1538 *Bull. Chem. Soc. Jpn. Vol. 82, No. 12, 1538–1547 (2009)*

Biomass Carbon Ratio of Biomass Chemicals Measured by Accelerator Mass Spectrometry

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The biomass carbon ratios of various chemical products were studied. The biomass carbon ratios of chemicals such as polymers, their monomers, starches, cellulose, calcium carbonate, charcoal, ethanol, and polymer blends were estimated by the ratios of ^{14}C to ^{12}C measured by accelerator mass spectrometry (AMS) based on ASTM D 6866. Preparations of the gaseous and liquid samples for the AMS measurements are described, and the pretreatment for carbonate is also explained. Repeatability and accuracy of the biomass carbon ratio evaluation by AMS are discussed. It was found that a new correction factor is necessary for cellulose other than 0.93, which is regulated as the correction factor for present modern carbon newer than 1950 in ASTM D 6866. The developed sample preparations of gaseous materials and carbonate were confirmed to be applicable for the AMS measurement of the biomass carbon ratio. The repeatability and accuracy of the biomass carbon ratio evaluation by AMS were confirmed for ethanol derived from biomass (bioethanol), a polymer blend of biomass-based poly(lactic acid) (PLA), and petroleum-based poly(butylene succinate) (PBS). Standard deviations of the bioethanol and the blend of PLA and PBS are 0.36 and 0.84%, respectively. The biomass carbon ratio evaluation by AMS has been proposed for the International Standard (ISO).

Recently, many chemical products are made from biomass in order to prevent global warming, since the total amount of carbon dioxide emission during the life of these products does not increase. The carbon dioxide during the disposal process of these products is originally derived from the photosynthesis of carbon dioxide emission in the modern atmosphere. Therefore, some kinds of chemicals such as surfactants, inks, and polymers, have been widely made from biomass. Polymers have been used in various industrial fields, due to their merits such as light weight, melt processability, and resistance to corrosion. Polymers are chemical products mainly derived from petroleum and they are difficult to dispose of after use due to their resistance to corrosion. This means that a lot of energy is required to treat polymers after use. Usually, polymers are burnt after use and carbon dioxide is produced during incineration. The total carbon dioxide emission into the atmosphere increases by burning polymers derived from petroleum. In order to maintain the amount of carbon dioxide during disposal, it is proposed that polymers derived from biomass should be used instead of those from petroleum.

In the USA, biomass products are promoted by governmental policies. The United States Department of Energy (DOE) selected a building block of twelve base units in order to produce many kinds of chemical products.[1] These basic materials are expected to be studied for effective production from biomass. The United States Department of Agriculture (USDA) introduced a Green Purchasing Affirmative Procurement Program (GPAPP).[2] The USDA's GPAPP has been developed to ensure that green products will be purchased to the maximum practicable extent and fulfills the applicable affirmative procurement requirements in the related sections of the U.S. Government.

The Japan Bioplastics Association (JBPA) is a voluntary organization founded by the main Japanese plastics producing companies and others focused on plastics, which was established with the aim of promoting the popularization of biodegradable plastics and biomass-based plastics, which play an important role in solving technical recycling problems. JBPA has established an identification system related to biomass-based plastic products. The BiomassPla Identification System was established in 2006.[3] Under this system, the products that meet the stipulated standards are certified as BiomassPla and given permission to use the BiomassPla logo shown in Figure 1.

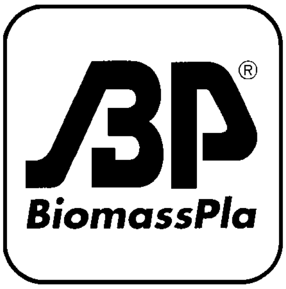

Figure 1. "BiomassPla" mark for BiomassPla Certification System by JBPA.

Published on the web December 10, 2009; doi:10.1246/bcsj.82.1538

The Organization for International Standards (ISO) was established as an international organization to publish and maintain international standards based on the World Trade Organization (WTO). ISO has Technical Committees (TC) in various industrial fields. TC61 is related to "Plastics" and has Sub-Committees (SC); SC5 is related to "Physical–chemical properties." Working Group (WG) 22 under SC5 is related to "Biodegradability."[4–8] Standards for the biodegradability of plastics in the ISO are discussed under TC61/SC5/WG22. Recently, a discussion about the biobased content of plastics was held. However, a new standard concerning the biobased content of plastic materials has not yet been proposed.

There are many kinds of chemical products which can be made from both biomass and petroleum. It is important for promoting the use of chemical products from biomass to consumers to establish a method to distinguish carbon atoms from biomass and those from petroleum. An evaluation method using the biomass ratio or biomass carbon ratio is necessary. It is difficult to determine for actual chemical products if their sources are biomass or petroleum based on physical properties such as mechanical properties, thermal properties, and others, since these properties of the chemicals including polymers derived from biomass are the same as those of the chemicals derived from petroleum. At this moment, there is no standard for the determination of the origin of chemical products in the ISO. There are some standards concerning the determination of the biomass content in the American Society of Testing and Materials (ASTM). ASTM D 6866-08 entitled "Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis" is one of these standards.[9] In ASTM D 6866-08, biomass-based carbons are evaluated by an analysis of the ^{14}C radioisotope of carbon atoms. The ^{14}C concentration is measured by accelerator mass spectrometry (AMS) and a liquid scintillation counter. The principle of this method using ^{14}C is based on a dating measurement for historical materials in archeology.[10,11] ^{14}C is a radioisotope of carbon atoms with a half life of 5730 years. ^{14}C atoms are continuously generated from ^{14}N atoms due to their interaction with cosmic radiation in the modern atmosphere. The ratio of ^{14}C to ^{12}C in modern air is constant at ca. 1×10^{-12} in spite of the period. Plants absorb carbon dioxide in the atmosphere and incorporate it in their structure by photosynthesis. The ratio of ^{14}C to ^{12}C in a plant is 1×10^{-12} immediately after photosynthesis. ^{14}C in the plant materials gradually decays into ^{14}N. The number of ^{14}C atoms continuously decreases and becomes half after 5730 years. Therefore, the age of materials including carbon atoms can be estimated using the ratio of the number of ^{14}C atoms to that of ^{12}C atoms and the half life of ^{14}C. The ratio of ^{14}C to ^{12}C can be measured by AMS, although this ratio is as low as 1×10^{-12}. A standard year is defined as 1950 according to these formulas for radiometric dating in ASTM D 6866-08. In ASTM D 6866-08, formulas of radiometric dating are applied to the determination of the biobased content. A percent modern carbon (pMC) value can be estimated by comparing the measured ratio of ^{14}C to ^{12}C, and the standard ratio of ^{14}C to ^{12}C determined the appropriate primary reference (oxalic acid) of SRM 4990c supplied by the National Institute of Standards and Technology (NIST), USA.[12] The percent modern carbon (pMC) can be slightly greater than 100% due to the continuing, but diminishing effects of the 1950's nuclear testing programs. Since all sample ^{14}C activities are referred to as a "pre-bomb" standard, all pMC values must be multiplied by 0.93 to correct for the bomb carbon and to subsequently obtain the true biobased content of the sample. The pMC value determined for the biomass produced in recent years is 108%. According to ASTM D 6866, the biomass ratio (biobased content) exceeding 100% is corrected to 100%. This regulation creates some problems. There is no problem for single materials, such as homopolymers to use this regulation. The origins of these materials are alternative biomass or petroleum. Most of the actual chemical products are not made of a single material. For a mixture, blend, or composites, it is necessary to more accurately evaluate the value of the biomass ratio. The method described in ASTM D 6866-08 is appropriate for solid samples, although the title of this standard includes "liquids" and "gaseous samples." In ASTM D 6866-08, a "liquid sample" means the benzene converted from the sample carbon by a synthesis procedure, and "gaseous sample" means the emission gas of carbon dioxide converted from the sample carbon and the flue gas from electric utility boilers.[13] For all the liquid and gaseous samples related to chemicals, an evaluation method of percent modern carbon is not regulated in ASTM D 6866-08. In order to evaluate the biomass carbon ratio of all the chemical products, we would like to propose an evaluation method widely applicable to the international standards of the biomass carbon ratio measurement. For this purpose, it is necessary to develop a method which can be applied to liquids and gaseous samples. A new evaluation method of the biomass carbon ratio is required for biofuels, such as biodiesel fuel (BDF). The biomass carbon ratios by determined a liquid scintillation counting (LSC) have been reported.[14,15] In these reports, bioethanol and BDF using a scintillator were measured by LSC. At the same time, the repeatability and accuracy of the evaluation method is required as an international standard. The biomass carbon ratios for various materials have been reported.[11,16–22] In these papers, the biomass carbon ratio is defined as the pMC value multiplied by 0.93 according to ASTM D 6866. Starches from corn, potato, and rice, and sugar from sugar beets were measured in terms of their biomass carbon ratio.[16] The biomass carbon ratios of wood powders from different parts of the same cedar tree were investigated. The biomass carbon ratios of blends and composites of poly(butylene succinate) (PBS) with cellulose or others have been investigated.[17–19] The biomass carbon ratios for PBS composites with furfural, starch and cellulose were measured. PBS blends with cellulose acetate–butyrate were also measured in terms of the biomass carbon ratio. The biomass carbon ratio of polycaprolactone (PCL) composites with cellulose and talc have been measured.[20] The biomass carbon ratio of the newly developed biodegradable polymer (Sorona®, DuPont) was also studied.[11] The biomass carbon ratios of polymer composites filled with inorganic fillers such as carbonates were investigated.[21] In ASTM D 6866, the carbon from carbonate is regulated and omitted in order to reduce errors. However, in order to confirm the applicability of our method to carbonate and composites including carbonate, the pretreatments and biomass carbon ratios were studied. In addition, the biomass carbon ratios of the evolved gas during the aerobic biodegradation test in the compost were studied.[22]

The biomass carbon ratios of samples were determined in this study. The biomass carbon ratio was determined as the biomass ratio of the origin of the samples in carbon atoms. The biomass carbon ratios were measured by AMS based on ASTM D 6866. However, the details are slightly different from those of ASTM D 6866. The sample preparation methods, which are not regulated for samples, such as the liquid and gas, in ASTM D 6866, are proposed in this paper. The biomass carbon ratio of the composite samples consisting of polymers and fillers of inorganic carbon were investigated. For this composite, the pretreatments for the AMS measurement were investigated. The biomass carbon ratios of various types of materials including gases were measured. The repeatability and accuracy of the measurements of the biomass carbon ratios were also investigated. The potential of the AMS measurements as international standards has been discussed.

Experimental

Materials. Various samples as representatives of chemical products were used for the biomass carbon ratio measurement. Methane gas, ethylene gas, and propylene gas of a calibration gas grade from GL Sciences, Inc., were used as gaseous fuels and monomers of polymers. Crude di-L-lactide from Tokyo Chemical Industry Co. was used as received. Purified di-L-lactide was made by recrystallization of the crude products. ε-Caprolactone from Tokyo Chemical Industry Co., Ltd., was used as a chemical derived from petroleum. Polypropylene, poly(butylene succinate) (PBS), and polycaprolactone were used as received from Sigma-Aldrich. Poly(lactic acid) was synthesized from purified di-L-lactide in the presence of tin(II) bis(2-ethylhexanoate) as catalyst and glycerol as an initiator. Starch, cellulose, calcium carbonate, and activated charcoal were employed as solid materials including carbon atoms for the biomass carbon ratio measurement. Two kinds of starches from potato and corn supplied by Wako Pure Chemical Industries, Ltd., were employed as received. Cellulose fibers of ashless pulp from Toyo Roshi Kaisha, Ltd., were used as received. Three kinds of fibers from palm oil trees were employed. Fibers from frond, trunk and empty fruit bunches of palm oil trees, which were provided by the Malaysia Palm Oil Board (MPOB), were used. These fibers were used as received and their powders were obtained by mechanical crushing. Powders of calcium carbonate from shells and from limestone were employed. Calcium carbonate from shells, Gofun, which is used as a coloring for Japanese painting, from Kissho, Nihonga Paint Co., Ltd., and Gofun from Matsujirushi, Nakagawa, were used as received. Calcium carbonates as chemicals of guaranteed reagent grade from Kanto Chemical Co., Inc., and an extra pure grade from Kanto Chemical Co., Inc., were used as received. Activated charcoal from Wako Pure Chemical Industries, Ltd., was used as received.

Crushing of Solid Samples. There is no regulation for sample preparation before combustion in ASTM D 6866-08. It is necessary for the solid samples to be reduced in size in order to prepare a ca. 10 mg sample for the accelerator mass spectrometry (AMS) analysis. In this study, some solid chemicals, such as polymer pellets and fibers, were crushed into powders. These samples were crushed by a mechanical mixer along with crushed dry ice. One cycle is a three-minute crushing and ten cycles of crushing for each sample with a one-minute interval. The crushed powders were separated from the small powders with a 125 µm mesh sieve. The powders were dried in a vacuum oven after the above elimination process.

Sample Preparation for Polymer Blend. Polymer blends were prepared by casting. That is to say, two kinds of polymers were weighed and mixed and then dissolved in a 10% chloroform solution. The solution containing the polymers was dried in air for 3 days and dried under reduced pressure for 1 day and a film sample of the polymer blend was formed.

Sample Preparation of Solid Materials for Biomass Carbon Ratio Measurement. The sample preparation for the AMS measurement is not clearly regulated in ASTM D 6866-08, since the standard should not exclude the sample preparation methods which are not clearly expressed in the standard. In this study, the sample preparation and measurements were performed at the Institute of Accelerator Analysis, Ltd. (IAA), Japan.[16–22] All carbon atoms in the samples were transformed into graphite carbons through serial oxidation and reduction reactions using a quartz glass tube and a vacuum manifold system. Solid samples, such as polymers and fillers, were ground into powder using sandpaper at various positions on the sample surface. For the polymer blend sample, small pieces of the specimens were taken from the bulk samples in order to limit the effect of the production process of the powders. Powder samples were used without undergoing the powder making process. These samples of 3–50 mg were put into a quartz glass tube with 1 g of copper oxide (CuO) connected to a vacuum line system, then the quartz glass tube was closed. The samples in the tube were oxidized at 500 °C for 30 min and at 850 °C for 2 h. Subsequently, the evolved carbon dioxide (CO_2) was cold-trapped. The collected CO_2 by pretreatment with ferrous (Fe) powders was reduced to graphite at 650 °C for 10 h by a deoxidization reaction. After the above procedures, pure graphite with oxidized iron (1 mg) was transferred to a sample holder (small rod shape; 1 mm hole) for AMS. In ASTM D 6866-08, the oxidation temperature is regulated at 900 °C, but there is no regulation for deoxidization.

Pretreatment of Calcium Carbonate for Biomass Carbon Ratio Measurement. In ASTM D 6866-08, the biobased content is regulated for samples without carbonate. Therefore, the carbonate in samples should be separated by a reaction with 10% HCl in ASTM D 6866-08. In this study, the separation method for carbonate during pretreatment was investigated. In order to separate carbon atoms of carbonate from those of other materials, carbonate, such as calcium carbonate ($CaCO_3$), was pretreated with acid, such as phosphoric acid (H_3PO_4). When it is not necessary to distinguish carbon atoms from carbonate, samples including carbonates were prepared for the AMS measurement according to the same procedure for the solid chemical product as already described. All carbon atoms of $CaCO_3$ were transferred to graphite carbons through serial vaporization and reduction reactions using a gas-tight glass tube with a closing cock which can be connected to a vacuum manifold system as indicated in Figure 2 for the pMC measurement of $CaCO_3$ powders by AMS. H_3PO_4 liquid (5 mL) was poured into the left round-bottom portion of the gas-tight glass tube, and $CaCO_3$ (20 mg) was placed in the right round-bottom flask. This tube was connected to the vacuum manifold line under reduced pressure ($<10^{-2}$ mbar) for 24 h at room temperature to remove the remaining water in the H_3PO_4 liquid. The H_3PO_4 liquid was slowly transferred to the right bottom one including the $CaCO_3$ powders. Additional liquid was added if the reaction was not active. After all the liquid was transferred, this tube was incubated in a hot water bath (ca. 90 °C) for 1 h.

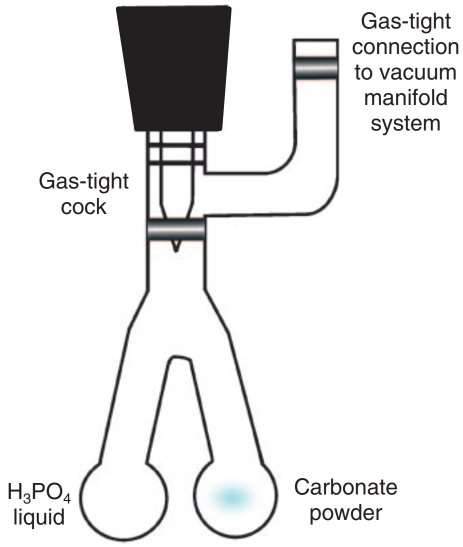

Figure 2. Gas-tight glass tube for pretreatment of carbonate with H_3PO_4.

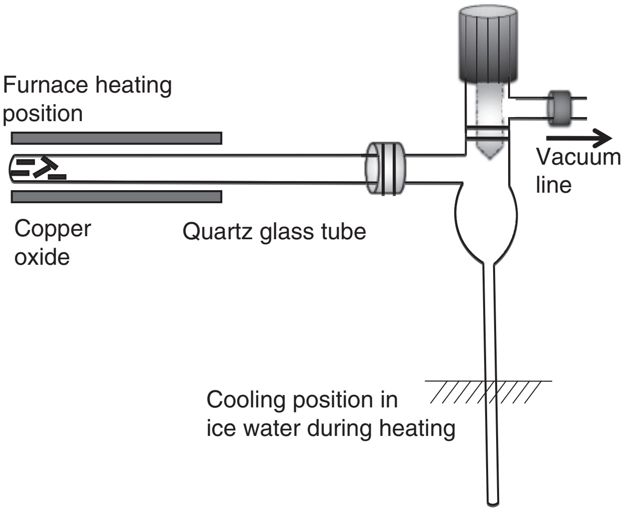

Figure 3. A reactor for oxidation of gaseous sample.

Sample Preparation of Gaseous Materials for Biomass Carbon Ratio Measurement. In ASTM D 6866-08, only gases from electrical utility boilers and waste incinerators are described as gaseous samples. Therefore, there is no regulation for general gas in ASTM D 6866-08.

Methane and biogas with methane cannot be trapped in a quartz glass tube using liquid nitrogen. Therefore, a special reaction tube with a quartz glass tube, cock and another glass tube having a buffer volume, which can be cooled in ice water when the quartz glass tube with CuO is heated, was used as indicated in Figure 3. The gaseous sample (ca. 7 mg) is cold-trapped with CuO in a special reaction tube (total volume, ca. 10 mL) using liquid nitrogen from a glass balloon server (1 L), connected to a vacuum line system, the volume and pressure of which are known in order to determine the amount of gas for the oxidation reaction.

Ethylene and propylene are trapped with CuO in a quartz glass tube connected to a vacuum line system using liquid nitrogen from a glass balloon server and then the quartz glass tube is closed. This tube is heated at 500 °C for 30 min and 850 °C for 2 h for the oxidation reaction. The other steps are the same as the pretreatment methods for the solid samples.

Sample Preparation of Liquid Materials for Biomass Carbon Ratio Measurement. There is no regulation for liquid samples in ASTM D 6866-08 except for the liquid scintillation analyzers. The liquid samples were used for the biomass carbon ratio measurement in this study. A quartz glass tube including CuO and sample was cooled at the liquid nitrogen temperature of about −196 °C. Ordinary liquid samples change to a solid at this temperature. The same procedure for the solid samples can be applied to the liquid sample, when the sample phase changes from liquid to solid.

Measurement of Biomass Carbon Ratio. In ASTM D 6866-08, there is no regulation for the measurement of the carbon isotope ratios using a specific apparatus, since ASTM D 6866-08 should not regulate the apparatus. If the standard regulates the apparatus, then other instruments cannot be used based on the standard. The measurement of the ratio of the three carbon isotopes (^{14}C, ^{13}C, and ^{12}C) using AMS was performed at the IAA. The AMS measurement procedure has already been reported in our previous studies.[16–22] The carbon in the graphite, transferred from the samples, was ionized using a cesium cation beam. The anionized carbons were accelerated using a 3 MV tandem accelerator. The accelerated carbon isotopes were separated using an analyzing magnet based on the different atomic masses. The amounts of ^{12}C and ^{13}C were detected as a current using multi-Faraday cups. The ^{14}C atoms were detected using a solid state detector with a semiconductor absorber. The ratio of the ^{14}C to ^{12}C concentrations ($^{14}A_s$) in the samples was calculated from the measured amounts of ^{14}C and ^{12}C. The percentage of modern carbon (pMC) for an oil-based carbon is 0%, since all of the ^{14}C in oil has already decayed during storage in the earth. The pMC for the biomass made from the fixation of CO_2 in the modern atmosphere through photosynthesis is 108–110% in 2002. Measurement of product's $^{14}A_s$ ($^{14}C/^{12}C$) is determined as relative to the modern carbon-based oxalic acid radiocarbon.[11] $\Delta^{14}C$ can be calculated using the following formula 1 and the pMC can be calculated from $\Delta^{14}C$ by formula 2. The biomass carbon ratio can be obtained using formula 3.

$$\Delta^{14}\mathrm{C} = [(^{14}\mathrm{A_s} - {}^{14}\mathrm{A_r})/{}^{14}\mathrm{A_r}] \times 1000\ (‰) \quad (1)$$

$$\mathrm{pMC} = \Delta^{14}\mathrm{C}/10 + 100\ (\%) \quad (2)$$

$$(\text{biomass carbon ratio}) = \mathrm{pMC} \times 0.93 \quad (3)$$

$^{14}A_s$ and $^{14}A_r$ are the ratios of ^{14}C to ^{12}C for the sample and reference (SRM 4990c), respectively. The above method is the measurement procedure of ratios for the three carbon isotopes (^{14}C, ^{13}C, and ^{12}C) in the samples at the IAA. Formulas 1 to 3 with the correction factor of 0.93 are regulated in ASTM D 6866-08. At the same time, the correction of $^{14}A_s$ using ^{13}C ratio to ^{14}C is also regulated in ASMT D 6866-08. However, this correction is not employed in this study.

Results and Discussion

Biomass Carbon Ratio of Monomers and Polymers. Among chemical products, it is difficult to confirm the source of polymers, particularly if they are biomass or petroleum. Both the polymers derived from biomass and those from petroleum are used in actual chemical products. The evaluation method of the biomass carbon ratio is important for chemical products which can be made from both biomass and petroleum. The biomass carbon ratios of various monomers and polymers

Table 1. Biomass Carbon Ratio of Monomers and Polymers

Entry	Material	Origin	Shape	Δ^{14}C /‰	pMC /%	Biomass carbon ratio /%
1	ethylene[a]	petroleum	gas	< -999[k]	<0.13[k]	<0.12
2	polyethylene[b]	petroleum	pellet	< -999[k]	<0.13[k]	<0.12
3	propylene[c]	petroleum	gas	< -999[k]	<0.13[k]	<0.12
4	polypropylene[d]	petroleum	pellet	< -999[k]	<0.13[k]	<0.12
5	di-L-lactide[e]	biomass	powder	44.04	104.4	97.09
6	di-L-lactide[f]	biomass	powder	82.32	108.23	100.65
7	poly(lactic acid)[g]	biomass	solid	63.4	106.34	98.90
8	caprolactone[h]	petroleum	liquid	< -999[k]	<0.13[k]	<0.12
9	polycaprolactone[i]	petroleum	pellet	< -999[k]	<0.13[k]	<0.12
10	poly(butylene succinate)[j]	petroleum	pellet	< -999[k]	<0.13[k]	<0.12

a) Ethylene, calibration gas, GL Sciences, Inc. b) Polyethylene, Mitsubishi Chemical Corporation. c) Propylene, calibration gas, GL Sciences, Inc. d) Polypropylene, Sigma-Aldrich. e) Di-L-lactide as received, Tokyo Chemical Industry Co., Ltd. f) Di-L-lactide purified by recrystallization, Tokyo Chemical Industry Co., Ltd. g) Poly(lactic acid) synthesized from di-L-lactide (f). h) ε-Caprolactone, Tokyo Chemical Industry Co., Ltd. [measured in 2007]. i) Polycaprolactone, Sigma-Aldrich [measured in 2007]. j) Poly(butylene succinate), Sigma-Aldrich [measured in 2007]. k) Less than detection limit of instrument.

derived from these monomers were measured by the accelerator mass spectrometry (AMS) method as described in the experimental section. The ratio of ^{14}C atoms to the number of ^{12}C can be measured by AMS. The difference between the ratio of ^{14}C to ^{12}C for the reference and that for the sample can be estimated as the Δ^{14}C value by formula 1. The percent modern carbon (pMC) can be calculated from Δ^{14}C according to formula 2. The biomass carbon ratios of samples can be derived from the pMC and correction factor of 0.93. The results of the biomass carbon ratios are shown in Table 1. The materials, origins of the samples, shape of the samples, Δ^{14}C, pMC, and biomass carbon ratios are shown in Table 1. The ^{14}C atoms were counted by a semiconductor absorber, since the number of ^{14}C atoms is very low compared to that of ^{12}C. The measured data ^{14}C by AMS in IAA is calibrated by a reference. The measurement limit of biomass carbon ratio related to this calibration is 0.12%, so that the lowest biomass carbon ratio value by AMS is 0.12%. This accuracy of the AMS measurement for the biomass carbon ratio corresponds to 0.13% percent modern carbon (pMC) and −999‰ Δ^{14}C. When no ^{14}C was detected for the sample, the Δ^{14}C, pMC, and biomass carbon ratio are shown as "< −999," "<0.13," and "<0.12" in the table, respectively. The biomass carbon ratios of the gaseous samples, such as ethylene and propylene, were measured after the sample preparation method for gaseous materials as described in the experimental section. Except for the di-L-lactide and poly(lactic acid), the resources for the materials are petroleum. The biomass carbon ratios of the oil-based materials are expected to be zero %. The experimental results well agreed with the expected values. The biomass carbon ratios of the two kinds of di-L-lactides are shown in Table 1 as Entries 5 and 6. The di-L-lactide of Entry 5 is the original chemical without purification. This di-L-lactide emits an ethyl acetate odor. This means that some amount of the solvent remained in the chemicals. Entry 6 shows the value for the purified di-L-lactide. For this di-L-lactide, the biomass carbon ratio is almost 100%. The biomass carbon ratio of the crude di-L-lactide (Entry 5) increased to that of the purified di-L-lactide (Entry 6) by purification. Based on these results, it was found that the amount of contamination of the oil-based chemicals during processing can be estimated by AMS measurement. Entry 7 is the result for polymerization from the purified di-L-lactide, an initiator and a catalyst in our laboratory. For this polymerized poly(lactic acid), the ratio of carbon atoms from the purified di-L-lactide is 99.4% based on our calculation. An estimated value for Entry 7 using this ratio and Entry 6 is 99.1%. This estimation agrees well with the result of 98.9%. From the above results, the biomass carbon ratios of the homopolymer and single monomer can be evaluated using the ^{14}C measurement by AMS. The biomass carbon ratios of the gaseous monomers besides carbon dioxide can be evaluated by the AMS method. The biomass carbon ratios of monomers and polymers derived from petroleum can be evaluated as zero % by AMS.

Biomass Carbon Ratio of Materials from Plants. The biomass carbon ratios of materials derived from plants were measured. The values of two kinds of starches from potato and corn, and five kinds of wood materials are shown in Table 2. There is a small difference between the two starches, although the biomass carbon ratios of the starches are almost 100%. The biomass carbon ratio of cellulose from filter paper is 102.67% and higher than 100%. The biomass carbon ratios of wood fibers from various parts of the oil palm tree in Malaysia were measured. It included the empty fruit bunch, trunk, and frond of the oil palm tree. There are small differences among the values of these fibers. These results mean that the biomass carbon ratios of plant materials are not equal to 100.0%. The types of plants and parts of plants affect the biomass carbon ratio. A correction is necessary for the biomass carbon ratios of plant materials. There is another effect for trees alive in the 1950's, since the nuclear test in the air generated artificial ^{14}C in the air. Entry 18 for wood powders from the core part of the cedar tree (Sugi) shows a 142% biomass carbon ratio.[16] This tree was cut down in 2000 and estimated to be 80 years old. This higher value seems to have been affected by nuclear testing in the atmosphere. One of the solutions correcting the biomass carbon

Table 2. Biomass Carbon Ratio of Materials from Plants

Entry	Material	Origin	Shape	Δ^{14}C /‰	pMC /%	Biomass carbon ratio /%
11	starch[a)]	potato	powder	64.84	106.48	99.03
12	starch[b)]	corn	powder	94.64	109.46	101.80
13	cellulose[c)]	filter paper	fiber	104.03	110.40	102.67
14	wood fiber[d)]	empty fruit bunch from oil palm tree	fiber	67.67	106.77	99.30
15	wood powder[e)]	empty fruit bunch from oil palm tree	powder	48.09	104.81	97.47
16	wood fiber[f)]	trunk of oil palm tree	fiber	59.41	105.94	98.52
17	wood fiber[g)]	frond of oil palm tree	fiber	49.38	104.94	97.59
18	wood powder[h)]	core part of cedar tree	powder	532.40	153.24	142.51

a) Starch from potato, Wako Pure Chemical Industries, Ltd. b) Starch from corn, Wako Pure Chemical Industries, Ltd. c) Ashless pulp, Toyo Roshi Kaisha, Ltd. d) Fibers provided by Malaysia Palm Oil Board (MPOB). e) Crushed fibers of d) by Malaysia Palm Oil Board (MPOB). f) Fibers provided by Malaysia Palm Oil Board (MPOB). g) Fibers provided by Malaysia Palm Oil Board (MPOB). h) Close to the core of an 80-year-old cedar tree (Sugi).[16]

Table 3. Biomass Carbon Ratio of Inorganic Materials

Entry	Material	Origin	Shape	Δ^{14}C /‰	pMC /%	Biomass carbon ratio /%
19	calcium carbonate[a)]	shell	powder	45.72	104.57	97.25
20	calcium carbonate[b)]	shell	powder	14.94	101.49	94.39
21	calcium carbonate[c)]	shell	powder	136.47	113.65	105.69
22	calcium carbonate[d)]	shell	powder	88.60	108.86	101.24
23	calcium carbonate[e)]	limestone	powder	−996.39	0.36	0.33
24	calcium carbonate[f)]	limestone	powder	−989.08	1.09	1.01
25	activated charcoal[g)]	sawdust	powder	138.25	113.83	105.86

a) Gofun, coloring in Japanese painting, Kissho, Nihonga Paint Co., Ltd.; pretreated by heating 500 °C for 30 min and at 850 °C for 2 h. b) Gofun, coloring in Japanese painting, Kissho, Nihonga Paint Co., Ltd.; pretreated by H_3PO_4.[21] c) Gofun, coloring in Japanese painting, Matsujirushi, Nakagawa; pretreated by heating 500 °C for 30 min and at 850 °C for 2 h. d) Gofun, coloring in Japanese painting, Matsujirushi, Nakagawa; pretreated by H_3PO_4.[21] e) Guaranteed reagent grade, Kanto Chemical Co., Inc. f) Extra pure grade, Kanto Chemical Co., Inc. g) Wako Pure Chemical Industries, Ltd., made from sawdust.

ratio of plant materials such as wood is the use of the other correction factor instead of 0.93, which is regulated in ASTM D 6866 as a correction factor for the calculation of the biomass carbon ratio from pMC. For this purpose, a lot of data should be measured as a database in order to accurately evaluate the biomass carbon ratio of materials such as cellulose. At the moment, edible components from plants, such as cornstarch, are widely utilized as resources for materials. In the near future, inedible components from plants, such as cellulose, especially cellulose from grasses and cellulose waists, will be utilized as resources for chemical products. Therefore, it is necessary to develop an accurate correction method for cellulosic biomass carbon ratios.

Biomass Carbon Ratio of Inorganic Materials. In order to estimate the biomass carbon ratio of actual products, not only the biomass carbon ratios of organic materials, but also those of inorganic materials should be evaluated. In ASTM D 6866, it is stated that carbonate, such as calcium carbonate, has to be omitted in order to reduce error. However, it is thought that the biomass carbon ratio of carbonate can be evaluated by the AMS method in this study, when the sample preparation for the AMS measurement and the correction factor are correctly selected. It is necessary for samples including carbonate to be pretreated for the AMS measurement in order to clearly distinguish the biomass carbon ratio of carbonate from that of other components in the sample. In this study, the phosphoric acid reaction (H_3PO_4) was employed as a pretreatment for the AMS measurement when the biomass carbon ratio of carbonate must be distinguished from that of other materials. The biomass carbon ratio of calcium carbonates and activated charcoal are shown in Table 3. Entries 19 to 22 are calcium carbonates derived from biomass. These materials are Gofun, which is a coloring in Japanese paint and is made of sea shells. Original shells for these two Gofuns are different from each other. Shells for Entries 19 and 20 are older than that for Entries 21 and 22. For Entries 20 and 22, the samples were pretreated with H_3PO_4 for the AMS measurement.[21] The biomass carbon ratios of Entries 19 and 20 are lower than 100% and those of Entries 21 and 22 are higher than 100%. The biomass carbon ratio of Entry 20 is slightly less than that of Entry 19, and that of

Table 4. Biomass Carbon Ratio of Gases

Entry	Material	Origin	$\Delta^{14}C$ /‰	pMC /%	Biomass carbon ratio /%
1	ethylene[a)]	petroleum	< -998.68[d)]	<0.13[d)]	<0.12[d)]
26	methane[b)]	petroleum	< -998.68[d)]	<0.13[d)]	<0.12[d)]
3	propylene[c)]	petroleum	< -998.68[d)]	<0.13[d)]	<0.12[d)]
27	propylene[c)]	petroleum	< -998.68[d)]	<0.13[d)]	<0.12[d)]
28	propylene[c)]	petroleum	< -998.68[d)]	<0.13[d)]	<0.12[d)]
29	biogas[e)]	digestion	24.22	102.42	95.25
30	biogas[e)]	digestion	18.9	101.89	94.76

a) Ethylene, calibration gas, GL Sciences, Inc. b) Methane, calibration gas, GL Sciences, Inc. c) Propylene, calibration gas, GL Sciences, Inc. d) Less than detection limit of instrument. e) Anaerobic fermentation of digestion.

Entry 22 is also less than that of Entry 21. It is thought that there is some amount of other materials other than calcium carbonate in Gofun, since Gofun is not a chemical product and is not pure calcium carbonate. Organic materials, such as protein, are included in these shells. These organic materials have a higher pMC due to the bomb effect on carbon derived from phytoplankton growing near surface of the sea. Calcium carbonate was produced from sea water inorganic carbon. Carbon dioxide derived from only calcium carbonate can be obtained by the reaction of H_3PO_4. The difference among the values of Entries 19 to 22 seems to be caused by this reaction. These results indicate the possible separation of the biomass carbon ratio of carbonate and that of other materials. Entries 23 and 24 are from limestone. The biomass carbon ratios of these are estimated to be 0%. Calcium carbonate is derived from limestone by chemical treatment, such as combustion. It is thought that some of the carbon atoms of calcium carbonates exchanged with biomass carbon atoms during the combustion process, since the biomass waste is usually used as fuel for combustion. Entry 25 is activated charcoal and is made from sawdust derived from trees. The biomass carbon ratio of Entry 25 is higher than 100%. The reason for this result seems to be the same as the results for Entry 18 of cedar trees, shown in Table 2. It was found that the pretreatment of H_3PO_4 for the AMS measurement is effective for the separation of carbonate with other materials. It was found that the biomass carbon ratio of the samples including the carbonate, such as calcium carbonate, could be measured by the AMS method with the appropriate pretreatment.

Biomass Carbon Ratio of Gases. The biomass carbon ratio evaluation by AMS is not suitable for gaseous materials, since the AMS measuring method has been developed as a dating measurement for historical materials in archeology. Carbon dioxide can be measured by the AMS method, since carbon dioxide is transformed into graphite during the usual pretreatment for the AMS measurement. Various kinds of gaseous chemicals are utilized as basic materials derived from the petrochemical complex and petrochemical industries. For example, methane, ethane, ethylene, propane, and propylene can be directly derived from petroleum. Methane gas from biomass will be used as a fuel instead of methane from petroleum. Recently, biobased ethylene (bioethylene) and biobased propylene (biopropylene) as monomers have been reported to be produced from bioethanol. Therefore, for these gaseous materials, it will be necessary to evaluate their biomass carbon ratios. The sample preparation method for gaseous materials for the AMS is newly developed at the IAA. In this method, the gaseous sample with copper oxide (CuO) in a quartz glass tube was cooled to liquid nitrogen temperature while controlling the pressure, and then the tube with an adequate amount of gaseous sample was closed. It was confirmed that this method could safely be applied to various kinds of gaseous samples. The biomass carbon ratios of various gases are investigated by the AMS measurement. These results are shown in Table 4. Entries 1 and 3 are shown in Table 1. The biomass carbon ratios of gases derived from petroleum and gases derived from anaerobic fermentation were investigated. The biomass carbon ratios of Entries 1, 3, 26, 27, and 28 derived from petroleum are almost 0% and agree with the expected values. Entries 29 and 30 are evolved gases during the anaerobic fermentation of digestion, which is derived from the biomass plant for caw drop treatment. The biomass carbon ratios of these biogases are expected to be 100%. The biomass carbon ratio of the original digestion was not measured, so that the experimental results are reasonable values. It is confirmed that the biomass carbon ratios of materials in the gas-phase can be evaluated by AMS measurement using the newly developed sample preparation method.

Biomass Carbon Ratio of Liquids. There is no particular regulation for the biomass content measurement for liquid samples in ASTM D 6866-08. Bioethanol is an ethanol which can be derived from biomass. At present, the chemical product from biomass, which is most commercially used, is bioethanol. In the near future, chemical products from biomasses, which will be most widely used, are glycerol from biomass. Bioglycerol, which is made from biomass, can be derived as a by-product of biodiesel fuel (BDF). In order to confirm the possibility of the biomass carbon ratio measurement of the liquid samples, biomass carbon ratios of bioethanol and bioglycerol as representatives of the liquid samples are measured by AMS. These samples are in the liquid phase; therefore, the sample preparation for liquid samples as described in the experimental section is applied to them. Results of the biomass carbon ratios are shown in Table 5. The measured results for one glycerol from the biomass and eight kinds of ethanols from biomass are shown in the table. Purities of all the bioethanols may be higher than 99%. All the biomass carbon ratios in Table 5 are almost 100%. These results suggest that

Table 5. Biomass Carbon Ratio of Liquids

Entry	Material	Country of origin	Δ^{14}C /‰	pMC /%	Biomass carbon ratio /%
31	bioglycerol[a)]	Philippines	44.7	104.47	97.16
32	bioethanol[b)]	Japan	93.9	109.39	101.73
33	bioethanol[c)]	Thailand	66	106.6	99.14
34	bioethanol[d)]	Thailand	69.2	106.92	99.44
35	bioethanol[e)]	China	80.9	108.09	100.52
36	bioethanol[f)]	Pakistan	82.6	108.26	100.68
37	bioethanol[g)]	Brazil	89.3	108.93	101.30
38	bioethanol[h)]	Brazil	95.8	109.58	101.91

a) Bioglycerol from palm oil production made in the Philippines. b) Ethanol from biomass made in Miyako Island of Japan. c) Ethanol from biomass made in Thailand, T332. d) Ethanol from biomass made in Thailand, T398-1. e) Ethanol from biomass made in China, C339. f) Ethanol from biomass made in Pakistan, P362-4. g) Ethanol from biomass made in Brazil, B341. h) Ethanol from biomass made in Brazil, B355.

the biomass carbon ratios of liquid samples can be evaluated by the AMS method. In other words, it is thought that the preparation method for liquid materials for AMS in this study is applicable to other liquid samples.

Repeatability and Accuracy of Biomass Carbon Ratio Measurement by AMS. It is necessary for the chemical products made of the biomass to evaluate the content of biomass resources in the product. A clear indication of these values for the products will help consumers who want to buy them. One of the evaluation methods for the biomass content is the biomass carbon ratio by AMS. It is important for this method to be published as an international standard in order for the evaluation method to be widely accepted. The repeatability and accuracy of the evaluation method have to be confirmed in order to propose it as an international standard. The repeatability and accuracy of the biomass carbon ratio were investigated for bioethanol. Bioethanol from Brazil, B355 shown as Entry 38 in Table 5, was employed as a representative sample. The ^{14}C ratios of this bioethanol were measured six times. Every time, sample preparation was performed according to the sample preparation method as described in the experimental section. That is to say, a ca. 10 mg sample was collected and was pretreated every time. As already mentioned, the lowest biomass carbon ratio value by AMS is 0.12%. This value is measuring limit of the biomass carbon ratio by AMS. Accuracy of the measured biomass carbon ratio data around 100% is ca. 0.3%. In other words, the ca. 0.3% value is the limit of the biomass carbon ratio around 100% by AMS. For example, the biomass carbon ratio of Entry 38 with error is expressed as $101.91 \pm 0.31\%$. The limitation of the biomass carbon ratio, which is due to the AMS apparatus and detector, is 0.12%. The accuracy (0.31%) of the biomass carbon ratio around 100% is sufficiently small compared to the 0.12% limitation of the AMS measurement. The standard deviation of these six results is 0.36% and sufficiently low compared to the limit of 0.3%. This fact indicates that the repeatability of the biomass carbon ratio by the AMS evaluation method is adequate for the evaluation method of biomass carbon ratio.

The biomass carbon ratios by AMS for another sample were investigated in order to confirm the repeatability and the accuracy of the biomass carbon ratio evaluation by AMS. For a liquid sample, the repeatability and the accuracy were discussed above. The polymer blend was employed for the confirmation of the repeatability and the accuracy as a representative of solid samples. Polymer blend samples consisting of poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) were prepared by the method described in the experimental section. The sample is a cast film. The biomass carbon ratios derived from the ^{14}C ratios of the film were measured six times. Every time, small specimens were cut from the film sample, pretreated, then measured. The standard deviation of these six results is 0.84% and is sufficiently low compared to 0.12% which is the limitation of the AMS measurement. The repeatability of the biomass carbon ratio by the AMS evaluation method is shown. The estimated value of the biomass carbon ratio calculated using molecular structure of PLA and PBS is 46.52%. Experimental results are smaller than this value. One of the possible reasons for this result is that the measured site by AMS is PBS rich and a small amount of chloroform in the cast film remains. A precise investigation is required for the confirmation, since the detailed compositions at the measured site by AMS in the cast film were not investigated. The ratio of the biomass resource can be evaluated by this method, although there is only a small difference between the measured biomass carbon ratio and the theoretical one. This method can be used as an evaluation method for the determination of the biomass content in chemical products. The standard deviation of the blend sample as shown in Table 7 is greater than that of bioethanol as shown in Table 6. The sample of bioethanol is liquid. The sample has a high level of homogeneity. The homogeneity of the polymer blend is not the same level as that of the liquid sample, even if the blend sample was made by the casting method. Differences in the homogeneity level affect their degree of accuracy, that is, the standard deviations. It is thought that the accuracy derived from the results of polymer blend is enough for actual polymer products. However, the actual chemical products including the polymer products usually consist of various kinds of chemicals. For the AMS measurement in this study, 5 to 10 mg samples were used for the exchange of graphite through carbon dioxide. In order to increase the accuracy of the measured data, the samples of

Table 6. Repeatability of Biomass Carbon Ratio of Bioethanol

Entry	Material	Country of origin	$\Delta^{14}C$ /‰	pMC /%	Biomass carbon ratio /%
38	bioethanol[a)]	Brazil	95.8	109.58	101.91
39	bioethanol[a)]	Brazil	87.62	108.76	101.15
40	bioethanol[a)]	Brazil	87.29	108.73	101.12
41	bioethanol[a)]	Brazil	93.94	109.39	101.73
42	bioethanol[a)]	Brazil	92.8	109.28	101.63
43	bioethanol[a)]	Brazil	97.62	109.76	102.08
Average			92.51	109.25	101.60
Standard deviation			3.88	0.39	0.36

a) Ethanol from biomass made in Brazil, B355.

Table 7. Repeatability for Biomass Carbon Ratio of Polymer Blends with Biobased PLA and Petroleum-Based PBS

Entry	Material	Shape	$\Delta^{14}C$ /‰	pMC /%	Biomass carbon ratio /%
44	PLA + PBS[a)]	film	−539.13	46.09	42.86
45	PLA + PBS[a)]	film	−547.23	45.28	42.11
46	PLA + PBS[a)]	film	−524.21	47.58	44.25
47	PLA + PBS[a)]	film	−534.5	46.55	43.29
48	PLA + PBS[a)]	film	−520.12	47.99	44.63
49	PLA + PBS[a)]	film	−532.16	46.78	43.51
Average			−532.89	46.71	43.44
Standard deviation			9.00	0.90	0.84

a) Cast film from chloroform solution (10%) of PLA/PBS (50/50 wt %).

greater than 10 mg should be initially used for the AMS measurement. It is necessary for this purpose to develop a new preparation method for the oxidation process for the AMS measurement. At the same time, it is necessary to collect the biomass carbon ratios of samples with lower values by AMS.

All the biomass carbon ratios for samples derived from biomass are not exactly equal to 100%. It is thought that these values are caused by the characterization of the materials themselves and not due to any error or accuracy of the measurements. For example, the biomass carbon ratios of the cellulose and wood samples are greater than 100%. Further investigation of this evaluation method by AMS is necessary. According to ASTM D 6866, only one correction factor, 0.93 is used for the biomass carbon ratio. One of the solutions for increasing the accuracy of the evaluation is to select a correction factor for each material. For this purpose, a large amount of data needs to be measured. Once a large amount of biomass carbon ratio data for various chemical products is obtained and the correction method for various kinds of materials is established, the evaluation method of the biomass carbon ratio by AMS can be proposed as an international standard.

Conclusion

The evaluation method of the biomass carbon ratios by measuring ^{14}C using AMS based on ASTM D 6866 was studied. The biomass carbon ratio of various chemical products in the solid, liquid, and gas phase was investigated. The biomass carbon ratios of cellulose and wood materials exceeded 100%. The biomass carbon ratios of the gaseous chemicals besides carbon dioxide can be evaluated using a new preparation method for gases. The carbon dioxide from calcium carbonate could be derived from samples separately reacted with phosphoric acid. The biomass carbon ratios of liquid samples, such as ethanol and glycerol, could be measured using the preparation method for liquid samples. The repeatability and accuracy of the biomass carbon ratio for ethanol and a polymer blend of poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) were investigated. The accuracies of ethanol and a polymer blend in these samples are 0.36% and 0.84%, respectively. The repeatability and accuracy for these samples compare well with the 0.12% limitation of the AMS measurement. Small amount of chemicals, such as chloroform, in the blend can be detected by AMS method. The biomass carbon ratio of blend of biobased polymer and petroleum-based polymer (PBS) can be evaluated by the AMS method. It is found that some of the biomass carbon ratios of the samples derived from biomass are not exactly equal to 100%. In order to accurately evaluate this value, the basic data of the biomass carbon ratio for homogeneous materials is required. It was thought that the biomass carbon ratios of actual chemical products will be able to be evaluated by the AMS method as described in this study based on the biomass carbon ratios of the resource materials.

The authors wish to thank the Malaysia Palm Oil Board (MPOB) for providing the fibers from the oil palm trees. The authors wish to thank for the financial support by New Energy and Industrial Technology Development Organization (NEDO) to Research Project entitled "Development of Preparatory Basic Bioenergy Technologies: Accelerated Technology Development for Biofuel: R&D of Method to Measure Biomass Carbon Ratio of Biopolyolefin."

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