METHODS FOR SULFATE REMOVAL IN LIQUID-PHASE CATALYTIC HYDROTHERMAL GASIFICATION OF BIOMASS

CROSS-REFERENCE TO RELATED APPLICATIONS

This invention claims priority from, and is a continuation of U.S. patent Ser. No. 13/541,003, filed Jul. 3, 2012, now U.S. Pat. No. 8,608,981, which is a continuation-in-part of U.S. patent application Ser. No. 12/339,876, filed Dec. 19, 2008, now U.S. Pat. No. 8,241,605 which claims the benefit of U.S. Provisional Patent Application No. 61,024,970, filed Jan. 31, 2008, all of which are incorporate herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with Government support under Contract DE-AC0576RL01830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

BACKGROUND

Conventional ways of gasifying of biomass can utilize thermal methods involving pyrolysis and/or partial oxidation to produce a fuel gas or a synthesis gas composed of carbon oxides and hydrogen. Many of the known methods use a dry biomass feedstock with less than 10 wt % moisture. However, much of the biomass resource that is actually available contains significantly higher levels of moisture, typically 50 wt %. Some biomass even consists of "wet" biomass, or biomass in water slurries at 85 wt % moisture or higher. One approach to efficiently process such wet biomass is gasification employing an active catalyst in a pressurized water environment (e.g., hydrothermal gasification).

However, hydrothermal gasification involving critical, or above critical operating conditions are expensive. Furthermore, when treating wet biomass by hydrothermal gasification, constituents that are commonly inherent in the feedstock can poison and/or foul the catalyst making long-term and/or continuous operation difficult to achieve. Accordingly, a need for improved methods for liquid-phase hydrothermal gasification of wet biomass exists.

SUMMARY

This document describes methods for treating wet biomass by liquid-phase catalytic hydrothermal gasification that address the problem of poisoning and fouling of the catalyst, especially by sulfate contaminants that are soluble in the liquid portion of the wet biomass feedstock. The methods involve operations at temperatures and pressures that maintain the wet biomass feedstock in the liquid phase without forming a critical or supercritical fluid. The wet biomass feedstock comprises solid and/or soluble biomass, soluble sulfate contaminants, and sub-critical liquid water. Some biomass feedstocks can also comprise inorganic wastes that can cause plugging and poisoning of the catalyst. These sulfate contaminants and inorganic wastes can be precipitated out before gasification by heating the wet biomass feedstock prior to exposure to the catalyst according to embodiments of the present invention.

Referring to FIG. **1**, treatment of the wet biomass feedstock comprises heating **100** the wet biomass with a heating unit to a pre-treatment temperature sufficient for organic constituents in the feedstock to decompose, for precipitates of inorganic wastes to form, for preheating the wet feedstock in preparation for removal of the soluble sulfate contaminants, or combinations thereof. The process further comprises reacting **101** the soluble sulfate with cations present in the feedstock in order to yield sulfate-containing precipitates and separating **102** the precipitates of inorganic wastes and the sulfate-containing precipitates out the wet biomass feedstock. After processing, the liquid of the wet biomass feedstock can have a decreased sulfate content. For example, accounting for the soluble sulfate and/or sulfate in the sulfate-containing precipitates, the feedstock can have less than 20 ppm sulfate content. Having removed much of the inorganic wastes and the soluble sulfate contaminants that can cause poisoning and fouling, the wet biomass feedstock can be exposed to the heterogeneous metal catalyst for gasification **103**.

As used herein, biomass refers to biological material that can be used for fuel or for industrial production. Exemplary biomass can include, but is not limited to, biosludge from wastewater treatment facilities, sewage sludge from municipal treatment systems, wet byproducts from biorefinery operations, wet byproducts/residues from food processing, animal waste and waste from centralized animal raising facilities. As used herein, biomass can also refer to various organic wastes. Examples include, but are not limited to organic chemical manufacturing wastewater streams, and industrial wastewater containing organics. Biomass commonly comprises organic matter that can be treated in a continuous reactor, according to embodiments of the present invention, to yield a gas containing hydrogen or useful for hydrogen production (e.g., methane). Common inorganic contaminants, which can poison and/or foul the catalyst, can include, but are not limited to minerals comprising Ca, Mg, P, and/or Fe. Sulfur-containing contaminants can occur in two different forms, reduced and oxidized. The reduced sulfur contaminants can occur in protein structures. The oxidized sulfur contaminants can occur as soluble sulfate contaminants. The sulfate contaminants can arise, for example, from oxidation of protein structures.

In some embodiments, the biomass can further comprise at least a partial source of the cations that react with the soluble sulfate contaminants to yield sulfate-containing precipitates. For example, the biomass can comprise certain compounds that yield cations in the feedstock at processing conditions. Alternatively, or in addition, the cations can be provided by adding **104** a salt to the feedstock. Examples of cations can include, but are not limited to, barium and calcium. In some embodiments, the salt added to the feedstock can be substantially water-soluble. An example of a water-soluble salt comprising calcium can include, but is not limited to, calcium ascorbate. Alternatively, the salt can be only partially water-soluble. Examples of calcium salts can include, but are not limited to, calcium oxide, calcium hydroxide, and calcium carbonate.

In preferred embodiments, the heterogeneous catalysts comprise Ru, Ni, and/or Ni with added Na. The Na can be in the form of a sodium carbonate co-catalyst. In a particular embodiment, the catalyst comprises Ru on a carbon support. Furthermore, the catalyst can be configured to gasify the organic constituents into a hydrogen-containing feedstock for subsequent catalytic reformation.

Separation of solids, including the sulfate-containing precipitates, from the heated wet biomass feedstock can be