

Upgrading Properties of Biomass Fuels by Torrefaction Process: Applying to Existing Coal-fired Boilers

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Abstract

Biomass torrefaction is a thermochemical pretreatment process to improve properties of biomass solid fuels. Torrefaction is conducted usually at 200-350°C for 30 minutes to 2 hours in the absence of oxygen under atmospheric conditions. Most of biomass properties are changed after torrefaction. It can be found that the hemicellulose component in biomass is decomposed during torrefaction. The distributions of product yields for the solid torrefied biomass, torrefied liquid, and gases are around 85%, 10%, and 5%, respectively. The carbon content, ash content, fixed carbon content, higher heating value (HHV) and Hardgrove Grindability Index (HGI) of torrefied biomass increase with increasing operating temperature and residence time, however, hydrogen content, oxygen content, moisture content and mass yield of solid product show contrary results. Torrefied biomass shows the satisfying properties as a coal-like fuel for combustion, gasification, etc., such as homogeneous, hydrophobic, preserved, grindable, and higher energy content. Also, it becomes easy for transporting, handling, and feeding for energy applications.

Introduction

Woody biomass is an abundant organic renewable energy on earth. On the technical level, derived fuels similar to coal, oil, and gas could be created by converting biomass using thermochemical methods. Other advantages such as the ease of storage, transportation, wide application, net CO₂ emission, and low sulfur and nitrogen content would not only protect the environment but also increase energy efficiency.

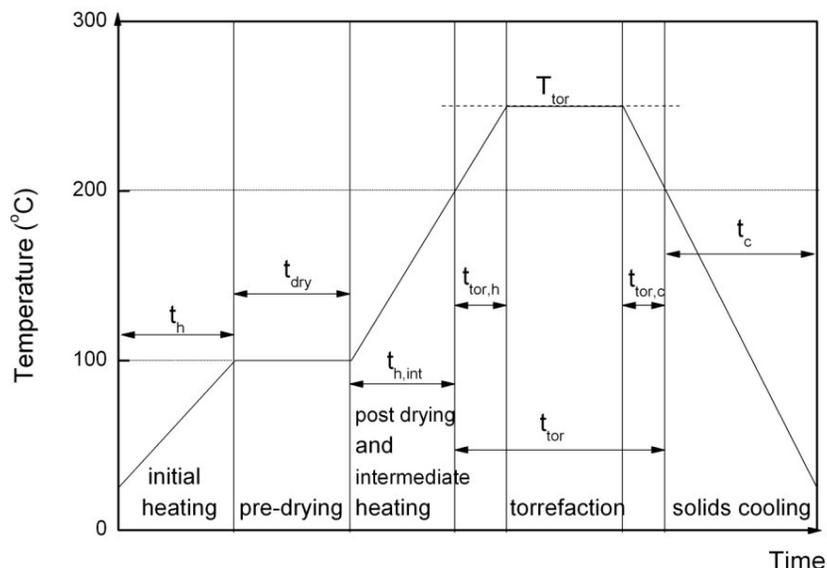
However, when using raw woody biomass as raw material for energy conversion, its structural heterogeneity and uneven physical properties result in low energy density, making it uneconomical for transportation, storage, and processing. Moreover, its high moisture content result in water absorption from the environment even after desiccation, ultimately resulting in its decay. The uneven sizes of the biomass also pose as a problem since it does not meet the current standard feed requirements of combustion and gasification. Lastly, wooden fibres are difficult to grind, and the grinding process takes up too much energy. All these problems end up making woody biomass an expensive renewable energy (Mani et al., 2004; Mani, 2005; Mani et al., 2006; Phanphanich and Mani, 2011). Based on the drawbacks and obstacles described above, new technologies are under development in order to obtain high quality biofuels.

To improve the biomass property, recently torrefaction is developed as a pre-thermochemical treatment technology that could increase combustion qualities when converting biomass into solid fuels. It is a mild pyrolysis process carried out under the atmospheric pressure and absence of oxygen, temperature ranging from 200 to 300°C, with a heating rate less than 50°C/min, and a short residence time (about one hour). It can also improve the quality of solid fuels simultaneously.

Torrefaction Process

There are clear restrictions on the reaction time and residence time of torrefaction. Therefore, the reaction temperature has a greater effect on the quality of the torrefaction process than its residence time. Bergman et al., (2005) utilized the changes of temperature and residence time to specify different stages of the reaction as shown in Figure 1. t_h represents the period of the initial heating stage, starting from the initial heating process to the drying process. In this stage, the moisture in the biomass evaporates fairly slowly, but the temperature continues to rise. t_{dry} is the drying time, mainly consisting of pre-drying in order to lower water content. Although the moisture level drops dramatically, the temperature holds still. $t_{h,int}$ is the transition heating time, starting from the drying stage until the temperature reaches the reaction temperature. During this post-drying and intermediate heating phase, the temperature would rise to 200°C, accompanied by the physical release of bound water. $t_{tor,h}$ is the time needed to heat from 200°C to the torrefaction reaction temperature (T_{tor}). t_{tor} is the

Figure 1: Stages of Biomass Torrefaction



Adopted from Bergman et al. (2005)

designated torrefaction reaction time. The torrefaction reaction starts when the temperature reaches 200°C, along with devolatilisation reactions. This is followed by $t_{tor,c}$, the time needed to cool from T_{tor} to 200°C. Lastly, t_c is the time needed to cool from 200°C to room temperature. Solid products start to cool during this phase.

Under room temperature, the products of torrefaction can be divided into solid, gas, or condensable liquid (Table 1). The distribution of product yields for the solid torrefied biomass, torrefied liquid, and gases are around 85%, 10%, and 5%, respectively. Solid consists of original and modified sugar structures, newly formed polymeric structures, char, and ashes. Products in gas form consist of permanent gases, such as H_2 , CO , CO_2 , CH_4 , C_mH_n , and some aromatic compounds with lower molecular weight. The liquids are produced from the condensation of volatile compounds, like water (formed from the dehydration reaction during heating), organic compounds (formed from devolatilisation and carbonization) and lipids.

Table 1: The Products of Biomass Torrefaction (Bergman et al., 2005)

Phase	Groups of Components
Solid	<ul style="list-style-type: none"> - Original and modified sugar structures - Newly formed polymeric structures - Char - Ash
Liquid (condensables)	<ul style="list-style-type: none"> - H_2O - Organics: sugars, polysugars, acids, alcohols, furans, ketones - Lipids: terpenes, phenols, fatty acids, waxes, tannins
Gas (permanent)	<ul style="list-style-type: none"> - H_2, CO, CO_2, CH_4, C_mH_n

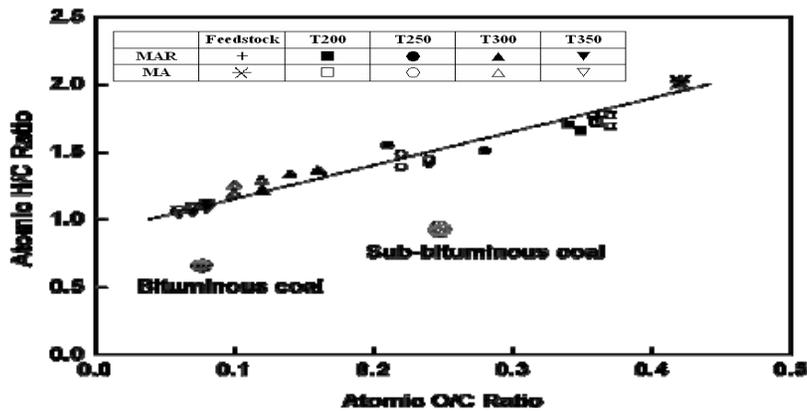
The cell wall of woody biomass is mainly composed of cellulose, hemicellulose, and lignin. Hemicellulose is the most reactive among the three, followed by cellulose, while lignin has the recalcitrant nature to be heated within the torrefaction temperature range. During torrefaction, low temperature (200–300°C) pyrolysis is mainly composed of the devolatilisation and carbonization of hemicellulose (Bergman et al., 2005). Hemicellulose is formed from a mixture of polysaccharides, mainly xylans, glucomannans and arabinogalactans. Hemicellulose is quite different from cellulose. Cellulose is composed of β -1-4 D-glucose, with hydrogen bonds between molecules, forming a high molecular weight polymer chain. Compared with cellulose, hemicellulose has a lower molecular weight, branched structures, and a low degree of polymerization (around 200). Also, since hemicellulose does not have crystalline structures, it is more prone to the influences of acids, bases, and heat.

Gaur and Reed (1998) summarized cellulose's degradation process into two main stages. Volatile compounds with small molecular weight are formed in the first stage through low temperature polymerization, creating polysaccharides. When the temperature reaches 250–350°C, the polysaccharides decompose into volatile compounds including monosaccharide, glycan fragments and dehydrosugars. Finally, these break down into CO_2 and CO with the catalytic effects of minerals. In the process of pyrolysis, several compounds containing carboxylic groups break down into acids. These acids promote reactions such as dehydration and pyrolysis to form CO_2 and compounds containing carbonyl structures, such as hydroxyl acetone, methanol and propanal.

Characteristics of Torrefied Biomass

All the solid products formed after torrefaction exhibit better fuel properties (e.g. lower moisture content, high heating value) than unprocessed biomass. A van Krevelen's diagram can be plotted by using atomic H/C vs O/C ratios from ultimate analysis shown in Figure 2 (Wu et al. 2011). It is clear that the H/C and O/C values decrease gradually with an increase in the torrefaction temperature and residence time. After torrefaction, the property of biomass feedstock approaches that of coal. Bridgeman et al. (2008) states that a large amount of elements released from torrefaction are O and H, thus the H and O contents in biomass gradually decrease. Also, from the work of Bergman et al. (2005), the decrease of O/C and H/C can reduce the thermodynamic loss of smoke and vapour from excessive oxidation. Therefore, torrefied biomass has potential in the application of co-firing with coal.

Figure 2: van Krevelen's Diagram



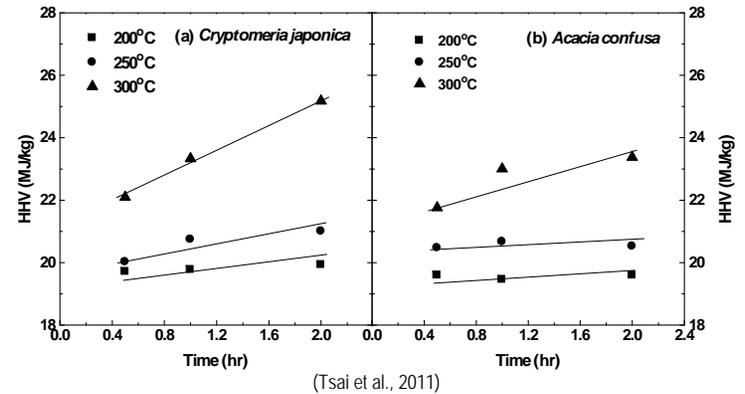
(MAR: microalgae residue; MA: microalgae)
(Wu et al., 2012)

As stated by Bergman et al. (2005) and Phanphanich and Mani (2010), after torrefaction process, the hydroxyl group (-OH) of the biomass feedstock is destroyed, and the biomass loses the capability to form hydrogen bonds with water. Thus, the torrefied biomass is the hydropho-

bic materials. Usually, if the moisture content in biomass is too high, the temperature for the ignition and combustion in combustors or boilers will be lowered, directly impacting energy usage. Prins et al. (2006) also states that torrefied products have less water content, lowering the enthalpy needed to evaporate the water in further applications, thus improving the efficiency of energy conversion.

Increasing the torrefaction temperature and residence time also increases the higher heating value (HHV) of the torrefied product (Figure 3). As pointed out in Chen and Kuo (2011), the oxygen in the feedstock is consumed during the torrefaction process. Thus, the C-O bonds in woody biomass decreases. Since the C-C bond energy is higher than that of the C-O bond, the carbon content increases and causes an increase in the heating value with increasing temperature and residence time.

Figure 3: Effect of Torrefaction Temperature and Residence Time on Higher Heating Value of Torrefied Biomass



(Tsai et al., 2011)

Grindability is also a property that contributes to the applications of torrefied biomass. The Hardgrove Grindability Index (HGI) represents the difficulty for grinding the solid sample into the powder. Higher HGI means easier to grind the sample into powder. Usually, the HGI increases with increasing temperature and residence time. Arias et al., (2008) states that the fibre structures of wooden materials are hard to grind. Phanphanich and Mani (2011) showed the evidence that the energy requirement to grind the torrefied biomass can be lower than grinding raw biomass directly. Improvement on grindability of torrefied biomass is attributed to

the weakening of the wooden fibre structure by torrefaction that can increase the brittleness of biomass (Mani, 2009).

Compared to original biomass, torrefied products have better grindability and other fuel properties. Therefore, if it could partially replace fossil fuels used in *pulverized coal* (PC) fired *boilers* or co-generations, the cost to produce energy would be lowered. Generally, the Hardgrove Grindability Index (HGI) of sub-bituminous coal is 50, which is an acceptable value for coal pulverizers. Torrefaction could enhance the HGI of biomass; hence with higher HGI, the torrefied biomass can be blended with coal directly for the grind before feeding into the boiler without modifying any part of the PC combustion system further.

Conclusion

Application of biomass for energy generation has become increasingly important. At the same time, there are already years of experiences in co-firing of agricultural and forestry waste to achieve the goal of energy-from-waste. To increase energy efficiency, biomass torrefaction will be a better solution for future application. After torrefaction, the carbon content, ash content, fixed carbon content, higher heating value and Hardgrove Grindability Index (HGI) of torrefied biomass increases with an increase in the operating temperature and residence time; however, hydrogen content, oxygen content, moisture content, and mass yield of solid product show contrary results.

Torrefied biomass shows satisfying properties as a coal-like fuel for combustion, gasification, etc., such as homogeneous, hydrophobic, preserved, grindable, and higher energy content. Also, it becomes easier for transporting, handling, and feeding for energy applications. Thus, it is expected that the biomass torrefaction process will promote the utilization of biomass energy.

During the torrefaction process, the water content is greatly lowered, causing the weight and volume to decrease. As a result, transportation costs are lowered. At the same time, using torrefied biomass as fuel could greatly increase its calorific value, making it more efficient undergoing co-combustion. Hence, torrefaction processes has the potential to produce economic and energy efficiency benefits.

References

- Arias, B., Pevida, C., Feroso, J., Plaza, M.G., Rubiera, F. and Pis, J. J. (2008) 'Influence of Torrefaction on the Grindability and Reactivity of Woody Biomass' *Fuel Processing Technology* 89: 169–175.
- Bergman, P. C. A., Boersma, A. R., Zwart, R. W. R. and Kiel, J. H. A. (2005) 'Torrefaction for Biomass Co-firing in Existing Coal-Fired Power Station' ECN report, ECN-C--05-013.
- Bridgeman T.G., Jones, J. M., Shield, I. and Williams. P. T. (2008) 'Torrefaction of Reed Canary Grass, Wheat Straw and Willow to Enhance Solid Fuel Qualities and Combustion Properties' *Fuel* 87: 844–856.
- Chen, W. H. and Kuo, P. C. (2011) 'Torrefaction and Co-torrefaction Characterization of Hemicellulose, Cellulose and Lignin as well as Torrefaction of Some Basic Constituents in Biomass' *Energy* 36: 803–811.
- Gaur, S. and Reed, T. B. (1998) 'Thermal Data for Natural and Synthetic Materials' Marcel Dekker, New York. 253 pp.
- Mani, S., Tabil, L. G. and Sokhansanj, S. (2004) 'Grinding Performance and Physical Properties of Wheat and Barley Straws, Corn Stover and Switchgrass' *Biomass and Bioenergy* 27: 339–352.
- Mani, S. (2005) 'A Systems Analysis of Biomass Densification Process' Ph.D. Dissertation, Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, Canada.
- Mani, S., Tabil, L. G. and Sokhansanj, S. (2006) 'Effects of Compressive Force, Particle Size and Moisture Content on Mechanical Properties of Biomass Pellets' *Biomass and Bioenergy* 30: 648–654.
- Mani, S. (2009) 'Integrating Biomass Torrefaction with Thermo-Chemical Conversion Processes' *Proceedings of The 2009 AIChE Annual Meeting*, Paper No. 160229, Nashville, TN.
- Phanphanich, M. and Mani, S. (2010) 'Drying Characteristics of Pine Forest Residues' *Bioresources* 5: 108–120.
- Phanphanich, M. and Mani, S. (2011) 'Impact of Torrefaction on the Grindability and Fuel Characteristics of Forest Biomass' *Bioresour Technology* 102:1246–1253.
- Prins, M. J., Ptasiński, K. J. and Janssen, F. J. J.G. (2006) 'More Efficient Biomass Gasification via Torrefaction' *Energy* 31: 3458–3470.
- Tsai, C. J., Chang, C. H., Tung, Y. C., Wu, K. T. and Yen, Y. H. (2011) 'Torrefaction and Carbonization of Woody Materials' Paper presented at *2011 Conference of the Chinese Forestry Association*, Ilan, Taiwan (27-28 October).
- Wu, K. T., Tsai, C. J., Chen, C. S. and Chen, H. W. (2012) 'The Characteristics of Torrefied Microalgae' *Applied Energy* 100: 52–57.

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Keng-Tung Wu received his doctoral degree in chemical engineering from University College London (UCL), University of London in 1997. Afterwards he went back to Taiwan as a post-doctoral researcher at Department of Chemical Engineering, Chung Yuan Christian University for one year working on coal and biomass combustion in fluidized beds. He then joined Industrial Technology Research Institute (ITRI) in Taiwan in 1999 as a Researcher at Clean Energy Technology Division of Energy and Resources Laboratories to develop the biomass gasification technology, and led a research team to build the largest circulating fluidized bed gasification pilot plant for biomass fuels in Taiwan. In 2005, Dr. Wu joined Central Taiwan University of Science and Technology as an Assistance Professor at the Department of Health, Safety and Environmental Engineering in Taichung. A year later, he transferred to the Department of Forestry at National Chung Hsing University (NCHU) as an Assistance Professor, and now heads the Bioenergy Research Core Laboratory supported by the College of Agriculture and Natural Resources at NCHU. Dr. Wu is also the leader of the Educational Laboratory of Ambient Experience for Bioenergy, Resource Center for Talent Training in Biomass Energy Technology supported by Ministry of Education. In addition, he is Adjunct Project Consultant (later Adjunct Distinguished Researcher) at ITRI since 2005. Currently he also holds the APEC New and Renewable Energy Technology Expert Group (EGNRET) Secretariat since 2011. Dr. Wu's research involves fluidization engineering and biomass thermochemical conversion technology including gasification, pyrolysis and torrefaction.

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