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Thermogravimetric analysis in steam and oxygen with gas chromatograph mass spectrometry for basic study of biomass gasification

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Abstract We modified a commercially available thermogravimetric analyzer to introduce helium alone or with steam, oxygen or both, atmosphere of which was controllable to be similar to that in a fixed-bed or an entrained-flow type gasifier, for studying basic properties of biomass gasification. We also connected it to a gas chromatograph-mass selective detector for identifying materials produced during the thermogravimetric analyses. Thermogravimetric analyses of Japanese cedar wood and identifications of the produced materials at around 365 °C were measured as demonstrations.

Keywords Thermogravimetric analysis in steam–oxygen · Gas chromatograph mass spectrometry · Biomass gasification

Introduction

Only biomass is a renewable source of hydrocarbon as other sources, such as petroleum, coal and natural gas, are fossil. Demands for biofuel have been rapidly growing because it is recognized to be carbon neutral and one of the most effective measures against the global warming. However, liquid biofuel fermented from foods such as corn or sugarcane, called as the first generation biofuel, causes unexpected and undesirable side effect of price rise. Developing technologies for gaseous and liquid fuel synthesis from non-edible biomass (second generation biofuel) is urgently required because of their advantages such as rapid conversions from large amounts and various kinds of whole biomass.

There are many types of gasifiers, from traditional to advanced ones. Biomass feedstocks are incompletely combusted in a fixed-bed type gasifier, to which insufficient air is supplied. It is thought that combustion mainly proceeds to produce heat near its air-intake (combustion zone) and pyrolysis proceeds using the heat to synthesize useful gases, such as CO, H_2 and CH_4 near gas-outlet (pyrolysis zone). Its conversion efficiency from carbon in the feedstock to gaseous components at room temperature (gasification rate) is low. And large amounts of by products, solid and liquid residues (char and tar), which are usually hydrocarbon of large mass numbers, are produced. Steam or steam and oxygen are used as gasification agents in an advanced gasifier such as an entrained-flow type one for improving gasification rate, in which hydrolysis and steam reforming mainly proceed [1–6].

Gasification processes are very complicated and gasification properties are dependent on biomass feedstock and gasification conditions. There are a lot of reports on thermal properties of biomass measured in air or nitrogen by using a common thermogravimetric analyzer, which is designed to use only air or nitrogen. However, it is very difficult to analyze gasification properties from such thermal properties, because conditions and reactions of thermogravimetric analyses in air or nitrogen are completely different from gasification with steam or steam and oxygen. Thermogravimetric analyzers with humidity controllers recently became available commercially, and humidity controlled thermal analysis was reported [7]. We modified one of them (model TG8120+HUM1, made by RIGAKU) and added an oxygen flow controller. It was the first

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thermogravimetric analyzer, atmosphere of which was controllable to be helium alone or with steam, oxygen or both and was similar to inside of the gasifiers.

We connected the thermogravimetric analyzer (TG) to a gas chromatograph mass selective detector (GCMS, model hp5890+hp5971A, made by Hewlett–Packard) in order to identify the produced materials in the gas, which were fed from the analyzer to the detector through a heated capillary. Biomass is generally composed of various materials, and consequently many kinds of materials are produced. A TG with a GCMS is more suitable for identifying the materials, like other applications [8, 9] than a TG with a mass selective detector [7, 10, 11].

Japanese cedar wood was thermogravimetrically analyzed and the produced materials at around 365 °C were mass spectrometrically analyzed as demonstrations. Thermal properties of the Japanese cedar wood and the produced materials were dependent on the atmosphere in the analyzer. Their dependences showed the same tendency of its gasification properties measured in our entrained-flow gasifier. This system, the thermogravimetric analyzer with steam and oxygen connected to the gas chromatograph mass selective detector, was experimentally certified to be very useful for analyzing gasification reactions.

Experiments

Biomass sample

Japanese cedar wood (*Cryptomeria Japonica*) pulverized to be smaller than 0.1 mm was used as it is one of the most popular woody biomass in Japan. Its elemental and chemical analyses were listed in Table 1.

Experimental instruments

Figure 1 shows schematic of the thermogravimetric analyzer. Gas helium passing through the temperature controlled bubbler (wet helium) and dry helium were mixed to each other in the mixing chamber, flow rates of which were automatically adjusted to control the humidity in it (HUM1). Total flow rate of the dry and wet helium was almost kept constant of about 500 sccm (standard cubic centimeter per minute), 500 cm^3/min at 0 °C and 0.1013 MPa. We added an extra-port to introduce dry oxygen into the mixing chamber, flow rate of which was controllable from 0 to 20 sccm. When introducing dry oxygen, flow rate of the dry helium in correspond reduced as expected. After mixed, humidity controlled gas (mixture of helium, steam and oxygen) was fed to the main chamber. Residence time of the gas in the chamber, dependent on its temperature, was shorter than several seconds as the chamber volume was about 60 cm^3.

Table 1 Elements and chemical components in the Japanese cedar wood

Element	C	H	O[a]	N	S	Ash
Content	48.58%	6.11%	45.06%	≤0.1%	≤0.1%	0.26%
Chemical component			Holocellulose		Klason lignin	
Content			64.26%		35.15%	

[a] Calculated by difference

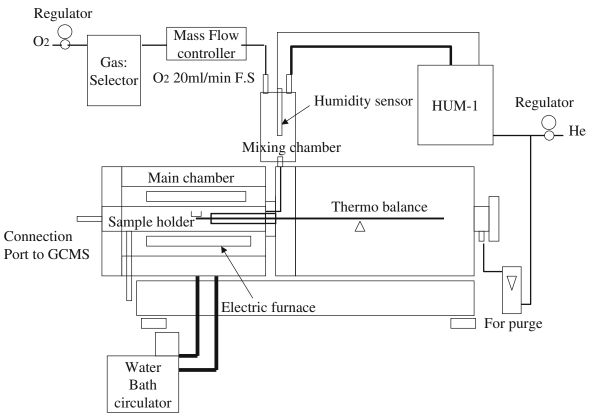


Fig. 1 Schematics of thermogravimetric analyzer

The biomass sample of about 1 mg was loosely packed in a shallow cylindrical pan made of alumina, whose diameter and depth were respectively 5 and 2.5 mm, for effective exposure of the sample to the gas because tightly packed or over weighted sample resulted poor repeatability. Temperature of the sample (T_s) was measured with a thermocouple attached to bottom of the sample holder. The pan was installed in an electric furnace, maximum temperature and heating rate of which were respectively 1,400 °C and controllable from 0 to 20 °C/min, and its weight change during heating was measured (thermogravimetric analysis, TG analysis). Resolution of the weight measurement was high, 0.001 mg, however, its offset drifted when heating (baseline drift). Its effect was numerically compensated by subtracting the baseline drift measured without sample (blank test).

The gas containing the produced materials was fed from the TG to the gas chromatograph mass selective detector through a heated capillary and syringe (Fig. 2). A U-shaped stainless steel pipe and a three-way connector were inserted between its injector and column of the gas chromatograph. Another export of the connector was connected to a vacuum pump through a valve, which automatically opened when the syringe was inserted to the injector. During the injection, the U-shaped pipe was cooled with liquid nitrogen, in which the produced materials were trapped, but through which helium passed. After the injection, the liquid nitrogen was removed and the produced materials were

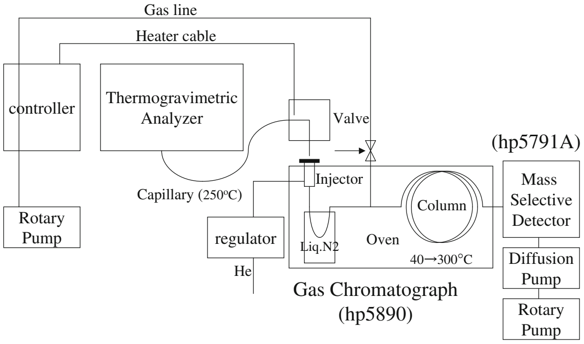


Fig. 2 Schematics of thermogravimetric analyzer and gas chromatograph mass selective detector

separated and identified using the GCMS: the produced materials were separated when passing through the column in the temperature controlled oven (gas chromatograph) and then each material was identified from its fragmentation pattern with the mass selective detector (mass spectrometry).

Atmospheric conditions in the TG of this series of measurements are listed in Table 2. Rate of the temperature rise was adjusted to be 20 °C/min. The produced materials in the temperature range of from 360 to 370 °C were analyzed: the injection started when $T_s = 360$ °C and ended when $T_s = 370$ °C. Period of the injection was about 30 s. A capillary column packed with 5% P ME Siloxane (Hewlett–Packard, HP-5), diameter and length of which were respectively 0.2 mm and 25.0 m, was used for the gas chromatograph. Pressure of helium carrier was set to be 100 kPa. Flow rate and velocity of the helium in the column were respectively 0.366 cm^3/min and 25.7 cm/s. Initial and final temperature of the oven were respectively controlled to be 40 and 300 °C, and rate of the temperature rise was 10 °C/min: oven temperature was initially kept at 40 °C for 5 min, then risen to 300 °C with rate of 10 °C/min, and finally kept at 300 °C for 11 min. Mass range of the mass selective detector was set to be 40–500 with 1.6 scan/s.

Table 2 Atmospheric conditions of the TG measurements

Atmosphere	He	He + H_2O	He + O_2	He + H_2O + O_2
H_2O	0	70%$_{rel}$ at 40 °C	0	70%$_{rel}$ at 40 °C
O_2	0	0	10 sccm[a]	10 sccm[a]

[a] cm^3 per minute at 0 °C and 0.1013 MPa

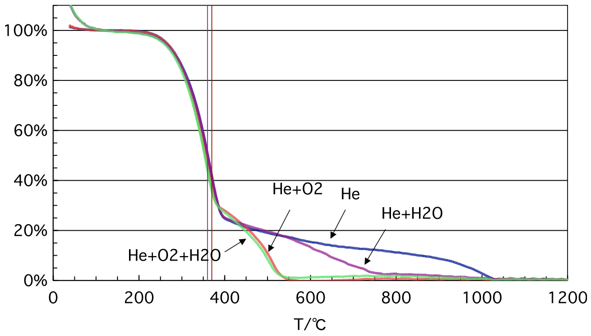


Fig. 3 Thermogravimetric analysis of Japanese cedar wood in helium alone or with steam, oxygen or both

Results and discussion

Thermogravimetric analysis

Figure 3 shows the TG analyses of the Japanese cedar wood. Its weight changes were strongly dependent on the atmosphere, especially above 450 °C. Weight of the cedar wood rapidly decreased above 450 °C in helium with oxygen or with oxygen and steam. It meant that the Japanese cedar wood reacted well with oxygen. The reaction finished and only ash remained at around 550 °C. In helium with steam, its weight gradually decreased and the reaction finished at around 750 °C, which meant that the cedar wood reacted with steam but not so well compared to oxygen. In helium only, its weight slowly decreased and certain amount of about 10% remained at around 900 °C.

These dependences had the same tendency of gasification properties of Japanese cedar wood when being gasified in an entrained-flow type gasifier at 900 °C with steam or steam and oxygen [3, 4]. Both steam and oxygen were good gasification agents, and oxygen was much more effective than steam. When increasing oxygen, carbon conversion rate from the cedar wood to the gas (gasification rate) increased, but useful gaseous components, H_2 and CO, decreased. Gaseous components were controllable by adjusting steam and oxygen. It is well known that huge amounts of solid and liquid residues, char and tar, are produced when the Japanese cedar wood is gasified in a fixed-bed type gasifier, inside temperature of which is usually lower than 900 °C. It corresponded to the TG analysis measured in helium: materials, more than 10% of the feedstock, remained below 900 °C.

Japanese cedar wood composed of various materials with complicated structures. Each of them melts, vaporizes or decomposes at certain temperature, and the decomposed materials are gasified, liquefied, solidified or polymerized. Its TG analysis reflected these reactions and completely differed from that of mono-material. As shown in Fig. 3, weight changes were little dependent on the atmosphere below 450 °C, and independent below 390 °C. It was expectable that the reacting materials were independent of the atmosphere below 390 °C and differences of the produced materials were corresponding to the effects of atmosphere. We sampled the gas in the temperature range of 360–370 °C and used the GCMS for identifying the produced materials in the gas. This temperature range was suitable for demonstrating combined operation of the TG and the GCMS.

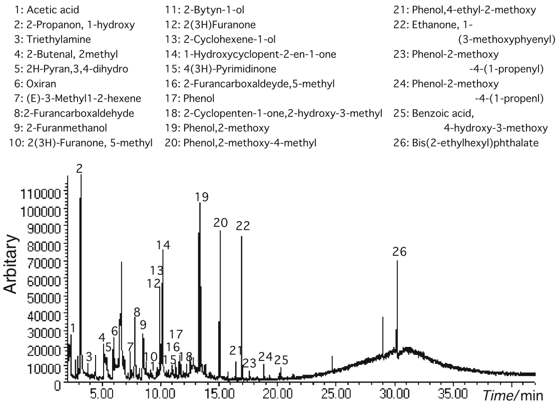
Gas chromatograph mass spectrometric analysis

The produced materials from the Japanese cedar wood in the temperature range of 360–370 °C were gas chromatographically separated and mass spectrometrically analyzed by using the GCMS. Figure 4 shows total ion chromatograms, traces of ions reaching to the mass selective detector, atmospheres of which were (a) helium, (b) helium with steam, (c) helium with oxygen and (d) helium with steam and oxygen. Identified materials from their fragmentation patterns are also listed, from which materials with low similarity indices are omitted.

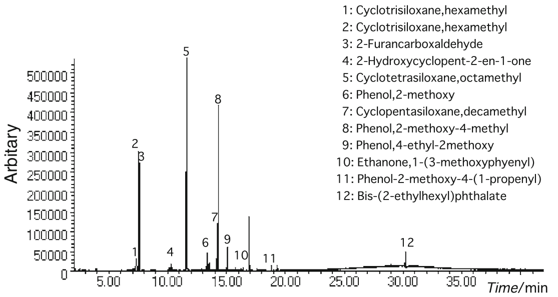
We categorized all these materials into four groups according to their atmospheric dependences: (1) produced only in helium (Table 3), (2) produced mainly in helium and helium with oxygen (Table 4), (3) produced only in helium with oxygen (Table 5), (4) produced in almost all atmosphere but more in helium with steam than helium with oxygen (Table 6). The listed areas were normalized by the initial weight of the Japanese cedar wood, which were proportional to their amounts produced from its unit weight. When corresponding materials had two peaks, sums of their areas are listed. Their dependences on the atmosphere indicated changes or progresses of the reactions by introducing steam, oxygen or both.

About 30 kinds of materials were produced in helium and 25 among them were identified (Fig. 4a). Although conditions in the TG with helium was similar to those in a fixed-bed gasifier or a dry distillator, kinds of materials (about 30) were much smaller than those contained in tar or pyrolized oil as reported before [12–14], probably because temperature in the TG (360–370 °C) was lower than that in a fixed-bed gasifier of 700–800 °C or in a dry distillator of around 500 °C. Amounts of almost all materials reduced or vanished when adding steam or oxygen, which corresponded to the high gasification rate (≥90%) of the Japanese cedar wood gasified in the entrained-flow type gasifier with steam or steam and oxygen [3].

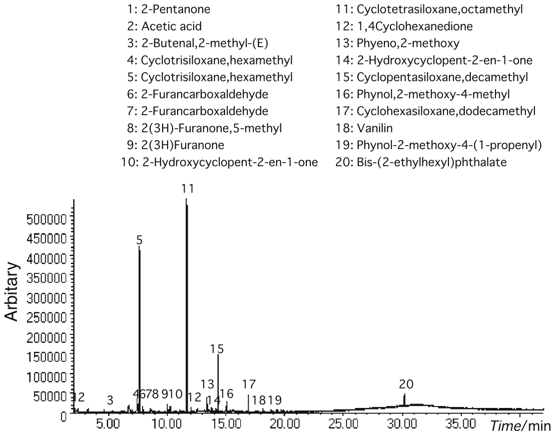
Furan and its compounds (2-Butenal,2-methyl is a opened ring of 2(3H)Furanon,5-methyl) were produced only in helium and helium with oxygen as listed in Table 4. Furan and its compounds were easily reacted with steam and hydrolyzed to gaseous components. 2-Pentanone, Vanillin and 1,4-Cyclohexanedione were produced only in helium with oxygen. These dependences suggested that both reactions and products of pyrolysis and combustion (without steam) were different from those of hydrolysis and steam reforming.



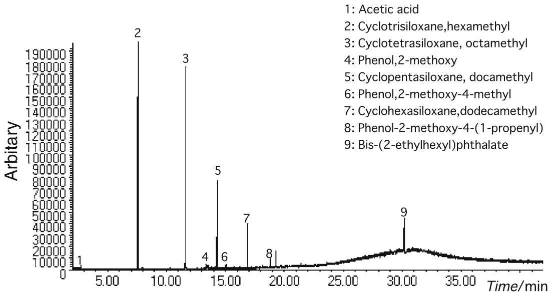
(a) Atomosphere: Helium



(b) Atomosphere: He+H$_2$O



(c) Atomosphere: He+O$_2$



(d) Atomosphere: He+O$_2$+H$_2$O

Fig. 4 Total ion chromatogram of the decomposed material from Japanese cedar wood in helium: **a** at around 365 °C, **b** with steam at around 365 °C, **c** with oxygen at around 365 °C, **d** with steam and oxygen at around 365 °C

Table 3 Peak areas of decomposed materials from Japanese cedar wood produced only in helium at around 365 °C

Material	Atmosphere			
	He/ area/μg^{-1}	He + H_2O/ area/μg^{-1}	He + O_2/ area/μg^{-1}	He + H_2O + O_2/ area/μg^{-1}
2-Propanon, 1-hydroxy	279	–	–	–
Triethylamine	13	–	–	–
2H-Pyran,3,4-dihydro	59	–	–	–
Oxiran,(propaxymethyl)	13	–	–	–
(E)-3-Methyl-2-hexene	38	–	–	–
2-Furanmethanol	139	–	–	–
2-Bytyn-1-ol	14	–	–	–
2-Cyclohexene-1-ol	40	–	–	–
4(3H)-Pyrimidinone	8	–	–	–
2-Frurancarboxaldeyde, 5-methyl	8	–	–	–
Phenol	17	–	–	–
2-Cyclopenten-1-one, 2-hydroxy-3-methyl	15	–	–	–
Benzoic acid, 4-hydroxy-3-methoxy	16	–	–	–
Thiocyanic acid, 5-alpha-cholestan-3beta-yl ester	33	–	–	–

Table 4 Peak areas of decomposed materials from Japanese cedar wood produced mainly in helium and helium with oxygen at around 365 °C

Material	Atmosphere			
	He/area/μg^{-1}	He + H_2O/area/μg^{-1}	He + O_2/area/μg^{-1}	He + H_2O + O_2/area/μg^{-1}
Acetic acid	99	–	19	8
2-Butenal, 2-methyl	130	–	20	–
2-Furancarboxaldehyde	103	11	64	–
2(3H)-Furanone, 5-methyl	16	–	10	–
2(3H)Furanone	133	–	51	–

Table 5 Peak areas of decomposed materials from Japanese cedar wood produced only in helium with oxygen at around 365 °C

Material	Atmosphere			
	He/area/μg^{-1}	He + H_2O/ area/μg^{-1}	He + O_2/ area/μg^{-1}	He + H_2O + O_2/ area/μg^{-1}
2-Pentanone	–	–	16	–
Vanillin	–	–	21	–
1,4-Cyclohexanedione	–	–	27	–

Table 6 Peak areas of decomposed materials from Japanese cedar wood produced in almost all atmosphere, but more in helium with steam than in helium with oxygen at around 365 °C

Material	Atmosphere			
	He/area/μg^{-1}	He + H_2O/ area/μg^{-1}	He + O_2/ area/μg^{-1}	He + H_2O + O_2/ area/μg^{-1}
2-Hydroxycyclopent-2-en-1-one	168	44	28	–
Phenol, 2-methoxy	153	94	55	13
Phenol, 2-methoxy-4-methyl	127	91	53	12
Phenol, 4-ethyl-2-methoxy	14	13	–	–
Ethanone, 1-(3-methoxyphyenyl)	121	200	–	–
Phenol, 2-methoxy-4-(1-propenyl)	21	21	1	14

Phenol compounds were produced in almost all atmospheres: in helium and in helium with steam, oxygen and both. Their amounts reduced when adding steam or oxygen and more effectively when adding oxygen. It suggested that decompositions of phenol compounds were accelerated by steam and oxygen and oxygen was more effective than steam. Phenol and its compounds were thought to be produced from lignin. It corresponded to that gasification rates of biomass feedstocks with high lignin contents were improved of about 5% or more when adding oxygen [5].

Bis-(2-ethylhexyl)phthalate was detected in all cases but omitted because it was thought to be a contamination. Compounds of Siloxan attributable to the gas chromatograph column were detected when supplying helium with steam, oxygen and both, however, none of them was detected when supplying helium only or without injection (background). Therefore, these compounds were produced through interfering steam, oxygen or both with the Siloxan in the column, although the reactions were not clear.

Conclusions

We modified a commercially available thermogravimetric analyzer (TG) with a humidity controller and added an oxygen controller, to introduce helium alone or with steam, oxygen or both. Inside atmosphere of the TG was controllable to be similar to that in a fixed-bed or an entrained-flow type gasifier. Atmospheric effects to thermal properties measured by this TG had the same tendency of effects of gasification agents. Both steam and oxygen were good gasification agents and oxygen was more effective than steam.

A gas chromatograph mass selective detector (GCMS) was connected to the TG: gas was fed from the TG to the GCMS through a heated capillary. Materials produced at around 365 °C were identified for demonstrating combined operations of the TG and the GCMS. Various kinds of materials were produced in helium. When adding steam or oxygen, amounts of almost all materials reduced or vanished. Effects of steam and oxygen were different. Furan and its compounds reacted well with steam. Phenol and its compounds reacted with steam and oxygen, and more effective with oxygen than steam. Simultaneous operations of the thermogravimetric analysis in helium alone or with steam, oxygen or both and the gas chromatograph mass spectrometry were useful for studying effects of gasification agents and reactions of biomass gasification.

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References

1. Ishii H, Fukui K, Takeno K. In: Proceeding of ICOPE-03; 2003.
2. Matsumoto K, Takeno K, Ichinose T, Ishii H, Nishimura K. In: Proceeding of the 15th Euro biomass conference and exhibition; 2007, p. 1945.
3. Ogi T, Nakanishi M, Inoue S. In: Proceeding of the 8th Japan-China symposium on coal and C1 chemistry; 2003, vol. 1, p. 227.
4. Ogi T, Nakanishi M, Inoue S. In: Science in thermal and chemical biomass conversion; 2005, vol. 1, p. 620.
5. Ogi T, Kawamura A, Nakanishi M, Inoue S. In: Proceedings of IAWPS2005; 2005, vol. 2, p. 257.
6. Ogi T, Nakanishi M. Renew Energy. 2006;1:1050.
7. Arii T, Kishi A. Humidity controlled thermal analysis: the effect of humidity on thermal decomposition of zinc acetylacetonate monohydrate. J Therm Anal Calorim. 2006;83:253–60.
8. Meszaros E, Jakab E, Varhegyi G, Tovari P. Thermogravimetry/mass spectrometry analysis of energy crops. J Therm Anal Calorim. 2007;88:477–82.
9. Ischia M, Perazzolli C, Dal Maschio R, Campostrini R. Pyrolysis study of sewage sludge by TG-MS and TG-GC-MS coupled analyses. J Therm Anal Calorim. 2007;87:567–74
10. Pappa A, Mikedi K, Tzamizis N, Statheropoulos M. TG-MS analysis for studying the effects of fire retardants on the pyrolysis of pine-needles and their components. J Therm Anal Calorim. 2006;84(3):655–61
11. Onishi A, Thomas PS, Stuart BH, Guerbois JP, Forbes S. TG-MS analysis of the thermal decomposition of pig bone for forensic applications. J Therm Anal Calorim. 2007;88:405–9
12. Wehlte S, Meier D, Moltran J, Faix O. The impact of wood preservatives on the flash pyrolysis of biomass. In: Bridgwater AV, Boocock DGB, editors. Developments in thermochemical biomass conversion, vol. 1. London: Blackie A&P; 1997, p. 206–29
13. Milne TA, Agblevor F, Davis M, Deutch S, Johnson D. A review of thechemical composition of fast pyrolysis oils, in developments in thermal biomassconversion. In: Bridgwater AV, Boocock DGB, editors. Developments in thermochemical biomass conversion, vol. 1. London: Blackie A&P;1997, p. 409–24.
14. Pasa VMD, Carazza F, Otani C. Wood tar pitch: analysis and conceptual model of its structure. In: Bridgwater AV, Boocock DGB, editors. Developments in thermochemical biomass conversion, vol. 1. London: Blackie A&P;1997, p. 448–61