and less acetic acid will be extracted with the HMF.

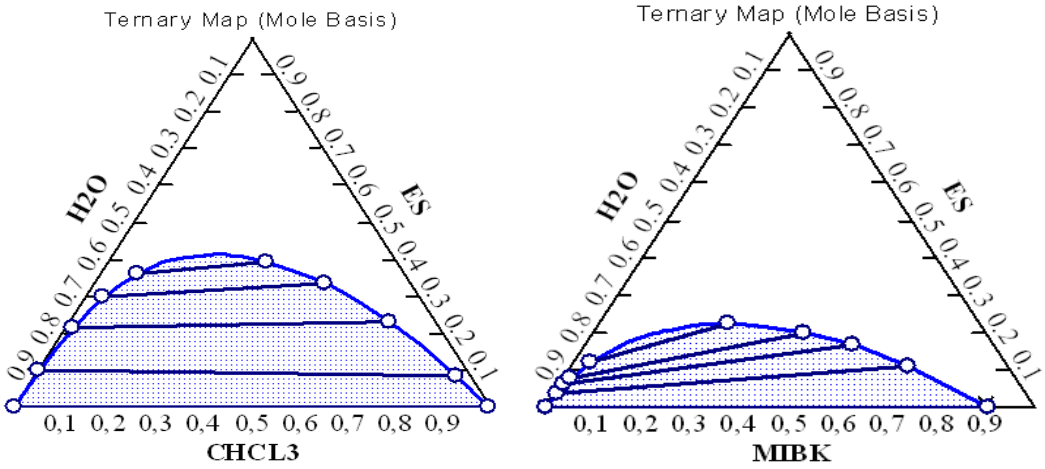


Figure 2.7: Calculated ternary phase diagram of water, acetic acid ("ES") and an organic solvent, here chloroform (left) or MIBK (right)

From these calculations of equilibrium data the number of necessary theoretical plates for a cross-flow continuous distillation is available. Fig. 2.8 for MIBK and Figure 2.9 for chloroform show, that around 8 theoretical plates are enough to extract HMF. At this point the acetic acid content is still low, especially for chloroform.

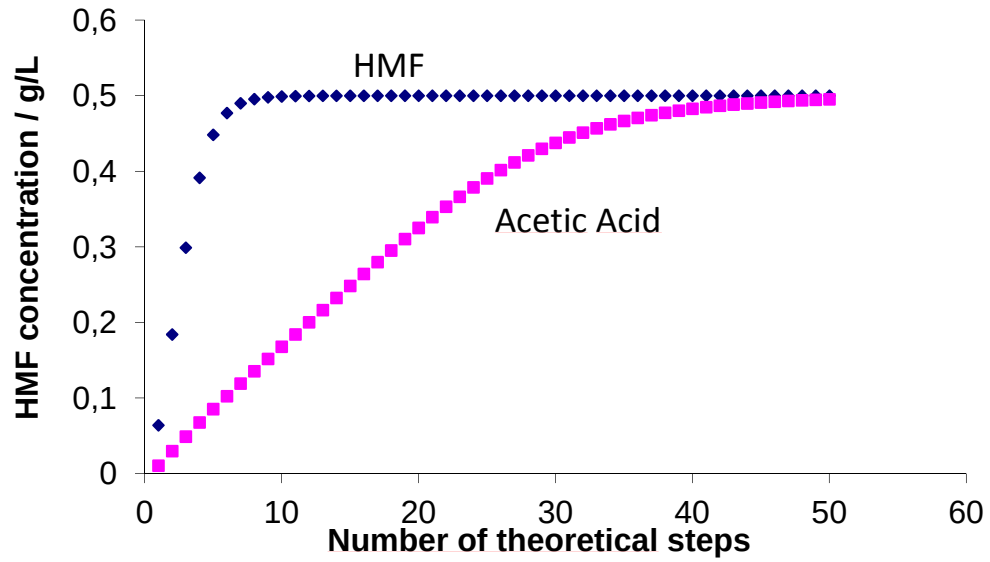


Figure 2.8: Content of HMF and acetic acid in the extracting solvent MIBK as function of the number of theoretical extraction steps

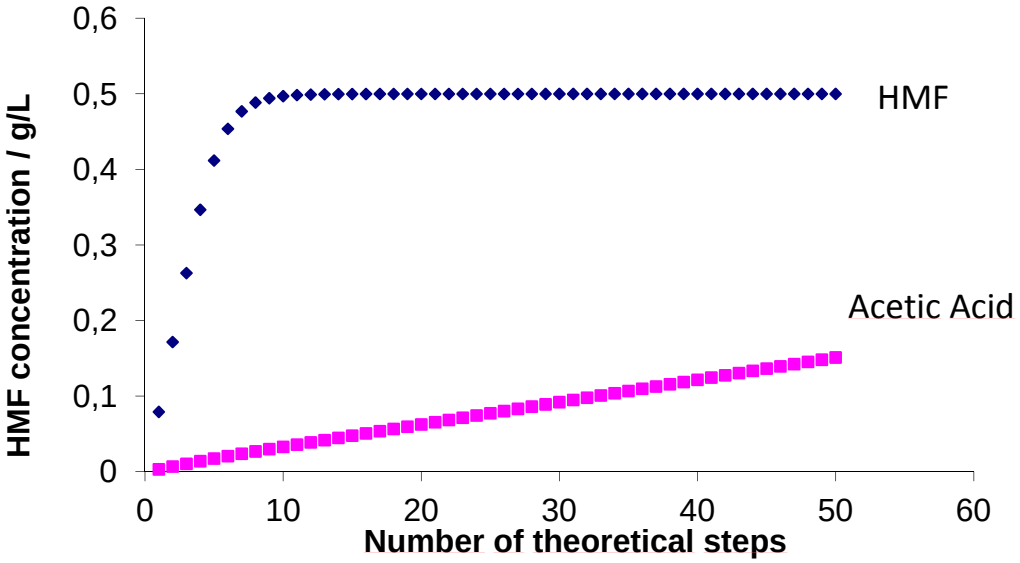


Figure 2.9: Content of HMF and acetic acid in the extracting solvent Chloroform as function of the number of theoretical extraction steps

These calculated results are compared to experiments with a mixer-settler with 8 theoretical plates (KIT, Fig. 2.10).

Figure 2.10: Settling part of a continuous cross-flow mixer-settler extractor

The results of the calculation and the experiments were found to be in good agreement. Unfortunately, the mixer-settler did not work perfect. This is seen in 2.11: The partition coefficient should be constant in all separation tubes of the mixer-settler. However, in the first and the last tube a too high and too low K-value is found, respectively.

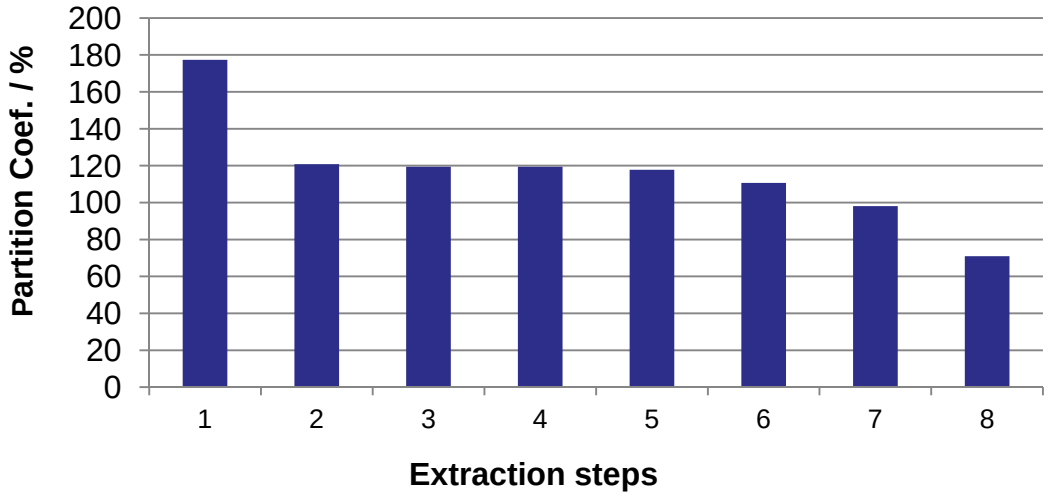


Figure 2.11: Partition coefficient measured in the settling tubes shown in Fig. 2.10.

2.3.3 Conclusion

The experiments and calculation show that chloroform is one of the most suitable solvents. A disadvantage is the problems to face, when halogen-containing solvents are used. The solvent choice has to be done after detailed investigation of the aqueous solution from an HMF-producing process, with all relevant organic and inorganic chemical species involved. A detailed work-out of the solvent system for HMF and furfural separation was not carried out, because the HMF content in the HTC process water was found to be too low for promising recovery.

2.4 Adsorption

An alternative method to recover HMF from water is by adsorption. Tests in KIT showed that charcoal is a suitable adsorbing medium for the removal of HMF from water. The results show also that the HMF can be removed from the charcoal with methanol, as following step for recovery. Methanol has a lower boiling point than water and by distillation, HMF can be isolated. The adsorption kinetics and the equilibrium is measured experimentally; from these data obtained the kinetic coefficients of desorption were calculated.

2.4.1 Adsorption experiments

As the adsorbent, activated charcoal Norit® GAC 1240 W has been used. Specification of the charcoal: alkaline, 0.6-0.7 mm effective size, 1150 m^2/g total surface area (BET), 9 wt.% ash content. HMF (> 95 %) and methanol (p.a.) were purchased from Sigma Aldrich.

The concentration of HMF in water or methanol was determined via measurement of UV- VIS- spectra. For that the spectra are measured on the photometer Dr. Lange DR 5000. For the determination of the extinction coefficients a stock solution of 1 g/l is prepared and to different concentrations diluted. The diluted solutions are measured on the spectrometer.

For the adsorption experiments only standard solutions are used. A solution of about 300 mg/l HMF in DI water or methanol is poured into a round bottom flask. The adsorbent is added while stirring with a magnetic stirrer. After specific times 150 µl are taken from the solution and diluted with DI water or methanol. From the diluted sample a UV-VIS- absorption is measured at the height of the HMF absorption maximum of 283 nm. The extinction coefficient according to Lambert-Beer´s law was determined to 13.05 m^2/g for HMF in water and in methanol.

2.4.2 Results and Discussion

Between HMF in solution $[HMF]_{aq}$ and on the charcoal adsorbed HMF $[HMF]_{ads}$, chemical equilibrium can be assumed:

$$[HMF]_{aq} \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} [HMF]_{ads}$$

In this chemical equation the rate constants k_{ads} and k_{des} describe the velocity of the adsorption or desorption. Evaluation of the rate equations leads to the time dependence concentrations.

$$[HMF]_{aq}(t) = \left([HMF]_{aq,0} - [HMF]_{aq,\infty}\right) \cdot \exp\left(-\left(k_{ads} + k_{des}\right) \cdot t\right) + [HMF]_{aq,\infty} \qquad (1)$$

$$[HMF]_{ads}(t) = \left([HMF]_{aq,0} - [HMF]_{aq,\infty}\right) \cdot \left(1 - \exp\left(-\left(k_{ads} + k_{des}\right) \cdot t\right)\right) + [HMF]_{ads,0} \quad (2)$$

It can be assumed that at the beginning of the reaction no HMF is adsorbed.
So Eq. (1) simplifies to:

$$[HMF]_{ads}(t) = \left([HMF]_{aq,0} - [HMF]_{aq,\infty}\right) \cdot \left(1 - \exp\left(-\left(k_{ads} + k_{des}\right) \cdot t\right)\right) \quad (3)$$

In Fig. 1.12 such a trend is shown. The mass m_{AK} of charcoal is 1.5 g. The mass $[HMF]_{ads}$ can be calculated via the law of conversation of mass.

$$[HMF]_{aq,0} = [HMF]_{aq}(t) + [HMF]_{ads}(t) \quad (4)$$

In this graph can be seen that after 30 min there are no more significant differences of the concentrations. That means the experiment can be stopped at this point.

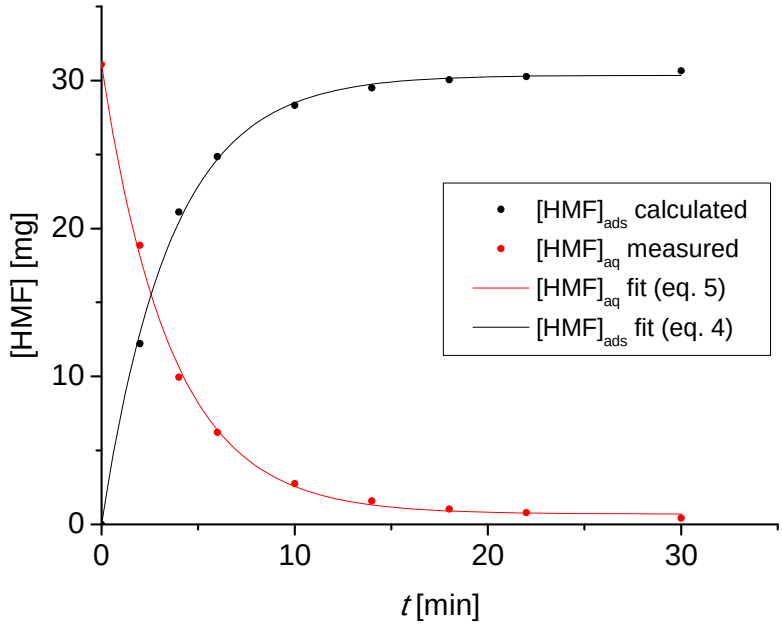


Figure 2.12: Time dependent trend of the adsorption experiment with m_{AK} = 1.5 g.

In Fig. 2.13 adsorption curves in dependence of different amounts of charcoal are shown. With increasing mass of the charcoal the chemical equilibrium is set faster. Also with increasing mass of the charcoal there is more $[HMF]_{ads}$ present. The constants $[HMF]_{aq,\infty}$ and $(k_{ads} + k_{des})$ can be calculated, when the curves are evaluated with Eq. (1). Furthermore the constant $[HMF]_{ads,\infty}$ can be determined with Eq. (4).

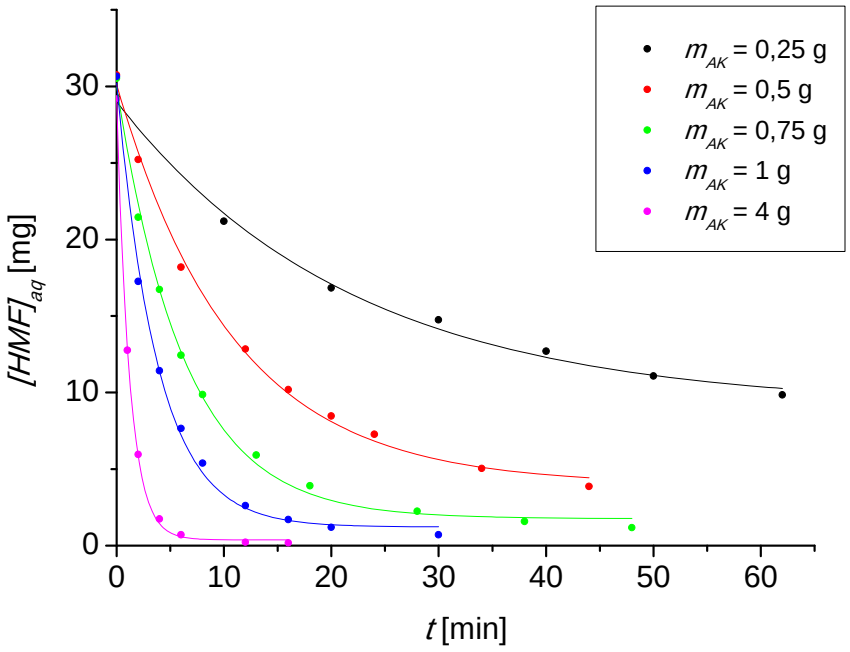


Figure 2.13: Adsorption curves for different weighs of charcoal.

With the following relation

$$K = \frac{[HMF]_{ads,\infty}}{[HMF]_{aq,\infty}} = \frac{[HMF]_{aq,0} - [HMF]_{aq,\infty}}{[HMF]_{aq,\infty}} \qquad (5)$$

the chemical equilibrium constant can be calculated. In Table 2.1, the measured and calculated values are shown.

Table 2.1: Thermodynamic and kinetic data for the adsorption experiments with water

m_{AK} [g]	$[HMF]_{aq,0}$ [mg]	$[HMF]_{aq,\infty}$ [mg]	$[HMF]_{ads,\infty}$ [mg]	$(k_{ads} + k_{des})$ [1/min]	K
0.25	29.25	9.20	20.05	0.047	2.18
0.5	30.76	4.19	26.57	0.097	6,34
0.75	30.53	1.83	28.70	0.163	15.68
1	30.65	1.26	29.39	0.268	23.33
1.5	31.06	0.71	30.35	0.279	42.75
2.5	30.77	0.56	30.21	0.565	53.95
3	30.36	0.48	29.88	0.658	62.25
3.5	30.21	0.46	29.75	0.751	64.67
4	29.17	0.39	28.78	0.829	73.79

The correlation between thermodynamic equilibrium constant and the kinetic rate constants is as follows:

$$K = \frac{k_{ads}}{k_{des}} \tag{6}$$

by which the corresponding desorption coefficients can be calculated. In Fig. 2.14, adsorption and desorption coefficients are shown in dependency of the amount of the charcoal.

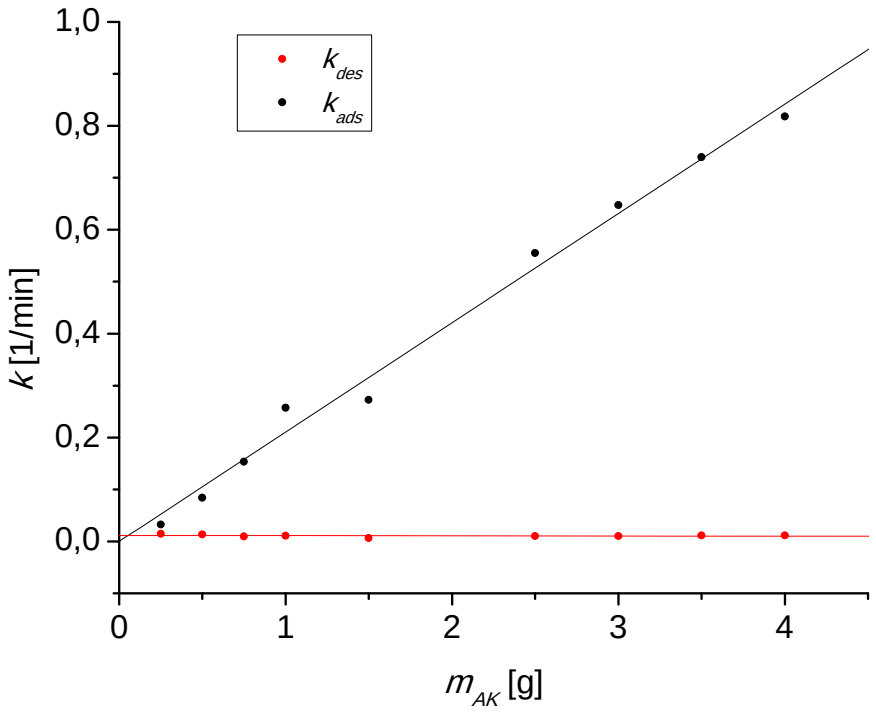


Figure 2.14: Rate constants of adsorption and desorption in dependency of the weight of the charcoal.

It can be seen, that the rate of the adsorption increases with rising amount of the charcoal. The anyway very slow desorption shows very less dependency. Over a wide range of the weight of charcoal it remains practically constant.

The activity of the charcoal is limited. The optimum amount of adsorbent material for an economic process is required. Therefore, in Fig. 2.15 the mass of adsorbed HMF relative to the starting mass versus the amount of the charcoal is shown. The adsorption curve can be modeled by a Langmuir type isotherm. Beyond a weigh of charcoal of 1 g the curve is practically constant. That means that there is nearly no further change of adsorbed HMF with increasing weight of charcoal. An optimum area for the adsorption of HMF is therefore between 1 and 2 g of charcoal.

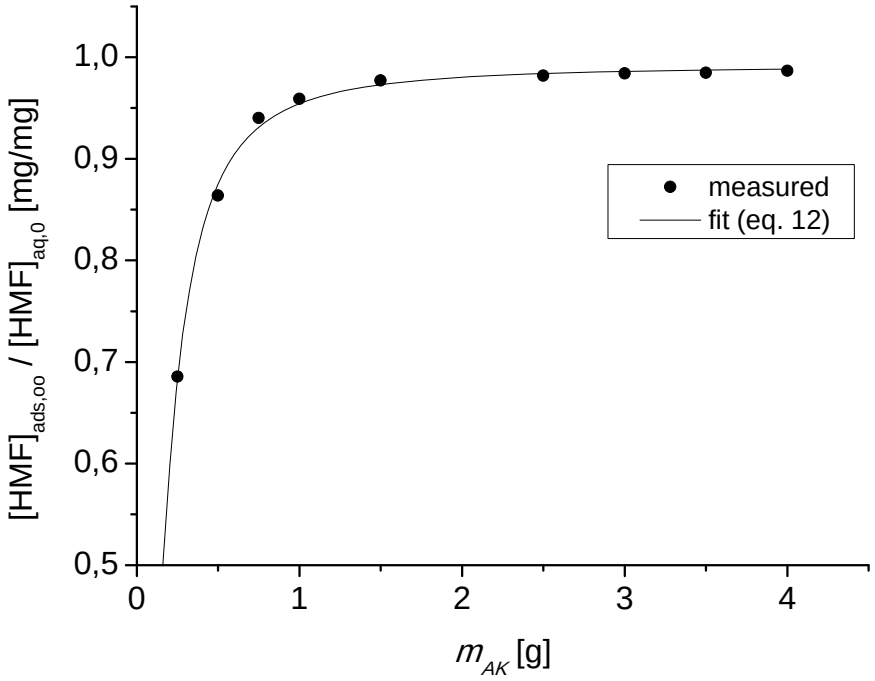


Figure 2.15: Mass of adsorbed HMF in dependency of the weight of charcoal

For the adsorption experiment of HMF (300 mg/l) in methanol 1 g of charcoal is used. The measurement and evaluation is performed in the same way as described above. In 2.16 is the time dependence for this adsorption experiment is shown.

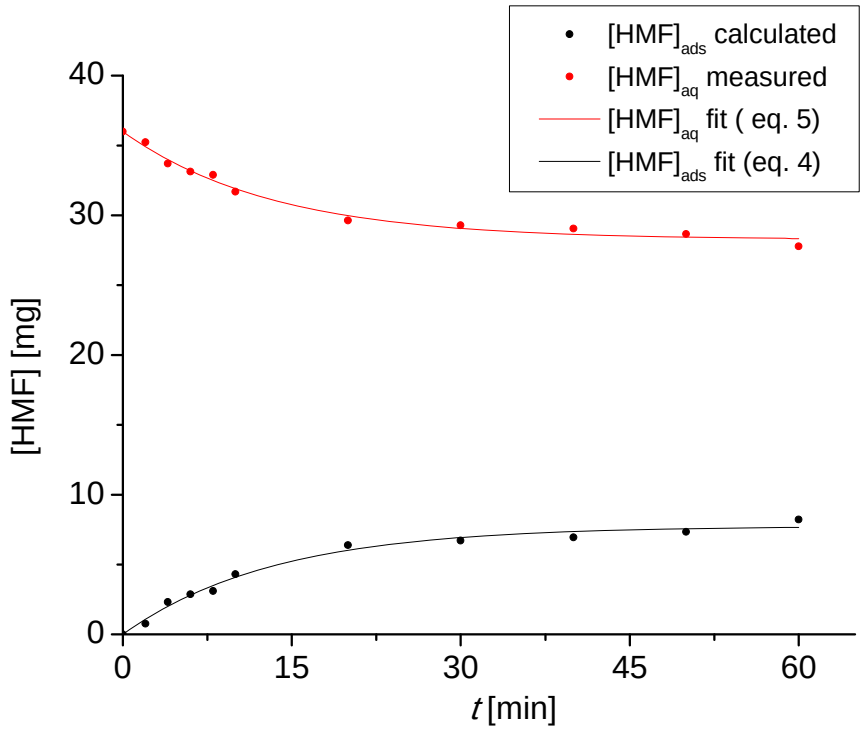


Figure 2.16: Trend of the adsorption experiment in methanol for 1 g of charcoal

In Table 2.2 the kinetic and thermodynamic data of the experiment in DI water and methanol are compared.

Table 2.2: Comparison of the thermodynamic and kinetic data of the adsorption experiments and according calculated desorption values

Solvent	m_{AK} [g]	K	k_{ads} [1/min]	k_{des} [1/min]
DI water	1	23.33	0.257	0.011
methanol	1	0.27	0.016	0.059

The equilibrium constant in water is about 100 times higher than the constant in methanol. Under these chosen conditions 96 % of the HMF solubilised in water is adsorbed. About 79 % of the adsorbed HMF can be solubilised in methanol. A comparison of these data leads to the conclusion, that methanol would be a good solvent for desorption of HMF. On the other hand, desorption of HMF in methanol is much slower than the adsorption of HMF in water, which has to be considered in a detailed process engineering.

2.4.3 Conclusion and future work

The experiments showed that the chosen activated charcoal is suitable for the adsorption of HMF from aqueous solutions. So far standard solutions had been used in the experiments. It is still be be investigated how the complex solute matrix of the HTC process water influences selectivity of HMF separation.

Furthermore it was shown, that methanol shows the properties of a good desorption reagent. In perspective, 79 % desorbed HMF is not satisfying for process development. However, additional knowledge is necessary on desorption behavior in dependence of the solvent quantity. Also, temperature has a strong effect. Desorption is an endothermic process. With rising temperature the amount of molecules released increases.

3 Recovery of nutrients from HTC process water

3.1 Introduction

In the BioBoost project the feasibility of nutrient recovery from the HTC process was studied by KIT and AVACO2 in order to improve the economic performance of the energy carrier by investigating methods for the recovery of valuable nutrients and to optimize HTC process parameters in regard to process water treatment or disposal.

From the work, carried out in Task 3.1 it became obvious, that only potassium is present in substantial amounts in the process water after carbonization of straw, namely 2800 to 3600 µl/ml according to ICP measurements of samples produced at

different process conditions. Calcium and magnesium are present in amounts of 150 - 310 and 110 - 200 µl/ml. Phosphorous was found to be lower than 100 µl/ml in most cases. So for direct recovery in particular of phosphorous and nitrogen appeared not to be promising. However, the behavior of nitrogen and phosphorous as well as of other components are relevant to the optimization of the HTC process. Therefore, the focus was set on

- phosphate behavior as one of the most prominent nutrients for growing plant,
- the determination of nitrogen species contained in the HTC process water, their amount and oxidation states
- recovery or disposal options for HTC process water treatment.

Also in view to potential nutrient recovery the results obtained are useful, when HTC process variants are considered, in which higher amounts of nutrient relevant components in the process water can be obtained. This may be the case of process combinations or subsequent, multistep processing of biomass, in which intermediates can be separated efficiently as discussed in the case of HMF.

3.2 Phosphate behaviour

Growing plant has nutrients, which should be recovered and recycled to the field. Here phosphates are of special interest because of the vanishing natural resources. Therefore, a focus of KIT´s work in this project has been the recovery of phosphates. Figure 1 as an example, the ratio of solved phosphate to the whole phosphate during conversion of horse dung is shown. The highest content of solved phosphates was found at rather low reaction time, too low to form HTC coal. The phosphates are solved when the biomass is degraded and precipitates when the HTC coal is formed. Potassium stays mainly in the aqueous phase, but this depends strongly on feedstock and reaction conditions. Magnesium and Calcium are found as salts mainly in the HTC coal. As for the hydroxymethyl furfural, occurring as an intermediate of HTC coal formation, a modified HTC process design would be necessary to obtain phosphates in larger quantities. Lower reactions times are required, contradicting high HTC yields. Also, the solubility of phosphate significantly depends on pH value.

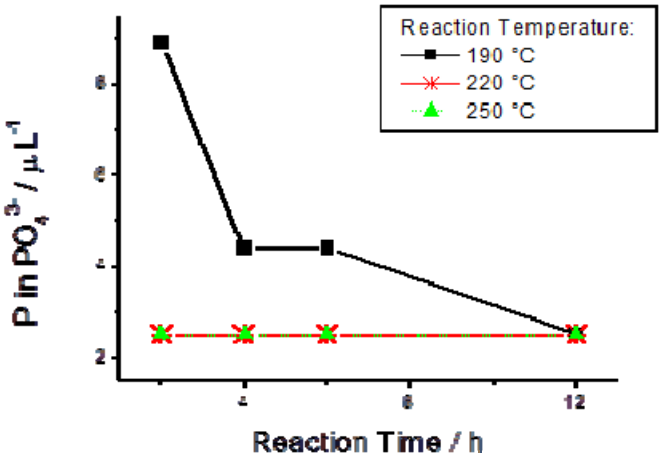


Figure 3.1: Relative amount of phosphate solved in water at 190, 220, and 250 °C in dependence of the reaction time (horse dung, micro autoclave).

3.3 Nitrogen behavior

As in the case of phosphate, the behavior of nitrogen in the aqueous HTC effluent is strongly linked to the optimized parameters of HTC-coal production. There, the potential formation of NO_x in combustion is a relevant issue in view to potential emissions. In this context the feasibility of separation/recovery of nitrogen containing compounds or, alternatively, a potential effluent water treatment have to be considered. Investigations of the nutrient content of process water of HTC are very complex. As an example and as substitute for biomass in household waste and agricultural waste, the green parts of carrots rich in nitrogen have been investigated at KIT as a model system. Figure 3.2 shows the ammonia content and Figure 3.3 and 3.4 that of nitrite and nitrate, respectively. In case of ammonium and nitrate, a maximum concentration of the nitrogen containing species can be observed with changing reaction temperature. For nitrate, a decrease is found with increasing temperature. Reaction time leads to a slow increase for ammonium and nitrate, but a decrease in nitrate concentrations. Obviously, for the fate of nitrogen the influence of temperature is most important, which is not completely understood until now but important to future work when considering nutrients to be recovered or waste water to be treated. It is assumed that some redox reactions between the nitrogen containing compounds occur.

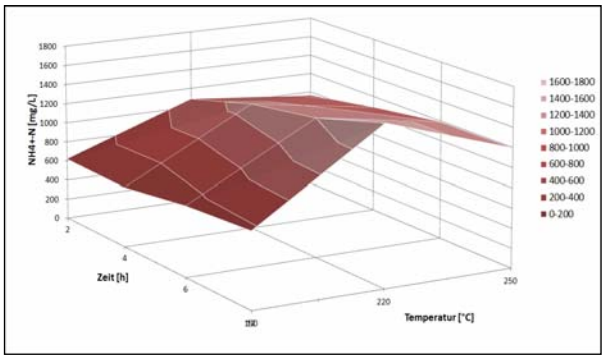


Figure 3.2: Ammonia content in HTC process water in dependence of reaction temperature and time

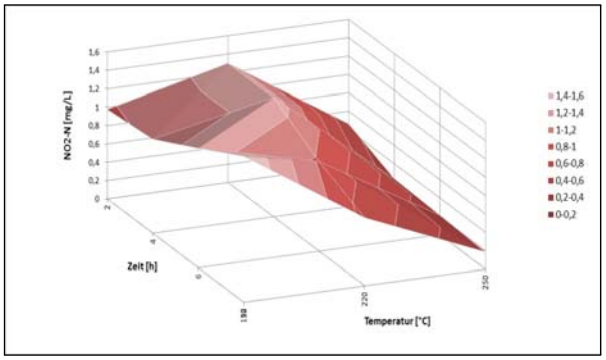


Figure 3.3: Nitrite content in HTC process water in dependence of reaction temperature and time

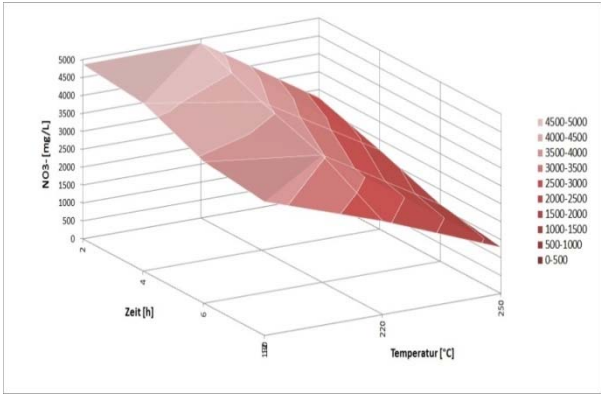


Figure 3.4: Nitrate content in HTC process water in dependence of reaction temperature and time

When biomass, impregnated with cysteine was used in HTC experiments at KIT, an interesting phenomenon could be observed (Figures 3.5 and 3.6). Obviously, the amino acid cysteine added to wood particles lead to an incorporation of nitrogen into the HTC coal formed. In particular, small raspberry-like structures could be observed on the bio-coal surfaces.

Concluding the behavior of nitrogen contained in biomass it can be stated:

- Addition of N leads to morphology changes
- With N-rich types of biomass around 60-70 % of the nitrogen is solved in the process water after HTC
- At higher temperatures N increasingly is incorporated into the coal
- Nitrate is nearly completely consumed at 250 °C
  (phosphate already at lower temperature).
- A maximum NH_4^+ content of ca. 1 g/l in the water phase is obtained at 250 °C.
- The temperature dependence of N-species concentrations is not exactly the same for NH_4^+, NO_2^-, and NO_3^-, most likely complex redox reactions occur

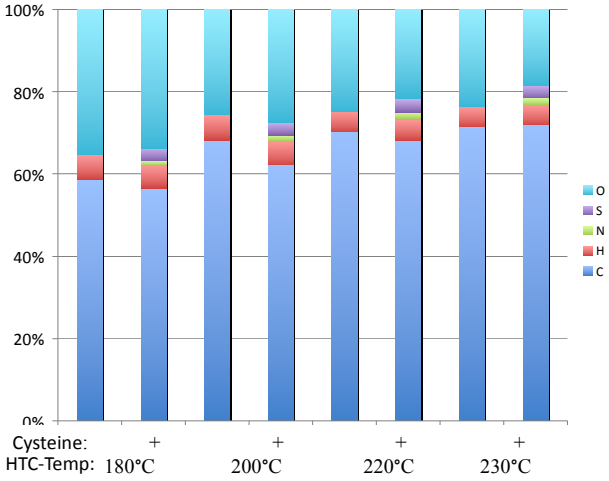
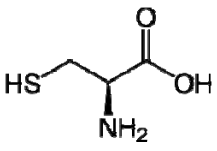


Figure 3.5: nitrogen content in HTC coal from wood without and with (+) addition of cysteine:



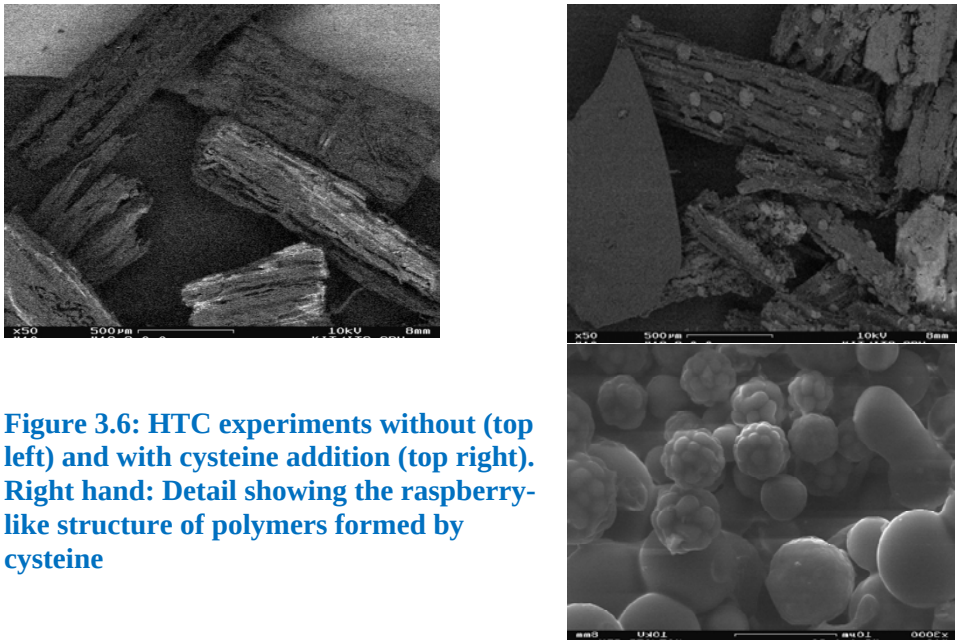


Figure 3.6: HTC experiments without (top left) and with cysteine addition (top right). Right hand: Detail showing the raspberry-like structure of polymers formed by cysteine

3.4 Treatment/disposal of HTC process water

The chemical analysis and tests showed that the amounts of chemicals in the process water directly correlate to the amount of carbon obtained. It will take substantial additional efforts to evaluate the possibility of an integrated energetic and chemical process (see chapter 5). However, by no means process water can be obtained, which is clean enough for direct disposal in municipal sewage systems. AVA-CO2 Forschung has set up a complete cleaning technology including reverse osmosis and nano-filtration in order to clean the process water (technical content in WP 2, refer to related deliverables). As a result the process water can be disposed via existing conventional waste water systems.

4 Polymers from phenols and furfurals

4.1 Background

4.1.1 Resins

Polymers changing irreversibly into hard rigid and infusible materials when heated are called thermosetting polymers. These polymers are usually prepared by heating relatively low molecular mass, semi fluid polymers, which become infusible and form an insoluble hard mass then. The hardening on heating is due to the formation of extensive cross-linking between different polymeric chains. This leads to the formation of a 3-dimensional network of chemical bonds between the polymer chains. Since the 3D network structure is rigid and does not soften by heating, the thermosetting polymers cannot be reprocessed. Some important examples of thermosetting polymers are resol phenol-formaldehyde (PF) resins [1]. Resols, which are the type of resins studied in this project, are prepared from the reaction of phenol with formaldehyde under alkaline conditions at low temperature (60 °C). This reaction results in ortho- and para-methylolated phenols. Methylolated phenols are more reactive with formaldehyde than the non-substituted phenol resulting in the rapid formation of 2,4-dimethylolphenol and subsequently, 2,4,6-trimethylolphenol.

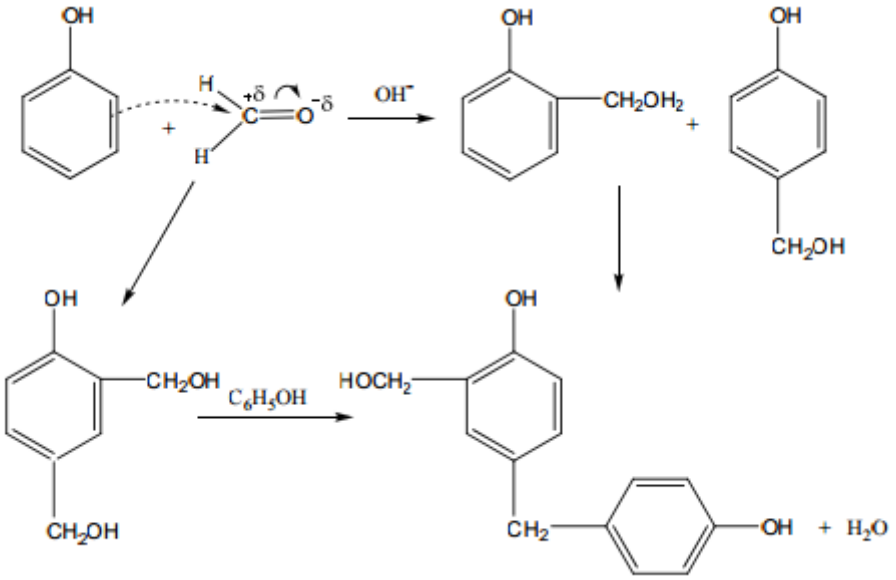


Figure 4.1: Phenol-formaldehyde polymerisation reactions

In a temperature range above 60 °C, condensation reactions of methylol phenols with phenol and/or methylol phenols occur and lead to the formation of the pre-polymer of the desired resole resin.

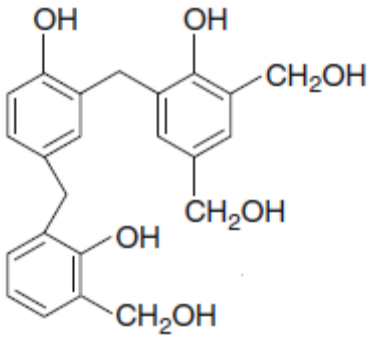


Figure 4.2: Resole structure

The final product of this synthesis is an aqueous mixture of methylol phenols, oligomers of varying molecular weights, and residual amounts of free phenol and formaldehyde [2, 3].

In the Bioboost project, resins of PF type were prepared by replacing phenol with phenolic fractions and formaldehyde by 5-hydroxymethul furfural (HMF) obtained from the thermochemical biomass conversion processes in WP 2. Apart from thermosetting resins of phenol-formaldehyde type, CHIMAR prepared also resins of urea-formaldehyde (UF) type, where the light phase obtained from the catalytic pyrolysis of biomass was used as acidification mean during the synthesis of the resin.

All resins were prepared by a batch process at lab scale and were analysed for their physicochemical properties according to methods applied as standards in the industry. All experimental resins were tested for their bonding ability via their application in the manufacturing of plywood and particleboard panels. The production processes and testing methods of panels are described below.

4.1.2 Particleboards

Particleboards were manufactured by mixing wood particles of certain size (chips) with a glue mixture which was comprised of resin, water, hardener (when needed) and paraffin.. The glued chips were formed in a mat of certain dimensions and then they were pressed under heating.. Next, the boards were cooled, trimmed and sanded before they were subjected to evaluation tests.

The boards were tested for their dry and wet properties as well as for their formaldehyde content according to the European standards mentioned in the following Table 4.1.

Table 4.1: European standards for the evaluation of particleboards

a\a	Properties	Unit	Test Method	Remarks
1	Internal Bond (IB)	N/mm^2	EN 319	-
2	Modulus of Rupture (MOR)	N/mm^2	EN310	-
3	Thickness Swelling (TS), 24h	%	EN 317	24 h, 20 °C
4	Formaldehyde content	mg/100g atro	EN 120	Perforator method

4.1.3 Plywood panels

Plywood panels are made from an odd number of constructional veneers, called plies or veneers, bonded face to face with the grains running in alternate directions (cross bonding). The center ply is known as the 'core', the outer plies as the 'faces' (or the 'face' and 'back') and the intermediate plies as the 'cross-bands'. Usually, a glue mixture from resin, water and additives is prepared and a certain quantity of it is spread on the veneers. The coated veneers are laid up into right angles with the uncoated face of the next veneer. The time from the spreading of the glue mixture until the plywood board is under pressure processed to develop glue line strength is called assembling time. Hereinafter, the ply boards are subjected to cold pressing followed by hot pressing until the glue is cured. After the pressing phase, the plywood panels are trimmed and cut in pieces that were subjected to certain tests in order to evaluate their properties.

In the BioBoost project, CHIMAR manufactured lab scale plywood panels of three layers where the face veneers were from Okumé, while the core veneer is from poplar.

Their testing and classification was carried out according to the following European standards:

- **EN 314-1:2004** Plywood - Bonding quality - Part 1: Test methods.
- **EN 314-2:1993** Plywood - Bonding quality - Part 2: Requirements

The standard EN 314-1:2004 describes the methods for the testing of the plywood panels, while the standard EN314-2:1993 categorizes the plywood panels and sets threshold values for their mechanical and wood failure performance. In particular, the standard EN314-2:1993 specifies requirements for bonding classes of veneer plywood according to their end use. The designated categories are:

Class 1 Dry Conditions: interior applications with no risk of wetting (12% or less moisture content at 20°C and 65% relative humidity).
Class 2 Humid Conditions: protected exterior conditions (20% or less moisture content, at 20°C and 85% relative humidity).
Class 3 Exterior Conditions: unprotected exterior conditions (above 20% moisture content).

For all bonding classes, each glue line must satisfy two criteria together: the values mean shear strength and mean apparent cohesive wood failure must have the following correlation (Table 4.2).

Table 4.2: EN314-2:1993 standard bonding performance requirements

Mean shear strength fv, N/mm^2	Mean apparent cohesive wood failure w, %
$0.2 \leq fv < 0.4$	≥ 80
$0.4 \leq fv < 0.6$	≥ 60
$0.6 \leq fv < 1.0$	≥ 40
$1.0 \leq fv$	No requirement

The above threshold values stand for any class of plywood panels but according to their intended application the panels are subjected to different pretreatments before their testing (EN314-1:2004).

The formaldehyde emissions were determined either with the Desiccator (ISO12460) or the Gas Analysis method (EN717-2).

4.2 Experimental Part

During BioBoost project CHIMAR tested phenolic fractions from the thermal and catalytic pyrolysis of biomass as well as 5-HMF from the HTC of biomass. These renewable chemicals were evaluated as substitutes of the petrochemical raw-materials used in the synthesis of Phenol-Formaldehyde (PF) resins. Besides, the light phase of the catalytic pyrolysis of biomass was evaluated as acidification mean during the synthesis of typical Urea – Formaldehyde (UF) resins.

4.2.1 Resins of Phenol – Formaldehyde type

In Bioboost project, all samples of phenolic fractions were provided to CHIMAR by CERTH/CPERI while 5-HMF was provided by AVACO2. The phenolic fractions were used as phenol substitutes at various levels up to 50% w/w, while 5-HMF was used as formaldehyde substitute reaching a 20% w/w maximum successful substitution level.
The resins were prepared smoothly according to technology of CHIMAR. However, it should be noted that the resins prepared with the phenolic fractions had an irritating smell, which however was disappeared after the complete curing of the resins during the production of panels.

The properties of the resins were determined with typical lab analysis methods and it was found that they are comparable with that of a typical PF resin.

Their adhesive ability was evaluated via their application in the production of lad scale wood-based panels. Most samples were tested in resins suitable for plywood production, while some samples were evaluated in both the production of plywood panels and particleboards. In each case, the panels were prepared following the industrial practice and were tested according to the relative European standards.

4.2.2 Resins of Urea – Formaldehyde type with the light phase of the catalytic pyrolysis of biomass

Apart from the phenolic fractions, CPERI/CERTH provided CHIMAR with the aqueous light phase of the catalytic pyrolysis of biomass that is rich in various acidic chemicals and especially in acetic acid.

These samples were used as acidification means during the synthesis of typical urea-formaldehyde resins.

The properties of all resins were determined with standard lab analysis as well as modern techniques like Size Exclusion Chromatography (SEC) and FTIR, while their

bonding ability was evaluated via their application in the production of lab scale particleboards following a simulation of the industrial practice. The properties of the panels were determined according to the relative EU standards.

Details of the work performed by CHIMAR in WP3 are reported in the deliverable D3.10.

4.3 Conclusions

Relatively with the resins of PF type, it is observed that the **various phenolic fractions** can replace successfully phenol up to the level of 50 %. The physicochemical properties of these resins are similar to the ones of a typical PF resin, while it is worthwhile to be noted that generally, as the phenol substitution level is increased the free formaldehyde content of the resins in decreased. These resins have also an irritating odour although the panels prepared with them have no smell.

In the case of plywood panels, most of the times, the experimental resins lack behind in performance as compared with a typical PF resin. The obtained testing results and especially the ones of wood failure are lowering as the phenol substitution level is increased. However, in all cases the experimental panels meet the requirements of the European Standard EN314-2:1993, even after they are subjected to the severest pre-treatment required for panels intended for use at exterior conditions (class 3).

As expected, the formaldehyde emissions of the experimental panels are at extremely low levels and in any case well below the emissions of a typical PF resin. Between the catalytic and fast pyrolysis phenolic fraction, it seems that the former one has the best performances as phenol substitute in PF resins at the level of 50 %

As a conclusion, it can be said that PF resins with partial replacement of phenol by a phenolic fraction up to the level of 50 % are suitable for the production of plywood panels rather than of particleboards. The phenolic fraction from the catalytic pyrolysis performed better than the sample received by the fast pyrolysis of biomass, since the plywood panels prepared with PF resins containing this phenolic fraction can be used both in interior and exterior applications.

When 5-HMF was used as formaldehyde substitute, problems came up with the synthesis of the resins, because of its higher chemical reactivity compared with the formaldehyde. Overall, it can be said that PF resins with partial replacement of formaldehyde by 5-HMF need further optimisation before their introduction to the industry.

Relatively with the use of the light phase of catalytic pyrolysis of biomass as acidification mean during the synthesis of a typical UF resin, it was found that such resins can be prepared without any problem while have properties relative to the UF resins prepared with a petrochemical acidification mean like acetic or formic acid. Particleboards produced with such resins have performance comparable with that prepared with a typical UF.

Hence, the BioBoost light phase fraction of the catalytic pyrolysis of biomass may be introduced to the industry as alternative acidification mean to the petrochemical ones currently used.

5 Feasibility of combined production of HTC and HMF

The original aim in WP 3 was to isolate Hydroxymethylfurfural (HMF) from the process water of the HTC process. It was found that the concentration was below 1 wt.% and therefore much too low for such an isolation. The reason is that HMF is an intermediate of the HTC reaction, and in a process optimized for HTC-coal production the concentration is therefore low. On the other hand, according to studies of NREL/DOE in USA and within the EU BREW project, HMF was identified as one of the most interesting platform chemical of bio-economy; no other chemical from biomass has such a high number of consecutive chemicals and applications. As a consequence, the company AVA and the KIT have developed a process to produce HMF from fructose, which is applied by the new-founded company AVA-Biochem. For HMF production, plants rich in fructose are used, because fructose is directly converted to HFM. This opened the opportunity for a promising option to combine HTC- and HMF-production: The water of the HMF-production process is used in a HTC-process (Fig. 5.1). Because of the key role of HMF in the HTC-process as intermediate an experimental proof was necessary to support the idea of a value added process. In 250 ml batch autoclave experiments with HMF process water, delivered by AVA-Biochem, have been compared with experiments using pure water (500 °C, 5 h reaction time, 15 wt.% feedstock dry matter content). The HTC was performed with draff (spent brewery grain) and the reproducibility was checked by repeating the experiments in each medium three times.
Compared to the addition of pure water, the coal yield is increased from around 53 to 63 wt.% when using the HMF effluent water and the coal showed slightly different properties like a lower content of volatile matter and an elementary composition with lower hydrogen content. The main advantage of such a combination is the avoidance of waste water treatment in the HMF production process. From the perspective of the HTC process, not only residual or “waste” biomass but also “waste water” is used, leading to a remarkable cost reduction.

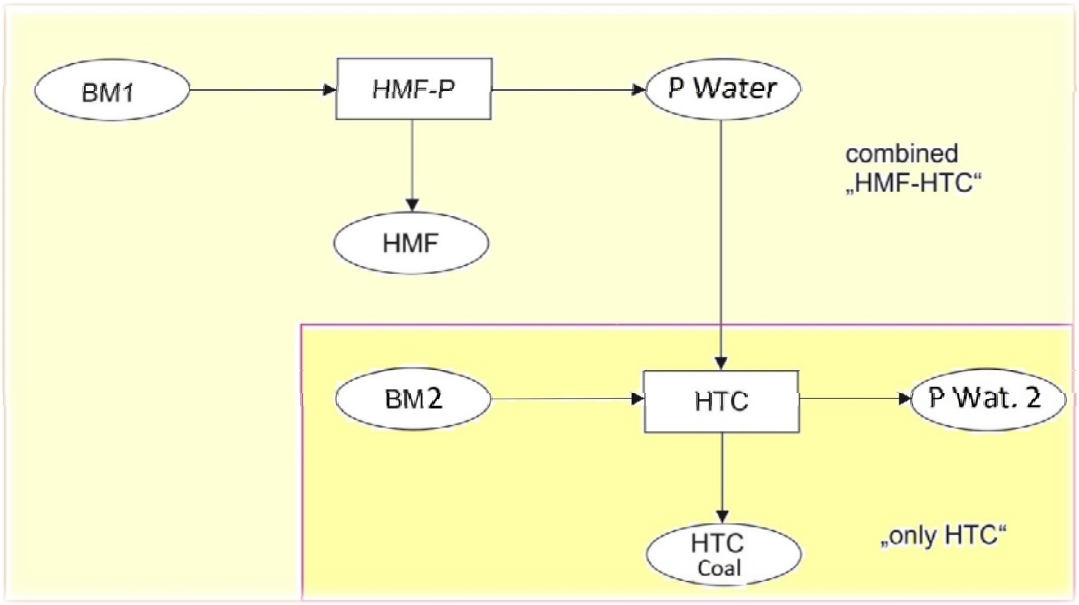


Figure 5.1: Coupling of HMF-production with HTC coal production