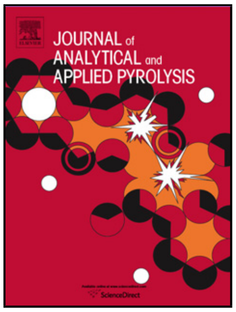

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Microwave assisted pyrolysis of crop residues from Vitis vinifera

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Highlights

- Crop residues from *Vitis vinifera* were pyrolyzed using a multimode microwave oven.
- A very fast pyrolysis was realized using Carbon as MW absorber.
- A high amount of bio-oil (34.9 wt%) was obatined in the presence of Fe as MW absorber.
- Large production of bio-char and gas were obtained using SiC as MW absorbers.

Abstract

A fast pyrolysis of crop residues of *Vitis vinifera* has been realized using a multimode microwave (MW) oven using various MW absorbers. The combination of absorber/reactor arrangement address the process towards a high formation of bio-oil (34.9 %) and gas (45.7 %) or the production of large amount of bio-char (up to 71.4%).

Bio-oils were collected as dark brown liquids with low viscosity and density. They were characterized through analytical and spectroscopic methods and the compounds present were identified and quantified. Large amount of acetic acid (up to 172.5 g/L) and appreciable amount of aromatics (up to 39.5 g/L) were formed in all experiments. Bio-oil obtained using carbon as MW absorber and set-up B showed the lower water concentration (39.5 wt%).

Bio-chars formed in all tests showed almost the same calorific values, close to that of commercial pellets.

The MAP of vine residues is a sound way to reduce environmental risks for their disposal and gave usefully chemicals, mainly acetic acid, aromatics and fuels through a fast pyrolysis process.

Keywords

Vitis vinifera, Microwave, Pyrolysis, Biomass, Quantitative bio-oil composition

1. Introduction

The primary energy demand was growing every year and in 2010 it was increased of 5% [1]. As a consequence the greenhouse gas emissions recorded a new peak, growing of 5.8% if compared to 2009 [2]. The increase of primary energy consumption between 2000 and 2009 was concentrated in few countries, mainly India and China, and it was driven by coal consumption even if this trend was decreased in the last years [3]. In Europe primary energy demand grew slowly in 2010 (3% if compared to 2009) [4] and the most interesting trend consists in an increased production from renewable sources [5].

In the same time the request of chemicals rises year by year and the use of renewable resource have been approached as a promising way to supply, at least partially, this demand [6]. Thermal treatments of biomass may give a contribution to the increasing request of energy and chemicals from renewable sources avoiding, in the same time, an increase in the production of CO_2 [7].

In the last 10 years Microwave assisted pyrolysis (MAP) gained a remarkable interest for processing waste/contaminate plastic materials in order to obtain fuels or raw materials [8-18]. Also MAP of biomasses was studied by several authors [19-22] to obtain high quality bio-oils thanks to a fast heating at moderate temperature (500-700 K) followed by a rapid quenching of the volatile products formed [23-25]. Furthermore MAP does not require the use of a finely milled feedstock because MW allows a volumetric heating of sample [26]. The presence of water inside the material may enhance the heating rate and mitigate the temperature reached during pyrolysis avoiding an advanced cracking degradation. Even if biomass may absorb MW, the addition of a MW absorber improve significantly the quality/quantity of the products formed [19]. Vine (*Vitis vinifera*) cultivation is one of the major business in the agrochemical industry [27] and they produce large amount of pruning and grape residues. In Italy, the annual pruning vineyard residues accounted to 1 oven dry ton (odt) per hectare with an estimated managing cost for the farms of 50 Euro per year [28]. There are a lot of available technologies to dispose these residues such as mechanical recycling or composting [29], but combustion is the most used. Several authors studied thermal pyrolysis of grapes bagasse to produce fuels with [30] or without a catalyst [31, 32]. In this work MAP of woody residues from vineyards was performed in a multimode batch oven using MW absorbers (carbon, iron powder, silicon carbide). A modified plant, containing a fractionating system inserted between the oven and the condensing system, was also tested. The aim of this work was to check an efficient disposal of waste residue of vineyards through a MAP process evaluating the yield of the pyrolyzed products using different reaction conditions. A great attention was devoted to the characterization of the three collected fractions (bio-char, bio-oil and gas) with particular attention to the liquid fraction.

2. Materials and methods

2.1 Materials and chemicals

Current-year shoots of *Vitis vinifera* (cv. cabernet) were collected on August 2015 from 10 years old plants growing in a vineyard located in Bolgheri, Tuscany, central Italy (43° 14’ 2” N, 10° 37’ 2” E, Altitude 96 m a.s.l.). Woody shoots were long 40-80 cm and they were cut into pieces of 2-3 cm and stored in sealed Erlenmeyer flask.

The carbon powder, employed as MW absorber was the solid from MAP of tires, metal wires depleted (C: 89.01 %, H: 0.83%, N: 0.48%, S: 2.0%). A more detailed characterization of the carbon powder was previously reported [16, 33].

Iron (fine powder, purity 99.9%, code 12310), SiC (400 mesh, purity 97.5 %, code 378097), hexadeutero dimethylsulphoxide (DMSO-d_6, isotopic purity 99.8%), analytical standard for GC-MS, acetonitrile (99.99%, GC grade), cyclohexane, chlorobenzene and 1,4-dimethylbenzene were supplied by Sigma Aldrich and used without any further purification.

2.2 Instruments and methods

Ultra Centrifugal mill ZM 200 (Retsch, Haan, Germany) equipped with a 12-tooth rotor and ring sieves or 0.75 and 0.25 mm trapezoid holes, respectively, was used for characterization of non structural carbohydrates, starch and lignin.

A Beckman Coulter DU 800 UV/Vis Spectrophotometer working at 280 nm was used to evaluate the lignin percentage.

Kinematic viscosity was detected, according to the ASTM method D 2854-00, using an Ostwald viscosimeter thermostated at 298.14 K with a Julabo model ME-18 V. Cyclohexane, chlorobenzene and 1,4-dimethylbenzene were used as standards [34].

Density was determined with a pycnometer thermostated at 298.14 K.

CHN analyses were performed using a Perkin-Elmer CHN/O analyzer model 2400 Series II, oxygen was calculated as difference.

Values of theoretical effective heat of combustion (EHC) were calculated according with Dorez et al. [35].

Proximate analysis was determined as follows: a weighted sample was heated at 378 K for 16 h to detect moisture; then volatile organic compounds (VOCs) were determined by heating the sample at 950 K for 6 min. Finally a total combustion of the sample was run and ash content was obtained by weighting the residue while fixed carbon was calculated by difference.

FT-IR spectra were collected using a Shimadzu model IRAffinity-1, equipped with a Golden Gate single reflection diamond ATR accessory supplied by Specac, for liquids analysis and a sapphire cell (length 10 cm) for gas analysis.

^{1}H-NMR spectra were recorded with a NMR Varian Mercury 400 using DMSO-d$_6$ as solvent. Residual hydrogens of the solvent were employed as internal standard and spectra were referenced to tetramethylsilane (TMS). Water suppression was employed to record ^{1}H-NMR spectra.

The water content was evaluated through ^{1}H-NMR spectroscopy using the standard addition method. Three spectra were recorded on the same sample: pure solvent; after the addition of a weighed sample of bio-oil, and after the addition of a known amount of Milli Q water. Integrals in each set of three spectra were referenced to the integral of the residual hydrogens of the solvent, used as internal standard [17, 24].

Gas chromatographic analysis were performed using a Shimadzu GC–MS QP5050A equipped with a capillary column Petrocol$^{\mathrm{TM}}$ DH 24160-U, (100 m length, 0.25 mm diameter, 0.5 µm stationary phase) using a 1:30 split ratio operating at 298 K for 15 min, then heated at 2.5 K/min up to 523 K and kept at this temperature for 15 min. A quadrupole mass (MS) detector, with a 70 eV ions generator, operating in the range 40–450 m/z was used. Other noteworthy peaks were not detected at higher temperature. Total ion chromatography (TIC) was obtained with a signal/noise ratio of five. Compounds were identified through standards, when available, or attributed using the MS spectra collected and the NIST mass spectral library. Concentration of each compound was determined as g/L using response factors experimentally detected, when the products were available, or calculated as reported by Bartoli et al. [38] according to an upgrade of the methodology previously proposed by Undri et al. [39].

Cellulose and lignin contents of vine samples were calculated as follow. Representative samples were stored in liquid nitrogen and then freezing-dried. A fine dried powder (< 0.25 mm) was obtained following the procedure proposed by Emiliani et al. [40].

Lignin was evaluated using the Klaison methodology. In the first step water extraction was run separating the supernatant from three subsequent incubations with hot water (358 K), one with ambient water (298 K), and then samples were dried (353 K) overnight. In the second step dried samples were cooled to room temperature, washed three times with ethanol, and then dried (378 K) overnight. The last step was the extraction with H_2SO_4 (72%) and the Klaison lignin was determined as the insoluble residue, after water and ethanol hydrolysis and drying.

α-Cellulose was detected following the sodium chlorite oxidation method [41]. Woody samples were dissected out from the main shoots and weighed into a labelled Teflon pocket. Samples (40–50 mg) were washed with $NaClO_2$ solution (1%) at 335 K for 30 h (five replacements of solution), and then transferred into a NaOH solution (17%) for 45 min at 300 K. Samples were neutralized rinsing with HCl solution (17%, three times for 5 min), with deionized water at 333 K (three times for 5 min), dried in an oven at 323 K for 72 h and then weighted. The α-cellulose content was estimated as the ratio between the weight of cellulose and the dry weight of the original sample.

2.3 MAP experimental set-ups

Pyrolysis were carried out in a MW oven designed and supplied by Bi.Elle s.r.l. (Italy), equipped with four magnetrons having a MW power of 6 KW, working at 2.45 GHz, Temperature measurement during a MAP experiment is quite challenging [42, 43]. A Raytek Thermalert MID infrared thermometer was used and a correlation between IR and mercury in glass thermometer were run using a silicon oil bath as described by Undri et al. [13]. The IR thermometer provides an average temperature of the biomass sample and the gas surrounding it during the experiment as reported in the previous papers. Two set-up equipments were used as shown in Figure 1.

INSERT Figure 1

Using the first arrangement, samples were placed in a 1000 mL borosilicate Erlenmeyer flask inside the oven and the flask was connected with two condensing systems cooled at 298 K and 263 K, respectively. Liquids were collected in another flask and gas in a gas holder. This equipment was called set up A. In the second arrangement, called set up B, a fractionating column, having a length of 0.2 m, internal diameter of 30.0 mm, filled with glass spheres with a diameter of 4.0 mm, was inserted between the oven and the condensing system.

Samples (100 g) were introduced in the Erlenmeyer flask and mechanically mixed with the MW absorber, the flask was introduced in the oven and heated using a MW power of 3 KW, according to the conditions reported in Table 1. All experiments were carried out in a N_2 atmosphere and pyrolysis was stopped when gas evolution was not further evidenced.

INSERT Table 1

At the end of the experiments when iron was the MW absorber, it was separated from bio-char using a magnet, then bio-char was weighted and characterized. Bio-chars containing carbon or SiC as MW absorber were characterized as recovered, taking into account the MW absorber present.

Each experiment was repeated three times and the mean value of these experiments was reported.

3. Results and discussion

3.1 Characterization of crop residues of Vitis vinifera

Representative crop residues of vine (*Vitis vinifera*) were initially characterized determining the amount of cellulose, lignin, and they proximate and ultimate analysis. They showed an interesting presence of cellulose (41.1 %) and lignin (23.2 %), a very low ash (4.4 %) and moisture (2.0 %) together with a high value of VOCs (75.4 %) and fixed carbon (18.2 %). Ultimate analysis showed a high content of carbon (45.5 %) and oxygen (47.8 %) together with a relatively amount of hydrogen (5.6 %), in agreement with proximate analysis and the high amount of cellulose.

3.2 Pyrolysis results

MAP experiments on crops of vine were carried out in a multimode MW batch reactor using different MW absorbers (carbon, iron, silicon carbide) and apparatus set-ups (A or B). Experimental parameters and results concerning the yield of bio-oil, bio-char and gas are shown in Table 1.

The use of carbon and set-up A (ID1) gave an yield of bio-oil over 30 wt% associated with a high yield of gas (up to 38.7 wt%) in agreement with previous results on other pyrolysis of biomass such as *Arundo donax* or short rotation coppice of poplar carried out using similar reaction conditions [17, 24]. The use of set-up B, that is inserting a fractionating system between the oven and the collecting system improved the residence time of high boiling materials inside the oven. In this conditions, using carbon as MW absorber (ID2) let to obtain an increased formation of bio-char (33.0 wt%) and a slightly lower formation of gas (34.7%) and bio-oil (32.1%). This behaviour may be attributed to the higher temperature reached in ID2 (644 K) and to a very low increase of the reaction time. The substitution of carbon with Fe as MW absorber, let to reach a higher reaction temperature independent on the set-up employed (A, 751 K in ID3 and B, 723 K in ID4). In these conditions an increase of biochar production (up to 36.9 wt%) and a decrease of gas fraction (down to 32.7 wt%) independent on the set-up employed was shown. Using SiC as MW absorber a lower temperature was reached using both set up A or B (475 K and 506 K, respectively) while the reaction time was increased (22 and 25 min, respectively). The lower efficiency of SiC as MW absorber, with respect to carbon and iron, is surprisingly considering the dissipation factor of the three materials. Infact, MW must be efficiently converted into heat by SiC, having a high value of dissipation factor. However this surprisingly behaviour has been reported in other pyrolysis experiments, and may be attributed to the shape of SiC particles or to the absence of impurities having a strong effect on the MW absorption [9]. Using SiC as MW absorber and set-up A (ID6) a very large production of bio-char was achieved (up to 71.4 wt%) associated with a low formation of bio-oils and gas, in agreement with previous results reported by Bartoli et al. [44] in the MAP of olive prunng residue. Furthermore the use of set-up B and SiC as MW absorber caused the largest gasification (up to 45.7%, ID 6).

3.3 Characterization of products

3.3.1 Bio-chars

Bio-chars were analysed through proximate and ultimate analysis, after iron removal or taking into account the amount of MW absorber present (Carbon or SiC, ID1, ID2, ID5 and ID6), in order to evaluate their main characteristics and results are shown in Table 2.

INSERT Table 2

All bio-chars showed interesting properties among which a high EHC, around 28 MJ/Kg, in agreement with the high amount of fixed carbon (close to 75 wt% with the only exception of ID4) and an amount of C, through elemental analysis, in the range of 78-85%. All samples had a relatively high ash content between 6.5 and 13.6 %, due to the concentration in the char of all the ash in the staring material.

These bio-chars may be employed as solid fuel or employed as substrate in a syngas coverter. It may be also employed for other applications such as soil remediation, carbon sequestration as well as absorber for gas or liquid purification or support for preparation of heterogeneous catalysts as reported by Nanda et al. [45]

3.3.2 Bio-oils

3.3.2.1 Physico-chemical properties and ultimate analysis

Dark-brown liquids having low density and viscosity were collected in all experiments, and their physico-chemical properties and ultimate analyses are reported in Table 3.

INSERT Table 3

Surpeisingly, bio-oils did not show any phase separation at room temperature but only after storage at 268 K and heating again at 298 K, two phases were formed, but this behaviour is just reported in other MAP of biomasses. Characterizations were run on bio-oil previous phase separations. All bio-oils showed a density in a close range around 1 mg/mL, and viscosities in the range among 2.33 (ID1) and 1.74 cp (ID6). Density and viscosity of bio-oils obtained with set-up A, that is in the absence of a fractionating system, was generally higher than those of bio-oil obtained with set-up B. These data were in agreement with the influence of the fractionating system to keep high boiling materials inside the oven, causing their further cracking. All samples showed low EHC_{calc} values, in the range of 7.5-8.1 MJ/Kg, and these low values were attributed to the large presence of water in the sample and to the high concentration of oxygenated compounds.

3.3.2.2 ^{1}H-NMR analysis

The composition of organic compounds present in bio-oils and the amount of water in the sample were evaluated through ^{1}H-NMR spectroscopy. The resonances of protons were attributed according to the ranges reported by Ozbay et al. [34] and to classical NMR data base [35]. The ranges were: δ 10.0-9.0 (aldehyde); 9.0-6.5 (aromatic, furan, and C=CH-OCC); 6.5-5.0 (phenolic OH or C=CH); 5.0-3.3 (CH_2-O-C; or CH_2-OOC; or Ar-CH_2-Ar); 3.3-2.0 (CH_3, CH_2, and CH linked to an aromatic ring); 2.0-1.6 (CH, CH_2 of alkyl groups; CH_2 and CH in β position to an aromatic ring); 1.6-1.0 (CH_2, CH_3 of alkyl groups, CH_3 in β−position and CH_2 and CH in γ-position to an aromatic ring or ethereal oxygen); 1.0-0.5 (CH_3 of alkyl groups or CH in γ-position or further of an alkyl chain linked to an aromatic ring). The collected spectra are shown in Figure 2, while the compositions of bio-oils as evaluated by integrals of the ^{1}H-NMR spectra are reported Table 4.

INSERT Figure 2

INSERT Table 4

The ^{1}H-NMR data (Table 4) showed a significant amount of substituted aromatic compounds (ethers, unsatured hydrocarbons and aldehydes) taking into account the integrals in the range 4.5-1.6 ppm. Mobile protons of carboxylic acids were not detected due to their exchange with the hydrogen of the solvent, but integrals of protons in α position to carboxylic groups were present in the region 2.5-2.3 ppm. Bio-oils contained a negligible amount of compounds having an alkyl moieties in agreement with the composition of biomass employed for these experiments.

Water content of bio-oils was evaluated by ^{1}H-NMR using internal standard technique as reported in experimental part and results are reported in Figure 3. Water content was in the range between 32.3% (ID4) to 45.6% (ID6), surprisingly it was lower in bio-oils obtained using the set-up B and carbon or Fe as MW absorber. These results may be explained assuming the concomitant water gas shift reactions between the water formed and carbon or char, catalysed by iron, when present or by a very rapid heat transfer from MW absorber to feedstock.

INSERT Figure 3

3.3.2.3 FT-IR ATR

Bio-oils were also analysed through FT-IR ATR and spectra are reported in supplementary materials (Figure 1SM). The presence of large amount of water in all bio-oils was confirmed by the wide band in the range of 3600-3200 cm-1 (ν_{OH}) while other bands in the range of 3600-3400 cm-1 were overwellmed by water bands. Bands due to alkyl mojety ($\nu_{C\text{-}H}$, 2900-2750 cm-1) were detected (ID5), as a proof of the presence alkyl moieties linked to aromatics or furans. In all spectra strong absorptions of carboxylic groups (free carboxylic acids and ester groups) were present in the range of 1800-1680 cm-1 ($\nu_{C=O}$) confirming the results obtained by $^{1H\text{-}NMR.}$ Further bands attributable to aromatics were shown as medium intensity absorptions in the range of 1680-1580 cm-1 ($\nu_{C=C}$).

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3.3.2.4 Quantitative GC-MS

Composition of bio-oils is a difficult task because a very large number of compounds are present and this happen also in samples from MAP of crop residues of vine. A GC–MS method was employed to identify the compounds present through their retention time and MS spectra. Concentration of compounds was calculated using their relative response factors (RRF), when available, while the RRFs of the other compounds were calculated according to the method proposed by Undri et al. [39] for GC-FID/MS and upgraded to GC-MS as reported by Bartoli et. [38]. The TICs of the GC-MS analysis of bio-oils are reported in Figure 4 where the peak of diphenyl, employed as internal standard, is marked by a star (*). The sixtyone most abundant identified compounds are reported in Table 5 with their experimentally found or calculated RRFs.

INSERT Figure 4

INSERT Table 5

GC-MS analysis let to identify more than 50% of compounds present, water depleted, with exception of ID6 where 85.1% of compounds were identified.

Acetic acid was the compound present in higher concentration but generally lower than that reported in MAP of *Oliva europaea* [44] or *Arundo donax* [17]. Its concentration reached a maximum of 130.5 g/L in ID3 when Fe was the MW absorber and set-up B was employed (Table 5) while the minimum concentration (75.5 g/L) was present in the bio-oil ID1 formed using set-up A and carbon as the MW absorber. One of the most striking results is found in ID6, where 85% of the bio-oil has been quantified by GC. This is substantially higher than the other 5 runs in the paper, and much higher than other MW pyrolysis studies, where typically 40-50% is volatile enough to get through the GC. This high percentage of compounds identified by GC-MS may be attributed to the contemporary use of SiC as MW absorber and set-up B. This combination causes a strong pyrolysis of low volatile compounds forming low boiling materials. This hypothesis is in agreement with the high yield of gas and the low presence of acetic acid, it was present at approximately half the amount of ID5 (same absorber, slightly different time, but different set-up B) while 1-hydroxy-2-propanone was strongly improved (19.4 g/l vs 0.1 g/l in ID5). Levoglucosan is also an intermediate initially formed from thermal degradation of cellulose but at the end of the experiment it is in very low concentrations (maximum of 2.6 g/L) due to its low thermal stability. Also furans derivatives (*i.e.* furfural, and 5-(hydroxymethyl)-2-furancarboxaldehyde) were detected but at concentrations lower than 10 g/L according to the low concentrations of other anhydrosugars.

Aromatic compounds were present in amount between 19.5 and 39.5 g/L as shown in Figure 5. Their concentrations were not particularly high with the maximum in the bio-oil obtained using SiC as MW absorber and set-up B (ID6, 39.5 mg/mL). The lower value obtained by GC-MS, if compared with those detected using NMR may be attributed to the presence of high molecular weigh aromatics that were not eluted by GC-MS while NMR detect all aromatics present in the sample. For instance the amount or aromatic present in ID4 was 5.3 % by NMR while a low amount (18.1 g/L, that is 1.81 %) was detected through GC-MS. This discrepancy may be attributed to the presence of aromatic oligomers having high molecular weight and not eluted by GC-MS. An analogous observation was reported by Undri et al. [39] in the analysis of bio-oil obtained from various feedstock, confirming the complexity of the analysis of bio-oils. A further support to this hypothesis is the relatively low amount of compounds identified, generally around 50 %, with the exception of ID6. In this last bio-oil the pyrolysis conditions (use of SiC and set-up B) promote a strong cracking of the feedstock with large production of biochar with respect to other absorbers and a higher amount of aromatics (39.5 mg/mL). Furthermore the identified aromatics were multi-substituted phenols such as vanillin, eugenol, isoegugenol or apocynin according with the above reported hypohesis and a not completed cracking process as happen in other biomass pyrolysis previous reported [24].

Useful chemical may be separated from bio-oils through selective extraction or distillation. For instance acetic acid may be selectively extracted from the mixture using a basic solvent than recovered from the solute by acidification and subsequent distillation. In the same way aromatics may be separated using a selective solvent such as sulpholane [46], N-methylpyrrolidone [47].

INSERT Figure 5

3.3.2.5 Yield of compounds

Other interesting information may be obtained by an evaluation of the yield, instead of concentration, of acetic acid and aromatics in bio-oils. Generally yields of the compounds present in bio-oils from *Vitis vinifera* are lower than those obtained using other biomass as starting materials.

Acetic acid was the product obtained with the highest yield, maximum 44.2 g/Kg when pyrolysis was carried out using carbon as MW absorber and set-up B.

Almost the same amount of acetic acid was formed using carbon as MW absorber and set-up B or iron as MW absorber and set-up A, while using SiC as MW absorber, independent on the set-up employed, yield of acetic acid was almost the same than using carbon and set-up A.

On the contrary the yield of aromatics was the highest using iron as MW absorber and set-up A, Figure 6, while it was strongly decreased using the set-up B. The highest yield of aromatics (11.3 g/Kg, ID3) was obtained when iron was the MW absorber using the set-up B. A different behaviour was shown with the other MW absorber because the set-up B gave higher yield of aromatics than set-up A.

These data show that many factors played a role in MAP influencing the yields and compositions of the bio-oils formed. As a consequence carbon and set-up B or iron and set-up A, let to obtain the better yields of acetic acid and aromatics in the MAP of crop residues of vine.

INSERT Figure 6

3.4 Gas

All gaseous fractions were analysed through FT-IR and spectra are shown in Figure 7. Thin bands were present in the range of 3750-3500 cm^{-1} in agreement with the presence of water vapour (ν_{OH}) while the presence of CO_2 and CO were confirmed by the strong bands at 2400 cm^{-1} (ν_{OCO}), and 2150-2000 cm^{-1} (ν_{CO}), respectively. The presence of light hydrocarbons such as methane, ethane, ethylene were evidenced by bands in the range of 3250-3000 cm^{-1} ($\nu_{CH=C}$) and 2950-2750 cm^{-1} (ν_{CH}) particularly in ID3 and ID6. The presence of light carbonyl compounds (such as formaldehyde or acetaldehyde) was evidenced by bands in the range of 1875-1750 cm^{-1} ($\nu_{C=O}$) in spectra of ID2 and ID5 while these absorptions were neglectable in the gas from other experiments, confirming the strong influence of MW absorber and experimental set-up on the products formed. The ratio between typical bands of CO_2 at 2400 cm^{-1} (ν_{OCO}) and carbonyl compounds at 1875-1750 cm^{-1} ($\nu_{C=O}$) was very close in all spectra.

INSERT Figure 7

4. Conclusions

Microwave Assisted Pyrolysis (MAP) of crop residues of vine was performed using different MW absorbers (carbon, Fe powder, SiC),) and two different experimental set-ups.

In all experiments clearly brown liquids were always obtained, having a density close to 1 mg/mL as well as low viscosity values (in the range of 1.88-2.33 cP). These data were lower than those of bio-oils collected from thermal pyrolysis of grapes bagasse in similar experimental conditions reported in literature. Generally the use of set-up A let to realize a very fast pyrolysis process (reaction time lower than 20 min) with the faster MAP when Fe was the MW absorber (ID3). Using SiC as MW absorber and set-up A let to realize the higher yield of bio-char (71.4 wt%). On the contrary the use of set-up B and the same MW absorber (SiC) gave a strongly deploy of bio-char yield (down to 31.1 wt%) but at the same time promoted a large gasification (up to 45.7 wt%).

The highest amount of bio-oil was obtained using iron as MW absorber and set-up A, while carbon as MW absorber gave slight lower yield of bio-oil.

GC-MS analysis of bio-oils, showed the presence of a large variety of compounds but the quantitative analysis showed that the total amount of detected compounds around 50% due to the presence of high molecular weight oligomers. Concentrations of aromatic compounds were lower that those observed in bio-oil obtained from MAP of other woody biomasses.

The amount of water was in the range between 32.3 wt% (ID4) and 45.6 wt% (ID6).

Crop residues of vine may be efficiently disposed through MAP obtaining several useful products such as acetic acid, hydroxypropanone and some aromatics, together with an high amount of bio-char as a function of the pyrolysis conditions selected. Furthermore the MAP process may be orientated to an increased production of one of three fractions with an appropriate combination of apparatus (set-up) and MW absorber.

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Figures

Figure 1: The two set-ups used during MAP experiments.

Figure 2: ^{1}H-NMR spectra of bio-oils from MAP of crop residues of *Vitis vinifera*, water signal suppressed.

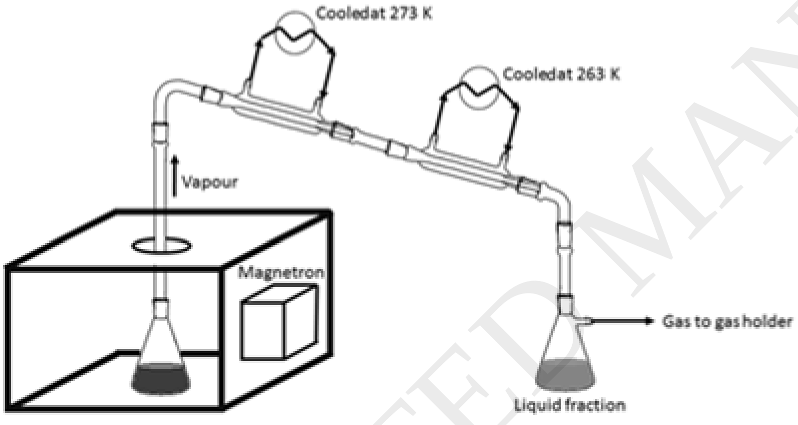
Figure 3: Water content of bio-oils collected from MAP of crop residues of *Vitis vinifera*

Figure 4: GC-MS analyses (TIC) of bio-oils from MAP of *Vitis vinifera*. Diphenyl, as internal standard, is marked with a star (*).

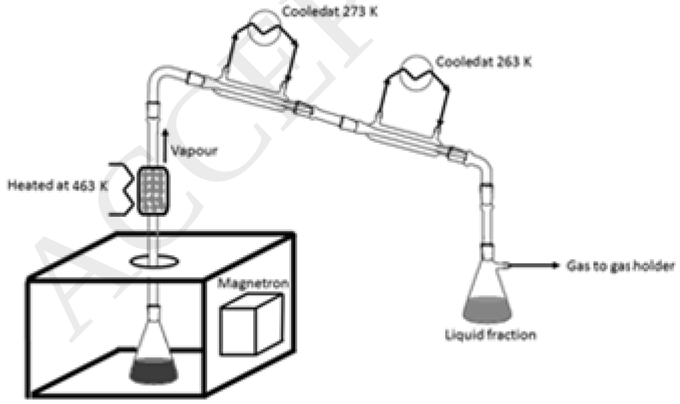
Figure 5: Acetic acid and aromatics compounds present in bio-oils from MAP of *Vitis vinifera* by quantitative GC-MS

Figure 6: Yield (g/Kg of biomass) of acetic acid and aromatics from MAP of *Vitis vinifera* residues

Figure 7: FT-IR spectra of gaseous fractions collected from MAP of *Vitis vinifera* residues



Set-up A



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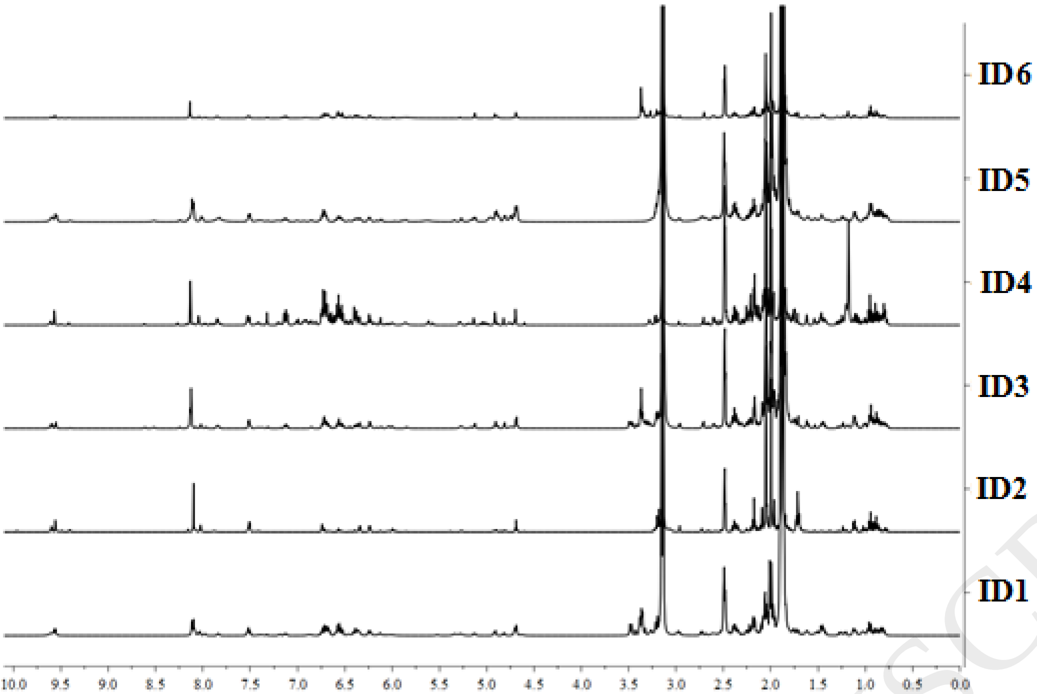
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6.0
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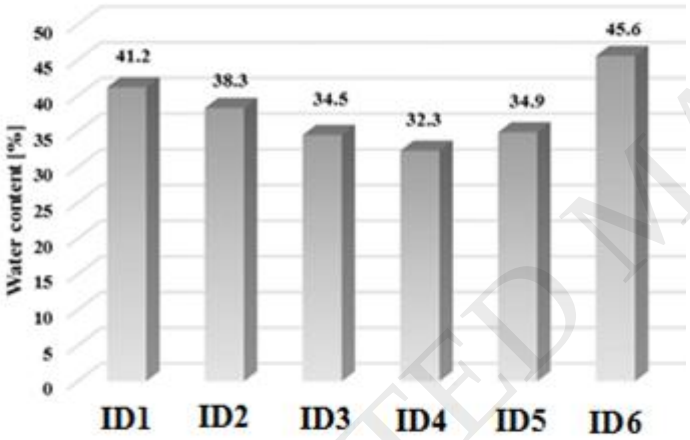
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40
35
30
25
20
15
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5
0
41.2
38.3
34.5
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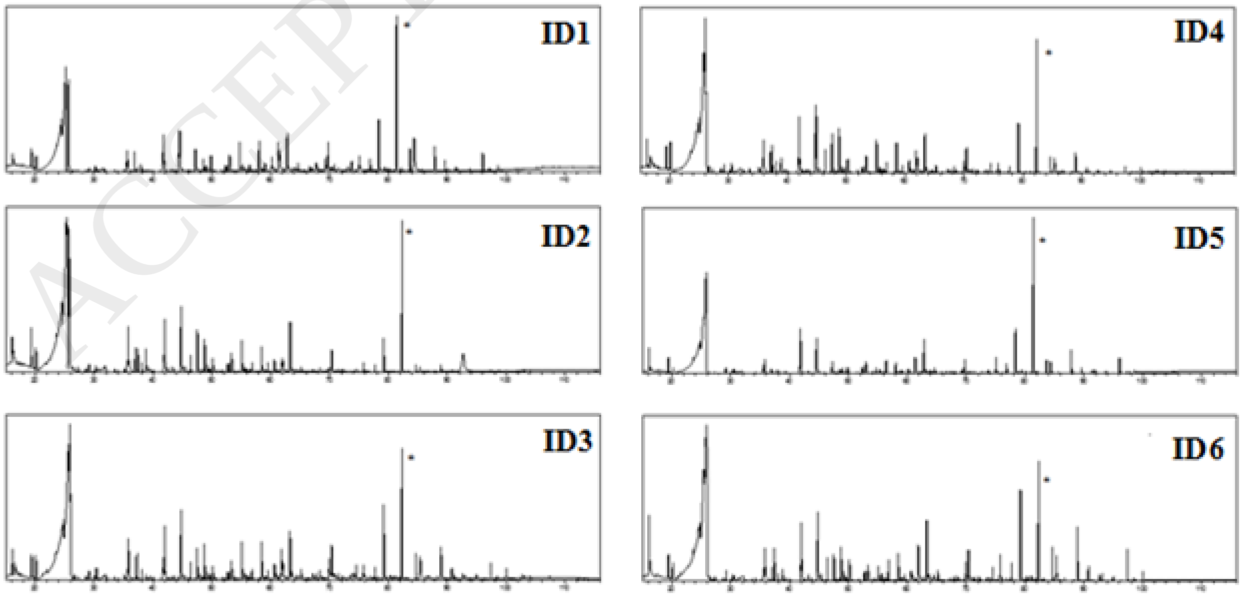
34.9
45.6
ID1
ID2
ID3
ID4
ID5
ID6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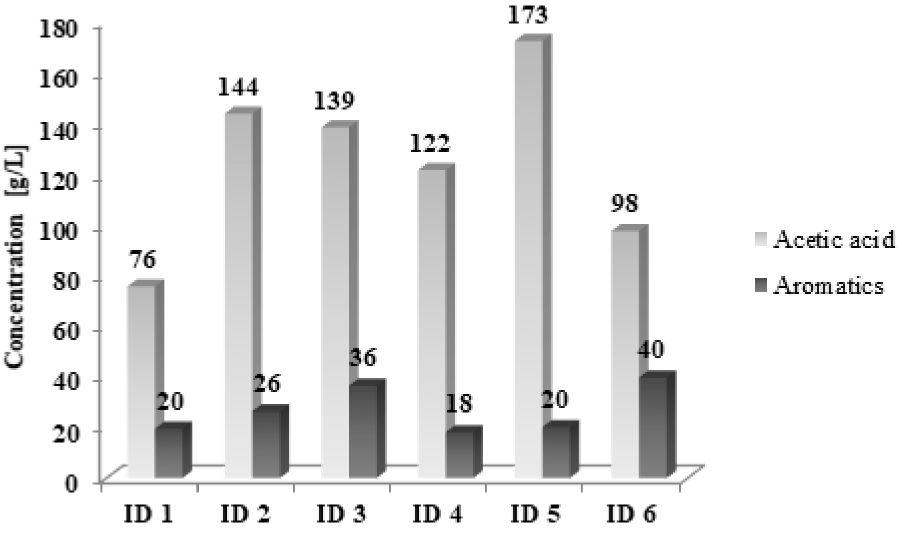
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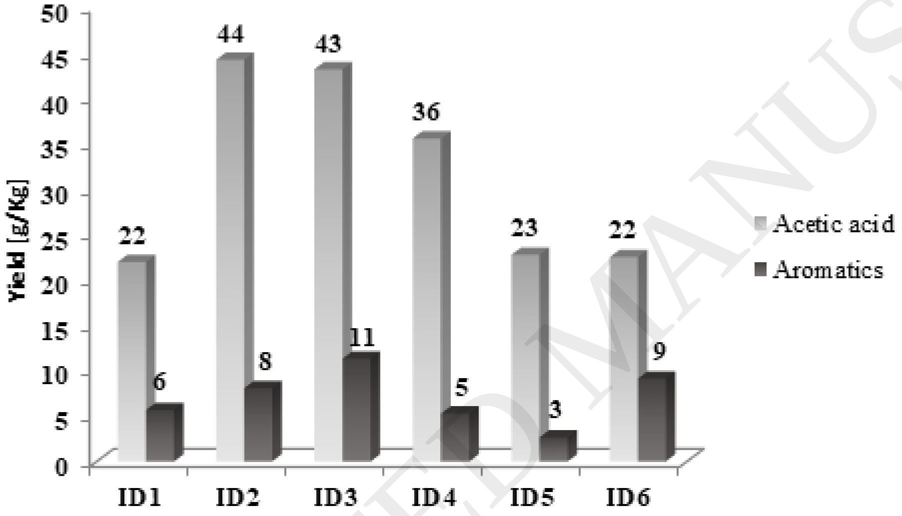
20
40
60
80
100
120
140
160
180
76
20
144
26
139
36
122
18
173
20
98
40
ID 1
ID 2
ID 3
ID 4
ID 5
ID 6
Acetic acid
Aromatics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5
10
15
20
25
30
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40
45
50
22
6
44
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43
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Aromatics

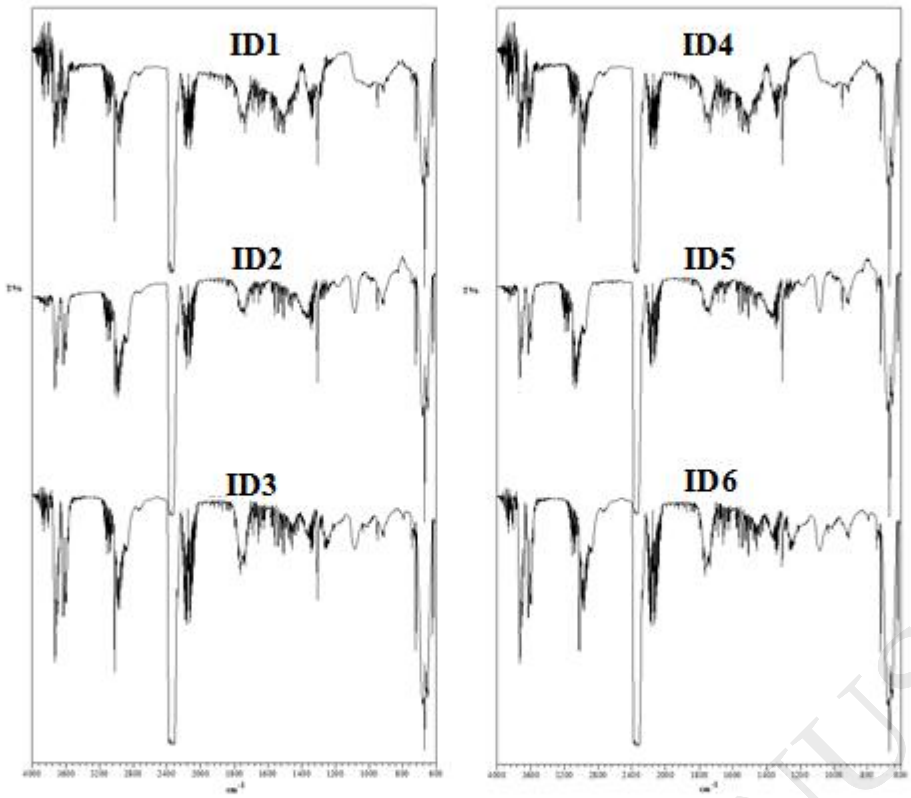

Table 1: Experimental conditions and mass balance of MAP of *Vitis vinifera*

	Set-up	Time [min]	Absorber		T	Products (%)		
			type	Adsorber/Biomass [wt/wt]	[K]	Bio-char	Bio-oil	Gas
ID1	A	16	Carbon	0.5	499	28.3	33.1	38.7
ID2	B	18	Carbon	0.5	644	33.0	32.3	34.7
ID3	A	14	Fe	0.5	751	30.7	34.9	34.3
ID4	B	20	Fe	0.5	723	36.9	30.4	32.7
ID5	A	22	SiC	0.5	475	71.4	15.3	13.3
ID6	B	25	SiC	0.5	506	31.1	23.3	45.7

Table 2: Ultimate and proximate analyses of char from MAP of *Vitis vinifera*

Proximate analysis [wt%]	Ultimate Analysis [wt%]	EHC_{calc} [MJ/Kg]

	Moisture	***VOCs***	***ASH***	***Fixed Carbon***		***C***	***H***	***O^a***	
ID1	3.1	14.1	8.8	74.0		80.4	1.1	18.5	28.1
ID2	3.4	13.1	10.1	73.4		84.9	1.0	14.1	29.7
ID3	3.0	12.0	11.9	73.1		78.8	1.4	19.8	27.5
ID4	3.1	15.9	12.0	68.9		85.1	1.4	13.5	29.7
ID5	3.3	9.4	6.5	74.8		83.2	1.6	15.2	29.1
ID6	3.1	7.9	13.6	75.4		85.7	1.8	12.5	29.9

a) Calculated as difference

Table 3: Physico-chemical properties and ultimate analysis of bio-oil from MAP of crop residues of *Vitis vinifera*

	Density [g/mL]	Viscosity [cP]	Ultimate Analysis (%)			EHC_{calc} [MJ/Kg]
			C	***H***	***O***^{a}	
ID1	1.14	2.33	21.4	7.8	70.8	7.5
ID2	1.05	2.01	24.3	5.3	70.4	8.5
ID3	1.12	1.96	23.2	6.8	70	8.1
ID4	1.04	1.88	22.9	7.9	69.2	8.0
ID5	1.16	1.93	23.1	7.3	69.6	8.1
ID6	1.01	1.74	23.1	6.4	70.3	8.1

a) Calculated as difference

Table 4: Composition (area %) of bio-oils from MAP of crop residues of *Vitis vinifera* through ^{1}H-NMR .

	Aldehydic protons	**Aromatic, furan, and C=CH-OCC**	**Phenolic "OH" and C=CH olefin**	**CH_2-O-C; CH_2-OOC; ring-join methylene, and Ar-CH_2-Ar**	**CH_3, CH_2, and CH linked to aromatic ring and in α–position to carboxylic groups or ethereal moiety**	**CH, CH_2 of alkyl groups; CH_2 and CH in β–position to an aromatic ring**	**CH_3 in β–position and CH_2 and CH in-γ position to an aromatic ring or ethereal moiety**	**CH_3 of alkyl groups or further of an alkyl chain linked to an aromatic ring**
δ (ppm)	**10.0-9.0**	**9.0-6.5**	**6.5-5.0**	**4.5-3.3**	**3.3-2.0**	**2.0-1.6**	**1.6-1.0**	**1.0-0.5**
ID1	1.0	3.7	1.5	0.1	43.6	45.2	1.9	2.9
ID2	0.3	4.7	2.4	1.5	34.2	51.3	2.7	2.9
ID3	0.8	4.7	2.3	8.9	31.8	46.3	2.3	2.9
ID4	0.6	11.8	4.7	2.1	32.1	37.1	7.5	4.0
ID5	0.4	3.8	1.7	3.2	35.8	50.4	2.1	2.6
ID6	0.7	5.3	2.8	3.1	30.9	51.4	3.4	2.4

Table 5: The main compounds (sixty one) identified in bio-oils from MAP of crop residues of *Vitis vinifera* by quantitative GC-MS

Compounds	RRF	Concentration [g/L]					
		ID 1	**ID 2**	**ID 3**	**ID 4**	**ID 5**	**ID 6**
Acetaldehyde	0.04	0.6	1.1	1.8	2.5	2.7	0.7
Methyl acetate	0.10	0.5	1.8	1.7	1.9	4.7	2.4
Formic acid	0.05	2.8	2.9	3.7	2.1	2.9	1.1
2,3-Butanedione	0.07	2.0	3.2	3.6	2.9	3.4	1.9
2-Butanone	0.11	1.2	2.1	1.6	2.4	1.7	0.6
Acetic acid	0.18	75.6	143.7	138.5	121.6	172.5	97.5
1-Hydroxy-2-propanone	0.09	11.9	9.8	21.6	7.7	0.1	19.4
Benzene	0.16	0.2	0.4	0.2	0.5	0.3	0.0
3-Methyl-3-buten-2-one	0.15	0.4	0.5	0.5	0.6	0.7	0.3
2-Pentanone	0.21	1.2	0.7	0.3	0.6	0.5	0.2
2,3-Pentanedione	0.14	0.4	0.8	0.6	0.7	0.9	0.7
3-Hydroxy-2-butanone	0.13	0.2	0.5	0.3	0.3	0.4	0.1
Propanoic acid	0.12	0.5	0.8	0.5	0.8	0.6	0.4
2-Propenoic acid	0.11	0.0	0.0	0.0	1.7	0.0	0.0
Methyl butanoate	0.23	0.3	0.3	0.4	0.2	0.3	0.1
Isopropyl Alcohol	0.29	0.3	0.4	0.4	0.4	0.3	0.2
Pyrrole	0.15	0.0	1.1	0.0	1.1	0.0	0.0
2-Methyl-2-butanone	0.26	1.0	1.3	1.6	0.0	0.9	0.0
2-Methylpropanoic acid	0.16	2.1	3.8	0.0	3.2	4.1	2.7
Cyclopentanone	0.25	1.5	5.3	2.8	0.0	1.3	0.7
2-Methylbutanoic acid	0.23	0.7	0.0	0.7	0.6	0.0	0.4
Furfural	0.13	1.9	1.2	2.2	1.4	1.8	0.9
3-Methyl-2-butanone	0.08	0.0	1.2	0.0	0.8	0.0	0.0
2-Methyl-1-pentanol	0.31	0.1	1.7	0.5	0.3	2.8	0.0
1,2-Ethanediol, diacetate	0.11	0.1	0.0	0.0	1.9	0.0	0.0
Oxopropanoyl acetate	0.39	2.2	0.0	0.5	0.0	0.0	0.0
2-Furanmethanol	0.25	0.0	0.0	3.2	4.8	3.3	2.8
5-Methyl-2(3H)-furanone	0.20	3.1	7.9	6.0	6.0	7.7	4.1

Ethylbenzene	0.36	0.2	0.7	3.0	1.6	1.7	0.0
Butyrolactone	0.19	0.0	1.5	1.1	1.9	0.6	0.0
3,3-Dimethoxy-2-butanone	0.25	0.0	0.0	0.0	4.6	0.0	0.0
1-(2-Furanyl)-ethanone	0.24	0.0	3.7	2.8	3.9	3.6	0.0
2,5-Hexanedione	0.27	0.8	1.2	0.8	1.0	1.3	0.8
Cyclohexanone	0.31	0.5	0.8	0.4	0.6	0.0	0.0
3-Methylcyclopentanone	0.33	1.9	0.0	1.8	0.0	0.0	0.9
Oxobutyl acetate	0.28	0.4	0.6	0.6	0.5	0.7	0.6
5-Methyl-2-furancarboxaldehyde	0.24	0.4	0.8	0.8	0.7	1.0	0.9
4,6-Dimethyl-2H-Pyran-2-one	0.52	0.0	0.0	0.0	0.0	2.7	2.2
3-Methyl-2-cyclopenten-1-one	0.32	2.3	0.0	2.3	0.0	0.0	0.0
α-Methylstyrene	0.47	0.0	0.0	0.4	0.0	1.3	0.0
Benzofuran	0.45	0.7	0.0	0.0	0.0	0.0	1.8
4-Methyl-5H-furan-2-one	0.26	2.9	4.2	2.5	2.8	2.7	1.4
3-Ethyl-2-hydroxy-2-cyclopenten-1-one	0.37	1.4	2.0	3.6	1.6	0.2	0.4
Indene	0.57	1.2	1.8	0.0	1.0	3.3	1.0
5-(Hydroxymethyl)-2-furancarboxaldehyde	0.28	2.6	3.2	0.0	2.1	0.0	0.0
Maltol	0.27	3.1	4.5	3.9	3.4	5.6	3.9
2,6-Dimethylphenol	0.48	0.1	0.6	0.0	0.2	0.9	0.3
1,4-Dimethoxy-benzene	0.44	1.9	3.1	0.2	1.8	3.0	0.7
Pyrocatechol	0.32	2.9	3.5	0.0	2.5	3.5	1.7
3-Methyl-1,2-benzenediol	0.42	1.2	1.6	0.3	1.1	1.6	0.4
4-Ethyl-2-methoxy-phenol	0.55	0.0	2.1	0.0	0.7	0.0	0.0
4-Hydroxy-2-methylacetophenone	0.55	1.2	1.4	0.5	0.3	2.4	2.0
2,3-Hexanedione	0.27	1.0	1.0	0.5	0.5	1.6	1.1
Eugenol	0.63	4.3	5.7	2.3	3.5	7.8	5.6
3,4-Dimethoxyphenol	0.45	0.2	0.0	1.7	0.0	0.5	0.2
Levoglucosan	0.38	1.5	1.9	0.5	1.0	2.6	1.5
Apocynin	0.55	6.6	2.5	0.0	3.0	0.0	0.0
Levulinic acid	0.38	0.7	0.0	0.0	0.0	0.0	0.7

Acetophenone	0.66	0.4	3.0	0.4	0.4	0.0	0.0
Isoegugenol	0.64	0.0	0.9	0.0	0.0	1.1	0.0
Vanillin	0.34	1.8	3.4	5.2	0.4	6.7	3.8
Total assignment [wt%]		50.1	50.0	60.2	59.4	53.2	85.1

a) Total assignment was calculated with formula: 100*(summa of weight of assigned compounds-weight of water)/(1 mL bio-oil)