Characterization studies of Waste- bio-derived feedstocks

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Abstract
The WAVES project aims on exploring new and emerging technologies in heterogeneous catalysis towards the production of aviation and road transportation fuels (i.e., gasoline, kerosene, diesel) via hydroprocessing (hydro-isomerization, hydrocracking or hydrodeoxygenation) of waste and/or renewable bio-feedstocks (vegetable oil, F-T waxes, algae oil and bio-oil) via the development of new and selective catalysts with tuneable properties. In the present study biomass pyrolysis oil from 5 different biomass feedstocks, have been collected and characterized in CPERI (elemental analysis, gross calorific value, composition, acidity, bulk density and moisture, etc.), in view of elucidating how each feedstock's varying properties matches the different needs for quality improvement - upgrading towards fuel production. An in-depth characterization of the 'major components' in the bio-oil feeds were performed with a, hyphenated high resolution chromatographic techniques like GCxGC-ToFMS.

1. Introduction

Lignocellulosic biomass is a promising sustainable source for the production of environmentally friendly bio-fuels and bio-chemicals. Biomass can be converted by thermal or biological processes into a range of energy carriers such as liquid fuels and synthesis gas. Lately research efforts are focused on the valorization of waste bio-feedstocks towards the selective production (via refining processes like hydroconversion, catalytic cracking etc.) of specific cuts of higher value, such as diesel and jet fuels. Thus, hydrocracking and especially hydroisomerization of long chain paraffins over novel, bifunctional catalysts are receiving increasing attention. Moreover, pyrolysis and in particular fast pyrolysis is a promising technology as it allows the transformation of solid biomass into a dense liquid energy carrier known as bio-oil or pyrolysis oil. In this case, hydrodeoxygenation (HDO) concepts are known promising approaches for the further upgrading of pyrolysis oil. Via the current WAVES project, new and emerging technologies are explored in heterogeneous catalysis towards the production of aviation and road transportation fuels (i.e., gasoline, kerosene, diesel) via hydroprocessing of waste and/or renewable bio-feedstocks (vegetable oil, F-T waxes, algae oil and bio-oil).
During biomass pyrolysis the bio-oil yield and its composition are affected by the biomass, the pyrolysis conditions (residence time and temperature) and the use of a catalyst [1,2,3]. Most importantly, the produced bio-oil is a mixture of various chemical compounds including carboxylic acids, carbonyl compounds, phenolics, sugars, water etc., produced from the rapid depolymerization and the chemical fragmentation of lignin, cellulose and hemicellulose during fast pyrolysis. Depending on its composition, bio-oil may have different applications, however in order to evaluate its potential uses, it is important to determine its composition both qualitatively and quantitatively [4].
The compounds that consist bio-oil belong to different chemical groups, rendering its complete analysis a challenging task [5]. Among the analytical techniques employed thus far, hyphenated chromatographic techniques appear to provide the most comprehensive analysis for such a complex mixture. In particular, GCxGC combined with ToFMS or FID has been employed with promising results, as it allows the qualitative identification of the majority of the existing compounds [6-8].
The present study includes the qualitative and quantitative analysis of bio-oils originating from different biomasses by GCxGC-ToFMS. A calibration method using an internal standard has been developed and employed for the analysis of bio-oils produced after the fast pyrolysis of five distinctively different biomass samples. The presented work highlights the ability of the GCxGC-ToFMS technique to characterize the bio-oils both qualitatively and quantitatively.

2. Experimental part

2.1 Materials

Five different biomass samples were collected from the local market and pyrolyzed in CPERI at a bench scale fixed bed reactor. The experimental apparatus along with a process diagram have been described in detail elsewhere [3].

2.2 Chromatographic analysis of bio-oils by GCxGC-ToFMS and GC-FID

The GC×GC analytical system was an Agilent 7890A GC with injector Agilent7683B series (Agilent Technologies, PaloAlto, CA, USA) connected to a Pegasus 4D time-of-flight mass spectrometer from Leco Instruments (St. Joseph, MI, USA). The first dimensional chromatographic separation was performed by an apolar column BPX-5 (5% phenyl polysilphenylene-siloxane) while the second dimensional column was situated in a secondary internal oven and was a BPX-50 (50% phenyl polysilphenylene-siloxane), both from SGE Analytical Science Pty Ltd (Australia). Cryofocusing by liquid nitrogen and a quad jet dual stage modulator (Zoex, Houston, TX, USA) was applied. Instrument control, data acquisition and data processing were done by the ChromaToF (Leco) software and custom Microsoft Excel spreadsheets. The ToFMS operated at an acquisition rate of 100 spectra/s and a mass range of m/z 45–400 amu. The carrier gas (He grade 5) flow rate was 1 mL/min; split injection of 0.5 μL sample solution at a split ratio of 1:20 and an injection temperature of 250 ºC. Total run time was 102.0 min.

For the purpose of quantification, the internal calibration method was followed. Phenol-d_6 was selected as IS and it was added at a constant concentration of 50 μg/g in a standard solution of 39 compounds. The standard solution consisted of 11 aromatic hydrocarbons, 5 PAHs, 1 aliphatic hydrocarbon, 4 furanoics, 4 carbonyl compounds (including cyclopentanones and aromatic aldehydes), 12 phenolic compounds and 2 anisoles (considered as ethers). The concentration of the standard solution ranged from 6 to 80 μg/g. For each of the 39 compounds, their relative response factor (RRF) value was determined and used thereof for their quantification, and that of structurally related compounds in bio-oil samples.

The analysis of acetic acid was performed on an HP5890II gas chromatograph equipped with an FID. The carrier gas was Helium at a flow rate of 2mL/min. The injection volume was 0.4μl on-column at a DB-WAX column and at an injector temperature of 200ºC. The total run time was 20min.

3. Results and discussion

The effect of the biomass type on the bio-oil quality is reflected at their different aqueous content and elemental analysis as presented in table 1. It appears that the woody biomasses result in bio-oils with lower aqueous content than the grassy biomasses.

Table 1: Elemental composition and water content of the bio-oils

	Bio-oil analysis (%wt)			
Biomass	*H_2O (%)*	*C (%)*	*H (%)*	*O(%)*
Pine	39,29	60,00	12,73	27,27
Cardoon	57,60	60,30	22,19	17,51
Olive kernel	33,39	64,19	14,81	20,99
Jatropha	44,52	62,17	14,54	23,28
Miscanthus	45,78	58,28	13,58	28,14

In the GCxGC-ToFMS analysis, the data acquisition, peak identification and group type classification were done as previously reported by our group [9]. In short, NIST05 library was used for the identification of the peaks and as identification criteria similarity of 700 and S/N ratio of 50 were established. Even with these limitations, the increased separation ability and sensitivity of the GCxGC-ToF-MS resulted in chromatograms with more than 400 peaks. The distribution of peaks identified and quantified in each sample are presented in table 2

Table 2: Distribution of peaks identified and quantified in bio-oils

Biomass	**Total number of peaks**	**Quantified compounds**	**Unidentified compounds**
Pine	869	340	240
Cardoon	468	244	90
Olive kernel	1377	673	266
Jatropha	891	311	234
Miscanthus	1034	426	272

An inherent advantage of GCxGC analysis is that the chromatograms maybe be considered as a 'map' of the sample, allowing an initial qualitative assessment of its composition, since peaks of similar structure elute in particular areas of the chromatogram. The elution area of each class of compounds is determined via classification. In this work the classification of the compounds was done by borderline group type classification. In total, seven discrete areas were determined on the chromatographic space corresponding to specific groups: 1) Acids and esters, 2) Aldehydes and ketones (including furanoics and cyclic carbonyls), 3) Hydrocarbons (saturated and unsaturated non-aromatic), 4) Aromatic hydrocarbons, 5) Phenolic compounds, 6) PAHs and 7) Sugars. The furanoic compounds eluted in between aliphatic carbonyls, so a clearly defined area could not be determined. The same applied for the guaiacols, syringols, anisols and catechols that were grouped together under the phenolics. The compounds that were not identified by the library and/or did not meet the required identification criteria were classified as 'unidentified'. The density of the peaks in each area is an indication of the abundance of the particular class of compounds in the sample.

The quantification method developed was based on the use of an internal standard, in particular phenol-d_6, and the analysis of a standard solution consisting of 39 compounds. The standard solution was analysed at five concentration levels for the determination of the linear range and the relative response factor of each compound. A detailed analysis on the quantification method can be found in detailed elsewere [10]. The developed quantification method allows an insight in the hereby presented bio-oils' composition, to the best of the authors' knowledge, to a greater extent than previously reported in the literature.

The chromatogram corresponding to pine bio-oil is presented in figure 1. The fast pyrolysis of pine yielded a bio-oil rich in furanoic compounds and in particular furanone and furfural as well as cyclopentanones as indicated by the peak density in the aldehydes and ketones area, while it is also very rich in phenolic compounds. This bio-oil also presents a high intensity peak in the sugars area, which corresponds to levoglucosan, a sugar anhydrite common in thermal bio-oils. The detailed quantification of this sample showed that its total determined concentration of carbonyl compounds was almost 7%wt. The phenolic content of this bio-oil amounts up to 8.6%wt and consists mainly of methoxy-phenols, which are a characteristic product of the pyrolysis of softwood lignin that is the main component of this biomass. To total determined concentration of this bio-oil amounted up to 21%wt.

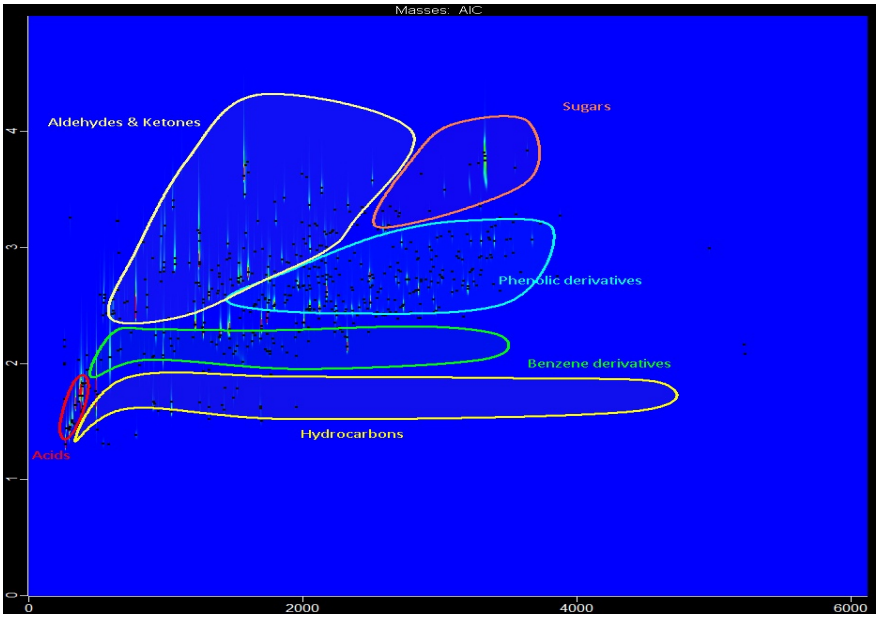

Figure 1: *GCxGC-ToFMS chromatogram of pine bio-oil*

The cardoon bio-oil shows a completely different chromatographic profile compared to pine bio-oil. The overall peak number is low, the carbonyl compounds are very few and only in the area of the phenolics a higher number peaks appear, while the levoglucosan peak is missing from the sugars area. A high intensity peak appears in the acids area, corresponding to acetic acid whose calculated concentration is 6.42%wt thereby being the most abundant compound in this sample. The total determined phenolic content of this sample was calculated as 4.5%wt and was attributed mostly to benzendiols. The carbonyl content of this sample was only 2%wt. The cardoon bio-oil had a very high aqueous content (table 1) which, combined with the absence of levoglucosan and the high acetic acid

content, are indications of a diversified pyrolysis route for this sample. Those differences are attributed to the increased ash content of this biomass that probably acted catalytically.

Table 3: *Quantitative results of pine bio-oil per compound and per group of compounds.*

Pine bio-oil			
Compound	**% w/w in bio-oil**	**Group**	**Total %w/w**
Acetic acid	3,55		
2(5H)-Furanone	1,98	AR	0,04
Phenol, 2-methoxy-	1,45	ALI	0,10
1,2-Benzenediol	1,39	PH	8,63
3-Furaldehyde	0,97	FUR	0,85
2-Cyclopenten-1-one, 2-hydroxy-	0,60	AC	3,55
2-Cyclopenten-1-one	0,55	EST	<0,01
Furan, tetrahydro-2,5-dimethoxy-	0,45	AL	<0,01
Phenol, 2-methoxy-4-methyl-	0,45	ETH	0,89
Phenol, 3-methyl-	0,41	ALD	1,63
1,2-Benzenediol, 4-methyl-	0,33	KET	5,33
2-Methoxy-4-vinylphenol	0,29	PAH	<0,01
Vanillin	0,26		
Eugenol	0,24		
4-Ethylcatechol	0,23		
Phenol, 3-methyl-	0,23		
Phenol, 4-ethyl-2-methoxy-	0,23		
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0,22		
Phenol, 2,5-dimethyl-	0,21		
Hydroquinone	0,21		
Phenol, 2-methoxy-4-(1-propenyl)-	0,20		
Total $_{\text{Top 20 compounds}}$ (wt.%)	14,45		
Determined wt.% of total bio-oil	21,04		
Determined wt.% of organic phase	34,66		

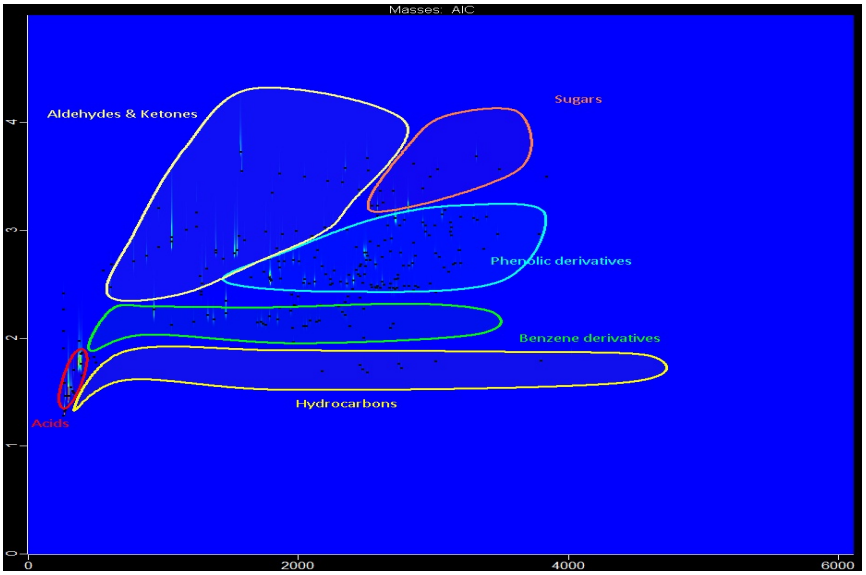

Figure 2: *GCxGC-ToFMS chromatogram of cardoon bio-oil*

Table 4: *Quantitative results of cardoon bio-oil per compound and per group of compounds.*

Cardoon bio-oil			
Compound	**% w/w in bio-oil**	**Group**	**Total %w/w**
Acetic acid	6,42		
Hydroquinone	0,87	AR	0,28
1,2-Benzenediol	0,76	ALI	0,04
Phenol	0,45	PH	4,50
2(5H)-Furanone	0,41	FUR	0,11
2-Cyclopenten-1-one, 2-methyl-	0,31	AC	6,42
Phenol, 4-ethenyl-, acetate	0,26	EST	0,26
Phenol, 3-methyl-	0,17	AL	<0,01
Phenol, 2,6-dimethoxy-	0,15	ETH	<0,01
1,2-Benzenediol, 3-methoxy-	0,13	ALD	0,07
Phenol, 2-methoxy-	0,13	KET	1,82
1,4-Benzenediol, 2-methyl-	0,13	PAH	0,08
Ethanone, 1-(2-furanyl)-	0,13		
4-Ethylcatechol	0,12		
2-Cyclopenten-1-one	0,12		
Phenol, 3-ethyl-	0,12		
Cyclopentanone	0,11		
2-Cyclopenten-1-one, 3-methyl-	0,09		
1,2-Benzenediol, 4-methyl-	0.06		
Resorcinol	0.06		
Phenol, 2,5-dimethyl-	0.06		
Total $_{\text{Top 20 compounds}}$ (wt.%)	11,07		
Determined wt.% of total bio-oil	13,59		
Determined wt.% of organic phase	32,05		

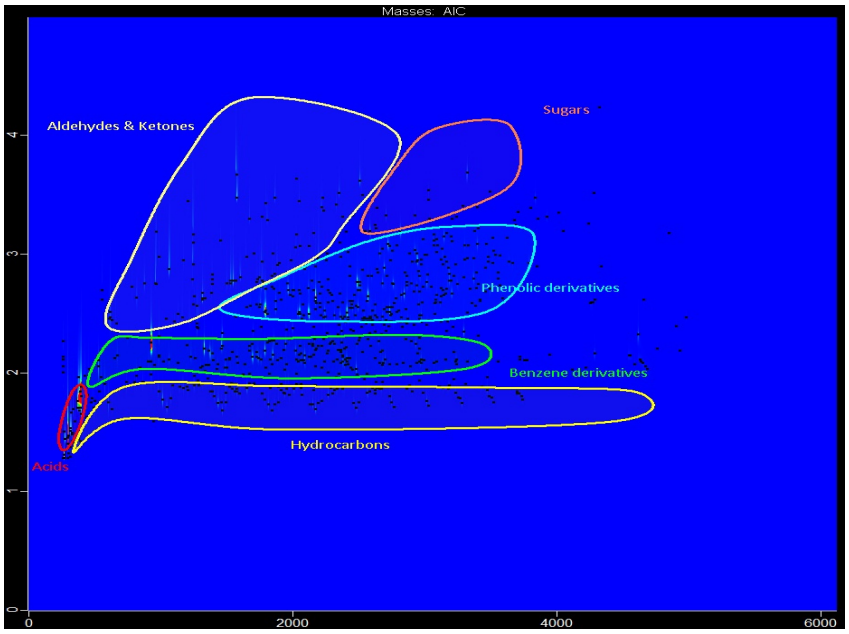

Figure 3: *GCxGC-ToFMS chromatogram of olive kernel bio-oil*

Among the analysed bio-oils, the olive kernel bio-oil had the highest number of peaks. As is evident from the chromatogram (figure 3) this bio-oils is very rich in phenolic and aromatic compounds while a fair amount of peaks appears in the hydrocarbons area. The presence of the latter could be attributed to the increased oil content of the olive kernels, since these hydrocarbons are mainly identified as linear hydrocarbons higher than C10 and alkyl derivatives of cyclic hydrocarbons, which could originate from the decomposition of triglycerides. However, these compounds could not be accurately quantified, with the developed method. As far as the rest of the compounds are concerned, guaiacol, syringol and benzendiol derivatives are prevalent among the phenolics. The concentration of the carbonyl compounds is very low. Among the aromatic hydrocarbons, toluene appeared to be the most abundant with a concentration of 0.07%wt.

Table 5: *Quantitative results of olive kernel bio-oil per compound and per group of compounds.*

Olive kernel bio-oil			
Compound	**% w/w in bio-oil**	**Group**	**Total %w/w**
Acetic acid	4,72		
1,2-Benzenediol	0,83	AR	0,32
Phenol, 2-methoxy-	0,35	ALI	0,73
1,2-Benzenediol, 3-methoxy-	0,30	PH	5,04
Phenol, 2,6-dimethoxy-	0,28	FUR	0,29
Phenol	0,27	AC	4,72
Phenol, 3-methyl-	0,22	EST	0,12
Hydroquinone	0,19	AL	<0,01
4-Ethylcatechol	0,19	ETH	<0,01
Phenol, 3-ethyl-	0,17	ALD	0,23
2(5H)-Furanone	0,16	KET	1,48
2-Cyclopenten-1-one	0,16	PAH	0,08
Benzaldehyde	0,15		
Phenol, 4-ethenyl-, acetate	0,11		
1,2-Benzenediol, 3-methyl-	0,09		
1,2-Benzenediol, 4-methyl-	0,09		
Phenol, 2-methyl-	0,09		
Phenol, 4-ethyl-2-methoxy-	0,08		
3-Furaldehyde	0,07		
2-Methoxy-4-vinylphenol	0,07		
Toluene	0,07		
Total $_{\text{Top 20 compounds}}$ (wt.%)	8,65		
Determined wt.% of total bio-oil	13,08		
Determined wt.% of organic phase	19,64		

The jatropha bio-oil chromatogram is presented in figure 4 and similar to that of cardoon bio-oil. The qualitative analysis of this sample showed that it contained a lot of nitrogen compounds, scattered in the chromatogram eluting close to oxygenated compounds of similar structure (e.g. pyridines eluted closer to the phenols). The presence of the nitrogen compounds can only be explained if the original biomass had a high N content, which unfortunately could not be confirmed by the available elemental analysis. The nitrogen compounds however were not quantified due to the absence of a similar compound in the standard solution, thereby lowering the total quantifiable percentage of this sample. However, among the quantified compounds acetic acid, phenol and 1,2 benzendiol were the most abundant.

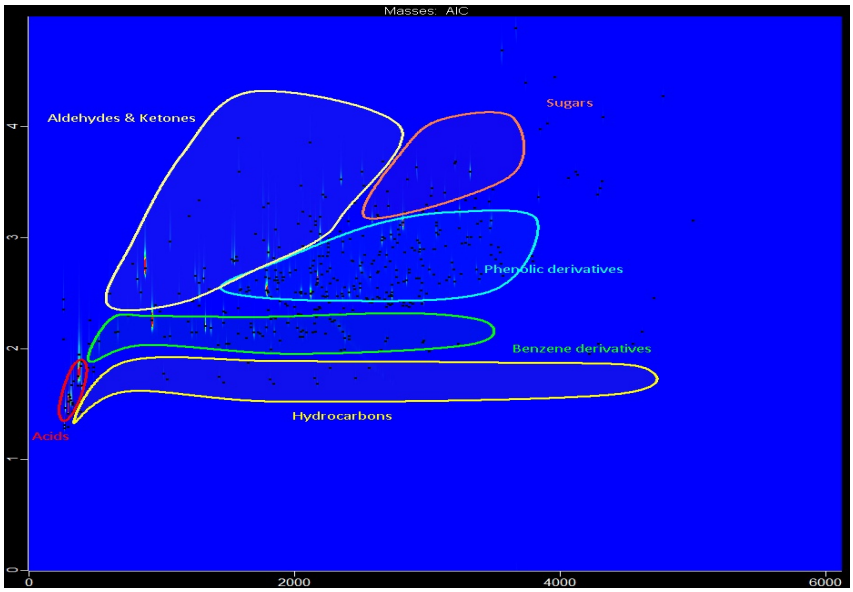

Figure 4: *GCxGC-ToFMS chromatogram of jatropha bio-oil*

Table 6: *Quantitative results of jatropha bio-oil per compound and per group of compounds.*

Jatropha			
Compound	**% w/w in bio-oil**	**Group**	**Total %w/w**
Acetic acid	3,88		
1,2-Benzenediol	0,81	AR	0,30
Phenol	0,43	ALI	0,15
Phenol, 2-methoxy-	0,41	PH	4,39
Phenol, 3-methyl-	0,33	FUR	0,39
Hydroquinone	0,21	AC	3,88
Phenol, 2,6-dimethoxy-	0,21	EST	<0,01
Phenol, 4-ethyl-2-methoxy-	0,13	AL	<0,01
1,2-Benzenediol, 3-methoxy-	0,13	ETH	<0,01
Toluene	0,11	ALD	0,06
2-Methoxy-6-methylphenol	0,10	KET	0,64
Phenol, 3-ethyl-	0,08	PAH	<0,01
4-Ethylcatechol	0,08		
1,2-Benzenediol, 4-methyl-	0,07		
2-Furanmethanol	0,07		
5-tert-Butylpyrogallol	0,07		
2-Cyclopenten-1-one, 2-methyl-	0,07		
2-Methoxy-4-vinylphenol	0,07		
2-Cyclopenten-1-one, 3-methyl-	0,06		
Furan, 3-methyl-	0.05		
Ethanone, 1-(2-furanyl)-	0.05		
			-
Total $_{\text{Top 20 compounds}}$ (wt.%)	7,41		
Determined wt.% of total bio-oil	9,90		
Determined wt.% of organic phase	17,84		

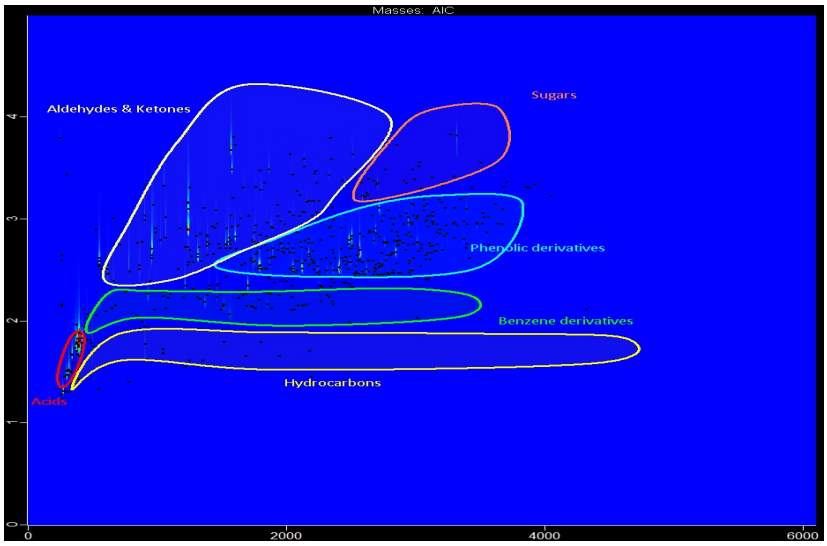

Figure 5: *GCxGC-ToFMS chromatogram of miscanthus bio-oil*

Table 7*: Quantitative results of miscanthus bio-oil per compound and per group of compounds.*

Miscanthus bio-oil			
Compound	**% w/w in bio-oil**	**Group**	**Total %w/w**
Acetic acid	8,65		
1,2-Benzenediol	1,19	AR	0,06
Phenol, 4-ethenyl-, acetate	0,99	ALI	0,08
Phenol, 3-ethyl-	0,57	PH	6,89
Phenol	0,53	FUR	0,47
3-Furaldehyde	0,51	AC	8,65
2(5H)-Furanone	0,46	EST	1,00
Phenol, 2-methoxy-	0,46	AL	0,04
Phenol, 2,6-dimethoxy-	0,34	ETH	0,09
Hydroquinone	0,32	ALD	1,04
1,2-Benzenediol, 3-methoxy-	0,32	KET	2,41
2-Cyclopenten-1-one	0,30	PAH	>0,01
Phenol, 3-methyl-	0,25		
2-Methoxy-4-vinylphenol	0,19		
2-Cyclopenten-1-one, 2-hydroxy-	0,16		
2-Furanmethanol	0,14		
Benzaldehyde, 4-hydroxy-	0,13		
1,2-Benzenediol, 3-methyl-	0,12		
Phenol, 2-methyl-	0,12		
2-Cyclopenten-1-one, 2-methyl-	0,12		
Vanillin	0,11		
Total $_{\text{Top 20 compounds}}$ (wt.%)	15,97		
Determined wt.% of total bio-oil	20,65		
Determined wt.% of organic phase	38,09		

The miscanthus bio-oil presented in figure 5, appears to have the majority of its peaks in the phenolics area. Very few peaks appear in both the hydrocarbons and aromatic hydrocarbons areas, while the carbonyl compounds are also few. As estimated by the quantification results, this sample has a very high acetic acid content of 8.65%wt and a total phenolics content of 6.89%wt with 1,2-benzendiol having the highest concentration, while the concentration of guaiacol and syringol derivatives was low. Regarding the thermal pyrolysis of miscanthus it could be noted that it shows a selectivity towards phenolic compounds as the determined carbonyls content is less than 50% of the phenolics one.

4. Conclusion

Fast pyrolysis is an effective process for biomass valorization as the resulting bio-oil can be considered both as an energy carrier and a renewable source of chemicals. Therefore detailed analysis of the bio-oil's composition and physicochemical properties is of paramount importance for its proper exploitation. GCxGC-ToFMS is a powerful analytical technique that can be employed for the analysis of complex mixtures such as bio-oils. Among the examined biomasses, olive kernel and miscanthus seem to result in bio-oils of added value, as they are both enriched in either aromatics or phenolics respectively that could be correspondingly exploited for the production of fuels or chemicals.

Acknowledgments

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