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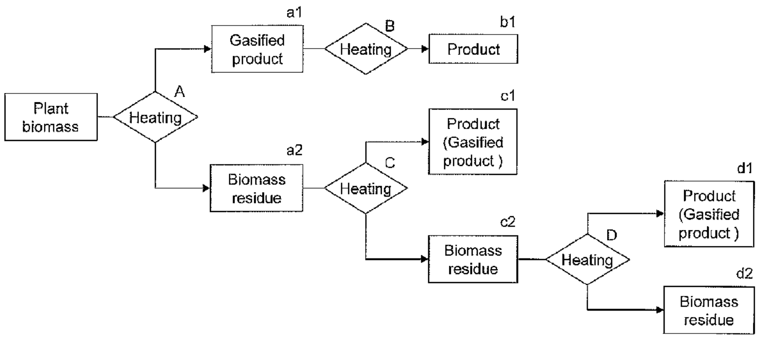
(54) Title: PYROLYSIS METHOD FOR PLANT BIOMASS

[Fig. 1]



(57) **Abstract**: An object of the present invention is to provide a convenient method for extracting a useful organic compound from plant biomass. According to the present invention, a method for pyrolyzing plant biomass comprising a 1st heating step in which biomass is heated at a 1st heating temperature and a 2nd heating step in which either a gasified product or a biomass residue obtained in the 1st heating step is heated at a 2nd heating temperature higher than the 1st heating temperature is provided. The method of the present invention makes it possible to extract useful organic compounds such as phenols from plant biomass with heat treatment alone.

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Description

Title of Invention: PYROLYSIS METHOD FOR PLANT BIOMASS

Technical Field

[0001] The present invention relates to a method for obtaining a useful organic compound by pyrolyzing plant biomass.

Background Art

[0002] Pyrolysis (thermal decomposition) of plant biomass results in the generation of many decomposition products originating from cellulose, hemicellulose, lignin, fats and oils, and the like contained in the plant biomass. Decomposition products contain useful organic compounds such as phenol, in addition to many other substances with poor usefulness. Extraction of a specific compound alone from such a miscellaneous mixture requires significant effort and thus is inappropriate for industrial applications. To address such a problem, cellulose alone can be extracted through pretreatment of a raw plant biomass material and then subjected to pyrolysis, for example. However, such pretreatment itself requires much effort and thus is inappropriate for industrial applications.

[0003] Non-patent literature 1 discloses compounds that are generated through pyrolysis of beechwood at 600K-900K and the fact that the resulting compounds differ depending on pyrolysis temperatures. Patent literature 1 discloses a process for extracting useful compounds through steps of separation, condensation, hydrogenation, and the like from pyrolyzed oil obtained from plant biomass.

Citation List

Patent Literature

[0004] PTL 1: WO 2007/128800

Non-Patent Literature

[0005] NPL 1: Ind. Eng. Chem. Res., 2003, vol. 42, pp. 3190-3202

Summary of Invention

Technical Problem

[0006] Although decomposition products of plant biomass contain many useful organic compounds, there is no known method for conveniently and effectively extracting a desired compound from the products. A convenient method that enables extraction of desired organic compounds from plant biomass and is appropriate for industrial applications is required for effective use of plant biomass.

Solution to Problem

[0007] As a result of studies, the present inventors have found that the pyrolysis of plant biomass via at least two heating stages makes it possible to separately extract a group of compounds or a specific compound originating from each of the components contained in plant biomass, such as lignin or hemicellulose, through heat treatment alone. The gist of the present invention is as follows.

(1) A method for obtaining a useful organic compound by pyrolyzing plant biomass, comprising:

a 1st heating step wherein biomass is heated at a 1st heating temperature; and

a 2nd heating step wherein either a gasified product or a biomass residue obtained in the 1st heating step is heated at a 2nd heating temperature higher than the 1st heating temperature.

(2) The method according to (1), wherein:

in the 1st heating step, plant biomass is heated at the 1st heating temperature of 400 degrees C or lower; and

in the 2nd heating step, the biomass residue is heated at the 2nd heating temperature of 500 degrees C or higher to obtain a lignin-derived decomposition product.

(3) The method according to (1) or (2), wherein:

in the 2nd heating step, the biomass residue obtained in the 1st heating step is heated; and

the method further comprises a 3rd heating step wherein the further generated biomass residue obtained in the 2nd heating step is heated at a 3rd heating temperature higher than the 2nd heating temperature.

(4) The method according to (3), wherein:

the 1st heating temperature is 400 degrees C or lower;

the 2nd heating temperature ranges from 500 degrees C to 600 degrees C; and

in the 3rd heating step, the biomass residue is heated at a 3rd heating temperature of 600 degrees C or higher to obtain a lignin-derived decomposition product.

(5) The method according to any one of (1) to (4), wherein the lignin-derived decomposition product contains at least phenol or cresol.

(6) The method according to any one of (1) to (5), wherein:

in the 1st heating step, plant biomass is heated at the 1st heating temperature ranging from 280 degrees C to 320 degrees C; and

in the 2nd heating step, the gasified product obtained in the 1st heating step is heated at the 2nd heating temperature ranging from 600 degrees C to 800 degrees C to obtain a hemicellulose-derived decomposition product.

(7) The method according to (6), wherein the hemicellulose-derived decomposition product contains at least furan.

Advantageous Effects of Invention

[0008] According to the method of the present invention, it becomes possible to separately extract a group of compounds or a specific compound originating from each of components such as lignin or hemicellulose contained in plant biomass through heat treatment alone. Therefore, according to the present invention, a useful compound with a certain level of purity can be extracted from plant biomass, and the preparation of organic compounds such as phenols becomes possible without the use of petroleum or the like.

This specification incorporates the content of the specification of Japanese Patent Application No. 2010-292630, for which priority is claimed to the present application.

Brief Description of Drawings

[0009] [fig.1]Fig. 1 is a flow chart showing the outline of the method of the present invention.
[fig.2]Fig. 2 is a chart obtained by GC/MS measurement of volatile components resulting from pyrolysis of cedar at 500 degrees C.
[fig.3]Fig. 3 is a chart showing the change in the weight reduction rate of a cedar sample when the temperature was increased at 50 degrees C/minute and then held at 370 degrees C.
[fig.4]Fig. 4 is a chart obtained by GC/MS measurement of volatile components resulting from pyrolysis of cedar at two temperature stages (370 degrees C and 500 degrees C).
[fig.5]Fig. 5 is a chart obtained by GC/MS measurement of volatile components resulting from pyrolysis of Japanese cypress at 500 degrees C.
[fig.6]Fig. 6 is a chart obtained by GC/MS measurement of volatile components resulting from pyrolysis of Japanese cypress at the two temperature stages (370 degrees C and 500 degrees C).
[fig.7]Fig. 7 is a chart obtained by GC/MS measurement of volatile components resulting from pyrolysis of Japanese cypress at 270 degrees C or 330 degrees C.
[fig.8]Fig. 8 is a schematic view of an apparatus having two heating zones, which was used in Example 2-2.
[fig.9]Fig. 9 is a chart obtained as a result of GPC analysis of decomposition products that were obtained by pyrolyzing Japanese cypress at 300 degrees C and then reheating the thus generated gasified product at 600 degrees C to 800 degrees C.
[fig.10]Fig. 10 is a chart obtained by GC-MS measurement of volatile components resulting from pyrolysis of eucalyptus at the three temperature stages (370 degrees C, 500 degrees C and 600 degrees C).
[fig.11]Fig. 11 is a chart obtained by GC-MS measurement of volatile components resulting from pyrolysis of palm kernel shells at the two temperature stages (500

degrees C and 600 degrees C).

[fig.12]Fig. 12 is a chart obtained by GC-MS measurement of volatile components resulting from pyrolysis of palm kernel shells at the three temperature stages (350 degrees C, 500 degrees C and 600 degrees C).

Description of Embodiments

[0010] Fig. 1 is a flow chart showing the outline of the present invention. The method of the present invention will be described using this flow chart.

[0011] The method of the present invention comprises a 1st heating step (A) of heating plant biomass at a 1st heating temperature and a 2nd heating step (B or C) of heating either a gasified product (a1) or a biomass residue (a2) obtained in the 1st heating step at a 2nd heating temperature higher than the 1st heating temperature. Also, the method of the present invention may comprise a 3rd heating step (D), in which a biomass residue (c2) generated in the 2nd heating step (C) is heated at a 3rd heating temperature higher than the 2nd heating temperature.

[0012] The term "plant biomass" as used herein refers to a plant-derived raw material containing cellulose, hemicellulose, lignin, and the like, including both woody biomass and herbaceous biomass. Examples of woody biomass include materials originating from plants having lignified stem tissues such as Japanese timbers, North American timbers, Russian timbers (North Pacific timbers), South Pacific timbers, African timbers, South American timbers, Oceanian timbers, Chinese timbers, and European timbers (e.g., cedar, cypress, pine, sawtooth oak, cherry, Japanese ash, zelkova, beech, oak (nara), maple, ginkgo, empress tree, oak (kashi), the trees of the genus Castanea of the family Fagaceae (kuri), eucalyptus, teak, mahogany, Hinoki cypress or Sawara cypress (hiba), poplar, acacia, Abies firma (momi), birch, lauan, walnut, Sawara cypress, Torreya nucifera (kaya), Japanese Yew, oak, Cercidiphyllum japonicum (katsura), Abies firma (momi), and barbados nut. Examples of herbaceous biomass include materials originating from plants lacking lignified stem tissues, such as rice, the cereals of the family Gramineae including barley and wheat (mugi), sugarcane, corn, rapeseed, soybean, palm, reed, bamboo grass, bamboo, sugarbeet, potates, legumes (plants of the family Leguminosae), and algaes. Naturally, examples of plant biomass also include residues of the above woody biomass and herbaceous biomass, such as bagasse (sugarcane residue after squeezing) and residues obtained by oil squeezing of soybean, rapeseed, palm tree, and the like. As plant biomass to be used in the method of the present invention, lignin-rich woody biomass is more preferable for the production of large amounts of phenols, as described later.

[0013] The term "useful organic compound" in the method of the present invention refers to an organic compound useful as a raw material in chemical industry or as a fuel for engines or fuel cells, for example. Specific examples of a useful organic compound include monohydric phenols, dihydric phenols, trihydric phenols, furans, levoglucosan, and cellobiose. Examples of a useful organic compound that is obtained by pyrolyzing plant biomass include particularly phenol, cresol, and furan.

[0014] In each of the heating steps (A to D) of the method of the present invention, a raw material to be heated (biomass, a gasified product, or a biomass residue) is pyrolyzed. Accordingly, excessive water should be absent in the system when heating is performed, in order to suppress the hydrolysis reaction as far as possible and to cause the pyrolysis reaction to proceed. Each heating step is preferably performed under conditions where an inert gas is present but water other than the one originally contained in the raw material is absent, for example. If necessary, a raw material may be dried before the heating step so as to remove water in advance.

[0015] The method of the present invention comprises separating a gasified product resulting from pyrolysis from a residue that has remained ungasified, following each of the heating steps (A to D). Separation is performed by a general method known by persons skilled in the art such as a method that involves installing a condenser in an exhaust system of a furnace for heating, liquefying and collecting a gasified product contained in exhaust gas, and separately collecting residues remaining in the furnace after heating.

[0016] In the 1st heating step (A), plant biomass is preferably heated at a temperature of 400 degrees C or lower and particularly at a temperature of 380 degrees C or lower. This is based on the finding that cellulose and hemicellulose, among the components contained in plant biomass, are pyrolyzed even at relatively low temperatures. At such temperatures, among components composing plant biomass, lignin is almost never pyrolyzed, but rather, only cellulose and hemicellulose are pyrolyzed to be converted to gasified products (a1). If the temperature is too low, pyrolysis does not proceed. Hence, plant biomass is heated preferably at a temperature of 275 degrees C or higher and particularly preferably at temperatures of 280 degrees C or higher.

[0017] Optimum heating temperature in the 1st heating step (A) (1st heating temperature) differs depending on plant biomass type, and it is generally 400 degrees C or lower. For example, when plant biomass originates from woody biomass, such as cedar or cypress, the 1st heating temperature is preferably 380 degrees C or lower, more preferably 375 degrees C or lower, and particularly preferably 370 degrees C or lower. Also, for the purpose of mainly obtaining a hemicellulose-derived gasified product, the 1st heating temperature preferably ranges from 275 degrees C to 325 degrees C and particularly preferably ranges from 280 degrees C to 320 degrees C, for example, since hemicellulose starts to be pyrolyzed at a lower temperature than cellulose.

[0018] In the 2nd heating step (B or C), either a gasified product (a1) or a biomass residue (a2) generated in the 1st heating step is heated at a 2nd heating temperature that is higher than the 1st heating temperature. Here, the term "biomass residue" refers to a residue remaining after liberation of the gasified product that has been generated via pyrolysis from a heated material. The 2nd heating temperature is preferably set at 450 degrees C or higher and particularly preferably set at 500 degrees C or higher.

[0019] When plant biomass is heated at a 1st heating temperature of 400 degrees C or lower in the 1st heating step (A) and then a biomass residue (a2) is heated at a 2nd heating temperature of 500 degrees C or higher in the 2nd heating step (C), a lignin-derived decomposition product is obtained as a gasified product (c1). A lignin-derived decomposition product contains phenols such as phenol, cresol, guaiacol, hydroxy methoxy toluene, hydroxy methoxy ethyl benzene, hydroxy methoxyvinyl benzene, hydroxy methoxy propyl benzene, dimethoxy phenol, hydroxy dimethoxy toluene, hydroxy dimethoxy ethyl benzene, hydroxy dimethoxy propyl benzene, pyrocatechol, benzofuran, dibenzofuran, and vanillin. Of these phenols, phenol and cresol are particularly industrially important compounds. The lignin-derived decomposition product to be obtained herein contains at least phenol or cresol. The phenol and/or cresol content in the lignin-derived decomposition product to be obtained herein is preferably 20% by weight or more with respect to the total weight of the obtained gasified product (c1) after condensation. More preferably, the lignin-derived decomposition product to be obtained herein substantially consists of phenol and/or cresol. Here, the expression "substantially consist(s) of" means that impurities other than a target substance contained in a subject account for less than 5% by weight, preferably less than 3% by weight, and particularly preferably less than 1% by weight.

[0020] A biomass residue (c2) further generated after heating of the biomass residue (a2) in the 2nd heating step (C) and the following liberation of the gasified product (c1) may be subjected to a 3rd heating step (D). In the 3rd heating step (D), the biomass residue (c2) is heated at a 3rd heating temperature that is higher than the 2nd heating temperature in the 2nd heating step (C). The 3rd heating temperature is preferably set at 550 degrees C or higher, and it is particularly preferably set at 600 degrees C or higher, for example. However, if the 3rd heating temperature is set at an excessively high temperature, the biomass residue (a2) becomes carbonized. Hence, the 3rd heating temperature is preferably set at 650 degrees C or lower.

[0021] In the case where plant biomass is heated at a 1st heating temperature of 400 degrees C or lower (more preferably 380 degrees C or lower and particularly preferably 370 degrees C or lower) in the 1st heating step (A), the biomass residue (a2) is heated at a 2nd heating temperature ranging from 500 degrees C to 600 degrees C (more preferably ranging from 500 degrees C to 550 degrees C) in the 2nd heating step (C), and subsequently the biomass residue (c2) is heated at a 3rd heating temperature of 600 degrees C or higher (more preferably 620 degrees C or higher) in the 3rd heating step (D), lignin that has remained undegraded is pyrolyzed and then a lignin-derived decomposition product can be obtained as a gasified product (d1). The lignin-derived decomposition product to be obtained herein is similar to the one described above and contains at least phenol or cresol. The phenol and/or cresol content in the lignin-derived decomposition product to be obtained herein is preferably 50% by weight or more with respect to the total weight of the thus obtained gasified product (d1) after condensation. More preferably, the lignin-derived decomposition product to be obtained herein substantially consists of phenol and/or cresol. A biomass residue (d2) generated in the 3rd heating step (D) contains no useful compounds anymore and thus is generally used as a raw material serving as a heat source.

[0022] In the case where plant biomass is heated at a 1st heating temperature ranging from 280 degrees C to 320 degrees C (more preferably ranging from 300 degrees C to 320 degrees C) in the 1st heating step (A) and then a gasified product (a1) is heated at a 2nd heating temperature ranging from 600 degrees C to 800 degrees C (more preferably ranging from 630 degrees C to 660 degrees C) in the 2nd heating step (B), a hemicellulose-derived decomposition product is obtained as a product (b1). Such a hemicellulose-derived decomposition product contains furans such as furan and furfural. A hemicellulose-derived decomposition product to be obtained herein contains at least furan. The furan content in such a hemicellulose-derived decomposition product to be obtained herein is preferably 30% by weight or more with respect to the total weight of the thus obtained product (b1) after condensation. More preferably, a hemicellulose-derived decomposition product to be obtained herein substantially consists of furan alone.

[0023] Incidentally, for the purpose of obtaining furan with higher purity, the 2nd heating temperature is preferably set at 700 degrees C or higher and particularly preferably 750 degrees C or higher. In this case, the furan content in a hemicellulose-derived decomposition product to be obtained herein is preferably 50% by weight or more with respect to the total weight of the thus obtained product (b1) after condensation. Also, for the purpose of obtaining a high yield of furan with somewhat lower purity, the 2nd heating temperature preferably ranges from 630 degrees C to 660 degrees C and particularly preferably ranges from 640 degrees C to 660 degrees C.

[0024] To obtain a cellulose-derived decomposition product in addition to the above hemicellulose-derived decomposition product, the 1st heating temperature in the 1st heating step (A) may be 320 degrees C or higher and may range from 320 degrees C to 400 degrees C (more preferably may range from 350 degrees C to 380 degrees C), for example. A cellulose-derived decomposition product contains hydroxymethyl furfural, levoglucosan, and cellobiose.

The above described procedures:
(i) a procedure in which a biomass residue (a2) is obtained from plant biomass via the 1st heating step (A) and then a gasified product (c1) is obtained by subjecting the biomass residue (a2) to the 2nd heating step (C);
(ii) a procedure in which a biomass residue (a2) is obtained from plant biomass via the 1st heating step (A), and a gasified product (d1) is obtained by subjecting the biomass residue (a2) to the 2nd heating step (C) followed by the 3rd heating step (D) in which the further generated biomass residue (c2) is subjected to the 3rd heating step (D); and
(iii) a procedure in which a gasified product (a1) is obtained from plant biomass via the 1st heating step (A) and then the gasified product (a1) is subjected to the 2nd heating step (B) to obtain a product (b1);
may be performed in parallel or only one or two specific procedures thereof may be performed.

[0025] The expression, "all of these procedures are performed in parallel" means that while the gasified product (a1) generated in the 1st heating step (A) is used for the procedure (iii) above, the biomass residue (a2) is used for the procedure (i) above and the thus generated biomass residue (c2) is also used for the procedure (ii) above. By performing all of these procedures in parallel in such a manner, a useful organic compound contained in biomass can be extracted without loss.

[0026] On the other hand, the expression "only one of these procedures is performed" means that only the procedure (i) above is performed, a gasified product (a1) generated in the 1st heating step (A) and a biomass residue (c2) generated in the 2nd heating step (C) are not further treated, but are used as fuels in the form of miscellaneous mixtures or discarded, for example. Similarly, the expression "only two procedures are performed" means that only the procedures (i) and (iii) above are performed, and a biomass residue (c2) generated in the 2nd heating step (C) is not further treated, for example. By performing specific procedures only, it becomes possible to select conditions (e.g., heating temperature) under which a desired organic compound (e.g., phenol or cresol) can be obtained with good purity and/or the maximum yield.

[0027] Products to be obtained in each procedure (b1, c1, d1) may be further purified if necessary. According to the method of the present invention, the number of types of compound contained in these products is very few compared with decomposition products obtained when plant biomass is simply pyrolyzed in a single stage. Therefore, the resulting compounds can be purified without particular difficulties. Purification can be performed by a conventionally known method such as distillation.

Examples

[0028] The present invention will be specifically described in the following examples.

However, the examples are not intended to limit the present invention.

[0029] 1-1. Analysis of volatile components resulting from pyrolysis of cedar (500 degrees C)

Cedar was pyrolyzed at 500 degrees C and then the resulting volatile components were subjected to GC/MS measurement. Measuring apparatuses used herein are as follows.

Pyrolyzer: PY-2020iD (Frontier Laboratories)

GC/MS: GCMS-QP2010 (Shimadzu Corporation)

Column: DB-17 (Agilent Technologies)

A cedar sample was placed in a heating furnace (helium atmosphere) of a pyrolyzer set at 500 degrees C for 5 minutes. The thus generated volatile components were measured by GC/MS (1.5 minutes to 30 minutes after the start of pyrolysis). Fig. 2 shows a chart obtained by the measurement. As shown in Fig. 2, volatile components obtained by pyrolysis at 500 degrees C included many decomposition products originating from cellulose, hemicellulose, and lignin, respectively.

[0030] In addition, the retention times for major compounds in GC/MS measurement performed using apparatuses and measurement conditions used herein are as listed in Table 1 below. (The same applies to the following GC/MS measurements.)

[0031] [Table 1]

Retention time (minute)	Compound
3.9	Furfural
6.4	Phenol
7.3-8.9	Cresol*1
9.8	Guaiacol
15.7	Hydroxymehylfurfural
18.5	Syringol
20.6	Vanillin
23.4	Levoglucosan

*1 Ortho-, meta-, and para-cresol are included.

[0032] 1-2. Analysis of pyrolysis behavior of cedar (370 degrees C)

Thermogravimetric analysis (TG analysis) was conducted in order to analyze the pyrolysis behavior of cedar. Fig. 3 shows the change in the weight reduction rate of a cedar sample when the temperature was increased at 50 degrees C/minute and then held at 370 degrees C. The weight of the cedar sample started to decrease at around about 280 degrees C. The weight reduction rate had decreased within about 2 minutes after the temperature had reached 370 degrees C. The weight of the residue at this time point accounted for about 30% of the initial weight. This suggested that most volatile components are volatilized within about 5 minutes when a cedar sample is pyrolyzed.

[0033] 1-3. Analysis of volatile components resulting from pyrolysis of cedar (370 degrees C and 500 degrees C)

Pyrolysis of cedar was conducted at two temperature stages, and the thus generated volatile components were subjected to GC/MS measurement. Measuring apparatuses used herein are the same as those in 1-1 above. A cedar sample was placed in a heating furnace (helium atmosphere) of a pyrolyzer set at 370 degrees C for 5 minutes. Subsequently, the cedar sample was removed once from the heating furnace and then left to stand to room temperature. The heating furnace was set at 500 degrees C and the sample was again placed in the heating furnace and then maintained therein for 5 minutes. Volatile components generated at each temperature were measured by GC/MS. Fig. 4 shows the thus obtained chart. Components volatilized at 370 degrees C were found to include high levels of hemicellulose-derived and cellulose-derived decomposition products. On the other hand, components volatilized at 500 degrees C were found to include high levels of lignin-derived decomposition products (phenols). When the chart of Fig. 4 is compared with the chart of Fig. 2, unlike the case in which the sample had been directly heated at 500 degrees C, the levels of the hemicellulose-derived and cellulose-derived decomposition products were found to decrease when the sample had been kept at 370 degrees C and then heated at 500 degrees C. (In Fig. 4, see regions A and B enclosed with broken lines.)

[0034] 1-4. Analysis of volatile components resulting from pyrolysis of Japanese cypress (500 degrees C)

Generated volatile components were measured by GC/MS in a manner similar to that in 1-1 above except that a Japanese cypress sample was used. Fig. 5 shows the thus obtained chart. As in the case of the cedar sample, many decomposition products originating from cellulose, hemicellulose, and lignin were included.

[0035] 1-5. Analysis of pyrolysis behavior of Japanese cypress (370 degrees C and 500 degrees C)

GC/MS measurement was performed in a manner similar to that in 1-3 above except that a Japanese cypress sample was used. Volatile components generated at 370 degrees C and 500 degrees C were measured by GC/MS. Fig. 6 shows the thus obtained chart. As in the case of the cedar sample, components volatilized at 370 degrees C were found to include high levels of hemicellulose-derived and cellulose-derived decomposition products. On the other hand, components volatilized at 500 degrees C were found to include high levels of lignin-derived decomposition products (phenols). When the chart of Fig. 6 is compared with the chart of Fig. 5, unlike the case in which the sample had been directly heated at 500 degrees C, the levels of the hemicellulose-derived and cellulose-derived decomposition products were found to decrease in the case in which the sample had been kept at 370 degrees C and then heated at 500 degrees C (in Fig. 6, see regions A and B enclosed with broken lines).

[0036] 2-1. Pyrolysis test for Japanese cypress (270 degrees C or 330 degrees C)

Japanese cypress was pyrolyzed at 270 degrees C or 330 degrees C and then the thus generated volatile components were subjected to GC/MS measurement. Measurement conditions and the like employed herein were similar to those of 1-1 above. Fig. 7 shows the chart obtained by measurement. The temperature of 270 degrees C was too low, so that no peak was observed for decomposition products. On the other hand, at 330 degrees C, not only hemicellulose-derived decomposition products but also cellulose-derived hydroxymethylfurfural were found to be generated. It was revealed that the appropriate temperature range for obtaining hemicellulose-derived decomposition products is between 280 degrees C and 320 degrees C.

[0037] 2-2. Reheating of gasified product by pyrolysis of Japanese cypress (300 degrees C, and 600 degrees C to 800 degrees C)

A Japanese cypress sample (about 0.1 g) was set in a first stage portion of a tubular furnace having two heating zones (see Fig. 8), and then it was heated at 300 degrees C in a helium atmosphere. The thus generated gasified product was further heated (600 degrees C, 650 degrees C, 670 degrees C, or 800 degrees C) at a heating part (secondary pyrolysis reactor) of the second stage portion for pyrolysis. The thus obtained decomposition products were analyzed by GPC. Fig. 9 shows the chart obtained by GPC analysis. The indication "300-600" in the chart means that heating at the first stage portion was performed at 300 degrees C and heating at the second stage portion was performed at 600 degrees C (and the same applies to the other indications). In the chart, peaks corresponding to furan and water, respectively, appeared at positions indicated with arrows in the "300-800." The furan collection rate with respect to stoichiometric furan production is as shown in Table 2 below.

[0038] [Table 2]

Secondary pyrolysis temperature (°C)	600	650	670	800
Furan collection rate (%)	29.2	62.3	35.2	39.6

Furan was generated even at a secondary pyrolysis temperature of 600 degrees C, and peak furan production was observed when the secondary pyrolysis temperature was set at 650 degrees C. Also, when the secondary pyrolysis temperature was set at 800 degrees C, products obtained by condensation of decomposition products were found to contain only furan and water. These results demonstrated that the best secondary pyrolysis temperature for the furan collection rate is 650 degrees C and the best secondary pyrolysis temperature for the selective collection of furan is 800 degrees C.

[0039] 3-1. Analysis of volatile components resulting from pyrolysis of eucalyptus (370 degrees C, 500 degrees C and 600 degrees C)

Eucalyptus was pyrolyzed at three temperature stages and the thus generated volatile components were subjected to GC/MS measurement. Measuring apparatuses used herein were the same as those in 1-1 above. An eucalyptus sample was placed in a heating furnace (helium atmosphere) of a pyrolyzer set at 370 degrees C for 5 minutes. Subsequently, the eucalyptus sample was removed once from the heating furnace and left to stand to room temperature. The heating furnace was set at 500 degrees C and the sample was again placed in the heating furnace and then maintained therein for 5 minutes. Similarly, after the eucalyptus sample was removed once, the heating furnace was set at 600 degrees C, and then the sample was placed again in the heating furnace and maintained therein for 5 minutes. Volatile components generated at each temperature were measured by GC/MS. Fig. 10 shows the thus obtained chart. It was demonstrated when pyrolysis was performed at three temperature stages (370 degrees C, 500 degrees C and 600 degrees C), a decomposition product containing phenol and cresol as major components was generated at 600 degrees C.

[0040] 3-2. Analysis of volatile components resulting from pyrolysis of palm kernel shells (500 degrees C and 600 degrees C; or 350 degrees C, 500 degrees C and 600 degrees C)

Palm kernel shells were pyrolyzed at two temperature stages (500 degrees C and 600 degrees C) or three temperature stages (350 degrees C, 500 degrees C and 600 degrees C) and the thus generated volatile components were subjected to GC/MS measurement. Measuring apparatuses used herein are the same as those in 1-1 above. Procedures for pyrolysis at two temperature stages or three temperature stages were similar to those in 1-3 and 3-1 above. Fig. 11 and Fig. 12 show the thus obtained charts. When pyrolysis was performed at two temperature stages (500 degrees C and 600 degrees C) without a pyrolysis step with a low temperature, almost no phenol peak and almost no cresol peak were observed by pyrolysis at 600 degrees C. On the other hand, when pyrolysis was performed at three temperature stages (350 degrees C, 500 degrees C and 600 degrees C) including pyrolysis at a relatively low temperature of 350 degrees C, both phenol peak and cresol peak were observed as a result of pyrolysis at 600 degrees C.

[0041] All references, including any publications, patents or patent applications cited in this specification are hereby incorporated by reference in their entirely.

Claims

[Claim 1] A method for obtaining a useful organic compound by pyrolyzing plant biomass, comprising:
a 1st heating step wherein biomass is heated at a 1st heating temperature; and
a 2nd heating step wherein either a gasified product or a biomass residue obtained in the 1st heating step is heated at a 2nd heating temperature higher than the 1st heating temperature.

[Claim 2] The method according to claim 1, wherein:
in the 1st heating step, plant biomass is heated at the 1st heating temperature of 400 degrees C or lower; and
in the 2nd heating step, the biomass residue is heated at the 2nd heating temperature of 500 degrees C or higher to obtain a lignin-derived decomposition product.

[Claim 3] The method according to claim 1 or 2, wherein:
in the 2nd heating step, the biomass residue obtained in the 1st heating step is heated; and
the method further comprises a 3rd heating step wherein the further generated biomass residue obtained in the 2nd heating step is heated at a 3rd heating temperature higher than the 2nd heating temperature.

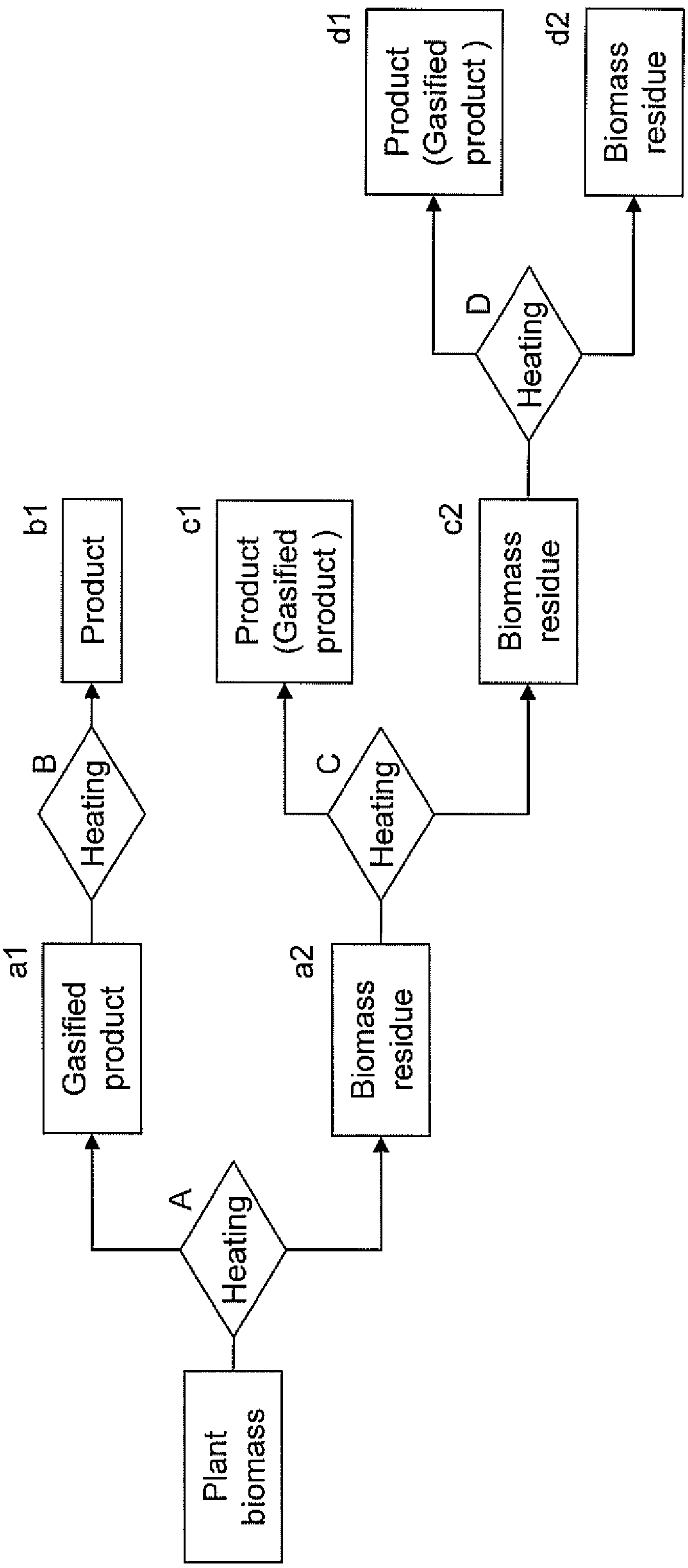
[Claim 4] The method according to claim 3, wherein:
the 1st heating temperature is 400 degrees C or lower;
the 2nd heating temperature ranges from 500 degrees C to 600 degrees C; and
in the 3rd heating step, the biomass residue is heated at the 3rd heating temperature of 600 degrees C or higher to obtain a lignin-derived decomposition product.

[Claim 5] The method according to any one of claims 1 to 4, wherein the lignin-derived decomposition product contains at least phenol or cresol.

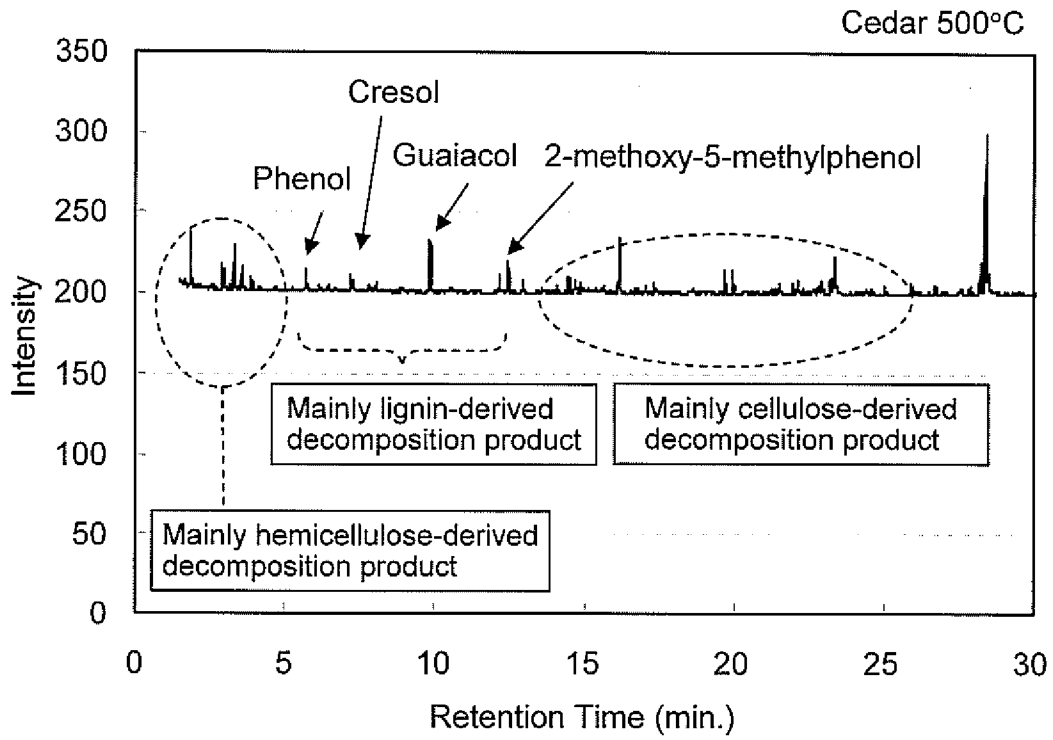
[Claim 6] The method according to any one of claims 1 to 5, wherein:
in the 1st heating step, plant biomass is heated at the 1st heating temperature ranging from 280 degrees C to 320 degrees C; and
in the 2nd heating step, the gasified product obtained in the 1st heating step is heated at the 2nd heating temperature ranging from 600 degrees C to 800 degrees C to obtain a hemicellulose-derived decomposition product.

[Claim 7] The method according to claim 6, wherein the hemicellulose-derived decomposition product contains at least furan.

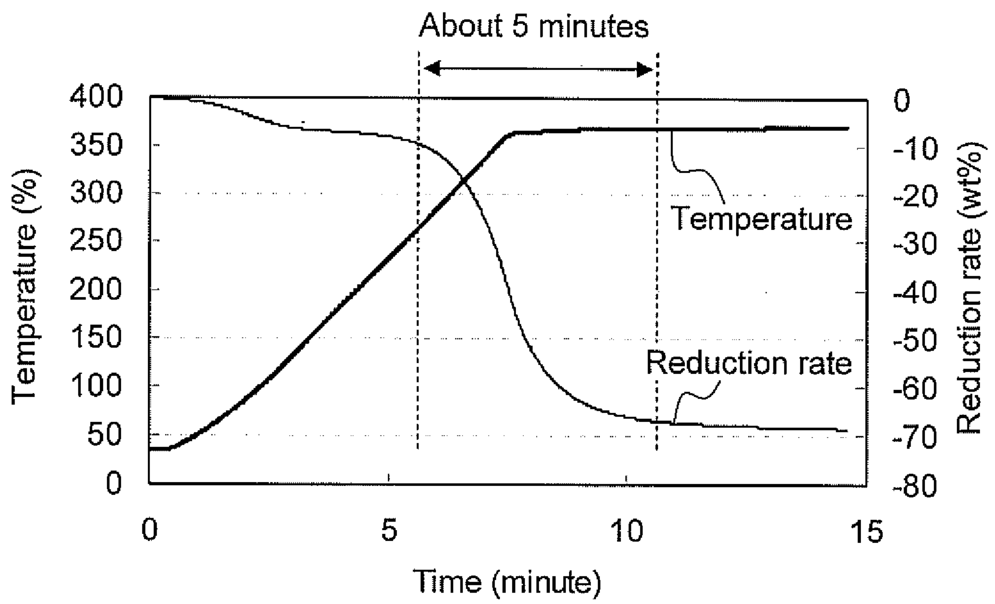
[Fig. 1]


Plant biomass
Heating
A
a1
Gasified product
a2
Biomass residue
Heating
B
b1
Product
Heating
C
c1
Product (Gasified product)
c2
Biomass residue
Heating
D
d1
Product (Gasified product)
d2
Biomass residue

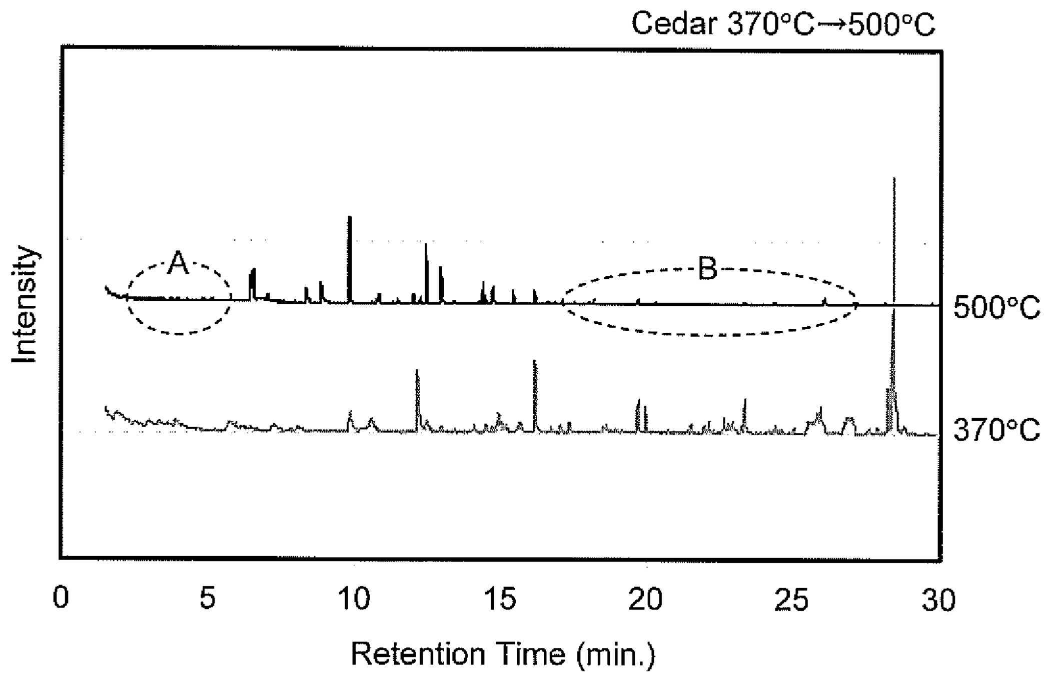
[Fig. 2]


Cedar 500°C
Cresol
Phenol
Guaiacol
2-methoxy-5-methylphenol
Mainly lignin-derived decomposition product
Mainly cellulose-derived decomposition product
Mainly hemicellulose-derived decomposition product
Intensity
350
300
250
200
150
100
50
0
0
5
10
15
20
25
30
Retention Time (min.)

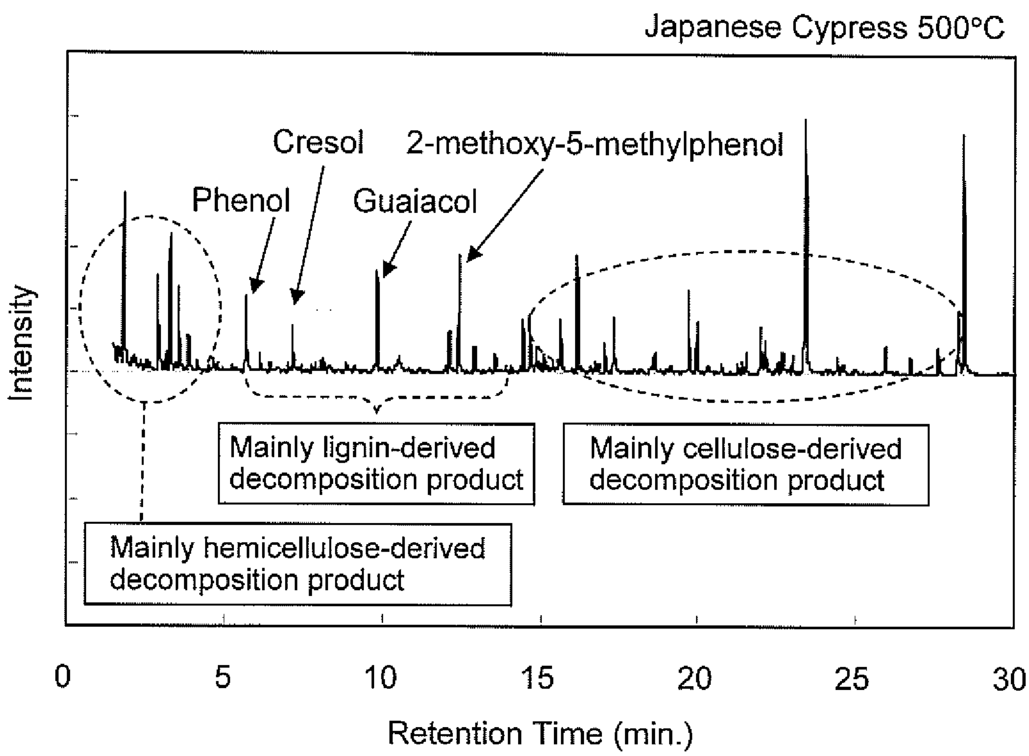
[Fig. 3]


About 5 minutes
Temperature
Reduction rate
Temperature (%)
Reduction rate (wt%)
400
350
300
250
200
150
100
50
0
-10
-20
-30
-40
-50
-60
-70
-80
0
5
10
15
Time (minute)

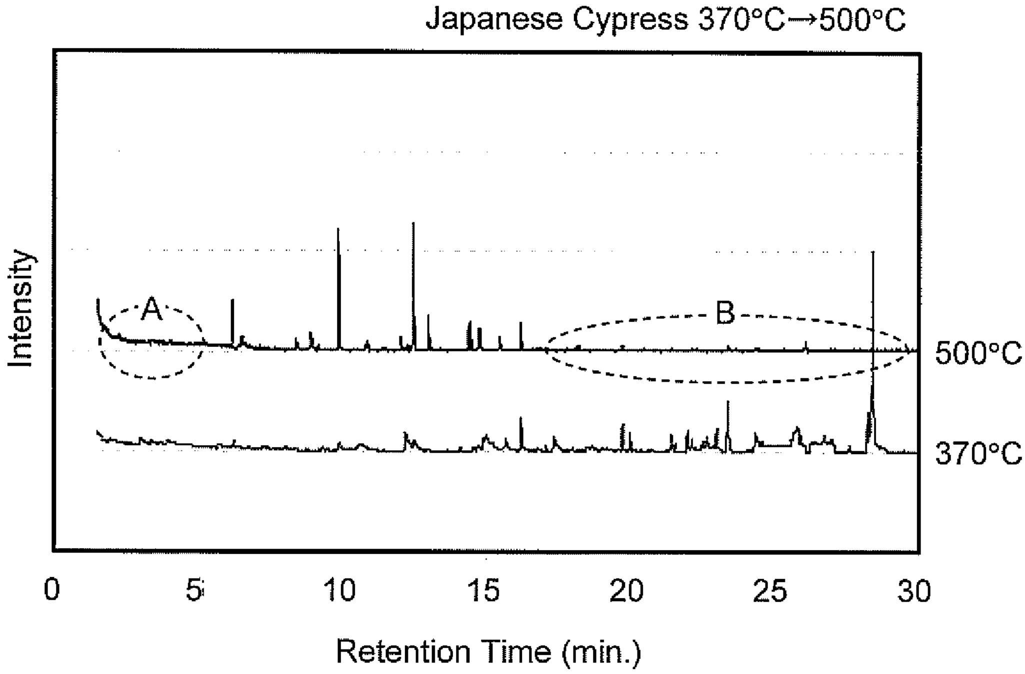
[Fig. 4]


Cedar 370°C→500°C
Intensity
A
B
500°C
370°C
0
5
10
15
20
25
30
Retention Time (min.)

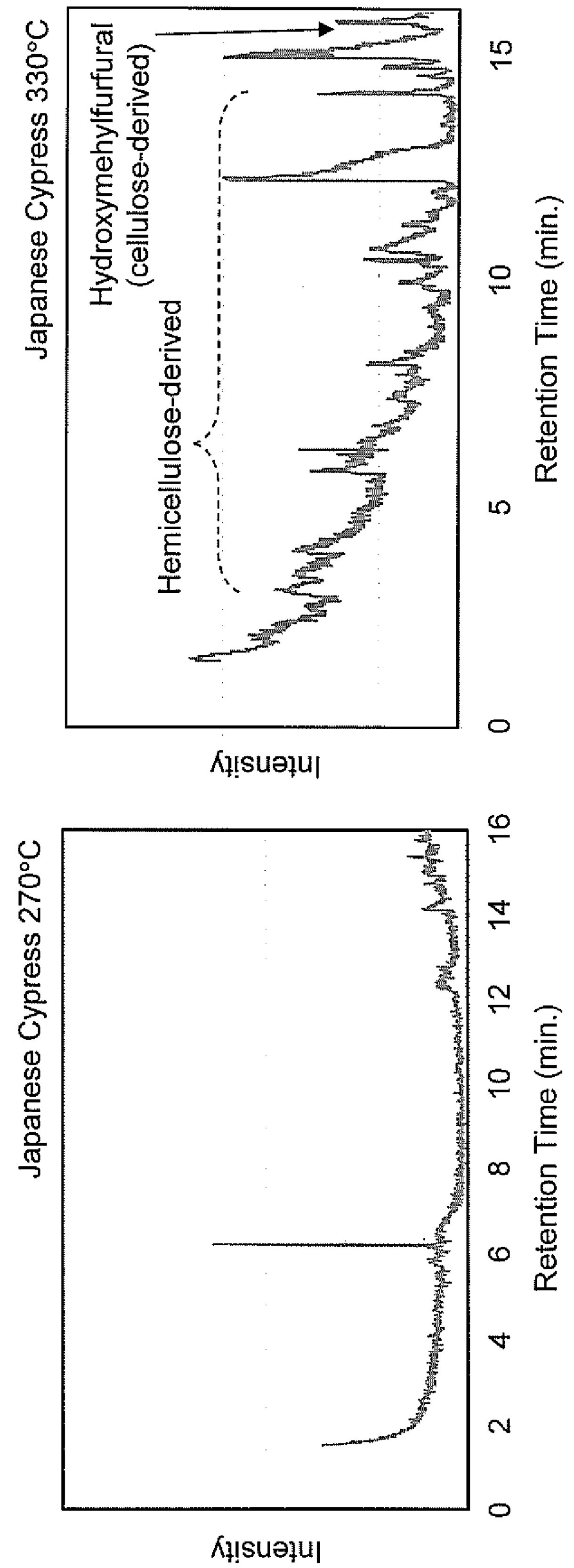
[Fig. 5]


Japanese Cypress 500°C
Intensity
Cresol
2-methoxy-5-methylphenol
Phenol
Guaiacol
Mainly lignin-derived decomposition product
Mainly cellulose-derived decomposition product
Mainly hemicellulose-derived decomposition product
0
5
10
15
20
25
30
Retention Time (min.)

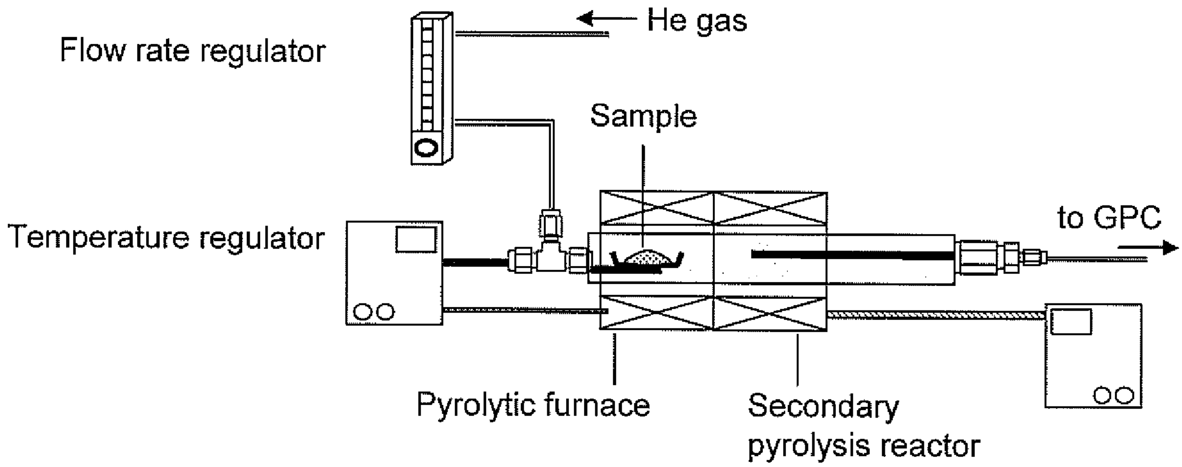
[Fig. 6]


Japanese Cypress 370°C→500°C
Intensity
A
B
500°C
370°C
0
5
10
15
20
25
30
Retention Time (min.)

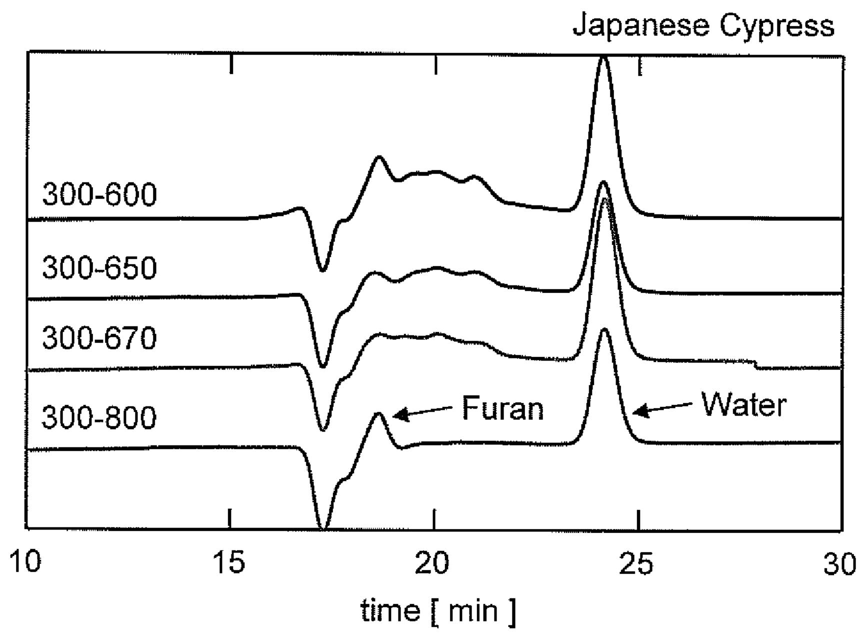
[Fig. 7]


Japanese Cypress 330°C
Hydroxymehylfurfural (cellulose-derived)
Hemicellulose-derived
Intensity
Retention Time (min.)
0
5
10
15
Japanese Cypress 270°C
Intensity
Retention Time (min.)
0
2
4
6
8
10
12
14
16

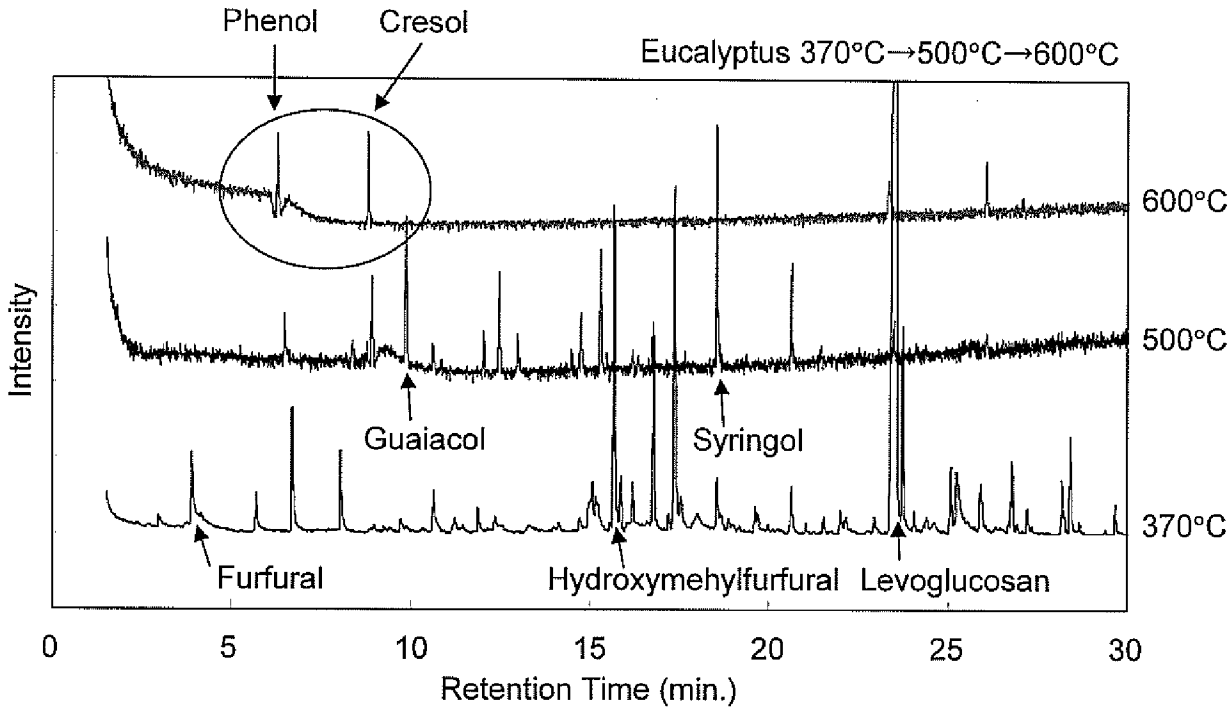
[Fig. 8]


He gas
Flow rate regulator
Sample
Temperature regulator
to GPC
Pyrolytic furnace
Secondary
pyrolysis reactor

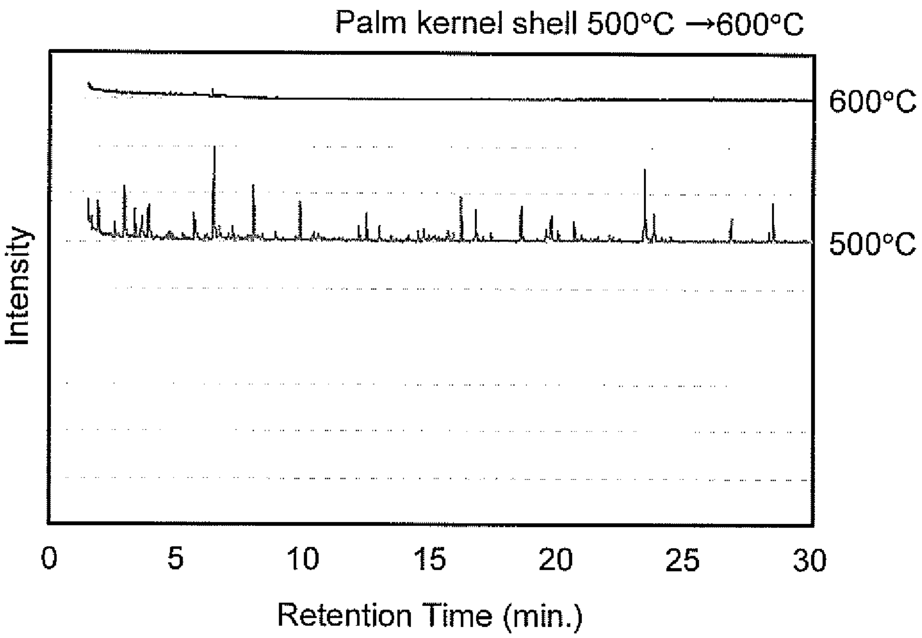
[Fig. 9]


Japanese Cypress
300-600
300-650
300-670
300-800
Furan
Water
10
15
20
25
30
time [min]

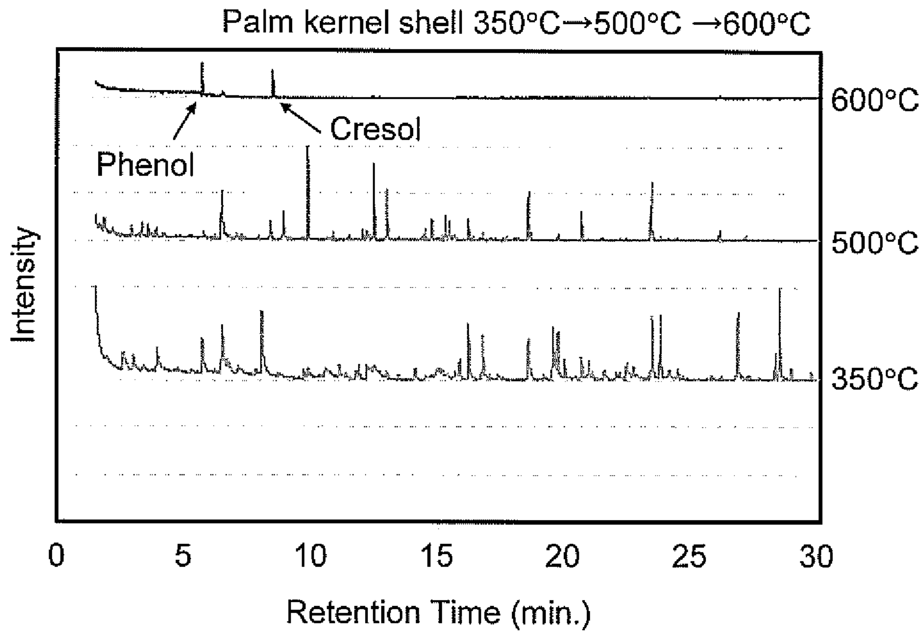
[Fig. 10]


Phenol
Cresol
Eucalyptus 370°C→500°C→600°C
600°C
500°C
370°C
Intensity
Guaiacol
Syringol
Furfural
Hydroxymehylfurfural
Levoglucosan
0
5
10
15
20
25
30
Retention Time (min.)

[Fig. 11]


Palm kernel shell 500°C →600°C
600°C
500°C
Intensity
0
5
10
15
20
25
30
Retention Time (min.)

[Fig. 12]


Palm kernel shell 350°C→500°C →600°C
600°C
Cresol
Phenol
500°C
Intensity
350°C
0
5
10
15
20
25
30
Retention Time (min.)

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2011/006030

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10B53/02 C10B57/02
ADD. C10C5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10B C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/130988 A1 (UNIV ASTON [GB]; HORNUNG ANDREAS [DE]; APFELBACHER ANDREAS [DE]) 18 November 2010 (2010-11-18) figures 1-8 page 16, line 4 - page 33, line 27 claims 1-18 ----- -/--	1-7

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 April 2012	16/04/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Zuurdeeg, Boudewijn

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE WILD P J ET AL: "Biomass valorisation by staged degasification. A new pyrolysis-based thermochemical conversion option to produce value-added chemicals from lignocellulosic biomass", JOURNAL OF ANALYTICAL AND APPLIED PYROLYSIS, ELSEVIER BV, NL, vol. 85, no. 1-2, 1 May 2009 (2009-05-01), pages 124-133, XP002603129, ISSN: 0165-2370, DOI: 10.1016/J.JAAP.2008.08.008 [retrieved on 2008-08-26] tables 1,2,5,6 figures 1,6 2. Materials and methods -----	1-7
X	WO 2010/102145 A1 (UNIV WASHINGTON STATE [US]; ZHOU SHUAI [US]; LIAN JIENI [US]; LIAW SHI) 10 September 2010 (2010-09-10) claims 1-20 page 8, lines 25-29 page 8, line 30 - page 9, line 32 page 6, lines 15-16 figures 1-13 -----	1-7
X	PRINS M J ET AL: "More efficient biomass gasification via torrefaction", ENERGY, PERGAMON PRESS, OXFORD, GB, vol. 31, no. 15, 1 December 2006 (2006-12-01), pages 3458-3470, XP024900326, ISSN: 0360-5442, DOI: 10.1016/J.ENERGY.2006.03.008 [retrieved on 2006-12-01] figure 4 table 3 -----	1,2,6,7
X	EP 1 277 825 A1 (INST FRANCAIS DU PETROLE [FR]) 22 January 2003 (2003-01-22) paragraphs [0001], [0066], [0070] figures 1,2 claims 1-7 -----	1,6,7

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/JP2011/006030

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010130988 A1	18-11-2010	EP 2430121 A1	21-03-2012
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		WO 2010130988 A1	18-11-2010
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		WO 2010102145 A1	10-09-2010
EP 1277825 A1	22-01-2003	AT 388213 T	15-03-2008
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		JP 2003147365 A	21-05-2003
		PT 1277825 E	29-05-2008