

Recent Research Activities in Solid and Liquid Bioenergy from Lignocellulosic Biomass

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Introduction

The increase in energy demand, the lack of petroleum resources, and concern over global climate change have placed great emphasis on the development of new alternative energy technologies that can be used to replace fossil transportation fuels (Himmel *et al.* 2007; Labbe *et al.* 2008; Lee *et al.* 2009a,b,c; Teramoto *et al.* 2008, 2009). In this context, many countries have initiated extensive research and development programs for bioenergy. Bioenergy can be classified into three kinds of solid, liquid, and gas bioenergy. For the effective production and utilization of these three types of bioenergy, different technologies are required (Figure 1). Lignocellulosic biomass, such as wood and agricultural residues, are widely distributed and easily accessible at relatively low costs. Of these, wood has the benefit of having a higher energy content per volume, lower ash content, and nitrogen content. In this review, recent research trends and advances in bioenergy from lignocellulosic biomass will be summarized from the author's point of view.

but burns rapidly. White charcoal, on the other hand, is covered with ash and is difficult to be ignited, but burns for a longer period. In addition, charcoal has attracted in many fields because of its unique characteristics. Charcoal has numerous tiny cavities resulting in a high surface area of approximately 300~600 m²/g. These cavities can absorb various substances including heavy metals. This property of charcoal has applications in various fields, such as soil modification, water purification, and the carbon industry. To obtain an effective carbonization process, it is important to understand the carbonization mechanism of wood.

The proposed mechanism involved in the transition from wood to charcoal is as follows: (1) water is evaporated up to a temperature of 150°C; (2) residual water is driven off of the wood structure between 150°C and 260°C; (3) decomposition and depolymerization of the wood begins breaking C-O and C-C bonds resulting in the evolution of water, CO, and CO₂, between 260°C and 400°C; and (4) graphitic layers are formed above 400°C. It is also known that thermally induced decomposition and rearrangement reactions are largely terminated above 800°C, leaving a carbon structure (Mopoung 2008). Analysis of the pyrolysis of wood using a heating rate of 5°C min⁻¹ suggests that hemicelluloses are decomposed at temperatures ranging from 170~240°C, cellulose between 240~310°C, and lignin between 320~400°C (Zerouh and Belkbir 1995). Kwon *et al.* (2010 and 2012) investigated the characteristics of the transition from wood to charcoal to understand the transformation mechanism and found that the volume, vessel diameter, and cell wall thickness of the wood decreased with increasing temperature.

Solid Bioenergy

Wood Charcoal

Wood charcoal is generally produced by pyrolysis at temperatures ranging from 600~1100°C under insufficient oxygen for complete combustion. Depending on the pyrolysis temperature and fire extinguishing system, charcoal can be classified into black and white charcoal (Kim *et al.* 2001). Generally, black charcoal is easy to ignite

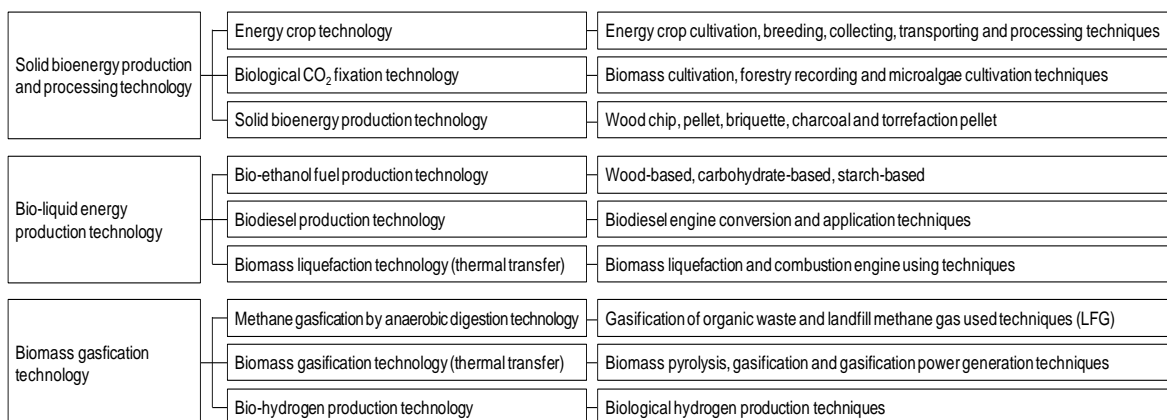


Figure 1. Classification of bioenergy technologies.
(New & Renewable Energy Center, Korea Energy Management Corporation 2016).

On the other hand, the weight loss, pH, and heating value increased with the increase in the carbonization temperature. SEM images indicated that the layering structure of the cell walls of wood fibers and parenchyma cells were present at 330~340°C. However, the cell wall layering structures disappeared at temperatures over 350°C and changed radically into an amorphous-like structure. X-ray diffraction patterns showed that the cellulose crystalline structure was present at 340°C, but it was not detected over 350°C. From FT-IR spectroscopy, signals from the vibration of aromatic

rings had maximum intensities at 390°C, and those from ether groups decreased with increasing temperature. The heating value gradually increased from 4530 to 8200 cal/g over the temperature range of 200~1000°C, as shown in Table 1. Rhee and Cho (2008) also reported that the fuel ratio (fixed carbon/volatile combustible), carbon content, and heating value of the carbonization residue increased, but the yield of the residue decreased, with increasing carbonization temperature.

Table 1. The heating value of *Quercus variabilis* charcoals prepared at different temperatures (Kwon *et al.* 2010)

Temp.	Control	200°C	250°C	300°C	350°C	400°C	600°C	800°C	1000°C
Heating value (cal/g)	4326	4530	4728	5099	5871	6699	7239	8183	8200

Wood Pellets

The pelletization of biomass involves the mass and energy densification of materials such as sawdust, straw, and other herbaceous energy crops with low bulk densities. This process reduces transportation costs and provides better handling, less dust formation, and more efficient feeding of the biomass into the pyrolysis process (Garcia-Maraver *et al.* 2011). In general, pellet quality depends on the chemical, mechanical, and physical properties of biomass in terms of thermal utilization (Kaliyan and Vance 2009; Oberberger and Thek 2004). Wood Pellets can be produced from roundwood but have mostly been made from cheaper waste residues derived from other wood processing activities, primarily sawdust and shavings from sawmills and

furniture factories. If made from roundwood, the full range of steps involving debarking, chipping, drying, and hammer milling must be done. Residues require less processing because they are already reduced in size, mostly bark-free, and dried (Spelter and Toth 2009). In either case, the moisture content is critical and must be confined within a range of approximately 12% to 17%. Pellets from different regions might be shown different properties (Kwon *et al.* 2009). Calorific value can be increased by the addition of other substrates, such as wood tar and wood vinegar (Kwon *et al.* 2010). Table 2 shows the characteristics of first-grade commercial wood pellets in several countries.

Table 2. Properties of first grade commercial wood pellets in several countries

Contents	United States ¹⁾	Germany ²⁾	Austria ²⁾	South Korea ³⁾
Thickness (mm)	5.84-7.25	4-10	4-10	6-8
Length (mm)	>38.1	50	5 x thickness	<32
Bulk density (kg/m ³)	640-737	1000-1400	>1120	>640
Moisture content (%)	<8	12	<10	<10
Ash content (%)	<1	1.5	<0.5	<0.7
Heating value (kcal/kg)	>4445	3704-4660	>4302	>4300

¹⁾ ISO 17225-1, 2014; ²⁾ Garcia-Maraver *et al.* 2011; ³⁾ Ahn *et al.* 2014.

Torrefied Wood Pellets

Torrefaction of wood can be described as a mild form of pyrolysis at temperatures typically ranging between 200°C and 320°C (Van der Stelt *et al.* 2011). During torrefaction, the wood properties are altered to produce a higher fuel quality for combustion and gasification applications. The main principle of torrefaction from a chemical point of view is the removal of oxygen to produce a final solid product, torrefied wood, which has a lower oxygen/carbon ratio compared to the original wood. The thermal treatment not only disrupts the fibrous structure and firmness of the biomass but is also known to increase the

calorific value. Torrefied wood has more hydrophobic characteristics that make storage of torrefied wood more attractive in comparison to non-torrefied wood, because of the tendency of non-torrefied wood to rot. During torrefaction, wood is partly devolatilized leading to a decrease in mass, but the initial energy content of the torrefied wood is largely preserved in the solid product. Therefore, the energy density of torrefied wood is higher than that of the original wood, making it less expensive to transport per unit of energy (Van der Stelt *et al.* 2011). Figure 2 shows a comparison of a typical pelletization and torrefaction process (Bergman *et al.* 2005). The pelletization process comprises the steps of drying, size reduction,

steam pre-conditioning, densification, and cooling. However, the torrefaction process only consists of three steps, drying, torrefaction, and cooling. Table 3 summarizes the main characteristics of wood, torrefied wood, wood pellets, and

torrefied wood pellets. In summary, torrefied wood pellets have a more hydrophobic characteristic, higher strength, and higher density than of wood pellets (Bergman 2005).

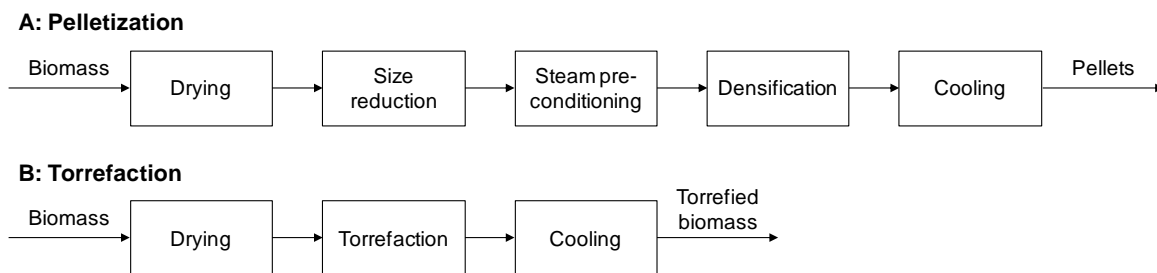


Figure 2. Schemes of pelletization (A) and torrefaction (B) processes.

Table 3. Characteristics of wood, torrefied wood, wood pellets, and torrefied wood pellets (Bergman 2005)

Contents	Wood	Torrefied Wood	Wood Pellets	Torrefied Wood Pellets
Moisture (wt%)	35	3	7	1
Net heating value				
Normal (MJ/kg)	10.5	19.9	16.2	21.6
Dry (MJ/kg)	17.7	20.4	17.7	22.7
Mass density (kg/m ³)	550	230	650	850

Liquid Bioenergy (Bioethanol)

Bioethanol is by far the most widely used biofuel for transportation worldwide. Production of bioethanol from lignocellulosic biomass is one way to reduce both the consumption of crude oil and environmental pollution. Biochemical conversion of lignocellulosic biomass through saccharification and fermentation is the primary pathway for bioethanol production. However, there are some difficulties in producing bioethanol from lignocellulosic biomass as a result of (1) the resistant nature of biomass to breakdown; (2) the variety of sugars that are released when the

hemicelluloses and cellulose polymers are broken down, and the need to find or genetically engineer organisms to efficiently ferment these sugars; and (3) the costs for collection and storage of low-density lignocellulosic biomass (Balat 2011). Figure 3 shows the basic process of producing bioethanol from lignocellulosic biomass, i.e., pretreatment, hydrolysis, fermentation, and product separation/distillation. A large number of pretreatment methods have been developed, including mechanical grinding, steam explosion, CO₂ explosion, ammonia fiber explosion, ozonolysis, hot water treatment, the organosolv process, and biological pretreatment (Kumar *et al.* 2009).

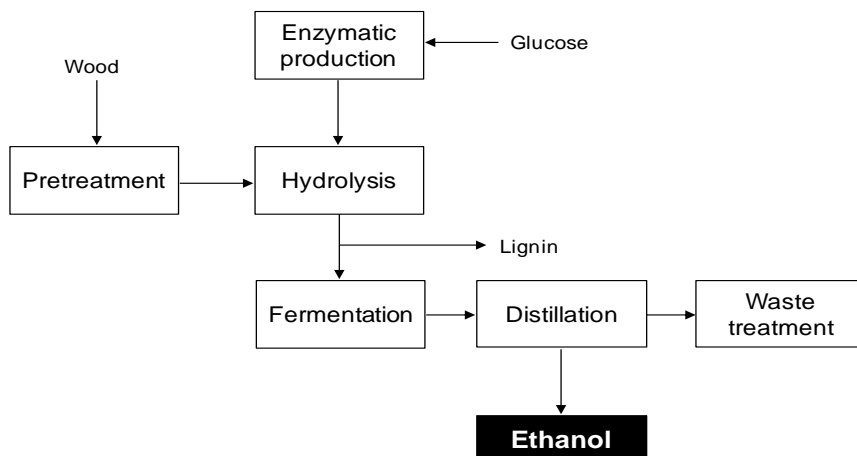


Figure 3. Production of bioethanol from lignocellulosic biomass.

The carbohydrate polymers in lignocellulosic materials must be converted to simple sugars before fermentation through a process called hydrolysis (Taherzadeh and Karimi 2007). The most commonly applied methods can be classified into two groups: chemical hydrolysis (dilute and concentrated acid hydrolysis) and enzymatic hydrolysis (Balat 2011). The dilute acid hydrolysis process involves a solution of approximately 1% H₂SO₄ in a continuous flow reactor at a high temperature. Most dilute acid processes are limited to a sugar recovery efficiency of around 50% (Farooqi and Sam 2004). The acid concentration used in concentrated acid hydrolysis processes is in the range of 10–30%. This process provides complete and rapid conversion of cellulose to glucose and the conversion of

hemicelluloses to five-carbon sugars with little degradation (Iranmahboob and Nadim 2002). In contrast, enzymatic hydrolysis is a slow process because enzymatic hydrolysis of cellulose is hindered by the structural parameters of the substrate, such as the lignin and hemicellulose content, and cellulose crystallinity (Pan *et al.* 2006). On the other hand, enzymatic hydrolysis is an environmentally friendly alternative that involves using carbohydrate-degrading enzymes (cellulases and hemicellulases) to hydrolyze lignocelluloses into fermentable sugars (Keshwani and Cheng 2005). A comparison of the process conditions and performance of three cellulose hydrolysis processes is given in Table 4 (Hamelinck *et al.* 2005).

Table 4. Comparison of conditions and performance of three hydrolysis processes (Hamelinck *et al.* 2005)

Contents	Consumables	Temperature(°C)	Time	Glucose Yield (%)
Dilute acid	<1% H ₂ SO ₄	215	3 min	50-70
Concentrated acid	30–70% H ₂ SO ₄	40	2–6 h	90
Enzymatic	Cellulase	50	1.5 days	75 → 95

References

- Ahn B.J., Cho S.T., Choi D.H. 2014. Quality standards of solid bioenergy from woody biomass. Proceeding of Annual Meeting of Korean Forest Bioenergy Society. May 16th, 2014. Seoul, South Korea. pp. 33-36.
- Balat M. 2011. Production of bioethanol from lignocellulosic materials via the biochemical pathway: A review. *Energy Conversion and Management* 52: 858-875.
- Bergman P.C.A. 2005. Combined torrefaction and pelletisation: the TOP process. Report ECN-C-05-073. Petten, The Netherlands: ECN; 2005.
- Bergman P.C.A., Boersma A.R., Zwart R.W.R., Kiel J.H.A. 2005. Torrefaction for biomass co-firing in existing coal-fired power stations "biocoal". Report ECN-C-05-013. Petten, The Netherlands: ECN; 2005.
- Farooqi R, Sam AG. 2004. Ethanol as a transportation fuel. Centre for applied business research in energy and the environment (CABREE) climate change initiative, University of Alberta, Canada, April 29 2004.
- Garcia-Maraver A., Popov V., Zamorano M. 2011. A review of European standards for pellet quality. *Renewable Energy* 36: 3537-3540.
- Hamelinck C.N., Van Hooijdonk G., Faaij A.P.C. 2005. Ethanol from lignocellulosic biomass: Techno-economic performance in short-, middle- and long-term. *Biomass Bioenergy* 28: 384-410.
- Himmel M.E., Ding S.Y., Johnson D.K., Adney W.S., Nimlos M.R., Brady J.W., Thomas D.F. 2007. Biomass recalcitrance: Engineering plants and enzymes for biofuels production. *Science* 315: 5813-5815.
- Iranmahboob J., Nadim F. 2002. Monemi S. Optimizing acid-hydrolysis: a critical step for production of ethanol from mixed wood chips. *Biomass Bioenergy* 22: 401-4.
- ISO 17225-1. 2014. Solid biofuels- Fuel specifications and classes, Part 1: General requirements.
- Kaliyan N., Vance R. 2009. Factors affecting strength and durability of densified biomass products. *Biomass and Bioenergy* 33: 337-359.
- Keshwani D.R., Cheng J.J. 2009. Switchgrass for bioethanol and other value-added applications: A review. *Bioresources Technology* 100: 1515-23.
- Kim N.H., Kwon G.J., Hwang W.J., Lee S.J., Park H.S. 2001. Development of an efficient process for manufacturing charcoal-variation of temperature in a traditional kiln during carbonizing process-. *Journal Industry University Regional Consortium Center, Kangwon National University* 5: 43-48.
- Kumar P., Barrett D.M., Delwiche M.J., Stroeve P. 2009. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. *Industrial & Engineering Chemistry Research* 48: 3713-29.
- Kwon G.J., Kim N.H., Cha D.S. 2009. Characteristics of the commercial wood pellets. *Journal of Forest Science*. 25(2): 127-130.
- Kwon G.J., Kwon S.M., Cha D.S., Kim N.H. 2010. Characteristics of pellet prepared from sawdust and wood-tar. *Journal of the Korean Wood Science and Technology* 38(1): 36-42.
- Kwon S.M. 2010. Transition characteristics of the wood cell walls during carbonization. Ph.D. thesis. Kangwon National University. Republic of Korea.
- Kwon S.M., Kim N.H., Cha D.S. 2009. An investigation on the transition characteristics of the wood cell walls during carbonization. *Wood Science and Technology* 43: 487-498.
- Kwon S.M., Kwon G.J., Jang J.H., Kim N.H. 2012. Characteristics of charcoal in different carbonization temperatures. *Journal of Forest Science* 28(4): 263-267.

- Labbe N., Lee S.H., Jeong M.K., Cho H.W., André N. 2008. Enhanced discrimination and calibration of biomass NIR data using nonlinear Kernel methods. *Bioresource Technology* 99: 8445-8452.
- Lee S.H., Teramoto Y., Endo T. 2009a. Enzymatic saccharification of woody biomass micro/nano-fibrillated by continuous extrusion process I-Effect of additives with cellulose affinity. *Bioresource Technology* 100: 275-279.
- Lee S.H., Teramoto Y., Endo T. 2009b. Enhancement of enzymatic accessibility by fibrillation of woody biomass using batch-type kneader with twin-screw elements. *Bioresource Technology* 101: 769-774.
- Lee S.H., Cho H.W., Labbe N., Jeong M.K. 2009c. Quick assessment of thermal decomposition behavior of lignocellulosic biomass by near infrared spectroscopy (NIR) and its statistical analysis. *Journal of Applied Polymer Science* 114: 3229-3234.
- New & Renewable Energy Center, Korea Energy Management Corporation. 2016. Classification of bioenergy technologies. <http://www.knrec.or.kr/knrec/11/KNREC110700.asp>. Accessed 11 July 2016.
- Obernberger I., Thek G. 2004. Physical characterization and chemical composition of densified biomass fuels with regard to their combustion behaviour. *Biomass and Bioenergy* 27: 653-669.
- Pan X., Gilkes N., Saddler J.N. 2006. Effect of acetyl groups on enzymatic hydrolysis of cellulosic substrates. *Holzforschung* 60: 398-401.
- Rhee S.W., Cho Y.H. 2008. A study on characteristics of carbonization residue produced from woody biomass. *Journal of Korea Solid Wastes Engineering Society* 25(6): 533-539.
- Spelter H., Toth D. 2009. North America's wood pellet sector. Research Paper FPL-RP-656FPL, USDA, USA.
- Taherzadeh M.J., Karimi K. 2007. Acid-based hydrolysis processes for ethanol from lignocellulosic materials: a review. *BioResources* 2: 472-99.
- Teramoto Y., Lee S.H., Endo T. 2008. Pretreatment of Eucalyptus wood chips for enzymatic saccharification using combined sulfuric acid-free ethanol cooking and ball milling. *Biotechnology and Bioengineering* 99(1): 75-85.
- Teramoto Y., Lee S.H., Endo T. 2009. Pretreatment of woody and herbaceous biomass for enzymatic saccharification using sulfuric acid-free ethanol cooking. *Bioresources Technology* 99: 8856-8863.
- Van der Stelt M.J.C., Gerhauser H., Kiel J.H.A., Ptasinski K.J. 2011. Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass and Biotechnology* 35: 3748-3762.
- Zerriouh A, Belkbir L. 1995. Thermal decomposition of a Moroccan wood under a nitrogen atmosphere. *Thermochim Acta* 258: 243-248.
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