



Report with Catalyst Evaluation Results

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1. EXECUTIVE SUMMARY

In the deliverable D4.1 catalysts screening studies were carried targeting to the selection of the best catalyst for the catalytic pyrolysis process of acid hydrolysis residues (AHR). This process focuses on the production of an upgraded biooil that could be used as diesel or diesel miscible biofuel and it is an upgrading process of AHR. Selection criteria for the best catalyst were the yield and the quality of the produced biooil (mainly its oxygen content). Moreover, in this deliverable the evaluation of various AHR was performed targeting to the selection of an AHR that could be used as potential feed in a pyrolysis or catalytic pyrolysis process. This selection can help to the optimization of the entire process chain from biomass to levulinic acid (LA) with the maximum valorization of the hydrolysis residues.

In this deliverable 11 different biomass feeds were used. Four of these feeds were raw biomass feeds (from miscanthus, sugarcane and beechwood), four AHR produced from hydrolysis under different severities (hydrolysis conditions) and 3 pre-treated Miscanthus. All biomass feeds were fully characterized at CERTH using elemental analysis, moisture content, ash content, chemicals analysis as well as TGA analysis. The characterization results showed that the acid hydrolysis and the oxidative pre-treatment conditions have a great impact on the actual structure of these feedstocks. The oxidative pretreatment appears to impact more the hemicellulose and the less crystalline parts of cellulose. Regarding lignin, the severity of the conditions appears to cause further aromatization of the lignin structure.

In this study we evaluated five different catalytic materials. Two of these catalysts were new catalysts synthesized at CERTH while the other 3 were commercially available catalysts. The catalytic materials were also fully characterized for surface area, pore size, pore volume and acidity. The pyrolysis experiments (thermal and catalytic) either for catalyst or for feedstock evaluation were carried on a pre-screening fixed bed pyrolysis unit. Full mass balances and biooil characterization results were obtained from these tests.

This deliverable showed that the thermal pyrolysis of the AHR could be a potential upgrading process for AHR only if the hydrolysis conditions (that produce the AHR) are mild. In this case oil yields up to about 40%wt (on AHR dry basis) can be produced. However, the quality of this thermal bio-oil is not satisfactory for a direct use as diesel miscible biofuel since it contains about 37%wt oxygen. Thus, a further downstream upgrading process is necessary. The AHRs that are derived from more severe treatment conditions appear to be more coke like in nature, their pyrolysis yielding more solid product and the minimum liquid biooil.

For the upgrading of AHR through catalytic pyrolysis, this deliverable showed that among the catalysts tested, the best catalyst is the ZSM-5. With this catalyst we can decrease the oxygen in the oil however, producing a lower yield of bio-oil. Of course as for the thermal biooil the quality of AHR is also crucial for the catalytic pyrolysis. From the evaluation of the various AHRs it was proved that only the AHR produced after hydrolysis at 200°C with 1%wt H₂SO₄ and for 10 min could be used for upgrading through catalytic pyrolysis. In this case a biooil with 13.5%wt yield and 15.5%wt oxygen can be produced. The quality of this bio-oil is also interesting since it contains a lot of aromatics and phenols.



2. INTRODUCTION

In this deliverable catalysts screening studies were carried targeting to the selection of the best catalyst for the catalytic pyrolysis process of acid hydrolysis residues (AHR). This process focuses on the production of an upgraded biooil that could be used as diesel or diesel miscible biofuel and it is an upgrading process of AHR. Selection criteria for the best catalyst were the yield and the quality of the produced biooil (mainly its oxygen content). Moreover, this deliverable was also used for the evaluation of various AHR qualities targeting to the optimization of the entire process chain from biomass to levulinic acid (LA) with the maximum valorization of the hydrolysis residues.

3. EXPERIMENTAL PART

In this paragraph we describe the various biomass feeds used in this study along with the experimental unit and the analyticals used for biooil characterization.

3.1. Feedstocks

Biomass feedstocks

The following biomass feedstocks were used in this deliverable for the catalytic pyrolysis experiments:

- ✓ Miscanthus feed from UL that is the raw material in the hydrolysis experiments.
- ✓ Sugarcane bagasse received from CTC
- ✓ Sugarcane trash from CTC,
- ✓ A standard CPERI feed (from beechwood) as reference materials

Acid Hydrolysis Residues (AHR)

Four different AHR samples were sent by UL to CPERI in order to investigate if these feeds could be used in a pyrolysis process for further production of biofuels. As we will present later these feeds were evaluated in both pyrolysis and catalytic pyrolysis. The University of Limerick has provided CPERI with AHR coming from Miscanthus feed and treated with various hydrolysis conditions. These feeds are the following:

- ✓ Miscanthus treated at 150°C, 1% H₂SO₄, 3 hours
- ✓ Miscanthus treated at 150°C, 1% H₂SO₄, 12 hours
- ✓ Miscanthus treated at 200°C, 5% H₂SO₄, 2 hours
- ✓ Miscanthus treated at 200°C, 1% H₂SO₄, 10 min

Pretreated Biomass

UL also sent to CPERI Miscanthus feeds pretreated under different conditions:

- ✓ Miscanthus pretreated with H₂O₂ + Fe₂(SO₄)₃
- ✓ Miscanthus treated with H₂O₂ and HCOOH
- ✓ Miscanthus pretreated with H₂O₂ and HCOOH, followed by 150°C, 1% H₂SO₄, 7 hours hydrolysis

All above different feedstocks were fully characterized at CPERI laboratory regarding the ash and moisture content, C and H content (elemental analysis), as well as their hemicellulose, α -cellulose and lignin synthesis (chemical analysis). The elemental analysis was conducted according to UOP 703 method on a CHN-800 elemental analyser (LECO). The moisture content was determined after heating at a furnace at 105°C for 15h while the ash content was calculated after burning in a muffle furnace at 640°C for 16h.



For the chemical analysis and before determination of hemicellulose, α -cellulose and lignin content of the biomass the extractives were determined with a mixture of EtOH:Toluene at a ratio of 1:2 for 16h. For the determination of the lignin content the official method TAPPI222 was followed. The holocellulose content was determined according to the well established Wise method, with small modifications. The α -cellulose content of the biomass samples was determined based on official method TAPPI203. Finally, the hemicellulose content of the samples was determined by subtracting the determined α -cellulose from the holocellulose.

TGA analysis was also conducted under air, in order to avoid the slow degradation peaks of lignin and have a clearer image of the sample's constituents. The analyses were performed on a SDT 2960 analyzer by TA Instruments. The samples were heated at a rate of 10°C/min up to 800°C.

3.2. Catalysts used in the catalytic pyrolysis tests

In this catalyst evaluation study we used new catalysts synthesized in CERTH and commercially available catalysts. Regarding synthesis of the new catalysts CERTH focused on two aluminosilicate mesoporous materials. More specifically an Al-MCM-41 and an Al-SBA-15 material were synthesized in CERTH following a typical synthesis method resulting in both cases in a Si/Al ratio equal to 30. A full characterization of these two materials is given in Table 1. These two mesoporous aluminosilicates were considered as promising catalysts for biomass pyrolysis due to their specific porosity and acidic properties (large surface area, relatively large pores of ca. 3nm pore diameter, and mild-to-moderate acidity). In this way large molecules derived during biomass pyrolysis are more accessible to the high mesoporosity of the catalytic samples, while their mild/low acidity can be tailored in order to avoid excessive cracking of the pyrolysis vapors leading to undesired products (e.g. water and coke). Known drawback of these mesoporous materials as compared to the corresponding zeolites (of similar Si/Al ratio) is their low hydrothermal stability.

The synthesis procedure of these aluminosilicates is the following: a mixture of tetraethylorthosilicate (TEOS) and aluminum isopropoxide (AIP) was slowly added under stirring at room temperature to an aqueous solution of cetyltrimethylammonium bromide (CTAB) which has been previously become alkaline (pH=10-11) by the addition of ammonia solution. The formed gel was further stirred for 1 hour and was then transferred to a polypropylene bottle and was hydrothermally aged at 100°C for five days. The white product was filtered, washed with double distilled water, dried at room temperature and calcined at 550°C. A similar procedure was applied for the synthesis of the SBA-15 material using in this case a mixture of tetraethylorthosilicate (TEOS) and sodium aluminate as the Si and Al precursors respectively and pluronic p-123 as the template, while the pH was initially adjusted to 1-3 using a HC solution and later to 2-4 using a NaOH solution. The formed gel was also hydrothermally aged at 100°C for five days, while the formed white product was filtered, washed with double distilled water, dried at room temperature and finally calcined at 500°C. Both mesoporous materials were fully characterised applying N₂ physisorption, XRD, SEM and TEM to examine their structural and porosity characteristics, ICP to check their elemental composition and finally ammonia TPD and FTIR of pyridine adsorption to examine their acidic characteristics. All these characterization results are given in Table 1. From this table it seems that the two catalysts have weak to moderate acidity with a low ratio of Bronsted to Lewis acidity. However, their total surface area (TSA) is very high at the level of about 900 m²/g. The Al-SBA-15 catalyst have higher TSA and higher Bronsted to Lewis acidity ratio.



Except of the new materials synthesized at CERTH, two commercially available catalysts (USY, ZSM-5) and an inert material (silica sand) were also used in this catalyst evaluation study. Characterization results of these catalysts are given in Table 1.

Table 1. Catalyst Characterization Results

	Si/Al ratio	SA, m ² /g	Pore size nm	Pore Vol. Cm ³ /g	Acid sites Mmoles NH ₃ /g	Bronsted/Lewis Molar ratio	Acidity strength
Silica Sand	-	-	-	-	-	-	-
ZSM-5	25	416	~0.55	0.23	0.6	3.2	Strong
USY	6	730	~0.74 and 4,16	0.48	0.25	1.4	Moderate/Strong
Al-MCM 41 (30)	30	860	2.75	0.96	0.28	0.50	Weak/Moderate
Al-SBA-15 (30)	30	1015	11.0	1.55	0.32	0.98	Weak/Moderate

3.3. Pyrolysis and catalytic pyrolysis tests

Thermal and catalytic pyrolysis experiments for the screening of catalysts and feedstocks were performed on a bench scale fixed bed reactor made of stainless steel 316. The reactor was heated by a three zone furnace and was purged with nitrogen to ensure an oxygen-free atmosphere and to carry the pyrolysis vapors through the catalyst. The reactor was loaded with 0.7 grams of catalyst and the catalyst bed temperature was constantly measured with a thermocouple. When the desired temperature was reached, approximately 1.5 grams of biomass were injected in the reactor with the help of a piston. The biomass was pyrolyzed and the pyrolysis vapors passed through the fixed catalytic bed where upgrading/cracking reactions took place. The liquid products were collected in a glass receiver, submerged in a cooling bath that was kept at -17°C. Solid (coke) and gas products were collected and measured as well. Pyrolysis products, namely solid (coke), gas and liquid (biooil) were analyzed in all cases for composition and elemental analysis with the help of GC, GCMS, Leco and Karl-Fischer.

3.3.1 Bio-oil characterization

Apart from the carbon and aqueous content of the produced bio-oils, their composition was elucidated by means of chromatographic analysis and in particular by GC-FID for the analysis of the aqueous phase of the biooils, and GC-MS and GCxGC-ToFMS for the analysis of the organic part and the whole bio-oil respectively.

Two-dimensional gas chromatography is a powerful analytical technique that allows better separation of the compounds of complicated mixtures, as bio-oils are, and increased identification of the compounds when hyphenated with a spectroscopic method such as time-of-flight mass spectroscopy. For the analysis of the bio-oils an analytical method was developed for the GCxGC that allowed complete separation of the bio-oil constituents. The analytical system used was an Agilent 7890 A GC with injector Agilent 7683 B series (Agilent Technologies, Palo Alto, CA, USA) connected to a Pegasus 4D time-of-flight mass spectrometer from Leco Instruments. The first dimensional chromatographic separation was performed by an apolar column while the second dimensional column was situated in a dual



internal oven. Instrument control, data acquisition and data processing were done by the ChromaToF (LECO) software and Microsoft Excel. The TOF-MS operated at an acquisition rate of 100 spectra/s and a mass range of m/z 45 – 400 amu. The modulation period was 10 s. The GCxGC analysis results were compared with a conventional GC-MS analysis, where the samples were also injected after proper dilution without any pretreatment. The GC-MS analysis was conducted using an Agilent 7890A Gas Chromatograph with a 5975C Mass Selective Detector System, equipped with a HP-5MS 5% phenyl methyl siloxane column with dimensions 30 m x 250 μm x 0.25 μm . The injection was performed in the split mode (split ratio 1:10), with the injector temperature at 280°C.

For the analysis of the aqueous extracts/phases, the analyses were carried out with a HP5890II gas chromatograph, equipped with an FID. The column used was a DB-WAX 30m x 0.53mm x 1 μm . The carrier gas was Helium at a flow rate of 2mL/min. The interpretation of the GCxGC analysis results has been done by both the semi-quantitative and the quantitative approach. The semiquantitative approach, commonly used for GCxGC analysis, approach focuses mostly on the qualitative characterization of the biooil and secondly on identifying which compounds and chemical groups are most abundant in the biooil. This approach allows for an estimate of the relative abundance of the different chemical groups present in the bio-oil, but is not representative of their actual concentration in the sample. External standard and internal standard (for GCxGC-ToFMS) calibration was developed in order to obtain accurate measurements of the actual concentration of the compounds contained in the bio-oil.

4. RESULTS AND DISCUSSION

4.1. Feedstock characterization

The elemental analysis, moisture and ash content for these samples were conducted according to the described (in the experimental paragraph) methods and the results are presented in Table 2. There are no big differences in the elemental analysis of the biomass feeds. All these materials have a carbon content of about 46-48%wt and an oxygen content of about 43-47%wt. In general sugarcane biomass has slightly more oxygen compared to Miscanthus feeds. The moisture content in all biomasses is around 6-7%wt while the ash content of the Miscanthus feeds is about 2.7%wt.

The acid hydrolysis treatment causes an increase in the carbon content of the biomass followed by a decrease in the oxygen content. The mild treated (at 150°C) AHR have a carbon content of about 47-49%wt however, the severe treated AHR (at 200°C) have very high carbon content of about 61-63%wt with much less oxygen of about 30%wt. On the contrary, the oxidative pre-treatment appears to have a smaller effect on the C, H and O content of the biomass. Probably, in the first case the severity of the applied conditions causes chemical reactions (e.g. condensations or oxidations) that lead to more carbon-like structures, while the milder oxidative treatment does not appear to impact the actual structure of the compounds, but only remove or transform them partly.

The ash content of the biomass is of importance for the pyrolysis process, as it affects greatly the pyrolysis reactions and products. The ash content of the oxidatively treated biomass is not affected greatly compared to original biomass, but in the case of the acid hydrolysis the ash content is diminished, as was expected, probably due to solubilization of some ash in the acidic environment. Only in the case of the most extreme acid hydrolysis conditions and the higher H_2SO_4 concentration is the ash content increased, probably due to residual sulfur or stable sulfuric salts that prevented the leaching of the metals.



The ICP analysis of the biomass feeds are given in Table 3. Miscanthus feed has a very high Calcium (Ca) content following by Potassium (K) and Sodium (Na). Sugarcane straw and bagasse have much lower Calcium and more Potassium.

Table 2. Elemental analysis, moisture and ash content of the received samples

Sample name	Elemental analysis (%) (moisture free)			Moisture (%)	Ash (%)
	C	H	O	105°C/15h	640°C/16h
Sugarcane Bagasse	46.59	6.80	46.47	6.84	-
Sugarcane Straw	45.81	6.76	47.06	6.36	-
Miscanthus raw	48.15	5.94	43.23	7.31	2.68
CERTH reference					
Misc. 3h, 150°C, 1% H_2SO_4	47.59	5.32	46.36	1.35	0.73
Misc. 12h, 150°C, 1% H_2SO_4	49.03	6.06	43.97	2.92	0.94
Misc. 2h, 200°C, 5% H_2SO_4	61.73	4.14	31.10	3.27	3.03
Misc. 10min, 200°C, 1% H_2SO_4	63.07	5.41	29.93	3.92	1.59
Misc. $H_2O_2+Fe_2(SO_4)_3$	42.18	6.18	48.84	6.22	2.80
Misc. $H_2O_2+HCOOH$	41.84	6.42	49.20	5.36	2.54
Misc. $H_2O_2+HCOOH$ followed by 7h, 150°C, 1% H_2SO_4	44.80	6.32	45.81	0.00	3.07

Table 3. ICP analysis of Feedstocks

Element (ppm)	Miscanthus	Sug. Straw	Sug. Bagasse
Potassium (K)	430±30	1250±100	1455±110
Sodium (Na)	380±25	240±40	122±15
Magnesium (Mg)	255±20	935±85	270±25
Iron (Fe)	0	1140±100	1050±100
Alumina (Al)	0	1100±100	440±30
Calcium (Ca)	8850±450	2380±140	830±70

The severity of the sulfuric acid treatment has a direct impact on the chemical composition of the biomass (Table 4). Compared to the untreated miscanthus, the treatment for 3h with 1wt% H_2SO_4 causes degradation of hemicellulose, which is reflected by the increased cellulose content while a small part of lignin is removed as well. The increase of the treatment time to 12h results in hydrolysis of hemicellulose, as is reflected by the increased extractives content and the lower hemicellulose and lignin content compared to the untreated miscanthus. However, the difference of the three biopolymer ratios compared to that of the milder treatment insinuates that some condensation reactions occur.

The increase of the treatment temperature to 200°C results in efficient removal of both hemicellulose and cellulose as it is evident by the high lignin content of these residues and the very low peak (below 350°C) corresponding to hemicellulose and cellulose along with the very sharp peak corresponding to lignin, that appears well above 400°C at the DTG graph (Figure 1). The sharpness of the peak corresponding to lignin implies some modification of the biopolymers structure, towards a more aromatized one.



Table 4: Extractives, hemicellulose, cellulose and lignin content of the received samples

Sample name	Extractives (%)	Hemicellulose (%)	α -Cellulose (%)	Acid Insoluble Lignin (%)	Acid Soluble Lignin (%)
Miscanthus raw	1.3	29.1	40.4	24.2	2.3
Misc. 3h, 150°C, 1% H ₂ SO ₄	4.1	17.8	52.1	22.8	1.7
Misc. 12h, 150°C, 1% H ₂ SO ₄	5.3	20.6	47.9	23.6	1.7
Misc. 2h, 200°C, 5% H ₂ SO ₄	4.2	2.3		87.8	2.7
Misc. 10min, 200°C, 1% H ₂ SO ₄	11.5	25.5		62.9	3.1
Misc. H ₂ O ₂ +Fe ₂ (SO ₄) ₃	1.3	69.7	10.7	12.1	3.4
Misc. H ₂ O ₂ +HCOOH	0.6	25.7	64.1	3.7	3.4
Misc. H ₂ O ₂ +HCOOH followed by 7h, 150°C, 1% H ₂ SO ₄	2.4	49.1	23.5	20.4	1.5

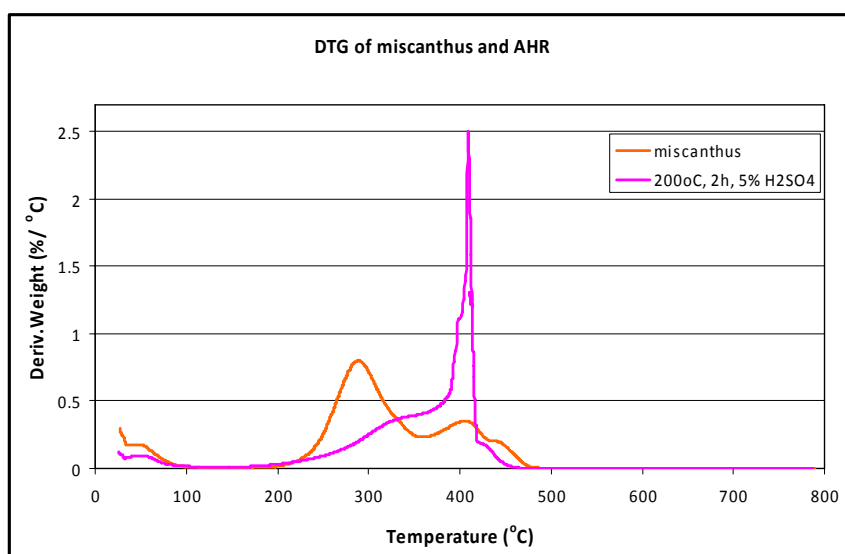


Figure 1: DTG curve of the acid hydrolysis residue at extreme conditions

The treatment of biomass with H₂O₂ and HCOOH or Fe₂(SO₄)₃ obviously impacts lignin as is reflected by this biopolymer's lower concentration in the samples. Formic acid is a lot more effective for delignification compared to sulfuric iron (III), however the treatment with H₂O₂ and Fe₂(SO₄)₃ appears to affect α -cellulose as well, probably by impacting on its crystallinity and degrading it to smaller molecules that are determined as hemicellulose, by the gravimetric method used. The increased lignin content of the last sample, where a combination of delignification and acid hydrolysis was applied, should be attributed to condensation products due to the acid hydrolysis of cellulose, which is greatly diminished.

To verify the above assumptions, TGA analysis was performed on these samples and the results are depicted in Figure 2. Comparing the DTG graphs of the untreated miscanthus with the oxidatively treated samples, it appears that both the hemicellulose-cellulose and the lignin peak, at ~300 and 400°C respectively, are shifted to higher temperatures. This means that either the materials become more crystalline or that more stable structures are formed. In fact in the case of the hemicellulose and cellulose, the shift of the peak indicates that the treatment impacts mostly on the less crystalline polymeric structures. In the case of lignin, the shift to the higher temperatures corroborates the earlier assumption that humin compounds are formed, due to condensation products of the cellulose hydrolysis.

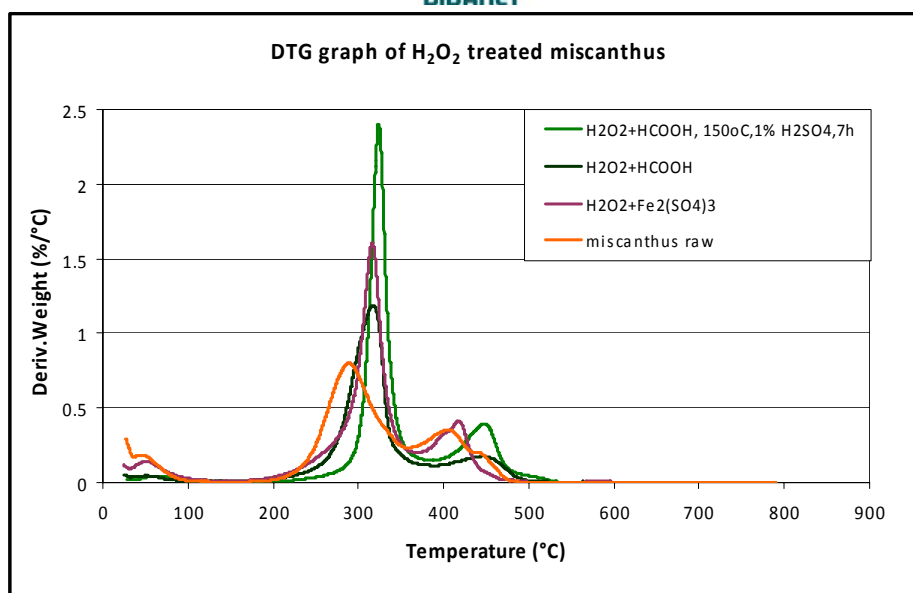


Figure 2: DTG curves of the oxidatively treated Miscanthus

4.2. Catalyst Evaluation with Biomass feeds

Bench scale pyrolysis tests were performed in this deliverable for catalyst testing using the Miscanthus feed that was the main DIBANET raw material for the production of AHR. For comparison purposes the CERTH standard feed (beechwood) was also used for catalyst pre-screening. The pyrolysis results with the beechwood feed and four catalysts (ZSM-5, MCM-41, SBA, USY) are given in Table 5.

Table 5. Catalytic pyrolysis runs with beechwood feed

	Silica Sand	ZSM-5	Al-MCM-41(30)	S13-Al-SBA-15	USY
Water, %wt on biomass	21.4	27.5	29.9	25.9	29.5
Organic oil, %wt on biomass	37.6	20.6	9.6	25.6	9.2
Gas, %wt on biomass	17.1	25.0	26.2	20.6	28
Coke, %wt on biomass	23.9	26.9	34.3	27.9	33.3
Elemental Analysis of Organic Biooil (%wt)					
C (Org.)	54.4	59.3	68.3	56.8	59
H (Org.)	7.2	9.6	12.7	9.7	6.5
O (Org.)	38.4	31.1	19.0	33.5	34.5

In this table we present the main product yields obtained from the pyrolysis runs along with the elemental analysis of the organic oil produced from the runs. From Table 5 it seems that compared to silica sand all catalysts decrease the yield of the organic oil producing more coke and gases and also more water. However, when catalysts are used we produce more deoxygenated bio-oil achieving up to about 20%wt oxygen in bio-oil. It is clear that the presence of catalyst favours the deoxygenation reactions producing a better quality biooil but with a lower yield. Comparing the performance of the catalysts it seems that USY gives very low yield with low deoxygenation and thus it is the worse catalyst. From the other catalysts the MCM material although achieved satisfactory deoxygenation it resulted in low oil yield. Based on the above screening the ZSM-5 seems to be the best catalyst since although it gives



lower yield than the SBA it has higher deoxygenation achieving bio-oil with less oxygen. The two best catalysts from the above screening study were also tested using the Miscanthus feed. The results are given in Table 6.

Table 6. Catalytic pyrolysis runs with Miscanthus feed from U.L

	Silica Sand	ZSM-5	S13-Al-SBA-15
Water, %wt on biomass	23.7	27.8	26.5
Organic oil, %wt on biomass	26.9	16.7	17.6
Gas, %wt on biomass	20.5	25.3	20.9
Coke, %wt on biomass	28.9	30.2	34.6
Elemental Analysis of Organic Biooil (%wt)			
C (Org.)	58.3	66.5	65.4
H (Org.)	8.0	10.1	10.1
O (Org.)	33.7	23.1	24.5

Table 6 validates the results from Table 4. Again the two catalysts present higher deoxygenation compared to silica sand. Moreover, the deoxygenation achieved with the ZSM-5 is better compared to SBA. Thus despite the fact that SBA gives slightly higher oil yield we selected the ZSM-5 catalyst as the best from this evaluation study.

4.3. Evaluation of AHR and pre-treated feeds

All received from UL AHR and pretreated biomasses were pyrolyzed both thermally and catalytically using the best catalyst from the above described pre-screening study (ZSM-5). Mass balances, yields and oxygen contents for the biooils are presented in Table 7. The effect of catalysis on product yields with the AHR is similar to that with biomass. Thus, comparing the thermal with the catalytic tests it is clear that in all cases the use of the ZSM-5 catalyst produces more water, less organic oil, more gases and more coke. In addition the oxygen content of the produced organic oil is reduced. Essentially, the oxygen content of the biooil is reduced via the production of more water, CO and CO₂. An increase in coke is also noted and is due to the overcracking/condensation reactions that take place on the catalyst's pores.

From the mass balances (Table 7) it is clear that the AHRs that were produced at mild conditions (150°C, 1% H₂SO₄) yield more biooil with pyrolysis. The Miscanthus treated at 200°C, 1% H₂SO₄ for 10 minutes also yields a satisfactory quantity of biooil, almost half compared to the mild conditions feeds and with lower oxygen content. The severely treated AHR on the other hand, 200°C, 5% H₂SO₄ for 2 hours, produces very little biooil, while coke production reaches up to 69 wt% in the case of ZSM-5. This is attributed to the extreme pretreatment conditions that were employed and probably caused condensation reactions and alteration of the lignin's structure resulting in an already more coke-like material, as has been indicated by the DTG graphs.

Table 8 summarizes the mass balances and biooil oxygen contents for the thermal and catalytic pyrolysis of the pretreated feeds. For comparison the pyrolysis results from Raw Miscanthus feed are also presented. From Table 8 it is clear that the same observations are made (concerning the thermal and the in situ catalytic upgrading pyrolysis as in the case of the AHRs). In general the biooils that are produced from pretreated delignified Miscanthus yield oils with higher oxygen contents which is to be expected since the starting material also has higher oxygen content (Table 1). This is attributed to the lower lignin and higher cellulose/hemicellulose content of the delignified samples, which is in contrast to the AHRs. Coke production is lower for the delignified samples compared to the AHRs. The last sample



(Miscanthus H₂O₂+HCOOH, 150°C, 1% H₂SO₄, 7h) yields more coke which is attributed to the fact that it has been acid hydrolyzed and therefore has higher content of lignin or humins/condensation products of cellulose, as was resulted from the initial characterization.

Table 7. Mass balances for thermal and catalytic pyrolysis of AHRs

	Miscanthus 3h, 150 °C, 1% H ₂ SO ₄		Miscanthus 12h, 150 °C, 1% H ₂ SO ₄		Miscanthus 2h, 200 °C, 5% H ₂ SO ₄		Miscanthus 10min, 200 °C, 1% H ₂ SO ₄	
	Sand	ZSM-5	Sand	ZSM-5	Sand	ZSM-5	Sand	ZSM-5
Product Yields								
Water	17.49%	24.94%	17.80%	23.03%	12.48%	11.61%	14.70%	19.40%
Organic Oil	41.75%	25.65%	40.29%	22.77%	6.09%	2.12%	25.57%	13.40%
Gas Yield	16.69%	25.29%	16.98%	26.37%	18.36%	17.41%	14.42%	18.41%
Coke Yield	24.07%	24.18%	25.00%	27.83%	61.10%	68.86%	45.30%	48.79%
Elemental analysis of organic oil								
C	54.57%	59.94%	56.56%	61.01%	66.28%	Organic yield too low for accurate measurements	66.04%	77.78%
H	7.68%	9.08%	6.93%	9.22%	11.60%		8.02%	6.84%
O	37.75%	30.99%	36.51%	29.78%	22.13%		25.93%	15.38%

Table 8. Mass balances for thermal and catalytic pyrolysis of raw and delignified Miscanthus

	Raw Miscanthus		Miscanthus H ₂ O ₂ + Fe ₂ (SO ₄) ₃		Miscanthus H ₂ O ₂ + HCOOH		Miscanthus H ₂ O ₂ +HCOOH, 150°C, 1%H ₂ SO ₄ , 7h	
	Sand	ZSM-5	Sand	ZSM-5	Sand	ZSM-5	Sand	ZSM-5
Product Yields								
Water	23.7%	28.46%	21.77%	27.17%	24.97%	31.21%	21.56%	27.92%
Organic Oil	26.9%	16.46%	38.07%	20.32%	39.57%	21.38%	34.86%	19.24%
Gas Yield	20.5%	25.38%	17.60%	18.58%	14.33%	23.71%	16.23%	24.27%
Coke Yield	28.9%	29.66%	22.52%	25.81%	21.13%	23.70%	27.35%	29.32%
Elemental analysis of organic oil								
C	58.3%	66.41%	54.59%	60.18%	53.58%	57.86%	53.64%	61.91%
H	8.01%	10.15%	7.49%	9.45%	8.08%	9.72%	8.54%	9.67%
O	33.7%	23.44%	37.92%	30.38%	38.34%	32.42%	37.83%	28.42%

In Figure 3 we summarize the results with all feeds regarding the organic oil yield vs oxygen content of the organic oil (for both silica sand and ZSM-5 catalyst). It seems that all feeds present the same behaviour and with this catalyst we obtain a better quality biooil (less oxygen content) but with less yield. Figure 3 shows that there is small difference between the various feeds regarding the effect of oil yield vs. deoxygenation. This is especially valid for the AHR received after 3 and 12 hours treatment with 1% H₂SO₄, for the severe treatment AHR (2hr, 200°C, 1% H₂SO₄) and the pre-treated Miscanthus. The AHR feed after 10 min, 200°C and 1% H₂SO₄ seems to have a very satisfactory performance giving the same organic oil yield with about 5% less oxygen.

4.3.1 Bio-oil characterization

Tables 9 and 10 present the GCMS analysis done on the organic oils produced from AHRs and pretreated Miscanthus, respectively. For the AHRs mostly aromatic chemicals such as aromatic hydrocarbons, phenols and Polyaromatic Hydrocarbons (PAHs) are detected. The existence of these compounds is attributed mostly to the increased content of lignin in the feed materials which has a highly aromatic nature. On the other hand the pretreated samples



produce some phenols, ketones, aldehydes and sugars. The ketones, aldehydes and sugars are attributed to cellulose and hemicellulose while the phenols are due to the lignin content as mentioned above. Catalytic pyrolysis produces high yields of aromatic hydrocarbons which attributed in part to the deoxygenation of the phenols that are derived from lignin and in part to the deoxygenation and dehydration of the sugar molecules.

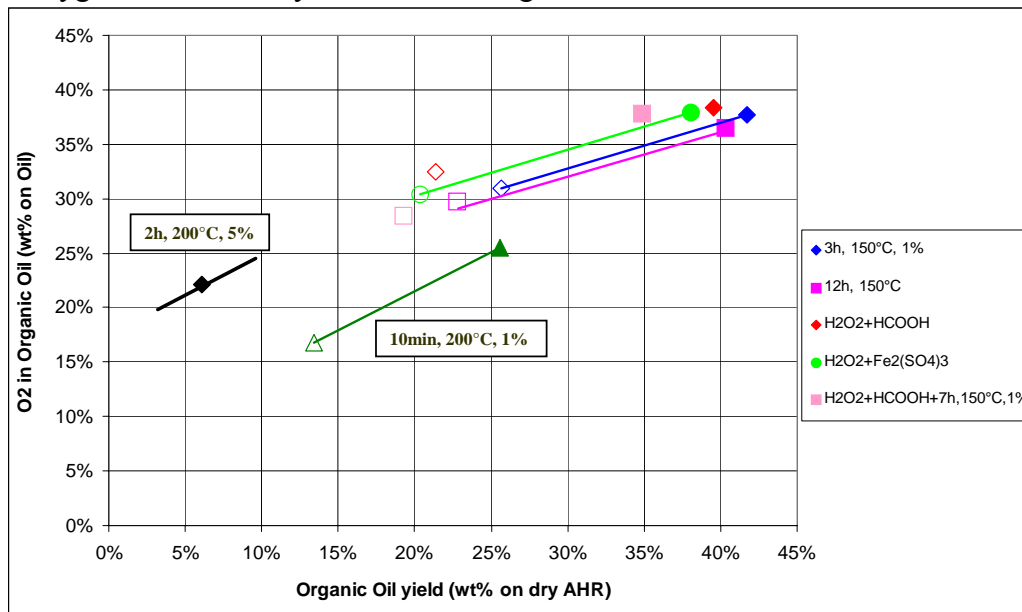


Figure 3. Organic oil yield vs Organic O₂ for AHRs and pretreated samples (solid symbol are from thermal runs while the empty are from catalytic runs)

Table 9. Semiquantitative GCMS analysis of biooil produced from AHRs

	Miscanthus 3h, 150 °C, 1% H ₂ SO ₄		Miscanthus 12h, 150 °C, 1% H ₂ SO ₄		Miscanthus 10m, 200 °C, 1% H ₂ SO ₄		Miscanthus 2h, 200 °C, 5% H ₂ SO ₄	
	Sand	ZSM-5	Sand	ZSM-5	Sand	ZSM-5	Sand	ZSM-5
	<i>Peak area %</i>							
AR	0.4	6.24	0.3	3.5	0.3	2.26	1.69	3.86
ALI	0.14	0.95	0.55	1.46	0.16	0	0.52	0.3
PH	28.09	50.3	36.49	54.86	27.39	46.16	66.7	67.04
FUR	0.84	1.75	2.32	1.03	0	0.67	3.05	3.53
AC	4	3.53	3.48	0.56	3.74	2.08	6.26	0.19
EST	0.78	0.41	1.03	0.76	0.29	0	1.12	2.19
AL	0.2	0.53	0.5	4.41	0	0.94	2.02	0.77
ETH	6.99	8.15	7.71	7.51	2.83	2.58	4.2	1.68
ALD	2.51	1.81	3.94	0.96	0.13	0.1	0	0
KET	13.38	8.89	13.91	5.47	1.17	0.76	0.95	0.81
PAH	0	2.66	0	2.82	0.32	2.01	2.41	6.85
SUG	10.1	0.39	7.17	0.47	0.58	0	0	0
NIT	2.28	2.31	2.71	3.89	1.39	0.27	1.17	1.97
UN	30.28	12.08	19.89	12.32	61.7	42.17	9.92	10.81



Table 10. Semiquantitative GCMS analysis of biooil produced from pretreated Miscanthus

	Misc. H ₂ O ₂ +Fe ₂ (SO ₄) ₃		Misc. (H ₂ O ₂ +HCOOH)		Misc. (H ₂ O ₂ +HCOOH) 150°C, 1%H ₂ SO ₄ , 7h	
	<i>Peak area %</i>					
	Sand	ZSM-5	Sand	ZSM-5	Sand	ZSM-5
AR	0	11.81	0.11	18.54	0	19.46
ALI	0.48	1.12	0	0	0.63	0.25
PH	18.46	31.08	4.15	13.13	5.38	18.11
FUR	0.89	3.38	0.29	4.15	1.04	4.22
AC	3.56	2.39	4.02	4.01	1.44	3.37
EST	1.07	1.18	0	0	0	0.25
AL	0.26	3.65	0.1	0.86	0	1.01
ETH	5.49	5.53	0	0.29	0.15	0.31
ALD	6.96	1.8	9.85	2.26	8.01	2.98
KET	17.29	11.89	7.6	7.56	8.73	9.28
PAH	0	4.9	0	4.86	0	6.31
SUG	17.2	0	2.58	0	10.11	0
NIT	2.47	4.05	0	1.58	1.08	0.82
UN	25.86	17.23	71.29	42.75	63.43	33.64

5. CONCLUSIONS

The acid hydrolysis and the oxidative pretreatment of biomass have a great impact on the actual structure of the biomass biopolymers as indicated by the characterization experiments performed in this study. The oxidative pretreatment appears to impact more the hemicellulose and the less crystalline parts of cellulose. Regarding lignin, the severity of the conditions appears to cause further aromatization of the lignin structure. Hydrolysis conditions affect also strongly the quality of the produced AHR as potential feedstock for further upgrading through biomass pyrolysis or catalytic pyrolysis. This has a direct effect on the quantity and quality of the produced bio-oil.

The results from this study showed that the thermal pyrolysis of the AHR can be used as an upgrading process if the AHR is produced under mild hydrolysis conditions, In this case oil yields up to about 40%wt (on AHR dry basis) can be produced. However, the quality of this thermal bio-oil is not satisfactory to be used as diesel miscible biofuel since it contains about 37%wt oxygen. The AHRs that are derived from more severe treatment conditions appear to be more coke like in nature, their pyrolysis yielding more solid product and the minimum liquid biooil.

For the upgrading of AHR through catalytic pyrolysis, the results showed that among the catalysts tested, the best catalyst is the ZSM-5. With this catalyst we can decrease the oxygen in the oil however, producing a lower yield of bio-oil. From the evaluation of the various AHRs only the AHR produced after hydrolysis at 200°C with 1%wt H₂SO₄ and for 10 min could be used for upgrading through catalytic pyrolysis. In this case a biooil with 13.5%wt yield and 15.5%wt oxygen can be produced. The pretreated samples produce less coke due to



their low lignin content and their biooil has higher oxygen content since the starting material also has more oxygen.

The organic biooil produced from the catalytic pyrolysis of AHR contains more aromatic chemicals such as phenols, aromatic and polyaromatic hydrocarbons due to their higher lignin content. The pretreated samples on the other hand contain more chemicals such as sugars, aldehydes and ketones all derived from the hemicellulose and cellulose of the feed.