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Editorial

## Hydrothermal Processing of Biomass for Biofuels

In recent years, significant research interests have been placed on the conversion of non-food biomass resources such as lignocellulosic biomass (terrestrial) and algae (aquatic) to biofuels. Among all the alternative or renewable energy options, biomass is the only resource which is carbon neutral and can potentially replace part of fossil fuels use as liquid transportation fuels as well as contribute to electricity generation. Therefore, it can play a significant role in partially replacing oil, natural gas, and coal utilization for heat and energy generation. However, high moisture content of fresh biomass or algae is one of the major challenges in developing logistics and downstream processing for an economical design of bio-refineries. In conventional conversion methods (e.g. gasification, pyrolysis, and combustion), drying of biomass is a required step which is a challenge in order to make biofuels production economically feasible.

Lots of efforts have been made to explore the role of liquid water as a reactant and/or reaction medium at high temperatures and pressures for the production of a variety of biomass-derived gaseous, liquid, and solid fuels. In fact, this eliminates the need of removing moisture from biomass. Hydrothermal or sub/super-critical water (critical point: 374°C, 22.1 MPa) technology can utilize wet biomass by capitalizing on the extraordinary solvent and tunable properties of water at elevated temperatures for converting biomass to biofuels. It is a non-toxic, environmentally benign, and relatively inexpensive medium for conducting chemical reactions. Another major advantage of this technology is that the large parasitic energy losses caused by moisture removal that can consume much of the energy content of the biomass are avoided. In sub- and supercritical water processes, water is kept in liquid or supercritical phase by applying pressure greater than the vapor pressure of water. Thus latent heat required for phase change of water from liquid to vapor phase (2.26 MJ/kg of water) is not needed. For a typical 250°C subcritical-water process, the energy requirement to heat water from ambient condition to the reaction temperature is about 1 MJ/kg, equivalent to 8-10% of energy content of dry biomass.

In the subcritical region, the ionization constant of water increases with temperature and is about three orders of magnitude higher than that of ambient water and the dielectric constant of water drops from 80 to 20. A low dielectric constant allows subcritical water to dissolve organic compounds, while a high ionization constant allows subcritical water to provide an acidic medium for the hydrolysis reactions. These ionic reactions can be dominant because of the liquid-like properties of subcritical water. Moreover, the physical properties of water, such as viscosity, density, dielectric constant and ionic product, can be tuned by small changes in pressure and/or temperature in the subcritical region. In the supercritical region, density of water drops down to lower values. This means that ionic product of water is much lower and ionic reactions are inhibited because of the low dielectric constant of water. The lower density favors free-radical reactions, which may be favorable for gasification. Therefore, subcritical water medium between 200-350°C and variable residence time is mainly used for the liquefaction of biomass for biocrude production or for the production of green coal/hydrochar/biochar. However, for gaseous fuels such as methane, hydrogen, and syngas production from biomass, supercritical water phase between 374-700°C is used.

Based on laboratory experiments, excellent results have been achieved and the technology possesses many potential benefits over the conventional methods of processing biomass to biofuels or chemicals. However, there are certain engineering issues involving the scale of the technology which need to be addressed. These challenges include feeding of biomass slurry, salt precipitation in supercritical water, corrosive medium, and possibility of deactivation of heterogeneous catalysts. The recent literature on lab/pilot-scale studies has shown that the sub- and supercritical water technology can be used in the production of liquid fuels (bioethanol, biocrude), gaseous fuels (methane, hydrogen, synthesis gas), and solid fuels (biochar, other functional carbonaceous materials) from terrestrial or aquatic non-food biomasses.

The U.S. DOE has identified subcritical water/hydrothermal process as a viable technology which can process wet biomass for biofuels. The National Advanced Biofuels Consortium (NABC) led by Pacific Northwest National Laboratory (PNNL) has published a report in 2012 on review and assessment of commercial vendors/options for feeding and pumping biomass slurries for subcritical water reactions in continuous reactor. The new feed and pumping options from the vendors presented in this report and the recent vendor experience pumping very challenging feedstock media have been shown to be successful in pumping biomass slurries at large scale. In fact, Elliott et al. at PNNL and NABC team has been leading the efforts of scaling up hydrothermal/subcritical water-based processing of biomass for biofuels. The recent (year 2013) pilot scale published studies on hydrothermal processing of macroalgal feedstocks in continuous-flow reactors also successfully demonstrated the technical feasibility of the subcritical water-based processes. Wet algae slurry was successfully converted into an upgradeable biocrude with high levels of carbon conversion to gravity separable biocrude product at 350 °C and 20 MPa in a continuous-flow reactor under subcritical water environment. The group reported that high conversions were obtained even with high slurry concentrations of up to 35 wt% of dry solids. Another example of technical feasibility of subcritical water-based process has been recently demonstrated by Sapphire Energy for processing algae at pilot-scale. The company is rapidly moving towards the commercial scale facility for algae-to-biofuels. The commercial-scale feasibility for solid fuels (green coal/hydrochar/biochar) production has been demonstrated by AVA-$CO_2$ Schweiz AG who succeeded as the first company to commission 8,400 tons per annum biomass processing capacity using hydrothermal/subcritical water technology.

Though the hydrothermal technology is being rapidly adopted for industrial scale applications, the expanded process development is still needed to take it to an appropriate scale for industrial applications.

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