# Catalytic Gasification of Pinewood in Hydrothermal Conditions for Hydrogen Production

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Lignocellulosic biomasses are gaining attention for biofuel production to supplement the increasing energy demands. This study is focused on identifying the candidacy of pinewood for hydrogen production through subcritical (300°C), near-critical (370°C) and supercritical (550°C) water gasification. Pinewood was gasified to study the impacts of temperature (300-550°C), feed concentration (20-30 wt%) and reaction time (20-60 min). The effects of metal catalysts (e.g., $Ni/Al_2O_3$, $Ru/Al_2O_3$, NaOH and KOH) were also examined to maximize hydrogen yields and carbon gasification efficiency. The individual gas yields, total gas yields and lower heating values were calculated for comparative evaluation between subcritical, near-critical and supercritical water gasification as well as between catalytic and non-catalytic gasification of pinewood. Supercritical water gasification at higher temperatures (550°C), longer reaction time (60 min) and lower feed concentration (20 wt%) improved water-gas shift reaction resulting in high hydrogen yields. Greater yields of hydrogen (0.52 mmol/g) and total gases (6.4 mmol/g) with lower heating value of 423 $kJ/Nm^3$ was found with 20 wt% of pinewood at 550°C and 60 min. $Ni/Al_2O_3$ at a concentration of 5 wt% showed highest yields for hydrogen (2.54 mmol/g) in the gas products when compared to other catalysts. The catalytic activity towards hydrogen production decreased as $Ni/Al_2O_3$ > KOH > $Ru/Al_2O_3$ > NaOH. The findings imply that pinewood is a promising feedstock for hydrogen production by supercritical water gasification.

## 1. Introduction

The consumption of fossil fuels is responsible for the increase in greenhouse gas emissions which have a great impact on the environment and moreover, lead to global warming. In addition to the resulting harmful environmental effects caused by fossil fuels, its limited supply motivates the proposition of an alternate source. The growing need for a renewable energy supply to replace fossil fuels shows a path to produce a clean form of fuel for transportation and other energy utilities. Fuels derived from waste biomass are considered to be carbon-neutral as the net $CO_2$ released during the combustion process is reused by plants during photosynthesis (Nanda et al., 2014).

Hydrogen ($H_2$) is also a clean fuel as its combustion results in water. It can be generated from lignocellulosic biomass through hydrothermal gasification. This makes it more attractive compared to other gaseous fuels, however; it is not readily available in nature and is generated through the reformation of natural gas. $H_2$ is a clean, energy dense and versatile fuel with highest energy content (120 MJ/kg) compared to conventional fuels. It can be produced from biomass through thermochemical conversion (pyrolysis and gasification), biological conversion (biophotolysis, photo-fermentation and dark fermentation) and electrolysis (Holladay et al., 2009).

Manipulation of lignocellulosic biomass through gasification processes is a viable option for producing $H_2$. When compared to other methods of biomass conversion, thermochemical gasification consumes large amounts of energy. Supercritical water (or hydrothermal) gasification, on the other hand, is energy efficient and does not require the biomass to undergo drying procedures and other pre-treatments, thereby reducing process expenditure (Reddy et al., 2014). Lignocellulose biomass components can break down into simple molecules during supercritical water gasification (SCWG) to produce synthetic gas or syngas. Syngas ($H_2$ and CO), the main product of the SCWG process, can be used as clean fuel or for the production of diesel fuel through gas-to-liquid (GTL) methods such as Fischer-Tropsch catalysis or syngas fermentation.

Depending on the critical temperature ($T_C$) and critical pressure ($P_C$) of water, hydrothermal gasification processes can involve subcritical ($T_C < 374°C$ and $P_C < 22.1$ MPa), near-critical ($T_C \sim 374°C$ and $P_C \sim 22.1$ MPa) and supercritical ($T_C > 374°C$ and $P_C > 22.1$ MPa) water. However, supercritical water (SCW) imparts enhanced mass and heat transfer properties with higher solvation potential. SCW is an ideal solvent for biomass processing and conversion because of its liquid-like densities and gas-like transport properties. SCWG has been immensely researched for the hydrothermal conversion of lignocellulosic biomass to generate $H_2$-rich gas products.

This paper focuses on the analysis of hydrothermal gasification performed with wood shavings of *Pinus banksiana*, commonly known as jack pine, which is native to Canada and the United States. The experiments are performed over a wide range of operating conditions such as temperature, pressure, residence time, feed concentration and catalysts. This paper presents an overview of the effects of each parameter on the hydrothermal gasification of pinewood with regards to the overall reaction mechanisms and $H_2$ yields.

## 2. Experimental

### 2.1 Biomass

Pinewood (*Pinus banksiana*) used in this study was obtained from Saskatchewan, Canada. As reported by Nanda et al. (2013), pinewood contained 48.9 wt% carbon, 6.2 wt% hydrogen, 0.1 wt% nitrogen, 0.1 wt% sulfur and 42.5 wt% oxygen. Cellulose, hemicellulose and lignin compositions in pinewood were 38.8 wt%, 23.6 wt% and 20.4 wt%, respectively. Pinewood was crushed to a particle size of 0.5 mm prior to its hydrothermal gasification.

### 2.2 Hydrothermal gasification

Hydrothermal gasification was performed in a stainless steel batch tubular reactor (length: 10 in., outer diameter: 0.5 in. and inner diameter: 0.37 in.). The schematics of the gasification reactor and its operational procedures have been comprehensively described by Nanda et al. (2016). The gasification reactor assembly consisted of pressure gauge, pressure relief valve, split furnace, tubular reactor, Type-K thermocouple, check valve, 2 μm filter and gas-liquid separator. All the tubing and accessories were of SS 316 grade and purchased from Swagelok® (Swagelok Central Ontario, Canada). Nitrogen gas was used as the inert gas to create an initial reactor pressure of 10-15 MPa depending on gasification temperature. The syngas was collected in gas sampling Tedlar® bags (Environmental Sampling Supply, USA). Hydrothermal gasification of pinewood was performed at a pressure range of 23-25 MPa to investigate the impacts of temperature (300-550°C), feed concentration (20-30 wt%) and residence time (20-60 min). For catalytic gasification experiments, heterogeneous catalysts (e.g., $Ni/Al_2O_3$ and $Ru/Al_2O_3$) and homogeneous catalysts (e.g., NaOH and KOH) were employed at concentrations of 3-6 wt%.

### 2.3 Characterization of gas and char

The gases were analysed in an Agilent 7820A gas chromatography (Agilent Technologies, USA). The system was equipped with a thermal conductivity detector consisting of three packed columns and one capillary column. The Ultimetal HayesepQ T 80/100 mesh column identified $H_2$, CO and $CH_4$, whereas Ultimetal Hayesep T 80/100 mesh column quantified $CO_2$ and $C_2H_6$. Argon was used as the carrier gas with a column temperature of 60°C. The individual gas yield (in mmol/g) was determined as the moles of each gas per mole of pinewood. The total gas yield (in mmol/g) was calculated as the moles of total gas products collected per gram of pinewood. The lower heating value or LHV (in $kJ/Nm^3$) of the gas phase was estimated using the formula described elsewhere (Nanda et al., 2016). Fourier transform infrared (FT-IR) spectroscopy of pinewood and its biochars was performed using a Bruker Alpha FT-IR spectrometer (Bruker Optics Ltd, Canada). Different surface organic functional groups were analyzed in the infrared range of 500-3500 $cm^{-1}$ with an average of 24 scans. Scanning electron microscopy (SEM) of pinewood biochar was performed using an FEI Quanta 3D FEG DualBeam microscope (FEI Company, USA) operated at 20 kV under high vacuum.

## 3. Results and Discussion

Pinewood was gasified at 300-550°C for 40 min to study the effect of subcritical, near-critical and supercritical water temperatures at 23-25 MPa. With the rise in temperature from 300 to 550°C, $H_2$ yield increased from 0.9 to 2.52 mmol/g (Figure 1a). The yields of $CO_2$ (4.92 mmol/g), $CH_4$ (1.2 mmol/g) and $C_2H_6$ (0.62 mmol/g) also increased at 550°C. The total gas yield increased from 3.5 mmol/g at 300°C to 9.6 mmol/g at 550°C with 20 wt% pinewood (Table 1). High gasification temperatures favour water-gas shift reaction resulting in greater yields of $H_2$ and $CO_2$ (Kruse, 2008). During water-gas shift reaction, CO reacts with water vapour at high temperatures to produce $CO_2$ and $H_2$. Therefore, CO yield shrunk from 0.8 mmol/g at 300°C to 0.3 mmol/g at 550°C. The temperatures above the critical point (≥ 374°C) lower the water density impacting the ionic product formation. This phenomenon favours the free-radical mechanism at supercritical temperatures (Guo et al., 2010). Hence, SCW at high temperatures of 550°C acted as a medium with the complete solubility of organic compounds resulting in higher gas yields. The LHV of the gas products also increased from 520 to 1135 kJ/Nm$^3$ as the temperature increased (Table 1).
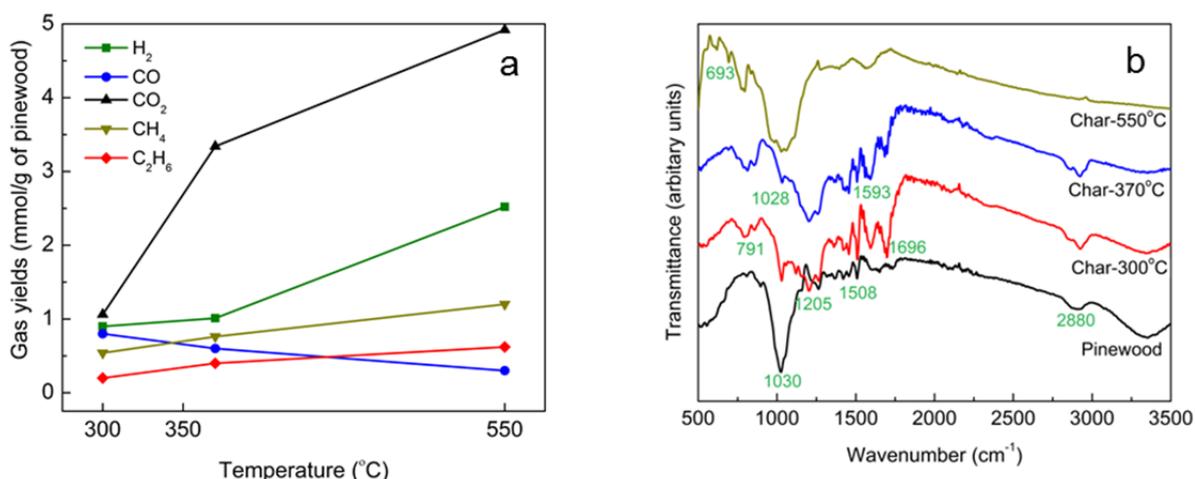


*Figure 1: (a) Effect of temperature on hydrothermal gasification of pinewood at 20 wt% feed concentration for 40 min; (b) FT-IR analysis of pinewood and biochar generated at different temperatures*

*Table 1:  Total gas yields and lower heating value of gas products from hydrothermal gasification of pinewood*

| Gasification conditions | Parameters | Total gas yield (mmol/g) | Lower heating value (kJ/Nm$^3$) |
|---|---|---|---|
| Effect of temperature (20% pinewood, 40 min) | 300°C | 3.5 | 520 |
| | 370°C | 6.1 | 712 |
| | 550°C | 9.6 | 1135 |
| Effect of feed concentration (550°C, 40 min) | 20 wt% pinewood | 9.6 | 1135 |
| | 25 wt% pinewood | 7.5 | 1047 |
| | 30 wt% pinewood | 5.6 | 961 |
| Effect of residence time (20 wt% pinewood, 550°C) | 20 min | 5.2 | 426 |
| | 40 min | 9.6 | 1135 |
| | 60 min | 11.2 | 1405 |
| Effect of catalysts (20 wt% pinewood, 550°C, 60 min) | 5 wt% Ni/Al$_2$O$_3$ | 14.2 | 1835 |
| | 5 wt% Ru/Al$_2$O$_3$ | 12.9 | 1619 |
| | 5 wt% NaOH | 12.5 | 1434 |
| | 5 wt% KOH | 13.1 | 1586 |
| Effect of catalyst concentration (20 wt% pinewood, 550°C, 60 min) | 3 wt% Ni/Al$_2$O$_3$ | 12.4 | 1601 |
| | 4 wt% Ni/Al$_2$O$_3$ | 13.4 | 1741 |
| | 5 wt% Ni/Al$_2$O$_3$ | 14.2 | 1835 |
| | 6 wt% Ni/Al$_2$O$_3$ | 14.8 | 1919 |

Figure 1b shows the FT-IR spectra of pinewood and its biochars generated at 300-550°C with 20 wt% feed concentration for 40 min. Pinewood contained a few distinctive components such as alcohols, ethers and esters (1028, 1030 and 1205 cm$^{-1}$), aromatic rings attributed by lignin (1508 cm$^{-1}$), carbonyls (1696 cm$^{-1}$) and alkanes (2880 cm$^{-1}$). These peaks progressively lost their intensity and disappeared in its biochar as the gasification temperature increased. The removal of these components was a result of higher SCW temperatures (550°C) that caused dehydration of organic functional groups, especially C–O, C=O and C–H (Nanda et al., 2016). Despite the exclusion of these peaks in the biochar, a few other peaks showed significant intensification such as those of 693 and 791 cm$^{-1}$. These two peaks represent C–C aromatic groups. Higher pyrolysis or gasification temperatures impact aromaticity to the biochar making them thermally stable as a result of the loss of moisture and volatile components (Peng et al., 2011; Azargohar et al., 2014). The SEM images of pinewood biochar obtained at 300°C and 550°C are similar to those of the FT-IR spectra (Figure 2). At 300°C, the pinewood surface displayed a more intact and fibrous structure. However, as the temperature increased to 550°C, the biochar surface showed a fragmented, porous and more distorted structure. As a result of increased gasification temperature, the organic components in pinewood decomposed and dehydrated leading to their loss during this process rending a cracked surface morphology.
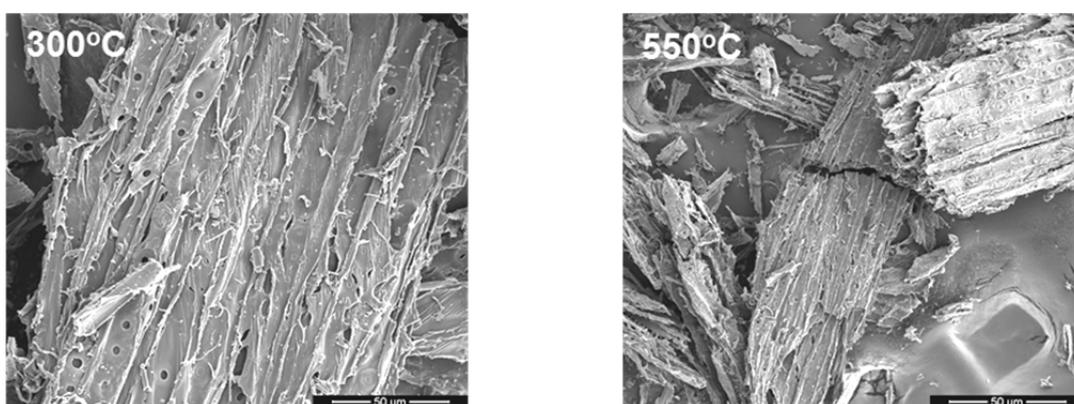


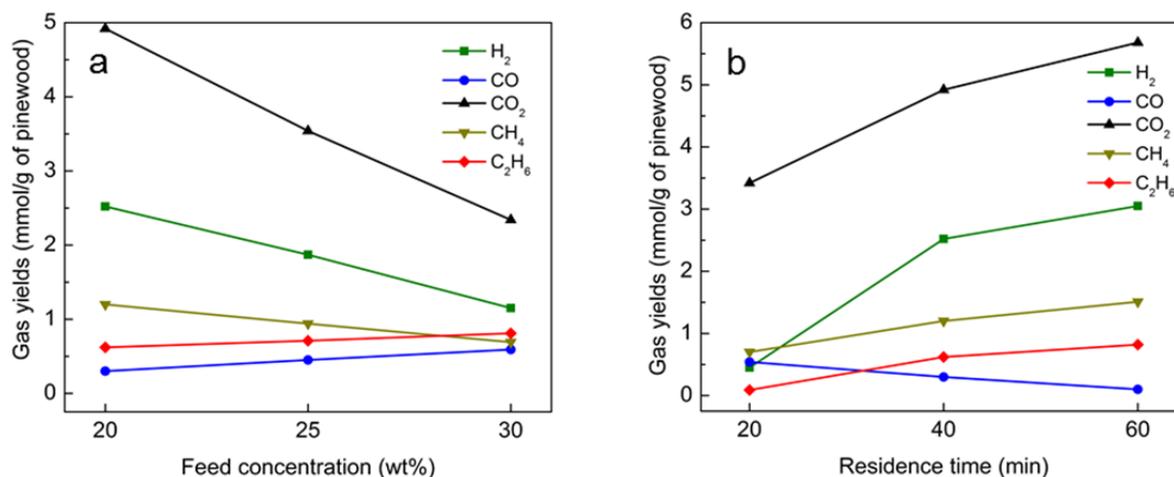Figure 2: SEM image of pinewood biochar produced at 300°C and 550°C for 40 min



Figure 3: (a) Effect of feed concentration on gasification of pinewood at 550°C for 40 min, (b) Effect of residence time on gasification of 20 wt% pinewood at 550°C

The gasification of pinewood with variable feed concentrations at 550°C for 40 min showed a typical trend in $H_2$ yields (Figure 3a). The $H_2$ yield at 550°C decreased from 2.52 mmol/g with 20 wt% feed concentration to 1.15 mmol/g with 30 wt% feed concentration. The yields of $CO_2$ and $CH_4$ also decreased while that of CO and $C_2H_6$ increased by 49% and 23% respectively, at 30 wt% feed concentration. The total gas yields at 20 wt% feed concentration (9.6 mmol/g) was relatively higher than 30 wt% feed concentration (5.6 mmol/g). There

was nearly a 42% decrease in total gas yields with the rise in feed concentration. The LHV of the gas products decreased from 1135 to 961 kJ/Nm$^3$ as the feed concentration increased from 20 wt% to 30 wt%, respectively (Table 1). Higher temperatures and lower feed concentration improve free-radical mechanism and steam reforming reaction in SCWG, thereby increasing $H_2$ and total gas yields (Reddy et al., 2014; Guo et al., 2010). The effect of residence time on the gasification of 20 wt% pinewood at 550°C is illustrated in Figure 3b. The $H_2$ yields increased from 0.45 mmol/g at 20 min to 3.05 mmol/g at 60 min of residence time. The total gas yield at 60 min (11.2 mmol/g) of residence time was relatively higher when compared to that of 20 min (5.2 mmol/g). While the yield of CO declined, the yields for $CO_2$, $CH_4$ and $C_2H_6$ amplified with the progression of residence time. Longer residence time enhances the gas yield by favouring thermal cracking reactions at higher temperatures (Chen et al., 2003). Higher temperatures and longer residence time favour methanation, hydrogenation and water-gas shift reaction that proceed at the expense of CO. $H_2$ and $CO_2$ are primarily produced from water-gas shift reaction, whereas $CH_4$ is predominantly obtained via methanation and hydrogenation reactions (Kruse, 2008). The LHV was higher for the gases obtained at 60 min (1405 kJ/Nm$^3$) compared to that of 20 min (426 kJ/Nm$^3$) and 40 min (1135 kJ/Nm$^3$).
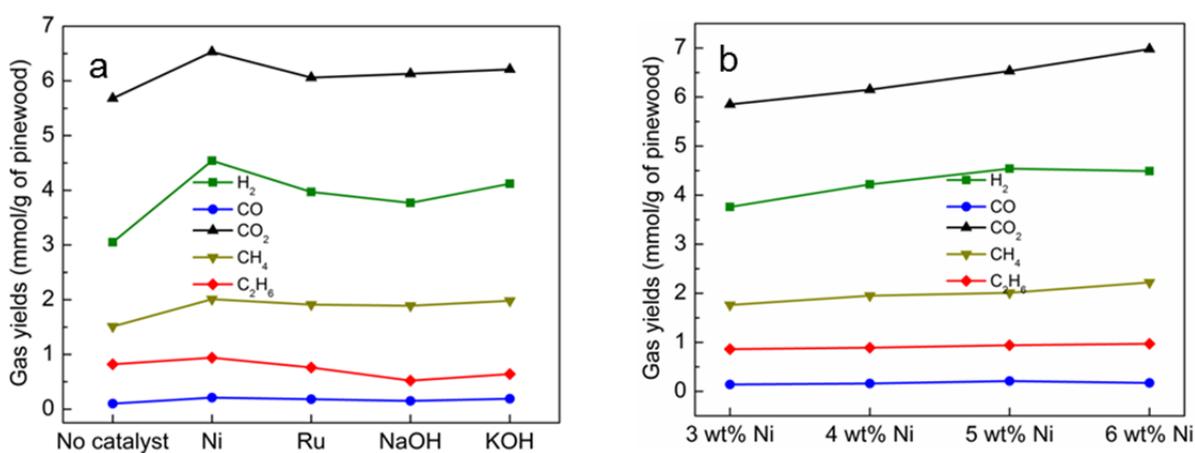


*Figure 4: (a) Effect of different catalysts on gasification of 20 wt% pinewood at 550°C for 60 min, (b) Effect of variable concentrations of Ni/Al$_2$O$_3$ on gasification of 20 wt% pinewood at 550°C for 40 min*

The effects of two homogeneous alkali catalysts (NaOH and KOH) as well as two heterogeneous metal catalysts (Ni/Al$_2$O$_3$ and Ru/Al$_2$O$_3$) were studied to evaluate their $H_2$ maximization potential. Figure 4a shows the trend of gas yields from 20 wt% pinewood with 5 wt% catalysts at 550°C for 60 min. Among all the catalysts, Ni/Al$_2$O$_3$ proved to be the most promising candidate due to its high $H_2$ yields. The catalytic activity based on $H_2$ production from pinewood varied as Ni/Al$_2$O$_3$ (4.54 mmol/g) > KOH (4.12 mmol/g) > Ru/Al$_2$O$_3$ (3.97 mmol/g) > NaOH (3.77 mmol/g). At 5 wt% catalyst concentration, the total gas yields were also highest in the case of Ni/Al$_2$O$_3$ (14.2 mmol/g) followed by Ru/Al$_2$O$_3$ (12.9 mmol/g), KOH (13.1 mmol/g) and NaOH (12.5 mmol/g) (Table 1). The LHV of the gas products also followed the pattern: NaOH (1434 kJ/Nm$^3$) < KOH (1586 kJ/Nm$^3$) < Ru/Al$_2$O$_3$ (1619 kJ/Nm$^3$) < Ni/Al$_2$O$_3$ (1835 kJ/Nm$^3$). Similar to $H_2$, Ni/Al$_2$O$_3$ also resulted in highest $CH_4$ yield of 2.01 mmol/g followed by KOH (1.98 mmol/g). This indicated that nickel not only promotes water-gas shift reaction but also favours methanation reaction at higher temperatures.

The effects of different concentration of Ni/Al$_2$O$_3$ were investigated to enhance $H_2$ yields (Figure 7b). With gradual increase in Ni concentration, the $H_2$ yields increased but it stabilized at 5 wt% and lowed at 6 wt%. More specifically, the $H_2$ yields increased from 3.76 mmol/g at 3 wt% Ni/Al$_2$O$_3$ to 4.54 mmol/g at 5 wt% Ni/Al$_2$O$_3$ and reduced to 4.49 mmol/g at 6 wt% Ni/Al$_2$O$_3$. The total gas yields varied in the sequence: 3 wt% Ni/Al$_2$O$_3$ (12.4 mmol/g) < 4 wt% Ni/Al$_2$O$_3$ (13.4 mmol/g) < 5 wt% Ni/Al$_2$O$_3$ (14.2 mmol/g) < 6 wt% Ni/Al$_2$O$_3$ (14.8 mmol/g) (Table 1). While $H_2$, $CO_2$ and CO yields decreased at 6 wt% Ni/Al$_2$O$_3$, the yield of $CH_4$ increased (2.22 mmol/g), and was the highest among all concentrations. This indicated that a higher concentration of nickel results in secondary reactions such as methanation reaction of CO and $CO_2$. Highest $CH_4$ yields also resulted in maximum LHV of the gas products from 6 wt% Ni/Al$_2$O$_3$ (1919 kJ/Nm$^3$) followed by 5 wt% Ni/Al$_2$O$_3$ (1835 kJ/Nm$^3$), 4 wt% Ni/Al$_2$O$_3$ (1741 kJ/Nm$^3$) and 3 wt% Ni/Al$_2$O$_3$ (1601 kJ/Nm$^3$).

## 4. Conclusions

Pinewood was hydrothermally gasified to study the effects of temperature, feed concentration, residence time and catalyst concentrations on $H_2$ and total gas yields. The yields of $H_2$ and total gases increased with the rise in temperature from 300°C to 550°C. High supercritical water temperatures (550°C) caused extreme degradation of pinewood through dehydration, decarboxylation and bond breakages rendering aromaticity to its biochar. Higher yields of $H_2$ (2.52 mmol/g) and total gases (9.6 mmol/g) with a LHV of 1135 $kJ/Nm^3$ was found with 20 wt% pinewood at 550°C and 40 min of residence time. Higher temperatures, longer residence time and lower feed concentration improved water-gas shift reaction resulting in high $H_2$ yields. A 5 wt% $Ni/Al_2O_3$ application resulted in highest $H_2$ yield of 4.54 mmol/g followed by KOH, $Ru/Al_2O_3$ and NaOH. An increase in $Ni/Al_2O_3$ concentration from 3 wt% to 5 wt% enhanced $H_2$ production. However, $H_2$ yield reduced at 6 wt% $Ni/Al_2O_3$ as a result of methanation reaction and higher yield of $CH_4$ (2.22 mmol/g). Due to high $CH_4$ yields, the LHV of the gas product also increased to 1919 $kJ/Nm^3$ at 6 wt% $Ni/Al_2O_3$. The results suggest that pinewood is a promising forestry biomass for the catalytic hydrothermal gasification to produce $H_2$-rich syngas.

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