



Catalytic supercritical water gasification of primary paper sludge using a homogeneous and heterogeneous catalyst: Experimental vs thermodynamic equilibrium results



Jeanne Louw, Cara E. Schwarz, Andries J. Burger*

Department of Process Engineering, Stellenbosch University, Private Bag X1, Matieland 7602, South Africa

HIGHLIGHTS

- Primary paper waste sludge (PWS) was gasified in supercritical water at 450 °C.
- Addition of K₂CO₃ catalysed the water-gas shift reaction to yield 7.5 mol/kg_{PWS} H₂.
- 90% conversion of carbon to the gas phase achieved with Ni–Al₂O₃/SiO₂ catalyst.
- 83% energy recovery achieved with Ni–Al₂O₃/SiO₂ catalyst.
- Gas product with HHV of 13.3 MJ/kg_{PWS} achieved with Ni–Al₂O₃/SiO₂ catalyst.

ARTICLE INFO

Article history:

Received 15 September 2015
Received in revised form 16 November 2015
Accepted 17 November 2015
Available online 23 November 2015

Keywords:

Primary paper sludge
Supercritical water gasification (SCWG)
Thermodynamic equilibrium yields
K₂CO₃
Ni/Al₂O₃–SiO₂

ABSTRACT

H₂, CH₄, CO and CO₂ yields were measured during supercritical water gasification (SCWG) of primary paper waste sludge (PWS) at 450 °C. Comparing these yields with calculated thermodynamic equilibrium values offer an improved understanding of conditions required to produce near-equilibrium yields. Experiments were conducted at different catalyst loads (0–1 g/g_{PWS}) and different reaction times (15–120 min) in a batch reactor, using either K₂CO₃ or Ni/Al₂O₃–SiO₂ as catalyst. K₂CO₃ up to 1 g/g_{PWS} increased the H₂ yield significantly to 7.5 mol/kg_{PWS}. However, these yields and composition were far from equilibrium values, with carbon efficiency (CE) and energy recovery (ER) of only 29% and 20%, respectively. Addition of 0.5–1 g/g_{PWS} Ni/Al₂O₃–SiO₂ resulted in high H₂ and CH₄ yields (6.8 and 14.8 mol/kg_{PWS}), CE of 84–90%, ER of 83% and a gas composition relatively close to the equilibrium values (at hold times of 60–120 min).

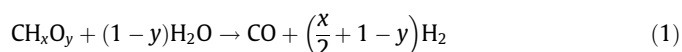
© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Increased electricity and disposal costs, stricter legislation regarding waste disposal, as well as the high organic content of paper sludge, have shifted the focus from considering paper sludge as a waste product to a possible feedstock material for thermochemical energy conversion processes such as pyrolysis (Ridout et al., 2015) and co-combustion (Yanfen and Xiaoqian, 2010). However, paper sludge contains high concentrations of water (typically 70–99 wt.% moisture) and needs to be dried prior to conventional thermochemical conversion processes. Since such drying consumes much energy, direct supercritical water gasification (SCWG) of paper sludge may be an attractive alternative energy recovery process.

SCWG (also commonly referred to as hydrothermal gasification) is a thermochemical process through which organic material can be converted to an energy-rich gas product (consisting mainly of H₂, CH₄, CO₂ and CO) in the presence of water above its critical point (374 °C and 22.1 MPa) (Kruse, 2008). Due to the change in the physical and transport properties of water above its critical point, minimal resistance to inter-phase mass transfer exists during SCWG. Additionally, a wide variety of feedstock material (containing lignocellulose, fatty acids and proteins) can be gasified in supercritical water (SCW) (Peterson et al., 2008).

The three main reactions taking place during SCWG of biomass are: steam reforming of biomass to form CO and H₂ (Eq. (1)); water-gas shift reaction between CO and water to form CO₂ and H₂; and methanation of CO and H₂ to form CH₄ and water.



* Corresponding author. Tel.: +27 21 808 4494.

E-mail address: ajburger@sun.ac.za (A.J. Burger).

Three operating temperature ranges generally exist for SCWG, namely subcritical water gasification (below 374 °C), low temperature SCWG (typically between 374 and 550 °C) and high temperature SCWG (typically between 550 and 700 °C) (Azadi and Farnood, 2011). When operating at temperatures higher than 550 °C, no catalyst is needed for complete gasification and the product gas will be rich in hydrogen. At lower temperatures (between 374 and 550 °C), the product gas will be richer in methane and a catalyst is required to achieve complete gasification (Elliott, 2008). One potential drawback of operating at high temperature SCWG conditions is that appropriate reactors require more robust and costly materials of construction at these temperatures, due to the general decrease in the yield strength of a metal with an increase in temperature. Hence, considering investment costs and safety requirements, operating at low temperatures, closer to the critical temperature of water, has a clear advantage over high temperature SCWG (Gasafi et al., 2008).

A wide variety of studies have shown that the use of both homogeneous alkali metal catalysts (such as K_2CO_3 , NaOH, KOH, $CaCO_3$, Na_2CO_3 and $KHCO_3$) and heterogeneous transition metal catalysts (such as Ru, Rh, Ni, Cr, Co, Zn, Pd, Pt, Ti and Mo) can greatly enhance the gasification efficiency during SCWG (Elliott, 2008). Generally, alkali metal catalysts enhance the water-gas shift reaction, resulting in a significant increase in the H_2 yield (Rönnlund et al., 2011). Sinağ et al. (2004) was the first to describe the catalytic effect of K_2CO_3 (probably the most widely used alkali metal catalyst) during SCWG. Firstly, K_2CO_3 reacts with water to form KOH and $KHCO_3$. Potassium formate (HCOOK) is then formed from the reaction of KOH with CO. HCOOK then reacts with water to form H_2 and $KHCO_3$. Finally, the $KHCO_3$ decomposes to water, K_2CO_3 and CO_2 .

Transition metal catalysts exhibit high catalytic activity and are believed to be more suitable for SCWG because they are easier to recover than homogeneous alkali catalysts. From the various transition metals used, Ru and Ni have shown to be the most active catalysts (Elliott, 2008). Although the activities of Ru catalyst have proven to be typically higher than that of Ni catalysts, Ni catalysts are most often preferred due to their significantly lower cost compared to Ru (Azadi and Farnood, 2011). Minowa and Ogi (1998) were the first to propose a reaction scheme for Ni-catalysed gasification of cellulose in sub- and supercritical water. Their work showed that Ni promoted the gasification of water soluble products to H_2 and CO_2 , as well as the methanation reaction of H_2 with both CO and CO_2 to form CH_4 and water.

The most popular commercial Ni catalyst used in SCWG studies is skeletal Raney nickel, a pyrophoric porous nickel catalyst with a small amount of aluminium residue, typically used for hydrogenation reactions (Afif et al., 2011; Azadi et al., 2009; Waldner and Vogel, 2005). However, other authors have shown that a commercially available, safer powdered Ni catalyst on Al_2O_3/SiO_2 support (a popular catalyst support material used in a wide variety of disciplines) can also be used as catalyst during SCWG (Guan et al., 2014; Taylor et al., 2009; Youssef et al., 2010).

A wide variety of studies focussed on the SCWG of waste sludge – specifically sewage sludge and secondary paper sludge, which consists mainly of microbial biomass, non-biodegradable lignin solids and cell-decay products (Afif et al., 2011; Chen et al., 2013; Gong et al., 2014; Xu et al., 2013; Zhang et al., 2010). However, only one study has previously focussed on the SCWG of primary paper sludge, which consists mainly of rejected wood fibres (Rönnlund et al., 2011). The work by Rönnlund et al. (2011) was conducted at high operating temperatures (500–650 °C) and low dry matter feed concentrations (2–3 wt.%) using three alkali catalysts, including KOH, NaOH, or K_2CO_3 . Amongst these, K_2CO_3 had the most significant effect on the energy recovery (ER) and the gas yields (especially on the H_2 and CO_2 yields). H_2 yields as high

as 25 mol/kg_{biomass} and an ER of 75% were achieved with the addition of 0.4–0.47 g_{catalyst}/g_{sludge} at 600 °C. Considering these experimental results, Myrén et al. (2011) postulated that, by integrating SCWG of primary paper sludge into an existing pulp and paper mill in Finland, the thermal energy efficiency of the paper mill can be increased by 50%.

Various experimental studies have been conducted in small-scale batch reactors at low gasification temperatures (e.g. Afif et al., 2011; Waldner and Vogel, 2005; Zöhler and Vogel, 2013). Typically, a batch reactor will not be used on industrial scale for SCWG. Experiments in small batch reactors can however be used to demonstrate the suitability and viability of a specific organic material as feedstock material for SCWG. Furthermore, optimum operating conditions can be determined, which may then later be confirmed in a continuous system.

Zöhler and Vogel (2013) suggested a residence time dependent biomass-to-catalyst ratio – to serve as first estimate of the minimum weight hourly space velocity (WHSV) when changing from a batch to a continuous setup (see Eq. (2)). The residence time τ was defined as the time that the temperature of the reactor content exceeds 300 °C. They showed that almost complete conversion of carbon can be achieved during SCWG of fermentation residue at 410 °C with $\zeta < 0.45 \text{ g} \cdot \text{g}^{-1} \text{ h}^{-1}$ when Ru/C catalyst is used at a reaction time of 25 min or less (this corresponds to a total catalyst loading of 6.3 g/g_{FR} Ru/C).

$$\zeta [\text{g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}] = \frac{m_{\text{feed}}}{m_{\text{catalyst}} \tau} \quad (2)$$

Thermodynamic equilibrium calculations can be used to predict the gas yields from SCWG for a specific biomass material (Tang and Kitagawa, 2005). Calculated equilibrium yields serve as important benchmarks for potential experimental yields, thereby assisting with the selection of suitable operating conditions (i.e. catalyst loading and reaction times) for a specific feedstock material.

This work is the continuation of a previous study by Louw et al. (2014) that characterised the effect of feedstock composition on the thermodynamic equilibrium yields during SCWG. The work presented here compares the thermodynamically predicted gas yields and gasification efficiencies for primary paper sludge with experimentally measured values. Reaction time and catalyst type and loading were used as factors. K_2CO_3 was selected as the homogeneous catalyst and the commercially available $Ni/Al_2O_3-SiO_2$ catalyst was chosen as the heterogeneous catalyst. Additionally, the energy-recovery potential of SCWG of primary paper sludge at low operating temperature (450 °C) is presented for the first time.

2. Methods

2.1. Calculation of thermodynamic yields

Aspen Plus[®] was used to calculate the thermodynamic yields of the gasification of paper waste sludge (PWS) in SCW at three operating temperatures (400, 450 and 500 °C) and five solid feed concentrations (2.5, 5, 10, 15 and 20 wt.%) and a pressure of 27 MPa. The Peng–Robinson equation of state with Boston–Mathias modification (PR–BM) was used. Details of the model implementation have been presented previously (Louw et al., 2014).

When considering the two energy-rich gases formed during SCWG, viz. H_2 and CH_4 , maximum H_2 yields are expected at low feed concentrations and high operating temperatures, while the opposite is true for CH_4 (see Fig. 1(a)). Although minimum CO_2 yields are expected at higher feed concentrations and lower temperatures, the CO yield seems to be more dependent on the temperature than the feed concentration throughout the ranges

Download English Version:

<https://daneshyari.com/en/article/679392>

Download Persian Version:

<https://daneshyari.com/article/679392>

[Daneshyari.com](https://daneshyari.com)