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Application of Microwave Technology for Utilization of Recalcitrant Biomass

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1. Introduction

Biomass is the sole organic material which is usable as an alternative to fossil resources on earth. Separation of constituent components (biorefinery) from biomass and their degradation are major steps for its practical use. Because of the diversity and recalcitrance of biomass, special techniques are required for these purposes. Microwave irradiation has been attracted much attention as a tool for degradation of biomass for its environment friendliness, known as green technology. Microwave heating is based on non-contacted irradiation of electromagnetic waves in a frequency range from 300 MHz to 300 GHz (wavelength about 1 m to 1 mm), which activate dipole molecules depending upon their dielectric constants (dielectric heating) and microwave sensitizers which induce electro-conductive heating by using modernized equipment with a computerized regulating system. In this Chapter authors introduce applicability of microwave technology for utilization of recalcitrant biomass as pioneers in this field.

2. Microwave apparatus for biomass utilization

Microwave irradiation method is a kind of autohydrolysis to separate hemicellulose and lignin from lignocellulose and it is utilizable as pretreatment before enzymatic saccharification to produce fermentable carbohydrates as well as an extraction method for biomass components such as polysaccharides. Fig. 1 shows the main concept of microwave irradiation technology for separation and applications of biomass components. In the simplest method, the heating medium is water since the water is the most environmental friendly and readily available solvent. The high temperature and pressurized water in a closed vessel provides decrease in dielectric constant and increase in ion products which enable solubilization of less polar substances and hydrolysis of biomass without catalyst. Moreover, the effects of microwave irradiation can be further enhanced by addition of organic acids, sulfuric acid, hydrogen peroxide, inorganic ion and aqueous alcohols to the medium depending on the targeting products. Recent sophisticated microwave ovens equipped with TFM vessel which can withstand <250°C, 55 bar satisfy use of these additives safely. Automatic temperature feedback system by PID is essential for precise control of reaction temperature, because the autohydrolysis of the biomass component is greatly dependent on the temperature. The feedback system also contributes to the safety of the reaction by quick shut down of microwave output in case of reaction overruns. Explosion

protection system is further required especially when running severe oxidation-reduction reactions.

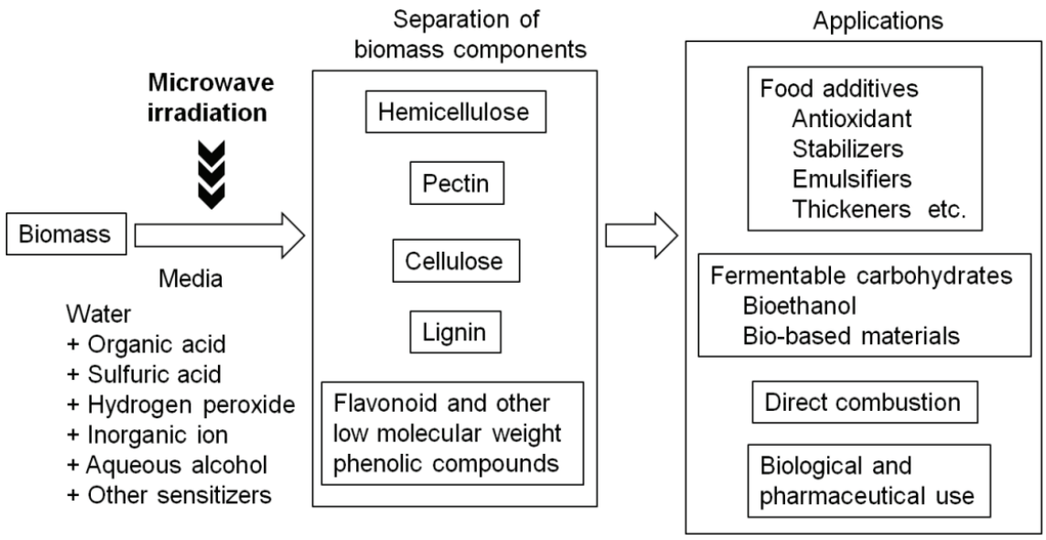


Fig. 1. Concept of microwave irradiation technology for refinery of biomass components.

Continuous flow system is crucial for scaling up of the microwave irradiation system. A continuous flow microwave irradiation apparatus was developed as shown in Fig. 2 (Tsumia & Azuma, 1994). The system provides 2.45 GHz of microwave with maximum output, temperature and flow rate of 4.9 kW, 240°C and 7-20 L/h, respectively. Generally, the powered materials are suspended in medium to give homogeneous slurry. The slurry is fed into the reactor at 20–30 kg/cm^2. The reactor is made of alumina fine ceramics (purity 99.7%, 2 m in length × 4 cm in diameter) to endure the high temperature and pressure reaction. The content inside the reactor was homogenized by rotating a stainless steel rod attached with blades. Finally the products are come out from a blow-down valve to atmospheric pressure. This final process gave a kind of defibrating effects like explosion.

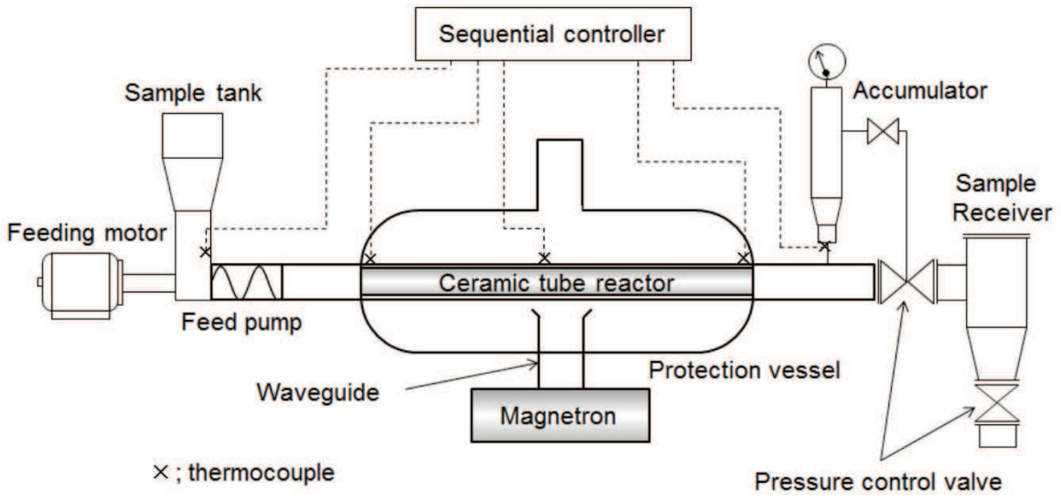


Fig. 2. Schematic illustration of continuous flow microwave irradiation apparatus.

3. Chemical composition of biomass

Biomass especially phytomass includes diverse group of plants which differed in chemical compositions, leading to difficulties in their utilization. Because about 70% (w/w) of phytomass was composed of carbohydrates, its utilization was usually directed to refinery (fractionate), decomposition and/or transformation of their carbohydrate moieties. For utilization of carbohydrates as biomass, polysaccharides were frequently targeted. In the phytomass two groups of polysaccharides were present, storage polysaccharides and constitutive polysaccharides present in cell walls consisting of primary cell wall and secondary cell wall in vascular plants. Primary cell wall is formed outside plasma membrane when daughter cell is separated from its mother cell and developed until the growth of cell cease. After finish of synthesis of primary cell wall, thick secondary cell wall is formed inside the primary cell wall. Lignification starts at cell corners and distributed throughout cell walls. Polysaccharides consisting of the primary and the secondary cell walls are different.

3.1 Storage polysaccharide

Starchy polysaccharides are typical storage polysaccharides present widely in plant tissues as an end-product of photosynthesis and accumulated in grains and tubers as crystallized granules (~1-100 μm). The predominant constituents in starch granules (98-99%, w/w) are amylose and amylopectin with a distribution of ~20-25% and ~80-75%, respectively. Amylose consists of a long linear chain having around 99% of α-(1→4) and a few α-(1→6) linkages (molecular mass in a range of 1.0×10^5 - 1.0×10^6) with around 9-20 branch points equivalent to 3-11 chains per molecule (Tester et al., 2004). Each chain contains 200-700 glucose residues having one reducing and one non-reducing ends. Amylopectin has a branched structure built from α-(1→4) linkages with 4.2-5.9% of α-(1→6) branch linkages (Tester et al., 2004; Robyt, 2008) and has 100-1,000 fold higher molecular mass (1.0×10^7 - 1.0×10^9) than amylose. Unit chain of amylopectin is much shorter than that of amylose and contains about 18-25 glucopyranose (Glc*p*) residues. Amylopectin molecule has thus one reducing and many non-reducing ends. It should be noted that the numerical values presented above differ in locations and species of plants. Exterior α-(1→4) linked chains of amylopectin form double helices to form crystalline region and branching point portions formed amorphous region leading to formation of radially oriented lamellae structure in 9 nm size (Fig. 3). Precise interactions between amylose and amylopectin are not known, but these polysaccharides attached together by intermolecular hydrogen and hydrophobic bonds in addition to intramolecular interactions to form water-insoluble granules. Three distinct X-ray patterns have been observed, A-, B- and C-types. Cereal grain starches showed A-type diffraction, and tuber, fruit and stem starches exhibit typical B-type diffraction. Root, bean and pea starches give intermediate diffraction profile between A- and B-types called as C-type. Although the double helical structures mostly due to exterior chains of amylopectin are common to all types, packing profiles of double helices are different between A- and B-types; A-type has a compact structure with a low water content, while B-type has a more open structure with a hydrated helical center.

Industrial enzymatic decomposition of starch proceeds through gelatinization (30-40% starch slurry, heating for 5 min at 105°C), liquefaction (1-2 h at 95-100°C) and saccharification (72 h at 60°C) to glucose whose concentration was 97% in the saccharified products (Van Der Maarel, 2010). Production of glucose from starch has economically

superiority but has a defect in competition with supply of food from starchy polysaccharides. In addition starch industries produce a huge amount of residues after extraction of starch. Although the residues contain residual starch, presence of recalcitrant lignocellulosic materials hampers their utilization.

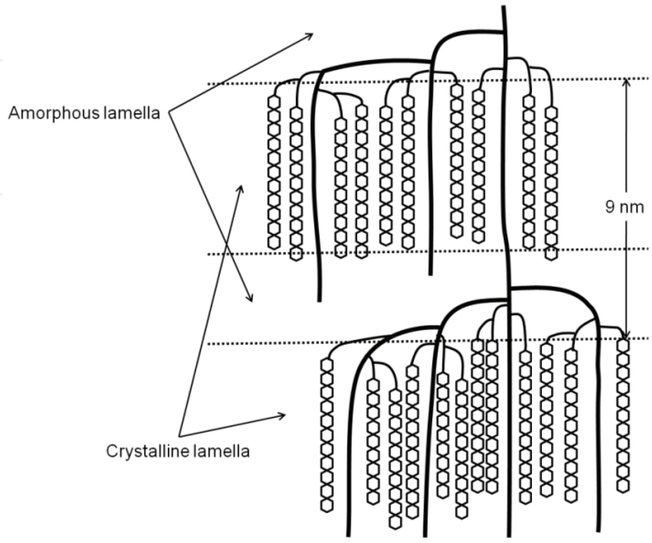


Fig. 3. Schematic illustration of lamellar structure of a starch granule.

3.2 Primary walls

Polysaccharides in the primary cell wall are grouped into three categories; skeletal polysaccharide such as cellulose, matrix polysaccharide mixture extractable with water and hot water, pectin fraction extractable with chelating agents, and hemicellulose fraction extractable with 1-24% sodium hydroxide or potassium hydroxide, and glycoconjugate rich in hydroxyproline such as extensin and arabinogalactan protein (AGP). Its composition was remarkably different in dicotyledonous and monocotyledonous plants. Typical constituent polymers are listed in Table 1. Plants grouped in gymnosperm have a similar composition as dicotyledonous plants. The primary cell wall is not lignified in the tissue cultured cells but is the most lignified of the whole cell wall layers to form middle lamella. Because of difficulty of separation of the middle lamellar structure from the other primary cell wall material, a whole region of primary cell wall is referred as compound middle lamella (CML).

Type	Monocotyledonous plant		Dicotyledonous plant	
Skeletal polysaccharide	Cellulose	(20-40)	Cellulose	(20-40)
Matrix polysaccharide	Pectin	(0.8-8)	Pectin	(20-35)
	(1→3,1→4)-β- Glucan	(12-16)	Arabinogalactan	(~10)
	Glucuronoarabino-xylan	(~30)	Gulucuronoarabino-xylan	(~5)
	Xyloglucan	(2-4)	Xyloglucan	(~20)
Glycoconjugate	Hydroxyproline-rich glycoprotein	(~10)	Hydroxyproline-rich glycoprotein	(~10)

Table 1. Polymers consisting primary cell wall of vascular plants (%, w/w)

Cellulose is a linear fibrous homopolysaccharide composed of β-(1→4) linked D-Glc*p* residues with cellobiose as a unit of fiber axis (1.03 nm) (Glasser, W.G., 2008; Wertz et al., 2010). Degree of polymerization (DP) of primary cell wall cellulose is ~2,000-6,000, varied depending upon origin, age and location of plant tissues. Cellulose molecules packed together to form microfibrils (width 2-2.5 nm in the case of cotton primary cell wall) by two intramolecular hydrogen bonds, *O*2′-*H*•••*O*6 and *O*3-*H*•••*O*5′, and one intermolecular hydrogen bond, *O*6-*H*•••*O*3. Crystalline form of the native plant cellulose (cellulose I) is a mixture of two crystalline allomorphs, Iα (one-chain triclinic unit cell) and Iβ (two-chain monoclinic unit cell), rich in the latter. Orientation of microfibrils inside the primary cell wall is random but more perpendicularly oriented to the cell axis close to the secondary cell wall. Tensile strength of fibrous structure of plant cells is largely depending upon the structure of the cellulose.

Pectins are composed of complex networks of three categories of acidic polysaccharides, homogalacturonan (HG), rhamnogalacturonan I (RG-I) and rhamnogalacturonan II (RG-II) (Willats et al., 2001). The HG has a fundamentally linear homopolysaccharide (Fig. 4) composed of α-(1→4) linked D-galacturonic acid (Gal*p*A) residues with partial acetylation and methyl-esterification (DP about 70). Insertion of L-rhamnosyl units sometimes occurred. The HG is covalently linked to RG-I and RG-II.

The RG-I is a branched acidic polysaccharide composed of backbone disaccharide repeating units of [→2)-α-L-Rha*p*-(1→4)-α-D-Gal*p*A-(1→]$_n$ with n of 100-300 (Fig. 4). About a half rhamnopyranose (Rha*p*) residue has substitution at *O*-4 with at least about 30 kinds of mono- and oligo-saccharides consisting of D-galactose and/or L-arabinose with trace amount of L-fucose. In addition the Gal*p*A residues are acetylated on *O*-2 and *O*-3.The RG-I molecules are usually obtained by pectinase treatment. In plants belong to *Chenopodiaceae* some of the side chains of RG-I are esterified with ferulic and coumaric acids and cross-linked by dimerization due to oxidative coupling (Harris & Stone, 2008).

HG: →4)-α-D-Gal*p*A-(1→4)-α-D-Gal*p*A-(1→4)-α-D-Gal*p*A-(1→4)-α-D-Gal*p*A-(1→

RG-I: →4)-α-D-Gal*p*A-(1→2)-α-L-Rha*p*-(1→4)-α-D-Gal*p*A-(1→2)-α-L-Rha*p*-(1→ (Backbone)

Fig. 4. Structures of homogalacturonan (HG) and rhamnogalacturonan I (RG-I)

The RG-II is a kind of substituted galacturonans having a backbone structure similar to HG. The RG-II molecules are usually obtained by pectinase treatment as RG-I and thus thought to be covalently linked to HG. Substitutions occur at both *O*-2 and *O*-3 positions of D-Gal*p*A residues with 4 types of side chains consisting of more than 12 kinds of glycosyl residues including rarely observed sugars such as D-apiofuranose (Api*f*). The two RG-II molecules form a dimer with boric acid as a tetravalent 1:2 borate-diol ester at *O*-2 and *O*-3 of the two Api*f* residues (Fig. 5) (Kobayashi et al, 1996; O'Neill et al., 2004). Acidic pectins are also known to form hydrogels by formation of egg-box structure with divalent cations such as Ca^{2+}.

β-Glucan (BG) is a linear polysaccharide mostly present in the primary cell wall of monocotyledonous plants especially in *Poaceae*. Its chemical structure is fundamentally composed of a mixture of cellotriose (~70%) and cellotetraose (~30%) units which are linked together by β-(1→3) linkages (Fig. 6). The ratio of β-(1→4) and β-(1→3) linkages vary depending upon species and location of plants. The BG has therefore a folded structure and shows viscous property in solution resulting in grouping into gum (Ebringerová et al., 2005).

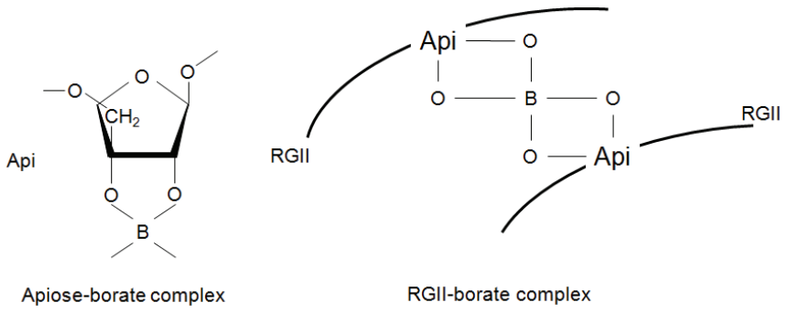


Fig. 5. Cross-linkage of two rhamnogalacturonan II (RG-II) chains by formation of a tetravalent borate ester at two apiofuranose residues

β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→4)-β-D-Glc*p*
(1↑ on the last Glc*p*; 1↑3 on the second Glc*p*)

β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→4)-β-D-Glc*p*
(3↑ on the first Glc*p*)

Fig. 6. Structure of (1→3,1→4)-β glucan (BG)

Arabinogalactans (AG) are grouped into two types; β-(1→4)-linked D-galactan having β-(1→5)-linked L-arabinofuranosyl *(Ara*f*)* short side chains at *O*-3 (Type I) (Fig. 7), and a highly branched arabino-3,6-galactan (Type II) (Ebringerová et al., 2005). The Type I AGs are pectinic and frequently considered to be originated from substituents in RG-I. The Type-II AG has an inner chain comprising β-(1→3)-linked D-Gal*p* residues which are substituted with β-(1→6)-linked D-Gal*p* residues. Other substituents such as D-Gal*p*, L-Ara*f*, L-Ara*p* and β-L-Ara*p*-(1→3)-L-Ara*f* are also attached at *O*-3/*O*-6 of 3,6-galactan moiety (Fig. 7). The Type-II AG which is linked to hydroxyproline is known as arabinogalactan protein (AGP).

Type 1 AG: →4)-β-D-Gal*p*-(1→4)-β-D-Gal*p*-(1→4)-β-D-Gal*p*-(1→4)-β-D-Gal*p*-(1→
(1↑3 on the third Gal*p*)
β-L-Ara*p*-(1→5)-α-L-Ara*f*

Type II AG: →3-β-D-Gal*p*-(1→3)-β-D-Gal*p*-(1→3)-β-D-Gal*p*-(1→3)-β-D-Gal*p*-(1→
(1↑6 on each Gal*p*)
β-D-Gal*p* R-3)-β-D-Gal*p* β-D-Gal*p* R
(1↑6 on the second Gal*p* and on the third Gal*p*)
R β-D-Gal*p*

Fig. 7. Structures of Type-I and Type-II agabinogalactans (AGs) (R: α-L-Ara*f*/*p*, β-L-Ara*p*-(1→3)-L-Ara*f* , β-D-Gal*p*)

The primary cell walls of both dicotyledonous and monocotyledonous plants including gymnosperm contain up to 10% protein. Hydroxyproline-rich glycoproteins (HRGPs) are the well-known glycoproteins present in the primary cell wall. Extensin belongs to this type of glycoprotein and acts as a cross-linker between cell wall polysaccharides and lignin by formation of oxidative couplings through its tyrosine residues to provide mechanical strength. Carbohydrate portion of extensin is composed of arabinotriose and arabinotetraose

linked α-glycosidic to hydroxyproline and monomeric β-D-Gal*p* residues linked to serine. In addition proline-rich and glycine-rich glycoproteins were also present in lignified cell walls.
Xyloglucan is a kind of substituted cellulose and has a backbone structure composed of linear β-(1→4)-linked D-Glc*p* residues. Substitutions occurred at *O*-6 by α-D-Xy*p* residues which are further connected to 1,2-linked Ara*f*, Gal*p* and α-L-Fuc*p*-(1→2)-linked-Gal*p* residues (Fig. 8). Substitution profile is different in species and location of plants. Xyloglucans are firmly attached to cellulose by hydrogen bonds and also covalently bonded to pectin (Hayashi, 1989; Harris & Stone, 2008).

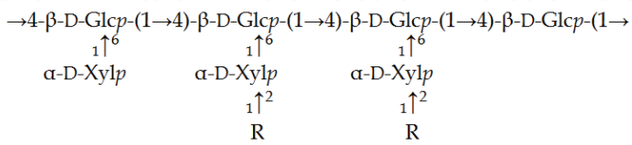


Fig. 8. Structure of xyloglucan (XG) (R: Ara*f*, Gal*p* and α-L-Fuc*p*-(1→2)-linked-Gal*p* residues)

3.3 Secondary walls

Secondary cell wall in the vascular plants is piled up by accumulation of layered structures in a concentric way inside the primary cell wall. In woods thickening of the secondary cell wall progressed in three steps mainly on account of cellulose synthesis to form three layers differing in orientation and thickness of cellulose microfibrils, a thin outer secondary wall (S_1) (0.1-0.2 μm, microfibril angle 50-70°), a thick secondary wall (S_2) (1-5 μm, microfibril angle 10-30° in earlywood and 0-10° in latewood) and a thin inner secondary wall (S_3) (~0.1 μm, microfibril angle 50-90°). DP of the cellulose in the secondary cell wall is higher than that in the primary cell wall (13,000~14,000 in cotton). Cellulose in wood has DP of 8,200-8,500 with width of microfibrils of 3-5 nm. Hemicelluloses are synthesized and deposited inside the secondary cell wall. Finally lignification starts from cell corner, then progressed into middle lamella, primary cell wall and secondary cell wall. Because of difficulty of separation of these cell walls, summative chemical compositions of softwoods and hardwoods in a temperate zone are listed in Table 2. Chemical composition of monocotyledonous plants is similar to that of hardwoods with peculiarly high content (1-3%) in hydroxycinnamic acids. Cellulose content in both woods is similar but softwoods are rich in lignin, in turn hardwoods are rich in hemicelluloses. Hemicelluloses are a group of polysaccharides extractable with alkali (Ebringerová et al., 2005). The most remarkable difference between both woods is in composition of hemicelluloses.
Xylans are ubiquitous in vascular plants having a common backbone structure of β-(1→4) linked D-xylopyranose (Xyl*p*) residues. Hardwood xylans have single 4-*O*-methyl-α-D-glucuronic acid (MeGlcA, α-D-4-*O*-Me-Glc*p*A) residues at *O*-2 with an average ratio of Xyl : MeGlcA being about 10 : 1 (distribution 4-16 : 1) and called as glucuronoxylan (4-*O*-methylglucuronoxylan, MeGX). In the native state Xyl*p* residues are partially acetylated at *O*-2 or *O*-3 and both positions (degree of substitution 0.3-0.7) and the native xylan is called as *O*-acetyl-4-*O*-methylglucuronoxylan (AcMeGX, Fig. 9). Some D-Xyl*p* residues bearing MeGlcA are further acetylated at *O*-3. In softwood xylans, no acetyl substitutions have been found and α-L-Ara*f* residues are further substituted at *O*-3 of Xyl*p* residues. Average ratios of Xyl : MeGlcA and Xyl : Ara*f* are 4-6 : 1 and 8-9 : 1, respectively. Thus softwood xylans are called as arabino-4-*O*-methylglucuronoxylan (AMeGX) or just arabinoglucurnoxylan (AGX) (Fig. 9). Presence of uronic acid substitutions on two contiguous D-Xyl*p* residues is noted in the

softwood xylans. Before the reducing end →4)-β-D-Xyl*p* residue of glucuronoxylan insertion of a peculiar disaccharide, →3)-α-L-Rha*p*-(1→2)-α-D-Gal*p*A-(1→, has been reported.

Component	Softwood	Hardwood
Cellulose	39-41	40-45
Lignin	25-36	18-25
Hemicellulose	15-26	23-38
Pectin	1	1
Extractives	1-5	1-5
Ash	0.1-1.0	0.1-1.0
Component of hemicellulose		
Glucuronoxylan	1-2	20-30
Glucomannan[a]	15-18	3-5[c]
Arabinoglucuronoxylan	8-10	-
Galactoglucomannan	1-4	Trace
Arabinogalactan	2-3	+

[a]Lower in Gal*p* content around a molar ratio of Gal*p* : Glc*p* : Man*p* = 0.1 : 1 : 3-4. [b]Higher in Gal*p* content around a molar ratio of Gal*p* : Glc*p* : Man*p* = 1 : 1 : 3-4. [c]A molar ratio of Glc*p* : Man*p* = 1 : 1-2

Table 2. Summative chemical composition of woods grown in a temperate zone (%, w/w)

Average DP_n of wood xylans is 84-108. Non woody dicotyledonous plants also bear a lot of xylans similar to the native hardwood xylans with frequent presence of glucuronic acid (GlcA). Monocotyledonous plants, however, contain partially acetylated arabinoglucuronoxylans (AcAGX) and neutral xylans containing α-L-Ara*f* residues at *O*-2 or *O*-3 and both positions of β-(1→4) linked D-Xyl*p* residues (AX). These xylans carry additional esterified hydroxycinnamic acids which are further linked to lignin (Harris & Stone, 2008). Substitution profiles in these xylans varied very much depending upon species and location of plants.

AcMeGX: →4-β-D-Xyl*p*-(1→4)-β-D-Xyl*p*-(1→4)-β-D-Xyl*p*-(1→4)-β-D-Xyl*p*-(1→
↑2; 3; 2,3 (Ac) ; $_1$↑2 (α-D-4-*O*-Me-Glc*p*A)

AMeGX: →4-β-D-Xyl*p*-(1→4)-β-D-Xyl*p*-(1→4)-β-D-Xyl*p*-(1→4)-β-D-Xyl*p*-(1→
$_1$↑3 (α-L-Ara*f*) ; $_1$↑2 (α-D-4-*O*-Me-Glc*p*A)

Fig. 9. Structures of hardwood native *O*-acetyl-4-*O*-methylglucuronoxylan (AcMeGX) and softwood arabino-4-*O*-methylglucuronoxylan (AMeGX)

Galactoglucomannans (GGM) showed a common structure consisting of a linear backbone of randomly distributed β-(1→4) linked D-Glc*p* and D-Man*p* residues with single substitutions of α-(1→6) linked D-Gal*p* residues at *O*-6 of D-Man*p* residues (Ebringerová et al., 2005). Softwoods contain two groups of galactoglucomannans differing in galactose contents, one has a low Gal*p* (Gal*p* : Glc*p* : Man*p* = 0.1 : 1 : 3-4), while the other has a high

Gal*p* (Gal*p* : Glc*p* : Man*p* = 1 : 1 : 3-4) (Table 2). In Table 2 content of the former is listed as glucomannan (GM). In the native state Man*p* residues are partially acetylated at *O*-2 or *O*-3 (degree of substitution 0.2-0.4) and the native galactoglucomannan is called as *O*-acetyl-galactoglucomannan (AcGGM, Fig. 10). The average DP_n of softwood galactoglucomannans is 90-102. Hardwoods contains glucomannans having a Glc*p* : Man*p* ratio of 1 : 3-4. Partial acetylation at D-Man*p* residues is also observed similar to the softwood galactoglucomannans. The average DP_n of softwood galactoglucomannans is 60-70. *O*-Acetyl-glucomannans having similar structure are also present in many tissues of monocotyledonous plants, such as bulbs, tubers, roots, seeds and leaves. Konjac mannan is a typical glucomannan used as a food.

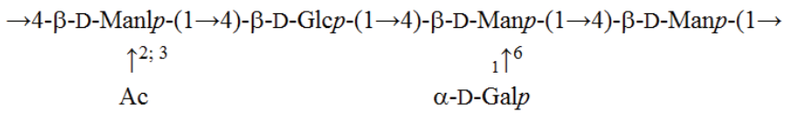


Fig. 10. Structure of softwood native *O*-acetyl-galactoglucomannan (AcGGM)

Linear β-(1→4) linked D-Mannans free of D-Glc*p* residues and highly substituted by α-(1→6) linked D-Gal*p* residues at *O*-6 of D-Man*p* residues are well known as galactomannans or gums. They are present in various kinds of plant storage tissues. Because of their high water-solubility with formation of very viscous transparent hydrogels, their industrial importance is high. The structure of arabinogalactan present in the secondary cell wall is similar to those belong to Type II AG. This kind of polysaccharide is abundantly present in the heartwood of the genus *Larix* and is called as larch gum. Because of its high water-solubility with low viscosity, its industrial importance is high.

3.4 Lignin and other components

Plant biomass contains polysaccharides, proteins and several groups of biopolymers which lack regular and ordered chemical structures like polysaccharides and proteins. Chemical properties of polysaccharides and glycoproteins in plant cell walls are reviewed above. Hydrophobic lignin, suberin and cuticular components such as cutin and cutan belong to the category of unordered polymers. These components wrap polysaccharides and glycoproteins inside the cell wall by direct covalent bonds and physical entanglements and indirect covering as hydrophobic layers, leading to give biomass recalcitrance. However, glass transition temperature of lignin (130-200°C) is usually lower than that of cellulose (230-250°C) and close to hemicellulose (160-200°C) under dry state. Glass transition temperatures of lignin and hemicelluloses unlike cellulose lowered with increase in moisture content. Therefore heating biomass in water close to the glass transition temperature of cellulose and extraction with solvents having various range of polarity is a strategy for refinery of biomass.

Lignins are radically coupled amorphous polymers having three fundamental monolignols, *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, and a number of minor monolignols such as coniferaldehyde, acetylated coniferyl alcohol, ferulic acid, etc., and have a peculiar optically inactive characteristic. Lignins are present in vascular plant cell walls. Based on degrees of contribution of monolignols lignins are usually grouped into three types, softwood lignin or guaiacyl (G) lignin, hardwood lignin or syringyl-guaiacyl (SG) lignin, and grass or hydroxyphenyl-syringyl-guaiacyl (HSG) lignin. Monolignol ratios are related with evolution of plants and varied depending upon location and species of

vascular plants. Polymerization of monolignols was previously proposed to progress by non-regulated couplings of peroxidase- or laccase-mediated monolignol radicals but recently a different theory was proposed by taking hypothetical low-molecular weight redox shuttle into consideration to regulate formation of monolignol radicals (Henriksson, 2009). Anyway inside lignins at least three kinds of ether bonds (β-aryl ether, diaryl ether and glyceraldehyde aryl ether types) and four kinds of carbon-carbon condensed bonds (dihydroxybiphenyl, phenyl coumarane, scoisolariciresinol and spirodienon types) connect the monolignols. In addition, hemicelluloses are covalently linked to lignins by ether and ester bonds at both benzyl and γ positions of the lignin moieties and also phenyl glycosides are formed to produce well-known lignin-carbohydrate complexes (LCCs) (Fig. 11) (Azuma, 1989; Harris & Stone, 2008). Presence of linkages between cellulose and lignin is also noted in woods. In monocotyledonous plant cell walls both ferulic and *p*-coumaric acids esterified to substituent sugars of hemicelluloses are further connected with lignins as described in 3.3.

Suberins are aliphatic-aromatic cross-linked polymers present in root, bark and fruit surface (Gandini et al., 2006). The contents of suberin in extractive-free outer bark of hardwoods of industrial relevance amount to 20-50%. Cork tissue contains suberin as the main constituent (Pinto et al. 2009). It serves as a protective barrier between the plants and environment. Their main aliphatic moieties are composed of C_{16}-C_{28} ω-hydroxy-fatty acids, C_{16}-C_{26} α,ω-dicarboxylic acids, C_{16}-C_{30} dihydroxy- or epoxy-fatty acids, and C_{16}-C_{26} aliphatic alcohols. Aromatic moiety is close to lignin but contains aromatic acids such as quinic acid, ferulic acid and 3,4-dihydroxybenzoic acid.

Cutin is an aliphatic polyester embedded with wax and cutan in the cuticular membranes of plant leaves, young stems and fruits, consisting of C_{16} and C_{18} hydroxy-fatty acids and hydroxyepoxy-fatty acids (Fig. 12) (Stark and Tian, 2006). Proportion of cutin and cutan varied based on maturity, location and species of plants. Its major functions are protection against microbial attack and intrusion of water and air. Supplying a polymer matrix for binding wax in the cuticle is also the primary role of cutin. Cutan is a common aliphatic biopolymer isolated as non-hydrolyzable and non-saponifiable residue in cuticular membrane (Boom et al., 2005). Presence of ether linkages was noted. Upon flash pyrolysis, cutan yields a series of C_7-C_{33} *n*-alkenes and *n*-alkanes with lack of cutin-derived C_{16} and C_{18} fatty acid monomers. Its function is in relation to drought resistance.

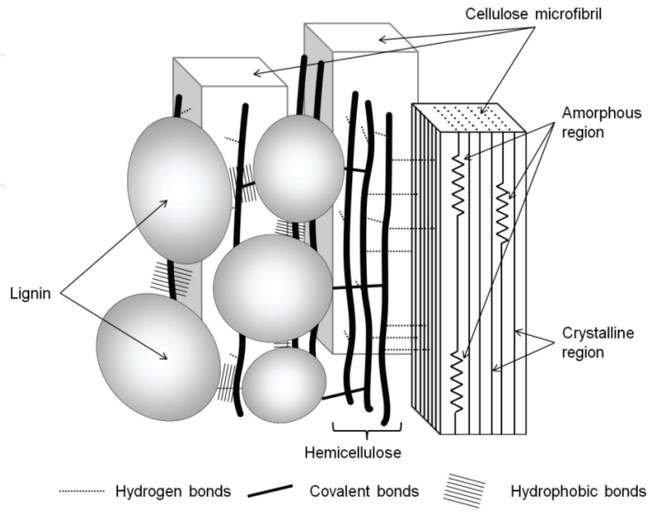


Fig. 11. Schematic illustration of lignin-polysaccharide network

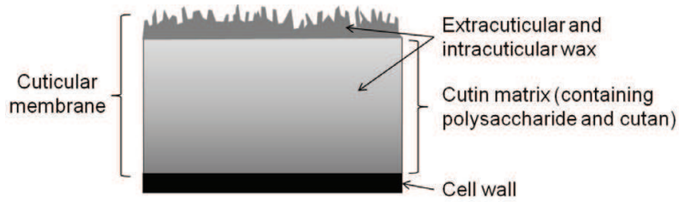


Fig. 12. Schematic illustration of cuticular membrane

4. Practical applications of microwave technology on biomass

This section summarizes microwave technology of three categories of biomass. The first category is a woody biomass including highly lignified softwoods such as cedar (Sugi, *Criptomeria japonica*), pine (Akamatsu, *Pinus densiflora*), etc., and hardwoods such as beech (Buna, *Fagus crenata*), birch (Shirakanba, *Betula platyphylla* var. *japonica*) etc. Treatments were also conducted in the presence of organic acids for saccharification and hydrogen peroxide for deliginification due to recalcitrant nature of woody biomass. The second category is monocotyledonous lignified biomass such as bamboo (Moso bamboo, *Phyllostachys pubescence*), rice straw, husk and hull, sugarcane bagasse, etc. The third category includes various kinds of non-utilized residues produced from food processing industries, agriculture and fisheries including *Okara* (soy bean residue), soy sauce residue, barley malt feed, tea residues, stones of fruits, waste of corn starch production, sea algae, fruiting bodies of mushrooms and peels of thinned fruits. Finally the microwave irradiation was applied to starch processing.

Although various kinds of biomass are present on earth, we are going to review the results we got on some typical woody biomass and agricultural and food residues. The chemical compositions of typical biomass we used are listed in Tables 3 and 4.

Component (%, w/w)	Pine (Akamatsu, *Pinus densiflora*)	Outer bark of Pine (Akamatsu, *Pinus densiflora*)	Beech (Buna, *Fagus crenata*)	Bamboo (Moso bamboo, *Phyllostachys pubescens*)
Ash	0.2	2.2	0.5	1.3
Alcohol benzene extract	3.2	5.8	2.2	3.3
1% NaOH soluble component	11.0	37.1	17.8	28.4
Water-soluble component	1.2	5.2	1.8	5.3
Hot-water soluble component	2.0	6.8	2.6	7.3
Lignin	26.6	47.4	21.3	22.6
Pentosan	11.3	8.5	23.8	23.7
Holocellulose	56.2	40.2	56.6	67.0
α-Cellulose	42.0	24.9	43.3	41.9
Relative monosaccharide composition (%, w/w)				
Rhamnose	0.4	10.3	0.7	Trace
Arabinose	3.7	1.4	1.5	2.2
Xylose	11.6	9.1	27.8	32.2
Glucose	59.8	57.1	64.5	65.6
Galactose	7.1	16.5	4.0	Trace
Mannose	17.4	5.6	1.5	Trace

Table 3. Chemical compositions of typical woody biomass used in this review

4.1 Lignified woody plants

As shown in section 3, lignified woody plants are highly resistant materials. Azuma et al. have utilized microwave irradiation technology for improvement of enzymatic susceptibility of these materials to produce fermentable sugars which can be converted into biofuels and bio-based materials. Several kinds of woody plants including softwoods, hardwoods and monocotyledonous plants were investigated for their reactivity by using batch-type microwave reactor.

Component (%, w/w)	Bagasse[a]	Coconut fiber[b]	Coconut coir dust[b]	Barley malt feed[c]	Green tea residue[d]	Stone of Japanese apricot[e]	Corn pericarp[f]	Soybean residue[g]
Ash	2.4	2.0	6.0	3.6	3.1	0.5	0.6	3.5-6.4
Extractive	2.9	0.9	0.6	10.7	10.4	1.4	7.7	6.9-22.2
1% NaOH soluble component	37.2	17.2	35.0	69.7	52.6	14.0	65.2	43.9-52.5
Water-soluble component	2.9	5.8	8.3	18.6	10.1	8.0	9.2	5.2-6.3
Hot-water soluble component	4.8	5.9	12.9	20.2	14.6	9.0	12.5	9.7-11.6
Lignin	19.5	30.9	51.8	24.8	30.8	25.3	4.0	Trace
Holocellulose	77.9	65.2	36.8	45.9	43.0	83.8	78.6	52.8-58.1
α-Cellulose	41.0	36.7	18.2	20.8	23.6	43.4	25.1	-
Protein	2.0	-	-	25.8	25.4	1.3	9.5	19.2-32.2
Relative monosaccharide composition (%, w/w)								
Rhamnose	0.2	0.9	1.4	-	0.8	0.3	Trace	0.5
Arabinose	5.8	9.1	24.9	14.1	12.7	0.6	20.0	10.2
Xylose	34.0	41.8	33.5	28.7	13.5	42.0	33.4	2.7
Glucose	57.4	41.3	29.8	53.2	54.3	56.0	36.8	52.0
Galactose	2.1	5.0	6.9	2.2	15.7	1.2	5.9	30.6
Mannose	0.5	2.0	3.6	1.7	3.0	Trace	4.1	4.1

[a]Including data listed in Kato et al., 1984; [b]Indrati & Azuma, 2000 [c]Matsui & Azuma, 2007; [d]Tsubaki et al., 2008; [e]Tsubaki et al., 2010a; [f]Yoshida et al., 2010; [g]O'Toole, 1999.

Table 4. Typical chemical compositions of food and agricultural biomass used in this review.

4.1.1 Hardwoods

For hardwoods, three kinds of sapwoods (Buna, Eucalypt and Shirakanba) and two kinds of green wood and dried chips (Poplar and Buna) were investigated for production of fermentable sugars by microwave irradiation (Azuma et al., 1984, 1985a, 1985b) (Fig. 13). Microwave irradiation was performed by using batch type glass tube sealed with stainless-steel stoppers connected together by screws and the microwave oven was equipped with 2 magnetrons (TMB-3210, Toshiba Co. Frequency; 2.45 GHz. Max output; 2.4 kW.). Heating

above 160°C with solid to liquid ratio at 2.0 : 16-20 (g : mL) and 5-11 min of irradiation time was effective for solubilization of components in wood. The solubilization rate and the carbohydrate yield from sapwoods attained 30-38% and 15-20% (weight basis) by microwave irradiation at around 220-230°C, respectively. The pH of the water soluble fraction decreased to around 3.0-3.3 at 230°C, due to production of acids during microwave irradiation. The predominant neutral monosaccharide in the solubilized materials was only Xyl*p* indicating release of xylan by microwave irradiation. The molecular weight distribution analysis by GPC revealed production of oligosaccharides having DP 2-8 and monosaccharide. This technology was further applied for production of xylo-oligosaccharides which has various biological effects (Azuma et al., 1994a,b). The microwave pretreated residues were further digested by a mixture of cellulose and hemicellulose degrading enzymes. The solubilization rate and carbohydrate production was widely improved to 70-80% at temperatures around 220-230°C. The carbohydrate recovery attained ≥90% of total hydrolysable carbohydrate content.

For practical application of hardwood refinery, green wood chips and dried chips were investigated for their reactivity under microwave irradiation (Azuma et al., 1985c). The saccharification rate increased above 160°C. The poplar green wood chips and Buna dried chips showed resistance to enzymatic saccharification, however, their enzymatic susceptibility could be improved by increasing the heating temperature up to 240-260°C.

4.1.2 Softwoods

For softwoods, ten kinds of sapwoods (Akamatsu, Ezomatsu, Hinoki, Karamatsu, Sugi, Todomatsu, Loblloy pine, Metasequioa, Bald cypress and Slash pine) and 5 kinds of barks (Akamatsu, Ezomatsu, Hinoki, Karamatsu and Sugi) were treated with microwave energy (Azuma et al., 1984b, 1985c, 1986a) (Fig.13). Sapwoods showed 24-33% (weight basis) of solubilization at temperatures around 230°C with microwave irradiation only. At the same condition, the production of carbohydrates attained 12-28% (weight basis). The major organic acid was acetic acid which was derived from acetyl ester of the native acetylated-hemicellulose. The most predominant carbohydrate released was mannose followed by glucose and galactose reflecting the native softwoods containing GM and GGM. Furfural was also produced 0.2-1.4% due to secondary degradation of released pentoses. These results showed that the hemicelluloses were released by autohydrolysis similar to steaming or steam explosion. The weight loss after enzymatic hydrolysis attained around 30-50%. The carbohydrate yield also attained around 30-50% (weight basis) and around 35-65% (total carbohydrate basis).

Softwoods are more resistant to microwave irradiation than hardwoods. Magara et al. has investigated the reason of low enzymatic susceptibility of softwoods by measuring pore size produced along microwave irradiation (1988, 1990). They have showed that hardwoods produced larger number of pores which are accessible by enzymes than softwoods leading to increase in the surface area of the treated cell walls. Proportion of condensed form in softwood lignins increased by microwave irradiation and limited the increase in surface areas accessible by enzymes.

In the case of softwood barks, microwave irradiation was also effective for production of carbohydrates (Azuma et al., 1986a). Microwave irradiation at 234-235°C produced 0.4–0.9 meq of acids and pH value attained to 3.6-4.0. The production of carbohydrates became predominant above 160°C, and reached 2.9% (Karamatsu outer bark) -8.6% (Akamatsu) at temperatures around 210-215°C. After successive enzymatic treatment, the maximum

saccharification rate attained 35.5% (Karamatsu outer bark)-73.5% (Ezomatsu). The decrease in pH and carbohydrates yield was slightly lower than the sapwoods mentioned above since barks contain suberin.

4.1.3 Microwave irradiation of wood components

Reactivity of individual components of woody materials was also investigated for elucidation of the mechanism of chemical reaction of biomass under microwave irradiation. Avicel SF cellulose and Cellulose Powder D was subjected to microwave irradiation (Azuma et al., 1985a Elongated irradiation time (10-12 min) was necessary to induce degradation at >230°C. Increase in heating temperature increased the production of acids (up to 0.09 meq) and decreased pH down to 3.0-3.2. Production of carbohydrates were only 10.5% (Avicel SF Cellulose) and 6.5% (Cellulose Powder D), however the enzymatic susceptibility was improved above 220°C and the saccharification rate attained 81% (Avicel SF Cellulose) and 60% (Cellulose Powder D) at 245°C. Azuma et al. further investigated the effect of acetic acid, lignin and monomeric lignin model compounds on the extent of saccharification of crystalline cellulose (Whatman CF11) (Azuma et al., 1985d). Presence of acetic acid increased production of carbohydrate from 43.2% to 69.2% at 240°C. Although lignin did not induce degradation of cellulose by microwave irradiation alone, it facilitated the enzymatic susceptibility below 200°C. Moreover, addition of both acetic acid and lignin or monomeric lignin compounds showed synergistic improving effects on enzyme accessibility.
Effect of microwave irradiation on neutral LCC from Pine (C-I-M) was studied to investigate the correlation of polysaccharide and lignin (Azuma et al., 1986b). Heating at 237°C produced 45.7% of carbohydrates accompanied with production of oligosaccharides having DP of 2-5 and monosaccharides. Substantial amount of β-*O*-4 linkages and lignin-carbohydrate bonds were split by microwave irradiation.

4.1.4 Microwave irradiation of woody plants by continuous system

Based on the batch-scale studies mentioned above, microwave irradiation technology was scaled up by employing continuous system as introduced in section 2 (Magara et al., 1988) (Fig. 13). One kg of ground wood of Akamatsu and Buna was soaked in 10 L of water and microwave irradiation was performed by continuous irradiation plant (Japan Chemical Engineering and Machinery Co., Ltd. Frequency; 2.45 GHz. Max output; 4.9 kW) at a flow rate of 10-15 L/h. Reaction media were water or 0.5% (w/v) acetic acid solution. The maximum saccharification rate attained 55.7% (Akamatsu) and 61.0% (Buna) (total carbohydrate basis). Addition of acetic acid reduced the threshold temperature for removal of hemicelluloses by 10°C. The results showed that continuous system was also effective as a pretreatment of woody biomass for saccharification.

4.1.5 Catalyst assisted conversion of woody plants

Beyond the environmental-friendliness of microwave-irradiation technology based on water catalyzed reaction, Okahara et al. has developed hydrogen peroxide assisted liquefaction of woody materials to reduce severity of the process (2008) (Fig. 13). Hydrogen peroxide degrades into non-toxic water and oxygen easily by manganese dioxide or catalase, therefore it is recognized as an environmental-friendly activator of microwave irradiation. Akamatsu and Buna was loaded in TFM vessel with 20 mL of 10% hydrogen peroxide. Microwave irradiation was performed at 120-160°C and <7 min by microwave oven

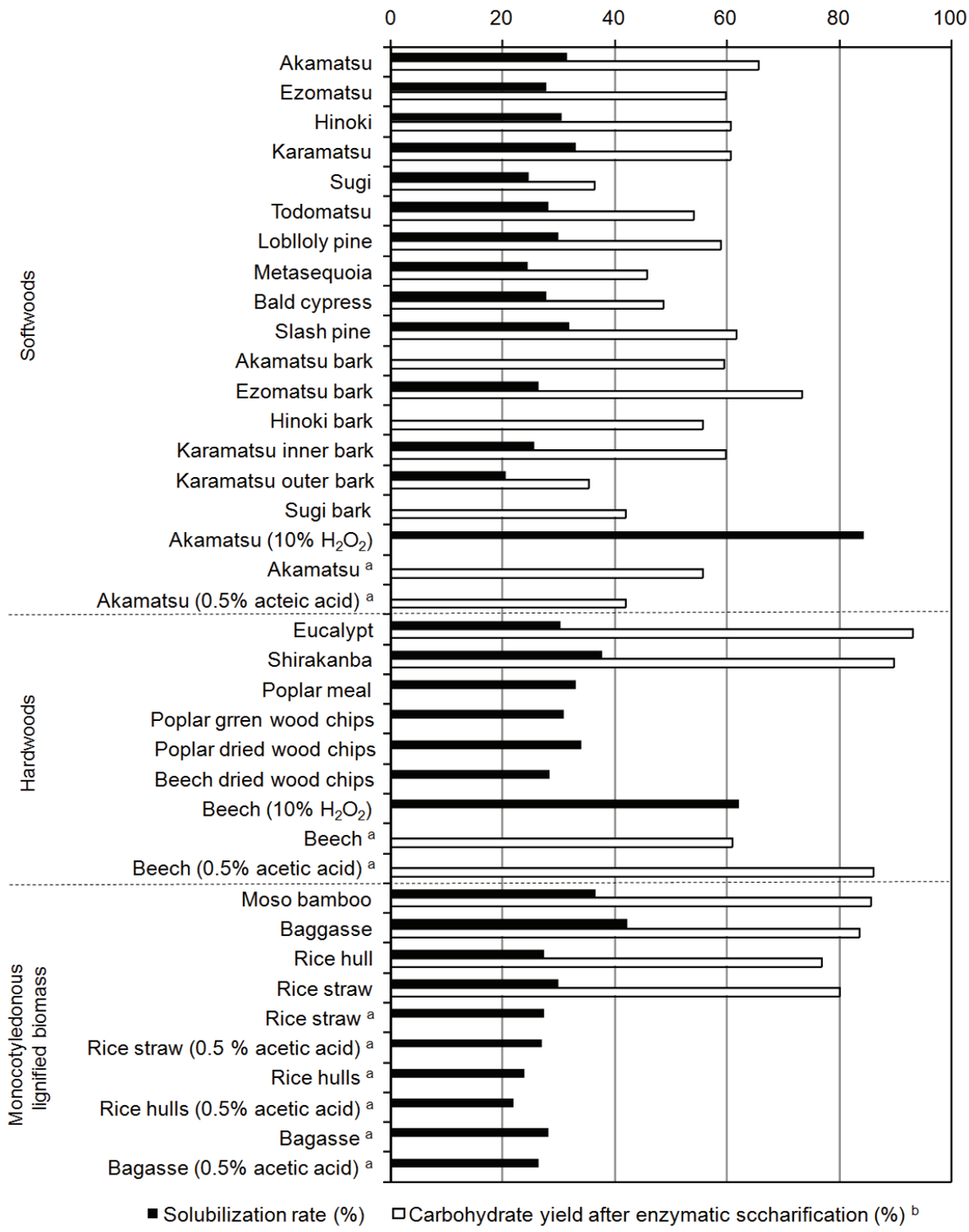


Fig. 13. Weight loss and carbohydrate yield after enzymatic saccharification (%, w/w) of softwoods, hardwoods and monocotyledonous lignified biomass. [a]Results obtained by using continuous flow system. [b]Results on the total carbohydrate basis.

MicroSYNTH (Milestone Inc., Shelton, CT, USA. Frequency; 2.45 GHz, Maximum output 1 kW. equipped with thermocouple thermometer and stirrer). Temperature was controlled by PID. The maximum solubilization rate attained 84.4% (Akamatsu) and 62.3% (Buna) at 160°C which were remarkably higher than reaction only with water or dilute organic acid solution. Neutral carbohydrate composition of extracted materials and residues showed that hemicelluloses were appreciably separated. The Klason lignin content decreased above 140°C and the lignin removal attained 61.1% (Akamatsu) and 91.7% (Buna) at 160°C. This technique was further applied to agricultural waste such as bagasse, rice straw, bamboo and lignified stone of Japanese apricot fruits (Azuma, Sakamoto & Onishi, 2009).

4.2 Monocotyledonous lignified biomass

Monocotyledonous plants such as rice, wheat, barley sugar cane and corn are important agricultural crops. Their productions reach 6.6×10^{14}, 6.1×10^{14}, 1.3×10^{14}, 1.6×10^{15} and 7.9×10^{14} tons in 2007, respectively (FAO, 2010). Agricultural residues of these crops such as husks, hulls, bagasse are important cellulosic resources to produce fermentable sugars. Furthermore, bamboo is one of the fast growing monocotyledonous plants. Therefore, it is valuable biomass feedstock. Although these plants are not classified to woods, they require pretreatment prior to enzymatic saccharification due to their lignified structures. Lab-scale microwave irradiation was demonstrated for Moso bamboo and three representative lignocellulosic wastes such as sugarcane bagasse, rice straw and rice hulls (Azuma et al., 1984a, 1984b) (Fig. 13). Moso bamboo shows 30-40% of weight loss at around 230°C. The released neutral carbohydrate fraction was mainly composed of Ara and Xyl reflecting the original carbohydrate composition (Table 3) and extraction of AX and/or AGX from these biomass. The maximal extent of enzymatic saccharification rate attained 85.7% (total carbohydrate basis), showing that the native material was comparably reactive to autohydrolysis by microwave irradiation as hardwoods. Sugarcane bagasse and rice straw showed almost the same saccharification rate (83.5 and 83.1%, respectively) as well as Moso bamboo (85.7%). In the case of rice hulls, the solubilization rate did not exceed 30%, since the recalcitrant nature of this biomass due to high content of Si.

Reactivity of lignin was further studied in detail for sugarcane bagasse, rice straw and rice hulls (Azuma et al., 1984a). Microwaved products were delignified by extraction with 90% aqueous dioxane or methanol. Bagasse lignin was the most susceptible to the pretreatment and approximately 70% of lignin became extractable in 90% aqueous dioxane at 226°C. In the case of rice straw and hulls, the maximal extents of delignification attained 58.8% and 54.4% at 226°C and 228°C, respectively. Delignification was accelerated above 180°C corresponding to release of hemicelluloses, supporting splitting of bonds between lignin and carbohydrates. The number average molecular weights of the solvent soluble lignin were measured by GPC. The extracted lignin showed smaller molecular weight (3,400-10,000) than the values of milled grass lignin isolated from the lignocellulosic wastes (5,000-15,000), showing the occurrence of sprit of bonds in lignin.

Three kinds of agricultural wastes (sugarcane bagasse, rice straw and rice hulls) were, further, pretreated by continuous microwave irradiation to scale-up the system (Magara et al., 1989). One kg of air-dried and ground material was suspended in 15 L of water and the slurry was fed to microwave irradiation at flow rates (8-20 L/h) and 160-225°C. Almost all of the hemicelluloses were removed by microwave irradiation at 210-220°C, and addition of acetic acid decreased the heating temperature by 10-30°C. Enzymatic saccharification was

satisfactory progressed after microwave irradiation and the produced glucose was fully converted to ethanol by alcohol fermentation (rice straw; 378 mL/kg and bagasse; 285 mL/kg).

4.3 Unutilized agricultural biomass from industries

Various kinds and enormous amounts of residues are discharged from food processing industries, agriculture and fisheries. They are unutilized biomass capable of producing fermentable sugars, chemicals and materials. However, in many cases, they are burnt or dumped into landfills. Since chemical components of this kind of biomass are widely different depending upon species and parts of the mother plants, characterization of these components and their chemical reactivity under microwave irradiation should be elucidated for each biomass. The chemical compositions we got on typical food and agricultural biomass were already summarized in Table 4. Now the results of application of microwave irradiation for refinery of them including the results of sea algae are summarized in Fig. 14.

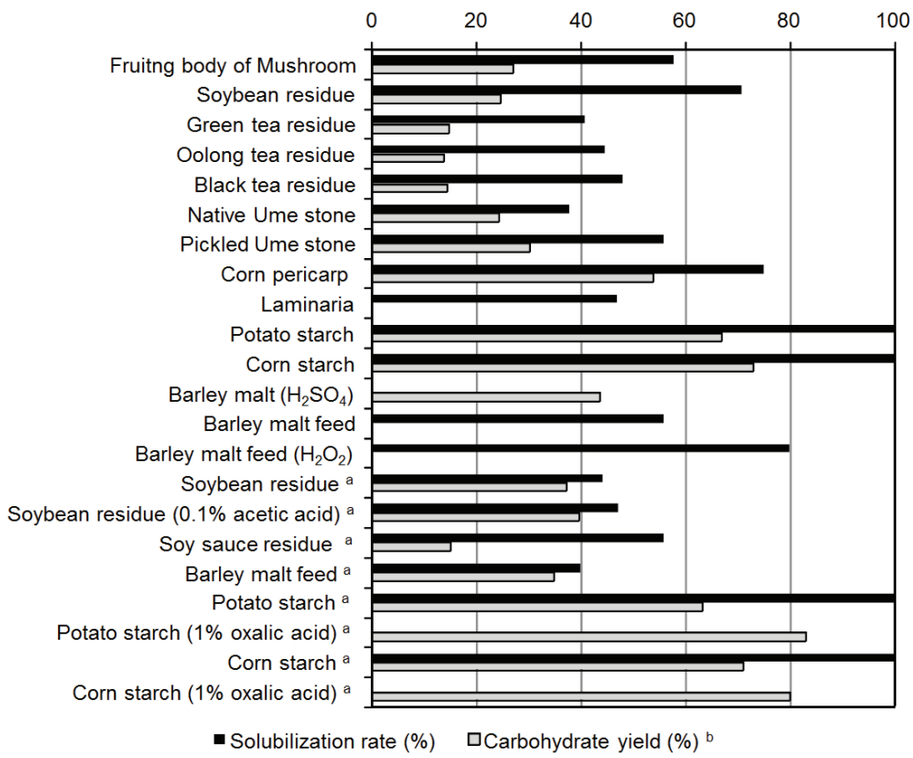


Fig. 14. Weight loss and carbohydrate yield after microwave irradiation (%, w/w) of unutilized biomass from food, agricultural and fishery industries. [a]Results obtained by using continuous flow system. [b]Data on weight basis.

4.3.1 Soybean residue

Soybean residue is a by-product from soybean curd (Tofu) production and its production reaches 700 thousand tons a year in Japan. Soybean residue is mainly composed of polysaccharide followed by protein and lipids. Microwave irradiation of soybean residue by using batch type oven (MicroSYNTH) at 200°C for 7 min (including 2 min of come-up time)

with 1 : 20 of solid : liquid ratio resulted in approximately 70% of solubilization (Tsubaki et al., 2009) (Fig.14). Due to high content of pectic arabinogalactan in soybean residue, the maximum carbohydrate production (24.6% at initial weight basis) was achieved at 160°C and 7 min. Pectic polysaccharides suffer autohydrolysis greatly easier than hemicellulose which is autohydrolyzed above 180°C. Moreover, pentoses in extracted arabinogalactan suffer further degradation into furfural and other secondary decomposed materials, therefore, 2-step microwave irradiation was investigated at 170°C, 2 min for first step and 180°C, 2 min with 4% of citric acid for second step. The first step mainly solubilized arabinogalactan and the solubilized material was removed to prevent secondary degradation. At the second step, addition of citric acid was effective for separation of protein and the extent of solubilization attained 85% at the maximum with producing minimum browning.

Scaling up of this system was successfully done by employing continuous microwave irradiation. Solubilization rate and carbohydrate yield attained 45% (240°C) and 37% (220°C) at the maximum by loading slurry of 5 kg/20 L in water. The continuous system required higher temperature to initiate autohydrolysis, however addition of acetic acid slightly decreased the severity.

4.3.2 Soy sauce residue

Soy sauce is a brown colored traditional Japanese flavoring which is essential to most of the Japanese foods. Soy sauce is a fermented food of soybean and wheat with addition of salts. The fermentation liquor becomes soy sauce and the residual material is discarded as soy sauce residue. Solubilization of soy sauce residue was investigated by continuous microwave irradiation as soybean residue with addition of 0.1% (w/v) acetic acid. The highest solubilization rate and carbohydrate yield were 56% (200°C) and 22% (220°C), respectively (Fig.14). Heating at 170-220°C also produced oligosaccharides. The predominant monosaccharide contained in the extracted polysaccharide at 230°C was glucose (45.9%) followed by xylose (22.3%).

4.3.3 Barley malt feed

Barley malt feed (730 thousand tons/year) is a by-product from beer production. Fifty six percent of the barley malt feed was solubilized in water by the same microwave system as soybean residue (Azuma et al., 2008). The predominant extracted polysaccharide was AX and/or AGX. Addition of hydrogen peroxide greatly facilitated the solubilization of this biomass and the almost all the carbohydrates were solubilized by heating at 140°C under presence of 10% hydrogen peroxide with the maximal solubilization rate of 80% (Fig.14).

Barley malt feed was also saccharified by using two-step sulfuric acid hydrolysis (Matsui et al., 2007). At the optimized condition, 1 g of barley malt feed was suspended in 70% (w/w) sulfuric acid solution and microwaved for 2 min as the first step, and then the solution was diluted to 30% (w/w) by addition of water and microwaved for 3 min as the second step. The maximum saccharification rate attained 95.1% (total carbohydrate basis).

Additionally, barley malt feed was also liquefied by continuous microwave irradiation with addition of 1% (w/v) acetic acid. Heating at higher temperature than threshold temperature (200°C) was necessary to initiate solubilization of barley malt feed by continuous system. The highest solubilization rate was 41% at 240°C. Carbohydrate yield gave the maximum value of 36% at 220°C. The production of xylo-oligosaccharide was observed at 200-220°C.

4.3.4 Tea residues

Tea residues are herbal biomass discarded from tea drink production. The total emission amounts for 100 thousand tons a year in Japan. Three kinds of tea residues (green, oolong and black tea) were subjected to microwave irradiation (Tsubaki et al., 2008). Green tea residue is a non-fermented tea, while oolong and black teas are half and fully fermented by oxidase naturally exist in the native leaves, producing polymerized polyphenols and brown color. Tea residues are composed of carbohydrate (29.6-36.7%), protein (20.3-25.4%), acid-insoluble component (30.8-40.1%) and phenolic compounds (10.4-12.4%) (Fig.14). The specific aspect of this kind of biomass can be summarized in the abundance in phenolic compounds.

Microwave irradiation of tea residues solubilized 40.8-48.1% of solids and produced 13.9-14.7% of carbohydrates (initial weight basis) at 230°C, 2-min of microwave irradiation with 1.0 : 20 (g : mL) of solid to liquid ratio. The production of polyphenols attained 8.7-14.4% (initial weight basis) which was comparable to the amount of extracted carbohydrates. The extracted liquor showed antioxidant activity against hydroxyl radicals suggesting its applicability as biologically functional materials. Although catechins were fragile to microwave heating, heating above 180°C interestingly improved the polyphenol extraction, therefore, the composition was determined by using GC/MS (Tsubaki et al., 2010). The predominant phenolic compounds extracted were pyrogallol followed by catechol and dihydroconiferyl alcohol, indicating that autohydrolysis was responsible for the degradation of catechins and lignin and the production of these phenolic compounds.

4.3.5 Stones of Japanese apricot

Japanese apricot (*Ume*) has been appreciated for medicinal plant. The fruits are processed into Japanese traditional foods such as pickles (*Ume-boshi*) and liqueur (*Ume-shu*). Japanese apricot is a kind of stone fruits since it contains lignified stone in the center of the fruits. Lignified stone is a by-product of Pickles which amounts for 500 tons a year in Wakayama Prefecture, a leading producer in Japan. The stones are rich in ash (9.1%) since the pickling process includes immersion of fruits in fruit juice with addition of sodium chloride.

Heating above 200°C was necessary to solubilize components in stones and the solubilization rate and carbohydrate yield attained 55.9% and 30.3% (initial weight basis) at 230°C and 2 min of microwave irradiation (Tsubaki et al., 2010a) (Fig.14). Predominant extracted polysaccharide was xylan. Lignin also suffered partial degradation at syringyl moiety by splitting of β-*O*-4 linkages releasing appreciable amount of syringaldehyde, sinapaldehyde and syringic acid in the extracted liquor. Pickling process improved the solubilization of the solid material and the extraction of carbohydrates and phenolic compounds by 1.5, 1.3 and 1.4 fold, respectively. Additionally, organic acids mainly citric acid and salts contained in the stones improved the microwave absorption of the reaction medium, showing pickling process of lignocellulose in weak acidic and saline solution is capable as simple pretreatment before microwave irradiation for synergistic effect of pre-hydrolysis and microwave absorption.

4.3.6 Corn pericarp

Corn pericarp is a by-product from corn starch production. AX present in the corn pericarp could be extracted by microwave irradiation (Yoshida et al., 2010). The extraction condition was optimized by using response surface methodology and the highest carbohydrate yield was obtained as 70.8% (total carbohydrate basis) at heating temperature 176.5°C, come-up

time 2min, heating time 16 min and solid to liquid ratio 1 : 20 (g : mL) (Fig.14). At the optimized condition, the solubilization rate attained 75% demonstrating high applicability of this method for utilization of corn pericarp.

4.3.7 Sea algae (*Makombu*)

Makombu (*Laminaria japonica*) is a kind of brown sea algae. Sea algae are regarded as potential renewable biomass widely distributed in the world. Makombu is capable of producing foods and polysaccharides such as alginate, fucoidan, etc. The solubilization rate increased with increase in heating temperature above 110°C. The maximum solubilization was achieved at 220°C attaining the value of 47% (Fig.14). Value of pH decreased from 6.2 to 3.8 which might accelerate autohydrolysis of the components.

4.3.8 Mushrooms

Mushrooms have been appreciated for pharmacological activities from ancient times. β-Glucan (BG) is one of the physiologically active polysaccharides. Ookushi et al. have investigated microwave-assisted extraction for BG from fruiting body of mushrooms (*Hericium erinaceum*) (2006, 2008a, b, 2009). The extraction of BG was improved by microwave irradiation for 7 min above 140°C, and the highest yield was achieved at 210°C (Fig.14). Comparing with the traditional conventional extraction method, microwave irradiation for 5 min at 140°C was equivalent to the heat conductive extraction for 6 h at 100°C. The difference in detailed structure was also investigated by methylation and ^{13}C-NMR analyses. Microwave-assisted extraction produced (1→3) rich (1→3;1→6)-β-D-glucan whereas conventional heating produced (1→6) rich (1→3;1→6)-β-D-glucan. Extraction of BG could be enhanced by treating with protease and chitin degrading enzymes.

4.3.9 Peels of thinned *Citrus unshiu*

Citrus unshiu is one of the most consumed fruits in Japan and 1 million tons are produced in 2009 in Japan (Statistics of Agriculture, Forestry and Fisheries, 2010). A large amount of green immature fruits are thinned to control the amount and quality of the fruits. Since *Citrus* peels are attracted as resource to produce pectin and flavonoids, Inoue et al. has employed microwave-assisted extraction for producing hesperidin from peels of thinned *C. unshiu* by using 70% aqueous ethanol as an extracting and crystallization solvent (2010). Hesperidin has been appreciated for biological and pharmacological activities such as antioxidant, hypocholesterolemic, hypoglycemic, protection against bone loss and antitumor activities. Fifty eight point six mg of hesperidin was extracted from 2 g of wet *C. unshiu* peels by microwave irradiation for 7 min at 140°C (Fig.15). The yield was comparable to that obtained by mixed solution of DMSO : methanol (1 : 1, v/v) for 30 min at room temperature, showing the effectiveness and environmental friendliness of this system. Storage of the extracted liquor at 5°C for 24 h produced significant amount of crystalline hesperidin as white precipitate. The maximum yield of the crystallized hesperidin attained 47.7 mg/g (86.6% of the total hesperidin).

4.3.10 Starch processing

Microwave irradiation of polysaccharides in water medium provides generation of oligosaccharide and glucose through autohydrolysis. As starches from potato, corn, wheat and tapioca are industrially important products, the effective processing of these materials could be done by employing microwave technology. The results indicate that both potato

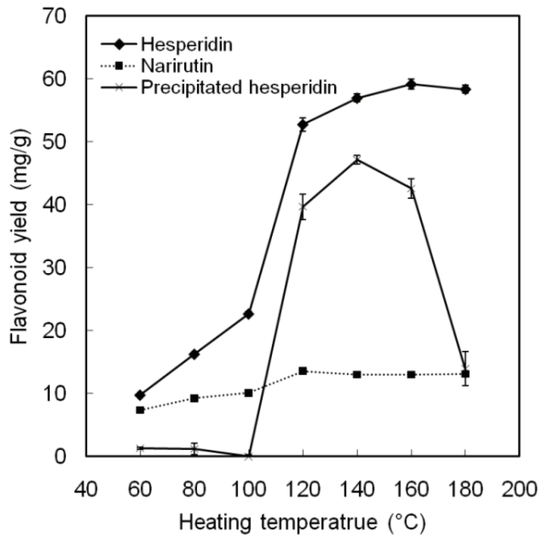


Fig. 15. Effect of microwave heating on extraction of flavonoids from thinned fruits peels of *Citrus unshiu*.

and corn starches have been saccharified by single microwave irradiation by using both batch and continuous type reactors. Gelatinization, liquefaction and saccharification processes could be done within 10 min. In the case of batch type reactor, efficient solubilization started above 120°C. Saccharification was started above 200°C accompanied with decrease in pH values. Maximal rate of saccharification of corn starch (73%) was given by batchwise microwave irradiation for 10 min at 220°C and solid to water ratio of 1 g : 20 mL. Corn starch was more susceptible to autohydrolysis than potato starch. In the case of potato starch maximal rate of saccharification (67%) was given at 230°C (Fig.14). Production of malto-oligosaccharides became prominent with increase in temperature and harder severity facilitated production of glucose. Scaling up of this method has been done by continuous system at 5-50% (w/w) and flow rate of 2.4-20.0 L/h. The results of saccharification rates of corn starch (71.0% at 220°C) and potato starch (63.6% at 225°C) were comparable to the values obtained by using the batch-type reactor. Addition of oxalic acid to 1% (w/v) was effective for lowering the severity of the process with increase in the saccharification rate.

Although microwave irradiation is a simple method for autohydrolysis of starch, secondary degradation of monosaccharides are unavoidable because the reaction was taken under elevated temperatures around 200°C. Addition of activated carbon is proved to be effective for removal of secondary degraded materials. Matsumoto et al. (2008) has applied such kind of activated carbons as sensitizers for reduction of secondary degradation and increase in microwave energy absorption. As a result, malto-oligosaccharides produced by heating for 10 min at 200-220°C were effectively adsorbed on the activated carbons. The malto-oligosaccharides adsorbed on the activated carbon could be recovered by elution with 50% aqueous ethanol. Additionally, the malto-oligosaccharides adsorbed on the activated carbon were stable and protected against microwave-assisted degradation.

5. The advantages of microwave irradiation

Microwave irradiation is different from the conventional heating in which thermal energy is delivered via conduction. Microwave energy is directly delivered to the materials and heat can be generated throughout their volumes, resulting in rapid and uniform heating. Although it is difficult to compare effects of microwave irradiation with conventional heating, some special effects notified by our results are summarized below.

5.1 Advantage of microwave irradiation over steam-explosion

Microwave irradiation in water is thought to be a kind of hydrothermal treatment. Is this microwave irradiation superior to usual hydrothermal treatment? Batch results on comparative analysis with steam-explosion shown in Table 5 indicate excellence of microwave treatment on account of enzymatic susceptibility in all three kinds of woody materials, hardwood (Japanese beech), softwood (Japanese red pine) and monocotyledon (Moso bamboo) (Azuma et al., 1984). The results on beech shown in Fig. 16A indicate further that continuous microwave irradiation is also superior to steam-explosion under the same duration of heating time of 3 min, enhancing enzymatic susceptibility at lower temperature after microwave irradiation (Yamashita & Azuma, 2010). The extents of methanol-extractable lignin are, however, similar in both treatments (Fig. 16B). These results indicate that microwave irradiation has more power to activate polysaccharides against enzymatic attacks than steam-explosion although the effects on lignin are similar.

Plant species		Temperature	Maximal extent of saccharification (%)
Pine (Akamatsu, *Pinus densiflora*)	Microwave	229 °C	65.6
	Steam explosion	227 °C	49.6
Beech (Buna, *Fagus crenata*)	Microwave	223 °C	93.0
	Steam explosion	227 °C	87.9
Bamboo (Moso bamboo, *Phyllostachys pabessence*)	Microwave	227 °C	85.7
	Steam explosion	227 °C	78.5

[a]Including data listed in Azuma et al. 1984.

Table 5. Comparison of microwave irradiation and steam explosion

5.2 Advantage of microwave irradiation over conventional heating

As described in 4.3.8 microwave irradiation shortens time necessary to extract valuable materials from biomass. Superiority of activating polysaccharides by microwave irradiation may be due to direct delivery of microwave energy to polysaccharides through molecular interactions with electromagnetic field. Similar to BG from mushroom microwave extraction was applied for extraction of hemicelluloses from plants (Ebringerová et al., 2005).

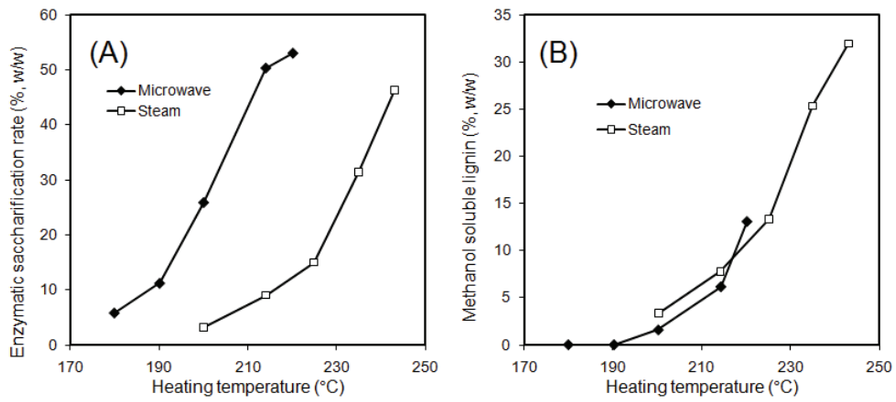


Fig. 16. Comparison of the values of saccharification rate (A) and methanol-soluble lignin content (B) got on continuous microwave irradiation and steam explosion (Parameter was set as duration of heating time 3 min, concentration 1 kg/L, flow rate of continuous microwave irradiation 8-15 L/h)

5.3 Advantage of microwave irradiation induced by electro-conductive reagents

As microwave energy is absorbed in electrically conductive materials, addition of any kind of sensitizers promotes heating. As described in 4.3.5 extraction efficiency of carbohydrates and phenolic compounds from fruits of Japanese apricot was improved for 1.4 fold by addition of sodium chloride for pickling. Furthermore addition of activated carbon was found to be useful for removal of secondary degradation products (4.3.10) with holding oligosaccharides inertly.

6. Conclusion

Effects of microwave irradiation on various kinds of recalcitrant biomass including woody and agricultural materials in aqueous media were reviewed. As a summary, microwave irradiation is demonstrated to have an efficient power for separation of biomass components. Its environment-friendliness, rapidity and easy to use safely opens unknown better ways for future welfare of human being. Finding new kind of sensitizers or catalysts which promote the power of microwave remarkably seems to be important for future innovation of this field of research. Development of scale up system for industrial use is also necessary.

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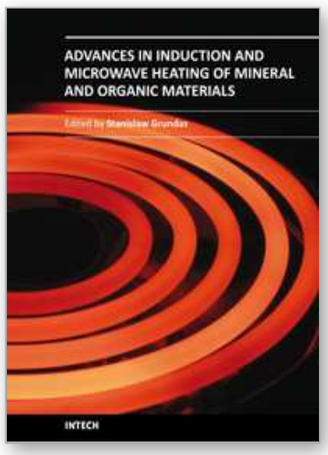
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