THEORETICAL PRINCIPLES OF PYROLYSIS OF LIGNOCELLULOSIC BIOMASS

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Abstract

Pyrolysis of lignocellulosic biomass is one of the currently investigated technologies applicable in the production of advanced biofuels. The desirable product of pyrolysis is pyrolysis bio-oil, which can become a precursor of the 2nd generation biofuels. The yield and composition of bio-oil depends on the mechanism of pyrolysis of the lignocellulosic biomass that is quite complex and strongly affected by the composition of biomass and pyrolysis process conditions, which determine the course of the fission reactions. Thus, by changing production conditions, the yields and chemical and physical properties of the desired products, such as gas, bio-oil or char can be varied. The scope of the work is (i) characterization of lignocellulosic biomass in terms of its composition, (ii) basic description of pyrolysis reactors and (iii) discussion of mechanism of pyrolysis.

Biomass

Biomass is an organic material obtained by sunlight-driven reactions between carbon dioxide and water in a process known as photosynthesis. Reaction products are mainly carbohydrates that form the building basis of plants. Solar energy needed for the photosynthesis to take place is saved in the form of chemical bonds between atoms in the structure of the molecules. Lignocellulose biomass consists of three major components: cellulose, hemicellulose and lignin.

Cellulose is the major constituent of plant cell walls and its content in biomass reaches up to 50 %wt. The polymeric structure of cellulose consists of glucose monomeric units linked β-(1,4)-glycosidic linkages. From the perspective of the energy stability, which is given by Van der Waals forces acting between different parts of the polymer, the weakest point in the glycosidic structure is the C-O bond. Long cellulose polymer chains are bound by hydrogen bonds to form a microfibril structure[1,2,3].

Hemicellulose comprises other polysaccharides in biomass, representing from the 15 to 35 %wt of biomass. Hemicellulose is a complex branched polymer which exhibits variations in composition and contains from 2 to 4 kinds of carbohydrates. Units of monomers contained in the hemicellulose may be divided into the following groups: pentose, hexose, hexuronic acid and deoxyhexose[1]. The main chain of hemicellulose contains one kind of sugar (homopolymer), which is represented e.g. xylan, or two or more types of carbohydrates (heteropolymer) e.g. glucomannan. xylan (polymer of xylose) is the dominant species of the polysaccharide in the hemicellulose of wood[4,5].

Lignin is the third major component of lignocellulose; its content in biomass ranges from 10 to 35 %wt. It is a highly-branched polymer of propyl and phenyl groups, formed by polymerization of three monomers (monolignols): p-coumaryl, coniferyl and sinapyl alcohol. The main function of lignin in lignocellulose is to bond the fibres of cellulose and hemicellulose, and thereby deliver strength to the timber[6].

Biomass pyrolysis

Pyrolysis of biomass is a thermal process resulting in thermal destruction / decomposition of organic molecules (polymers). Key characteristics of the pyrolysis process include heating of the material in the absence of air at temperatures higher than 300 °C. During the process, three main products are formed – gases, bio-oil and char. Depending on the pyrolysis temperature and heating rate, three types of pyrolysis processes are distinguished – conventional, fast and flash pyrolysis. Their main reaction conditions are shown in Table I.

At low reaction temperatures (300 °C), the yield of char is up to 60 %wt and the yield of bio-oil is about 30 %wt. Slow conventional pyrolysis has been used for a very long time to produce charcoal[3,7,8].

Fast pyrolysis is performed at temperatures up to 600 °C. The yield of liquid bio-oil after condensation of vapours and aerosols is in the range of 60 to 75 %wt. Yields of solid char and gas are in range from 15 to 25 %wt and from 10 to 20 %wt, respectively [9,10].

Table I
Types of pyrolysis processes

Pyrolysis type	Temperature (°C)	Heating rate (°C/min)	Reaction time	Bio-oil yields (%wt)
Conventional	300-500	10	5-30 min	30
Fast	<600	100	2 s	60-75
Flash	700-1000	1000	0.5 s	75-80

The mechanism of pyrolysis of lignocellulose biomass is quite complex and is strongly dependent on (i) the composition of the biomass (cellulose, hemicellulose, lignin), (ii) the pyrolysis process conditions which heavily influence the course of the fission reactions, (iii) the pre-treatment of biomass and (iv) the presence of a catalyst. A general mechanism of biomass pyrolysis is shown in Figure 1[1,2,11].

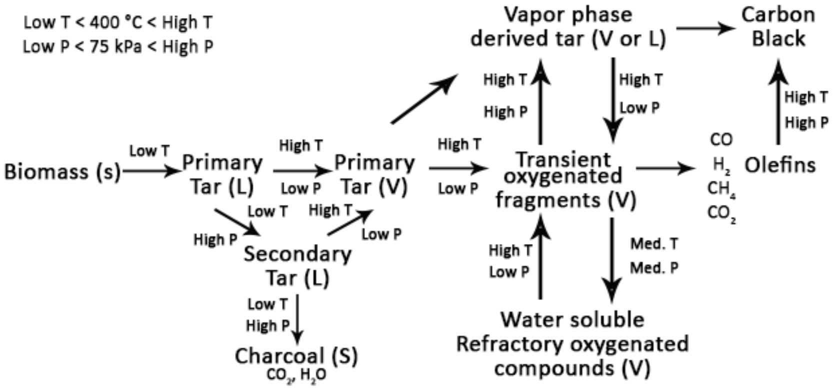

Figure 1. Mechanism of biomass pyrolysis (S-solid, L-liquid, V-vapour)[11]

The first step of pyrolysis of lignocellulosic biomass is its dehydration. This process takes place at low temperatures around 300 °C and causes the removal of water. Temperatures higher than 300 °C cause decomposition of biomass to produce a primary bio-oil.

Secondary depolymerisation reactions take place in the vapour phase because of the severe reaction conditions such as high temperature and low pressure. In the vapour phase, cracking reactions of the primary oil occur which result in the formation of intermediate oxygenated compounds consisting of a mixture of furan, acetic acid, methanol and other oxygenates. The next step is further thermal cracking of the intermediate oxygenates in the vapour phase, to produce hydrogen, methane, carbon monoxide and dioxide[1,10,12].

Pyrolysis of cellulose affords large amounts of cyclic compounds. One of the most important anhydrides formed is levoglucosan (1,6-dehydro-β-D-glucopyranose). It has been shown that the amount of levoglucosan present in the products of pyrolysis under reduced pressure was 20 to 60 %wt, as opposed to other carbohydrate-derived anhydrides, such as 2,3-dehydro-D-mannose, 1,6-dehydro-β-D-glucofuranose amounting to less than 1 %wt[13-16].

The mechanism of cellulose pyrolysis is complex and it can be described by a range of parallel reactions in which reaction conditions affect yields of each product. A mechanism of cellulose pyrolysis, that was proposed by Shen and Gu [15], is shown in Figure 2.

The experiments of cellulose pyrolysis were conducted in the temperature range of 400 to 900 °C in a fixed bed reactor. It was determined that the formation of levoglucosan begins at 450 °C and finishes at 650 °C. Levoglucosan maximum yield was achieved at 580 °C and was 58.7 %wt of the total mass of pyrolysis oil produced. Temperatures higher than 600 °C were shown to result in a significant decrease in the levoglucosan yield due to its further transformations. This is accompanied by a sharp increase in the content of lighter compounds[17,19].

In the process of cellulose pyrolysis, hydroxyacetaldehyde is formed by bond cleavage between C1 and C2 atoms of glucopyranose (D glucose), which is energetically more favourable than the cleavage of bonds between C2 and C3 atoms due to the shorter bond between C1 and C2 atoms[15]. According to Richards[20], hydroxyacetaldehyde does not arise from secondary cracking of levoglucosan, but is formed by reverse Diels-Alder reaction.

Pyrolysis of levoglucosan leads to the formation of lighter oxygenated products such as hydroxylacetoaldehyde and acetol[19]. According to Pikorza[22], during fast pyrolysis of cellulose in a fluidized bed reactor, hydroxylacetaldehyde is formed in a yield of 18 %wt, which attains its maximum at 610 °C. The experiment with pyrolysis of Whatman filter paper afforded hydroxylacetaldehyde yield of 3 to 19 %wt at reaction temperatures 450-930 °C[21].

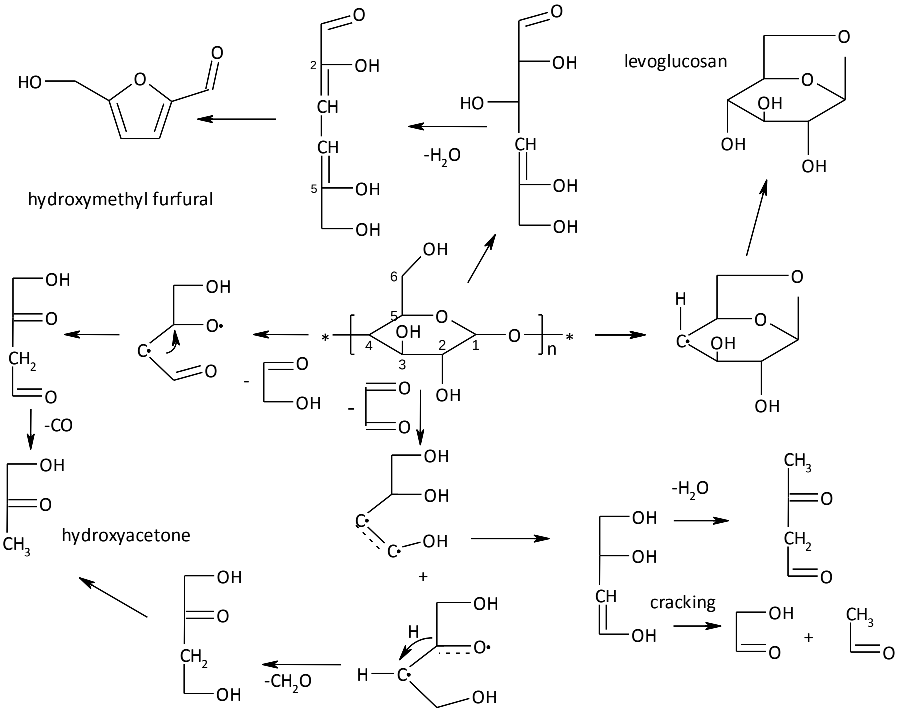

Figure 2. Cellulose pyrolysis mechanism[15]

Pyrolysis of hemicellulose and the composition of the products are discussed less than pyrolysis of cellulose, because of the lower abundance in biomass and the larger structure complexity[15]. Many researchers focused on determining the composition of each product phase in dependence on the used feedstock representing hemicellulose. D-xylose and O-acetyl-4-O-metylglukoronoxylan were used as reactants. The cracking mechanism of these compounds together with xylan has been shown by Shen and Gu[18] – see Figure 3.

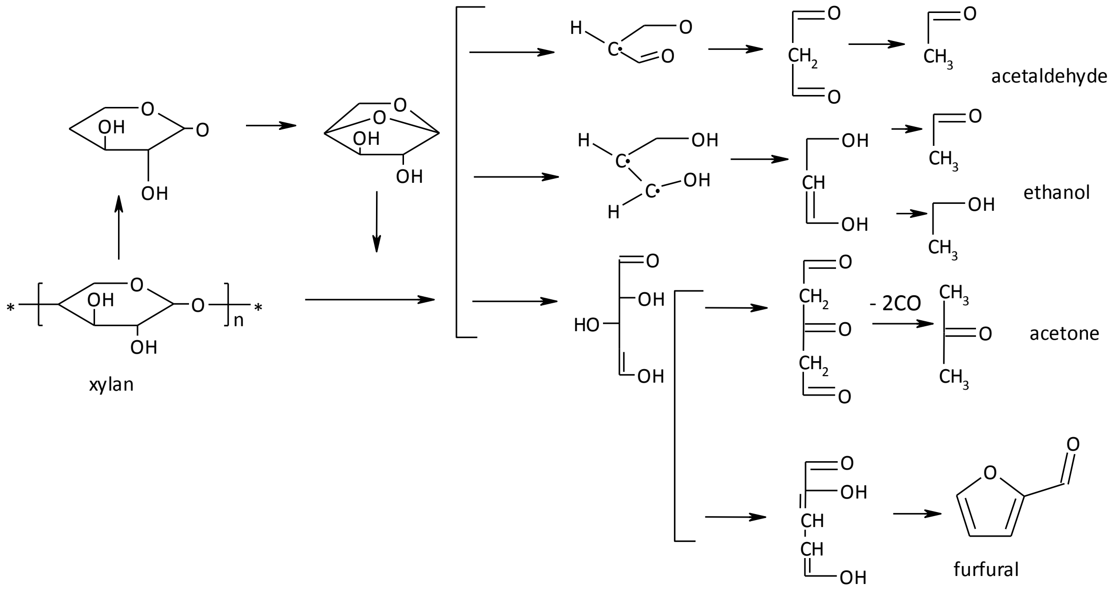

Figure 3. Xylan pyrolysis mechanism[15]

According to Shen and Gu[18], in the first pyrolysis step, the polymer structure of xylan is transformed into the monomeric units of 1,4-dehydro-D-xylanopyranose. The following reactions are accompanied by the formation of hydroxyacetaldehyde and glyoxal. Stabilization of the intermediate is performed via creation of a double bond or a rearrangement of a hydrogen atom, and followed by removal structural units to form ethanol and acetaldehyde.

Formation of furfural, reported also for cellulose pyrolysis, is accompanied by the opening of xylan monomer cyclic structure, dehydration of this intermediate structure leads to the formation of furfural, performed by the reaction of C2 and C5 atoms. Other pathway is characterized by the loss of two molecules of CO from the intermediate structure and formation of acetone. The composition of the pyrolysis products is significantly influenced by xylan branched structures, such as O-acetylxylan or O-acetyl-4-O-metylglucoronoxylan originated. Pyrolysis of O-acetylxylan leads to the formation of small oxygenated compounds, such as CO_2, acetaldehyde and acetic acid. Further, the formation of acetic acid occurs also upon pyrolysis of O-acetyl-4-O-metylglukoronoxylan, which is accompanied by formation of 4-metyl glucuronic acid and its cleavage affords methanol, formaldehyde, CO and CO_2, followed by decarbonylation of other products[23].

Pyrolysis of lignin yields more char and aromatics compounds in the liquid product in comparison with the pyrolysis of cellulose and hemicellulose when pyrolyzed at the same conditions. Lignin is the most thermostable component of lignocellulose, which decomposition starts at temperatures from 290 °C[24]. Lignin pyrolysis products can be divided into the following groups according to their chemical composition: (i) phenolic, (ii) xylene, (iii) pyrocatechol and (iv) cresylic compounds. Formation of phenolic and cresylic structures is caused by cleavage of the methoxy group from guaiacol and syringol structures, followed, in case of cresylic structure, by methylation. There is also a formation of hydrogen, hydrocarbons and acids[3].

Upon cleavage of the methoxy group off the aromatic ring structure of guaiacol and the subsequent reaction of the resulting phenolic structure and the methyl radicals, cresylic structure is formed. Cleavage of the CH_3- from the methoxy structure and the subsequent reaction between the formed oxygen radical and a phenolic structure causes the formation of pyrocatechol. Formation of methane, carbon dioxide and carbon monoxide is caused by the presence of free oxygen, hydrogen, and CH radicals in the system[13,25,26,27].

Results of thermal cracking of lignin from ground wood at a temperature of about 600 °C and a residence time of about 50-120 seconds in a closed reactor showed that the yield of bio-oil was about 30 %wt. The yield may be increased to 40 %wt during pyrolysis in the temperature range 350-600 °C. By using a flow reactor for pyrolysis of lignin, a yield of bio-oil in a range from 32 to 43 %wt can be achieved in the temperature range from 475 to 825 °C[25]. The maximum bio-oil yield is achieved at a temperature of 630 °C. A mechanism of the lignin pyrolysis is shown in Figure 4[15,25,27].

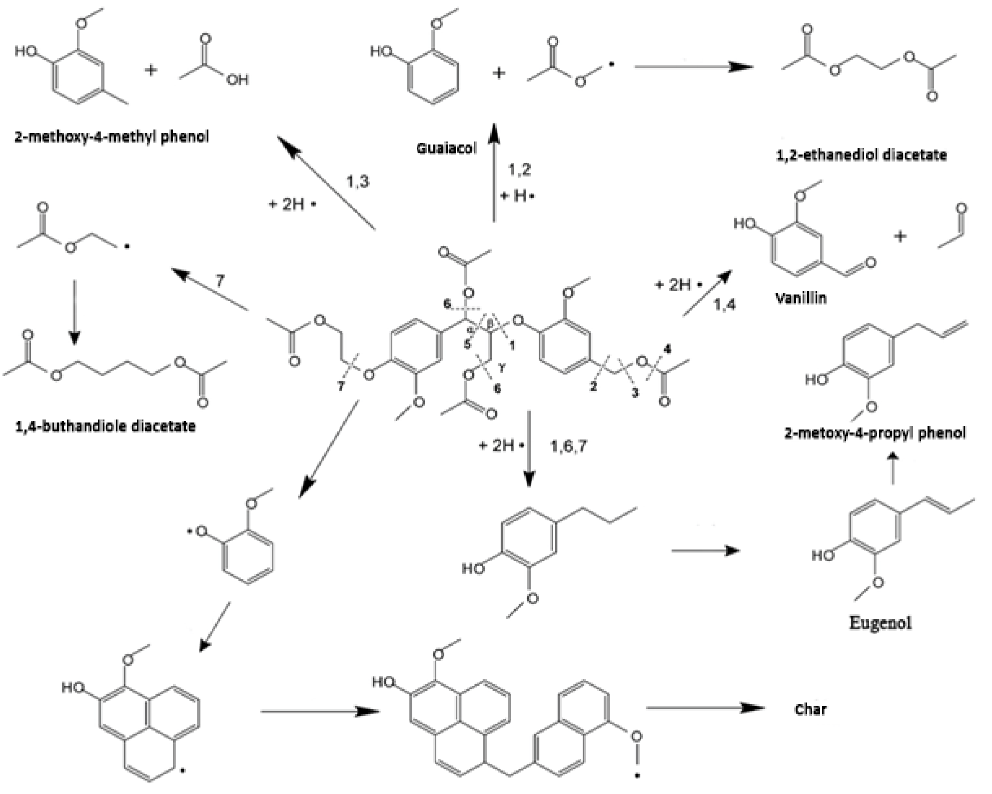

Figure 4. Pyrolysis mechanism of lignin[28]

Pyrolysis reactors of different type can be used. The simplest type of reactor is a reactor with particles free-fall. Feedstock is placed in a feeder above the top of the reactor. Particles fall through the entire body of the reactor. In the lower part formed char is removed and gaseous products pass through the cyclone, where small solid particles are removed. The gas passes through a condenser, in whose lower part bio-oil is captured. The technological setup is characterized by high heating rate and residence time of a few seconds. Its advantage is the absence of carrier gas and the resulting low costs[29].

Fluidized bed reactor is characterized by a carrier gas being fed to the bottom of the reactor and keeping biomass particles and hot sand in a fluidized suspension (bed). The key features of fluidized bed reactors include excellent heat and mass transfer and a quick heating of the raw material. Residence time of solids and vapours is controlled by the fluidizing gas flowrate and is higher for char than for vapours. As char acts as a cracking catalyst at fast-pyrolysis reaction temperatures, rapid and effective char separation/elutriation is important. This is usually achieved by ejection and entrainment followed by separation in one or more cyclones, so careful design of sand and biomass/char hydrodynamics is important. The high level of inert gases arising from the high permanent gas flows required for fluidization result in very low partial pressures of the condensable vapours. Thus, the design of efficient heat-exchange and liquid collection systems is crucial. In addition, the high inert-gas flowrates result in large equipment thus increasing the costs. In this type of reactor, bio-oil yield up to 70 %wt can be achieved[30].

High heating rate and short residence time are very important for fast pyrolysis that can be achieved in a rotating cone reactor. The configuration allows gaining cheaper pyrolysis process, due to the absence of a carrier gas. High yields of bio-oil (70 %wt) can be obtained. Heating sand carries the heat released by burning the formed char[28].

In the special process of ablative fast pyrolysis, the biomass feedstock is pressed against a hot surface, which is moving relative to the biomass. Upon contact with the hot surface, the biomass rapidly heats up, melts and yields a liquid layer on the hot surface, which evaporates instantaneously when leaving the contact area between biomass and hot surface. This principle does not need a heat carrier material nor a fluidizing gas, which would dilute the pyrolysis vapours and further hamper later condensation. Ablative reactors heat the surface of the wood blocks by thermal radiation (radiation ablative reactors), or by contact with hot surfaces (contact ablative reactors). As reaction rates are not limited by heat transfer through the biomass particles, larger particles can be used and in principle there is no upper limit to the size that can be processed. The process, in fact, is limited by the rate of heat supply to the reactor rather than the rate of heat absorption by the pyrolysing biomass, as in other reactors. For the ablative reactor construction, it is essential to achieve very fast removal of volatile components generated to prevent their secondary degradation reactions. Bio-oil yields up to 75 %wt[9,30] can be achieved.

Chemical composition of bio-oil from beech wood by GC-MS

Table II shows the composition of pyrolysis bio-oil produced by ablative fast pyrolysis of beech wood. The bio-oil was supplied by Fraunhofer UMSICHT. Prior to the analysis, the bio-oil sample was diluted in methanol to obtain a 1:1 (vol.) solution. No other sample pretreatment was performed. Instrument control, data acquisition and analysis were performed using Xcalibur 2.2 software (Thermo-Fisher Scientific). GC-MS spectra were interpreted using a mass spectral library (NIST 08). After comparison with the NIST library and subsequent manual inspection, only peaks with spectral matches better than 75 % were assigned with names. Structural isomers found in the GC-MS spectra were identified using Kovats retention indices from the NIST library.

Analysis of the bio-oil by GC-MS showed that the bio-oil was predominantly composed of oxygenated compounds. Light compounds such as glycol aldehyde and acetic acid were the most abundant. Other compounds such as 1-hydroxypropan-2-one, furfural, guaiacol and its derivatives formed by the pyrolysis of lignin were also identified. Levoglucosan was formed by the pyrolysis of cellulose and it was not completely converted by secondary fission reactions to lighter products. Type and concentration of compounds in detected bio-oil agrees with theoretical principles of cracking of lignocellulose biomass.

Conclusions

Lignocellulose biomass consists of three major components: cellulose, hemicellulose and lignin. Cellulose is the major constituent of plant cell walls and its content in biomass reaches up to 50 %wt. Other polysaccharides contained in biomass are called hemicellulose, and it represents from the 15 to 35 %wt of biomass. The third major component of lignocellulose is lignin. Its content in biomass ranges from 10 to 35 %wt. Pyrolysis of biomass is a thermal process resulting in thermal decomposition of organic molecules in the absence of air at temperatures higher than 300 °C. Fast pyrolysis is performed at temperatures up to 600 °C. The yield of liquid bio-oil after condensation of vapours and aerosols is in the range of 60 to 75 %wt. The first step of pyrolysis of lignocellulosic biomass is its dehydration-followed by primary depolymerisation. Secondary depolymerization reactions take place in the vapour phase together with cracking reactions of the primary oil resulting in formation of intermediate oxygenated compounds consisting of a mixture of furan, acetic acid, methanol and other oxygenates. Various types of reactor are used for fast pyrolysis of biomass. Among these, ablative fast pyrolysis reactors are advantageous due to the absence of heat carrier and auxiliary gases

Table II
Pyrolysis bio-oil compounds detected by GC-MS

#	RT [min]	Compound	M [g.mol^{-}	Formula	Rel. abund.
1	1.55	glycol aldehyde	60	$C_2H_4O_2$	12.79
2	1.95	acetic acid	60	$C_2H_4O_2$	18.17
3	4.71	1-hydroxy-2-propanone	74	$C_3H_6O_2$	8.81
4	5.95	furfural	96	$C_5H_4O_2$	2.04
5	7.02	acetoxyacetone	116	$C_5H_8O_3$	1.33
6	9.22	2-methyl-2-cyclopenten-1-one	96	C_6H_8O	0.90
7	9.29	5-methylfurfural	110	$C_6H_6O_2$	0.38
8	9.35	3-methyl-5H-furan-2-one	98	$C_5H_6O_2$	0.79
9	10.02	phenol	94	C_6H_6O	0.65
10	10.55	corylon	112	$C_6H_8O_2$	1.54
11	11.33	*o*-cresol and *m*- and/or *p*-cresol (RT 11.70)	108	C_7H_8O	1.11
12	11.78	guaiacol	124	$C_7H_8O_2$	1.48
13	12.87	dimethylphenol	122	$C_8H_{10}O$	0.27
14	13.29	6-methylguaiacol and 4-methylguaiacol	138	$C_8H_{10}O_2$	1.84
15	13.47	1,4:3,6-dianhydro-α-D-glucopyranose	144	$C_6H_8O_4$	0.30
16	13.63	benzenediol	110	$C_6H_6O_2$	0.60
17	13.71	5-hydroxymethylfurfural	126	$C_6H_6O_3$	0.79
18	14.77	4-ethylguaiacol	152	$C_9H_{12}O_2$	0.57
19	14.92	4-methyl-1,2-benzenediol	124	$C_7H_8O_2$	0.57
20	15.59	syringol	154	$C_8H_{10}O_3$	2.31
21	15.83	eugenol	164	$C_{10}H_{12}O_2$	0.54
22	15.93	4-propylguaiacol	166	$C_{10}H_{14}O_2$	0.46
23	16.12	vanillin	152	$C_8H_8O_3$	0.58
24	16.48	Isoeugenol, *cis*- and trans- (RT 16.98)	164	$C_{10}H_{12}O_2$	0.84
25	16.87	vanillic acid	168	$C_8H_8O_4$	1.41
26	17.13	levoglucosan	162	$C_6H_{10}O_5$	3.97
27	17.72	guaiacylacetone	180	$C_{10}H_{12}O_3$	0.70
28	18.14	coniferyl alcohol	180	$C_{10}H_{12}O_3$	0.13
29	18.89	syringaldehyde	182	$C_9H_{10}O_4$	0.51

Acknowledgement

The results were obtained in the BioMates project. This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 727463. The publication reflects only the authors' view and the Commission is not responsible for any use that may be made of the information it contains.

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