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Thermodynamic modelling of supercritical water gasification: Investigating the effect of biomass composition to aid in the selection of appropriate feedstock material

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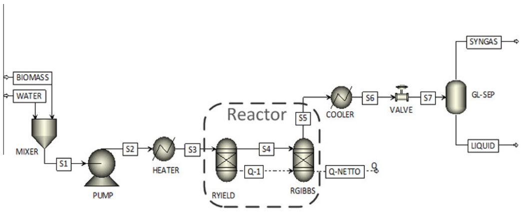
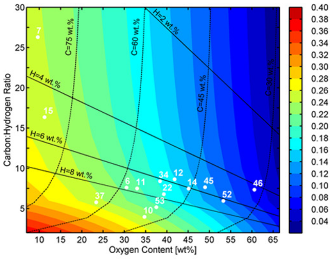
HIGHLIGHTS

- A thermodynamic model of a continuous SCWG experimental setup was developed.
- Effect of C:H and oxygen content of biomass are shown for product gas yields.
- Effect of C:H and oxygen content of biomass are shown for HHV_{gas}, CGE and Q_{Req}.
- Maximum H_2, CH_4 and total molar yields are achieved at low oxygen content and C:H.
- A screening method for selecting feedstock for SCWG experiments is proposed.

GRAPHICAL ABSTRACT



Aspen Plus ® thermodynamic process model of typical SCWG experimental setups



Effect of biomass composition (wt.% on a dry, ash-free basis) on the H_2 yield

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ABSTRACT

A process model developed in Aspen Plus®, was used for the thermodynamic modelling of supercritical water gasification (SCWG) using a wide variety of biomass materials as feedstock. The influence of the composition of the biomass material (in terms of carbon, hydrogen and oxygen content) on various performance indicators (such as gas yields, cold gas efficiency, calorific value of product gas and heat of reaction), were determined at various temperatures (600, 700 and 800 °C) and biomass feed concentrations (5, 15 and 25 wt.%). Generalised contour plots, based on the biomass composition, were developed for these performance indicators to provide the thermodynamic limits at various operating conditions. These plots can aid in the selection or screening of potential biomass materials and appropriate operating conditions for SCWG prior to conducting experimental work.

1. Introduction

The rapid depletion of fossil fuel resources together with the focus on limiting greenhouse gas emissions have led to an increased effort in the development of sustainable, alternative and renewable energy conversion processes. Hydrogen, a non-polluting, secondary energy carrier, has attracted great attention as an alternative fuel for future use in hydrogen fuel cells and combustion engines. Additionally, biomass is considered as a potential renewable and sustainable source from which hydrogen can be produced due to its CO_2 neutrality and lower emission of nitrogen oxides (NO_x) and sulphur dioxide (SO_2) during combustion (Zhang

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et al., 2010a). Biomass waste materials (i.e., organic industrial waste materials, generated from various industries such as agricultural activities, food processing plants, municipal sewage plants as well as the pulp and paper industry) typically have a high moisture content (80–99 wt.%) and are consequently not suitable as feedstock in typical thermochemical processes such as pyrolysis and gasification (Zhang et al., 2010a). Hence, these wet, organic waste streams are potential feedstock material for supercritical water gasification (SCWG), which requires an aqueous medium for gasification.

During SCWG, organic materials are converted to a fuel-rich gas, consisting of mainly H_2, CH_4, CO_2 and CO, in the presence of excess water above its critical point ($T > 374$ °C and $P > 22.1$ MPa). This conversion is made possible by the unique changes in the transport and thermo-physical properties of water observed above its critical point. The density of supercritical water (SCW) is much lower than that of ambient water (166.54 kg/m^3 at 400 °C and 25 MPa vs 997 kg/m^3 at 25 °C and 0.1 MPa, Lemmon et al., 2011), resulting in a decrease in the number and the strength of hydrogen bonds and causing SCW to lose its liquid-like properties. This results in a significant decrease in the dielectric constant (78.03 at 25 °C and 0.1 MPa to 2.52 at 400 °C and 25 MPa, Fernandez et al., 1997) allowing SCW to act as a good solvent for non-polar molecules such as organic compounds (Savage, 1999). Additionally, gases are highly miscible in SCW, allowing reactions to be homogeneous, resulting in the elimination of inter-phase mass transfer, which could delay reaction rates (Savage, 1999). Other advantages of SCWG include high gasification efficiencies and hydrogen yields as well as low or negligible tar formation (Zhang et al., 2010a). Furthermore, due to high-pressure operations, hydrogen can be made available at high pressures and can consequently be enriched easily due to the difference in solubility of hydrogen and carbon dioxide in pressurised water (Kruse and Dinjus, 2007).

Numerous experimental studies in both batch and continuous reactor setups, with and without the use of catalysts have shown that high gasification efficiencies can be achieved when model compounds (such as glucose, cellulose, methanol and ethanol, glycerol, iso-octane and xylose and phenol mixtures) as well as real biomass (such as pulp/paper mill sludge, sewage sludge and black liquor, algae, fruit shells and, corn, clover, wheat and other agricultural residues, livestock wastes as well as various wastewater streams compounds) are gasified by means of SCWG (Antal et al., 2000; Byrd et al., 2008; Hao et al., 2003; Kruse et al., 2003; Xu et al., 1996).

Various studies have performed thermodynamic equilibrium calculations of SCWG for the estimation of the equilibrium product gas compositions and yields, using several model feedstock materials (methanol, glycerol, ethanol, cellulose and phenol) as well as real biomass feedstock materials (paper residue, sewage sludge, microalgae, oak wood, pine wood, winery marc, wood saw dust and cow manure) (Castello and Fiori, 2011; Fiori et al., 2012; Gutiérrez Ortiz et al., 2011a; Letellier et al., 2010; Lu et al., 2007; Tang and Kitagawa, 2005; Withag et al., 2012). Although the results from these studies vary slightly, the general trends are in agreement and could be summarised as follow (Withag et al., 2012):

- An increase in operating temperature resulted in an increase in the hydrogen yield and a decrease in the methane yield;
- An increase in the biomass-to-water feed ratio resulted in a decrease in the hydrogen yield and an increase in the methane yield;
- An increase in the operating pressure above the critical pressure of water did not seem to have a significant effect on the gas yields.

Thermodynamic modelling of SCWG assumes that the reactions are controlled by equilibrium rather than kinetics. Although, in a practical sense, kinetics could play a definitive role in SCWG reactions (especially at temperatures below 600 °C and at short residence times), a proper knowledge of the thermodynamic limits provides valuable and critical information on the operating conditions that will favour the production of H_2 or syngas. By considering such information, experiments can be designed more effectively and the data can be compared with the equilibrium results (Gutiérrez Ortiz et al., 2011b).

Despite all of the work done on thermodynamic modelling of SCWG most of these studies only focussed on the effect of the operating conditions such as temperature, pressure and water-to-biomass feed ratio (also referred to as the biomass concentration in the feed stream) on the equilibrium product gas composition and gas yields (Castello and Fiori, 2011; Gutiérrez Ortiz et al., 2011a; Tang and Kitagawa, 2005; Yan et al., 2006). In only one of these studies, the effect of the elemental composition of the biomass was briefly examined, and it was suggested by Yan et al. (2006) that biomass with higher C/O ratio's will yield more H_2. However, no in-depth investigation on the combined effect of the composition of the biomass (in terms of its elemental composition) and operating conditions on the equilibrium gas composition or yields of SCWG have been reported thus far.

Knowledge of the thermodynamic limits of the gas yields that can be obtained from SCWG of a certain biomass material based on its elemental composition at specified operating conditions prior to conducting experimental work can be of great help. It can serve as a screening tool to indicate whether a specific biomass material is worth-while to be considered as a feedstock material for SCWG based on its equilibrium gas yields. Hence, the main objective of this study was to investigate the effect of biomass composition on the thermodynamic gas yields from SCWG at various operating conditions. This was done in order to develop a screening tool to aid in the selection of suitable biomass feedstock material for SCWG prior to conducting experimental work based on the biomass composition and its equilibrium gas yields. Even though a study on developing such a tool for the selection of appropriate feedstock material for conventional gasification of biomass has been proposed by Vaezi et al. (2012), no work has been done in developing such a tool for SCWG.

Aspen Plus® was used to simulate a typical SCWG process layout. The carbon (C), hydrogen (H) and oxygen (O) content of the biomass feedstock material were varied at various combinations of operating temperatures and biomass feed concentrations. Generalised contour plots for the total (Y_{Total}) and individual gas yields (Y_i), cold gas efficiency (*CGE*), calorific value of the product gas (*HHV*) and the heat required for the process (Q_{Req}) were generated. These plots can be used to obtain the maximum theoretical values for the performance indicators for any given biomass material with properties within the ranges used in this study at specific operating conditions.

2. Methods

2.1. Biomass feedstock properties

Five model biomass components (glycerol, ethanol, glucose, methanol and cellulose) and 49 real biomass materials (including, amongst others, sewage sludge, black liquor, grape residue, olive residue, pulp and paper mill sludge, various livestock manure, char from sugarcane bagasse, coffee waste, animal blood, leather waste, micro algae, organic wet fraction of municipal waste, crude glycerol from biodiesel production, palm leaves, straw and torrified wood chips) were considered as possible feedstock for the SCWG