



# Hydrogen production from cellulose, lignin, bark and model carbohydrates in supercritical water using nickel and ruthenium catalysts

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## ABSTRACT

In this study, the catalytic activity and hydrogen selectivity of Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Ni/hydrotalcite, Raney nickel, Ru/C and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts for hydrothermal hydrogen production from lignocellulosic biomass have been evaluated. The feedstocks included glucose, cellulose, fructose, xylan, pulp, lignin and bark. The experiments were carried out at 380 °C in a batch reactor with 2 wt% feed concentration. It was found that the gasification of glucose, fructose, cellulose, xylan and pulp resulted in comparable gas yields ( $\pm 10\%$  at 60 min), whereas lignin was substantially harder to gasify. Interestingly, gasification yield of bark which has a high lignin content was comparable to those of carbohydrates after 60 min reaction time. For a given feedstock, catalyst type affected both the gasification yield and the product distribution. Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ni/hydrotalcite catalysts were not only highly active for the gasification of carbohydrates, but also had better hydrogen selectivity when compared to Raney nickel, Ru/C and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In particular, gasification of bark in the presence of these catalysts resulted in negligible amounts of alkanes.

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## 1. Introduction

Supercritical water gasification (SCWG) is a promising process for the production of biorenewable hydrogen from biomass. In this process, wet biomass is decomposed to form hydrogen, carbon dioxide, methane and carbon monoxide. In comparison with the steam reforming process (e.g.,  $T > 650$  °C and low pressures), catalytic supercritical water gasification proceeds at milder temperatures (e.g.,  $T < 450$  °C) with little or no char formation [1]. In spite of major advancements over the past decades, there are still important challenges that need to be addressed to make catalytic SCWG technically and economically viable for hydrogen production. Poor hydrogen selectivity, catalyst deactivation, tar and char formation, heat recovery and precipitation of inorganic salts are among the most important issues that are yet to be addressed.

Since SCWG is operated at a high water content (typically 80–90%), and given the considerably high specific heat of water, it is of great importance to run the reaction at the lowest possible temperatures. It has been shown that homogeneous alkali and nickel and ruthenium-based solid catalysts are useful for

enhancing the gasification rates at moderate temperatures [2,3]. Supercritical water gasification of glucose in presence of different skeletal catalysts indicated that the inherent activity of the nickel is substantially higher than that of cobalt and copper [4]. In general, catalyst formulation along with the operating conditions such as temperature and feed concentration can significantly affect the conversion and product distribution. More detailed discussion regarding the current status of the catalytic SCWG can be found in [5,6].

Review of the literature illustrates that both real biomass and model compounds have been employed to evaluate the effectiveness of the catalytic SCWG process [5–7]. Investigations on real biomass provides practical information on the performance of the SCW gasifiers at various operating conditions while model compounds may be used in the laboratory for fundamental studies. The real biomasses considered for gasification in SCW include lignocellulosic biomass from different sources, sewage sludge [8–10], pulp and paper wastes [11], chicken manure [12], food wastes [13], and algae [14,15]. Given the fact that lignocellulosic biomass is the most abundant type of biomass on the earth, its conversion and upgrading is expected to play a significant role in the production of future fuels. Representative model compounds of various types of biomass such as cellulose, glucose, phenolics, glycerol and alcohols have been also considered in the literature. Earlier studies have shown that due to the fast hydrolysis of cellulose to glucose and other sugar oligomers, gasification of glucose and cellulose led to identical gas yields [16]. Osada et al. showed that ruthenium

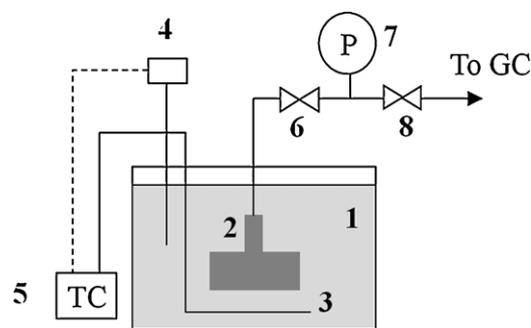
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is an effective catalyst for decomposition of organosolv lignin in SCW [17], but its activity decreased by the addition of sulfur to the feed [18]. The same behavior was observed when sulfur was added to a Raney-nickel catalyzed SCWG reaction [9]. Interaction among different reactants during the SCWG has been also studied using representative mixtures of model compounds as a feedstock. In the case of cellulose/lignin sulfonate mixtures at low catalyst loadings (0.4 g [Ni 5132P, Engelhard]/g feed), a strong negative deviation from the rule of mixtures in terms of carbon conversion was observed whereas mixtures of cellulose and xylan at any ratio were found to exhibit a very predictable gasification efficiency that closely matched the rule of mixtures [19,20]. The magnitude of the negative deviation for the cellulose-lignin sulfonate substantially decreased at higher catalyst to feed ratios [20] and the authors suggested that the possible mechanism for this deviation the catalyst deactivation by tarry products formed due to the reaction between cellulose and lignin. Moreover, Yoshida et al. [20] found that the gasification yield of saw dust was nearly 90% of the predicted value based on the rule of mixtures.

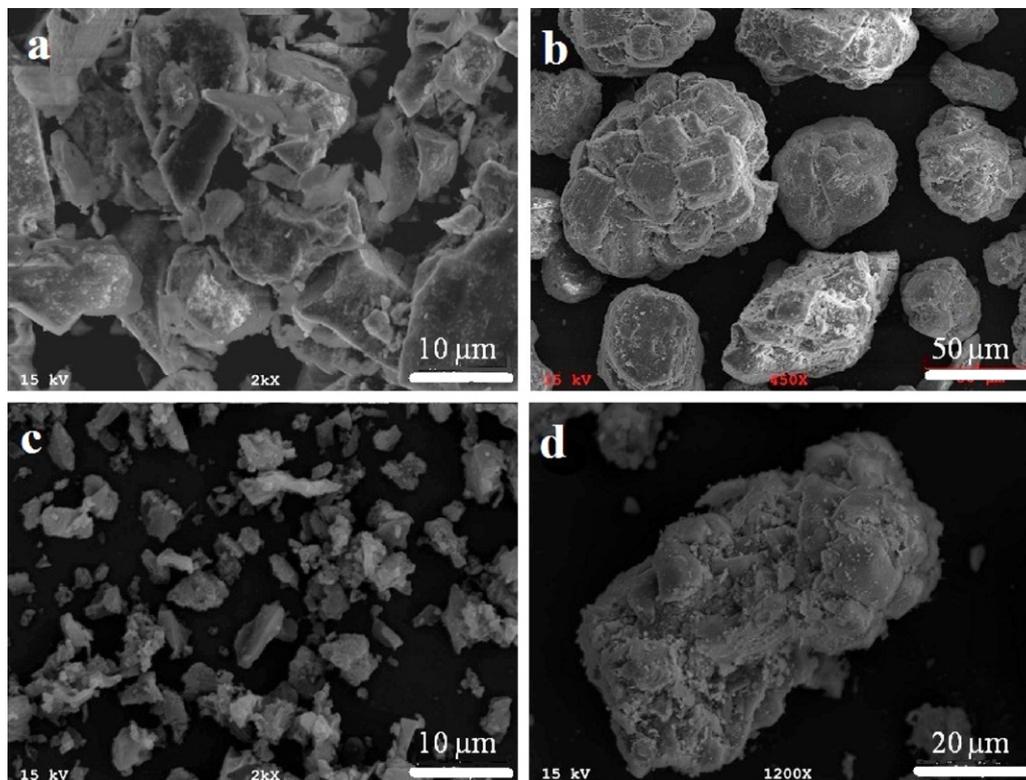
In general, SCWG of carbohydrates using supported nickel catalysts at temperatures below 400 °C typically results in 1–15 mmol H<sub>2</sub>/g dry feed [6], corresponding to 1.5–23% of the maximum stoichiometric value (not considering the thermodynamic equilibrium), while the SCWG of lignin at the same operating range generate 1–2 mmol/g dry feed [6]. We note that it is not possible to increase the hydrogen yield simply by extending the reaction time, as the hydrogen yield decreases due to methanation reaction in the presence of typical Ni and Ru catalysts. The low hydrogen selectivity is caused by the high activity of nickel and ruthenium to open the C–O bonds, which in turn would result in the formation of alkanes. Although many studies have been devoted to evaluate the short term activity of heterogeneous catalysts, limited work is done on enhancing the hydrogen selectivity and decreasing the alkane selectivity. In one of the few attempts, Dumesic et al. showed that the hydrogen selectivity of Raney nickel catalyst for aqueous phase



**Fig. 1.** Schematic diagram of the experimental set-up: (1) molten salt bath, (2) reactor, (3) electrical heater, (4) thermocouple, (5) PID temperature controller, (6) first valve, (7) low-pressure gauge, (8) second valve. The equilibrium gas yields were calculated using Gibbs free energy minimization using Aspen Plus (AspenTech, Burlington, USA).

reforming can be significantly improved by adding tin onto the surface of the Raney nickel catalysts [21–24]. Addition of molybdenum as a promoter to Raney nickel did not have a pronounced effect on the catalyst performance [4].

In this paper, we present a systematic study of SCWG of several lignocellulosic materials with five promising catalysts including three nickel and two ruthenium catalysts. Commercially available Raney nickel, Ru/activated carbon and Ru/ $\gamma$ -alumina along with two laboratory-made nickel catalysts supported on  $\alpha$ -alumina and hydrocalcite were considered. The relationship between hydrogen selectivity and carbon conversion for the gasification of glucose, cellulose, xylan, kraft lignin and birchwood bark is discussed in details. To the best of our knowledge, this is the first paper concerning supercritical water gasification of bark. Results of this study provide a better understanding of the performance of solid catalysts for the gasification of lignocellulosic biomass in supercritical water in terms of activity and hydrogen selectivity.



**Fig. 2.** SEM micrograph of the catalysts used in this work. (a) Raney nickel, (b) Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, (c) Ru/C, (d) Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

## 2. Materials and methods

A schematic of the experimental setup is shown in Fig. 1. A non-stirred 50 mL stainless steel batch reactor was used in the SCWG experiments. In all experiments, 0.2 g of feedstock was added to 9.8 g of deionized water to obtain a 2 wt% mixture. This mixture along with the desired amount of catalyst was introduced into the reactor and immersed in a molten salt bath containing sodium nitrate, sodium nitrite (General Chemical, USA), and potassium nitrate (Alphachem, USA). The heat transfer from molten salts to SCWG reactors has been discussed in [25].

The metal loadings of Ni and Ru (excluding the catalyst support) were set at 120 mg and 6 mg, respectively. These amounts were chosen in such way that the carbon conversions of about 60% can be obtained from SCWG of glucose in 15 min reaction experiments. The temperature of the salt bath was measured using a Type K thermocouple (Omega Engineering, Canada) and was maintained at 380 °C using a PID temperature controller (Hanyoung, Electronic Co. Ltd., Korea). The corresponding pressure in the reactor at 380 °C was estimated to be 230 bar. Four different reaction times were considered: 5, 15, 30 and 60 min. After a predetermined reaction time, the reactor was rapidly cooled by quenching in cold water and allowed to reach the room temperature. Then, the pressure in the reactor was determined using a digital pressure gauge (Cecomp Electronics) and was used to calculate the gas yield using the ideal gas law. The gaseous product was then collected in a gas bag for composition analysis. The data reproducibility was confirmed to be within  $\pm 5\%$  by performing at least one replicate run for each data point.

A gas chromatograph (Hewlett-Packard 5890 series) equipped with a thermal conductivity detector and argon as carrier gas was used to determine the product gas composition. A 5 m general SupelcoSS 60/80 CARBOXEN 1000 column (Sigma–Aldrich, Canada) was used for fractionation of the permanent gases. The oven, injector and detector in the GC were all set at 140 °C.

The model compounds investigated in our experiments included: glucose (CAS 50-99-7), microcrystalline cellulose (CAS 9004-34-6), alkali lignin (CAS 8068-05-1) and xylan from oat spelts (CAS 9014-63-5), all of which were obtained from Sigma–Aldrich, Canada. Kraft pulp was obtained from the National Institute of Standards and Technology USA, and bark from birchwood was kindly provided by Professor Ning Yan from the Department of Forestry at University of Toronto. The elemental analysis (2400 Series II CHNS Analyzer from Perkin Elmer operating at the C–H–N mode) indicated that the empirical formulas of lignin and bark were  $\text{CO}_{0.95}\text{H}_{0.63}\text{N}_{0.002}$  and  $\text{CO}_{0.88}\text{H}_{0.83}\text{N}_{0.01}$ , respectively.

The commercial catalysts including Raney nickel 4200 (received as aqueous slurry containing 50% solid content), 5% Ru/C and 5% Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$  as well as  $\alpha$ - $\text{Al}_2\text{O}_3$ , hydrotalcite (HT), and nickel nitrate were all obtained from Sigma–Aldrich Canada.

Ni/ $\alpha$ - $\text{Al}_2\text{O}_3$  and Ni/HT catalysts were prepared by incipient wetness impregnation with nickel nitrate solution. The catalyst precursors were dried at 110 °C over night and calcined in air at 350 °C for 3 h. The catalyst was then reduced in flowing hydrogen for 2 h (50 ml STP/min, 30%  $\text{H}_2$ , 70%  $\text{N}_2$ ) and stored in water before being used in the experiments. The SEM micrographs of the catalysts used in this study are depicted in Fig. 2. These images are obtained using JEOL JSM-840 scanning microscope. The BET surface area and metal dispersion were obtained using Quantachrome Autosorb catalyst characterization system (Quantachrome, USA). Fig. 3 shows the pore size distributions of  $\alpha$ - $\text{Al}_2\text{O}_3$  and hydrotalcite based on nitrogen adsorption. The supports materials were degassed under vacuum at 300 °C for 3 h prior to nitrogen adsorption. Based on this figure, a large fraction of the pores in the  $\alpha$ -alumina support were greater than 40 nm whereas hydrotalcite had a bimodal pore size distribution at  $\sim 5$

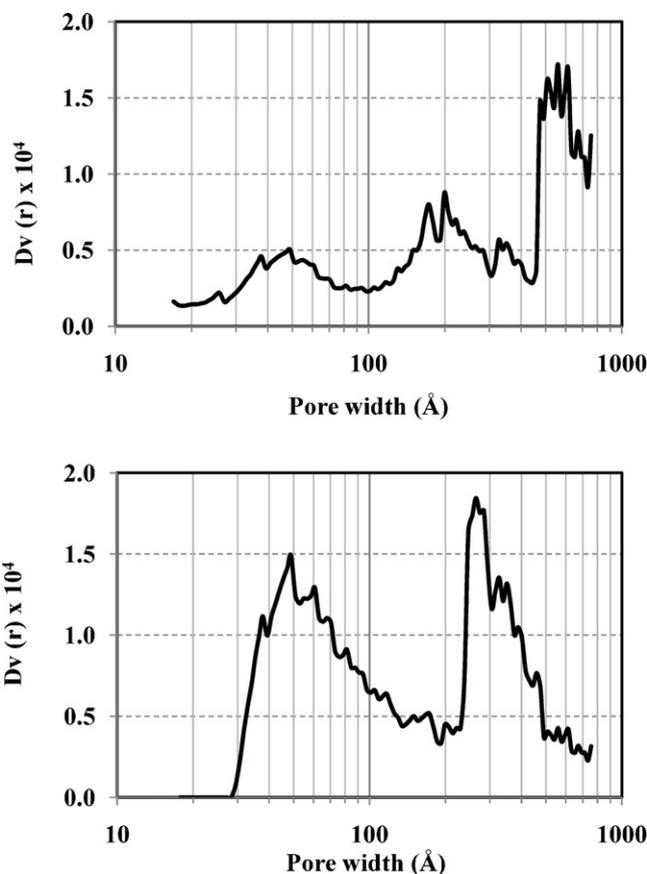


Fig. 3. Pore size distribution of  $\alpha$ - $\text{Al}_2\text{O}_3$  (top) and hydrotalcite (bottom). The unit of the Y-axis is  $\text{cm}^3/\text{A}/\text{g}$ .

and 20 nm. The characteristics of the utilized catalysts are listed in Table 1.

## 3. Results

The effects of catalyst type, feedstock, and the reaction time on the supercritical water gasification of several lignocellulosic materials have been systematically investigated. Experimental results are presented in terms of gas yields ( $\text{mmol gas/g feed}$ ), carbon gasification ratio (CGR) and hydrogen selectivity. Carbon gasification ratio is defined as the ratio of carbon in the gas products to the carbon in the initial feed. Hydrogen selectivity is defined as the number of moles of  $\text{H}_2$  to the number of moles of hydrogen in methane and it has been calculated as follow:

$$\text{hydrogen selectivity} = \frac{\text{moles of H}_2}{2 \times \text{moles of CH}_4}$$

Given the differences in the quantities of the active elements (i.e., Ni and Ru) and the metal dispersions, comparison was only made between the activities of catalysts with the same type of active metal. We also note that the CO yield in all catalytic SCWG experiments were below 1  $\text{mmol/g}$  and therefore not shown in the figures.

### 3.1. Thermodynamic considerations

The theoretical equilibrium concentrations of the gaseous products obtained using Gibbs free energy minimization at 380 °C and 230 bar for the mixtures of 98 wt% water and 2 wt% feed are given in Table 2. Under these operating conditions, the equilibrium hydrogen yield for the carbohydrates was limited to about 6  $\text{mmol/g feed}$

**Table 1**  
Physical characteristics of the catalysts used in this study.

Catalyst	Ni or Ru (wt%)	Particle size ( $\mu\text{m}$ )	BET ( $\text{m}^2/\text{g}$ )	Metal dispersion <sup>a</sup> (%)
Raney nickel	93	35	78	13.4
Ni/ $\alpha\text{-Al}_2\text{O}_3$	5	118	8	4.5
Ni/Hydrotalcite	5	1	12	1.3
Ru/C	5	18	900	41.0
Ru/ $\gamma\text{-Al}_2\text{O}_3$	5	40	90	16.7

<sup>a</sup> The metal dispersion obtained from [26] for Ru/C and [27] for Ru/ $\gamma\text{-Al}_2\text{O}_3$ .

and the methane yield varied from 15 to 17 mmol/g feed, with cellulose having the highest methane yield compared to other carbohydrates examined in this work.

As methane formation during gasification of biomass in SCWG medium does not have a pyrolytic origin and it is mostly formed through hydrogenation on the catalytically active metal surface [28], it is possible to minimize the methane yield through careful design of the reactor and the use of appropriate catalysts. Indeed, this highlights the need for design of selective catalysts with minimal activities for hydrogenation through cleavage of C–O bond.

### 3.2. Catalyst-free SCWG

In order to evaluate the effectiveness of the catalysts, the gas yields and carbon conversion obtained from catalyst-free supercritical water gasification in 15 min batch experiments are given in Table 3. It was found that without the addition of catalysts, the carbon conversions obtained from these compounds were typically between 6% and 22%, depending on the feedstock.

### 3.3. Nickel-catalyzed SCWG

Figs. 4–6 illustrate the yields of gaseous products obtained from the catalytic SCWG of different species using Raney nickel, Ni/ $\alpha\text{-Al}_2\text{O}_3$  and Ni/hydrotalcite, respectively. It was observed that the gasification yields and the product distributions of glucose and fructose were similar to those of cellulose ( $\pm 10\%$  at 60 min). However, SCWG of lignin was more difficult (i.e., lower yield) compared to carbohydrates. Although hardwood bark typically contains 40–50% lignin, 32–47% carbohydrates and 5–12% extractives [29], its gasification yield was found to be comparable to that of carbohydrates and significantly higher than that of lignin. Furthermore, we note that the decomposition of bark in the presence of Ni/ $\alpha\text{-Al}_2\text{O}_3$  and Ni/hydrotalcite catalysts resulted in low methane yields even after long reaction times. Yoshida et al. have previously shown that for the mixture of cellulose and lignin sulfonate, the negative deviation from the expected yields (obtained from the rule of mixtures) became less pronounced by increasing the catalyst loading and reported that the gasification yield of sawdust in near critical water and in the presence of nickel catalyst was nearly 90% of the theoretical value [20]. Similarly, Waldner and Vogel [30] reported near-complete gasification yield of bark-free fir and spruce sawdust at 400 °C with Raney nickel as catalyst. These observations imply that naturally occurring lignocellulosic compounds could be entirely gasified in supercritical water with sufficient amount of catalyst. Hence, the low conversion of lignin and also the negative

deviation of blends of lignin and carbohydrates from the rule of mixtures are likely caused by the catalyst poisoning due to the sulfur content and/or the condensed chemical structure of lignin sulfonate (compared to the original protolignin in wood).

In general, in order to interpret the results obtained from the SCWG of a binary mixtures of compounds A and B the following parameters should be considered: (i) the relative gasification rates of A and B, (ii) the rates of bimolecular condensation reactions between A–A, B–B and A–B, (iii) the rate of catalyst deactivation by A, B and the reaction intermediates, (iv) the amount of the produced hydrogen from the easier-to-gasify compound and (v) the initial feed to catalyst ratio.

### 3.4. Ruthenium-catalyzed SCWG

Ruthenium has been reported to be quite active for reactions involved in SCWG [6]. Figs. 7 and 8 depict the gas yields obtained from the catalytic SCWG of lignocellulosic materials using Ru/C and Ru/ $\gamma\text{-Al}_2\text{O}_3$  catalysts, respectively. After 60 min, Ru/ $\gamma\text{-Al}_2\text{O}_3$  resulted in a total yield of about 45–60 mmol/g for glucose, fructose, cellulose, xylan and pulp, whereas Ru/C resulted in a total yield of about 40–55 mmol/g for the SCWG of the same compounds. Furthermore, it is demonstrated that even at low catalyst loadings, ruthenium was highly active for the hydrogenation of  $\text{CO}_2$  and CO, and consequently, resulted in poor hydrogen selectivity. Similar to nickel catalysts, alkali lignin had the lowest total gasification yield likely due to catalyst poisoning and/or condensed chemical structure of lignin. Contrary to nickel-catalyzed reactions, use of ruthenium as catalyst resulted in a lower gas yield for gasification of bark ( $\sim 40$  mmol/g) compared to cellulose and glucose ( $\sim 50$ – $60$  mmol/g). However, the gas yields obtained from bark were still higher than the expected values based on the rule of mixtures between the carbohydrates and lignin. The difference in the gasification yield of bark may be due to the difference in the pore structure of catalysts. The pore size of nickel catalysts used in this study is in the order of tens of nanometers while activated carbon and  $\gamma\text{-Al}_2\text{O}_3$  are known to have a smaller pore structure. Therefore, the rate of gasification of larger molecules (e.g., lignin) generated by the hydrothermal degradation of birchwood bark could be lowered due to the reduced diffusion rate of these molecules in the smaller pore structure of Ru catalysts, reducing the total yield.

### 3.5. Hydrogen selectivity

Fig. 9 depicts the hydrogen selectivity obtained from SCWG of various feeds at 60 min reaction time. Lower hydrogen selectivity

**Table 2**  
Thermodynamic equilibrium of 2 wt% feeds at 380 °C and 230 bar.

Feed	Formula	C/O ratio	$\text{H}_2$ (mmol/g)	CO (mmol/g)	$\text{CH}_4$ (mmol/g)	$\text{CO}_2$ (mmol/g)	Hydrogen selectivity
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6$	1.00	5.7	0.008	15.2	18.1	0.19
Fructose	$\text{C}_6\text{H}_{12}\text{O}_6$	1.00	5.7	0.008	15.2	18.1	0.19
Cellulose	$(\text{C}_6\text{H}_{10}\text{O}_5)_n$	1.20	5.8	0.009	17.0	20.0	0.17
Xylan	$(\text{C}_4\text{H}_8\text{O}_4)_n$	1.00	5.7	0.008	15.2	18.1	0.19
Lignin	$\text{CH}_{0.63}\text{O}_{0.95}\text{N}_{0.002}$	1.05	4.8	0.009	11.0	24.8	0.22
Bark	$\text{CH}_{0.83}\text{O}_{0.88}\text{N}_{0.01}$	1.14	5.1	0.010	12.8	24.1	0.20

**Table 3**

Gas yield and CGR obtained from catalyst-free SCWG of 2 wt% feeds at 380 °C in 15 min batch experiments.

Feed	H <sub>2</sub> (mmol/g)	CO (mmol/g)	CH <sub>4</sub> (mmol/g)	CO <sub>2</sub> (mmol/g)	CGR (%)
Glucose	2.7	1.0	0.10	6.5	22
Fructose	1.5	0.7	0.02	4.9	17
Cellulose	1.1	1.0	0.10	6.3	20
Xylan	1.1	0.8	0.02	4.8	17
Lignin	1.6	0.1	0.14	1.8	6
Bark	1.3	0.4	0.03	3.2	9

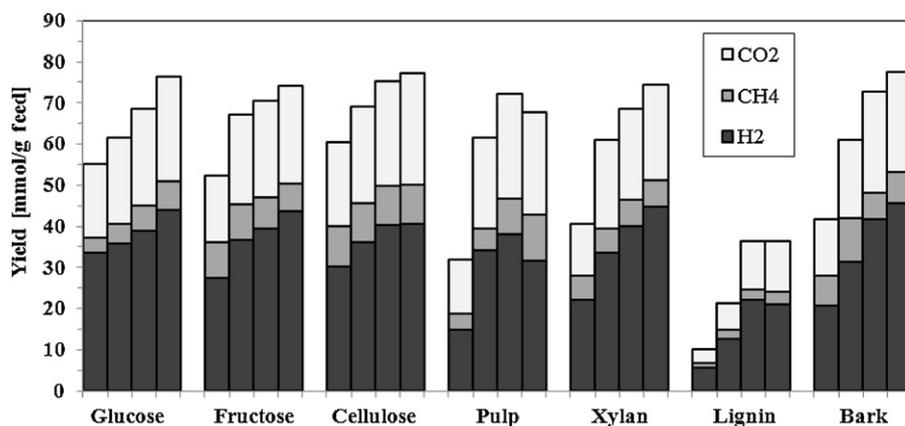
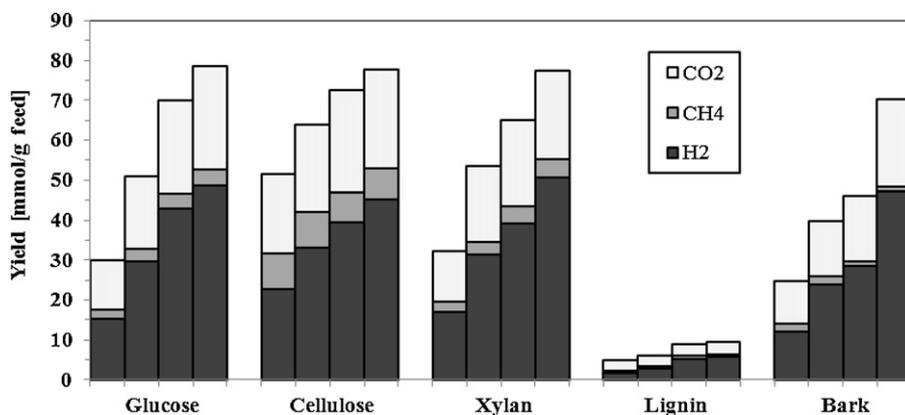


Fig. 4. SCWG of lignocellulosic feeds using Raney nickel catalyst. 380 °C, 2 wt% feed, 5, 15, 30 and 60 min (bars from left to right respectively), 120 mg Ni.

Fig. 5. SCWG of lignocellulosic feeds using Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. 380 °C, 2 wt% feed, 5, 15, 30 and 60 min (bars from left to right respectively), 120 mg Ni.

obtained from Raney nickel-catalyzed reactions implies that this catalyst is more active for cleaving C–O bonds compared to the other two nickel catalysts. This is likely due to the higher dispersion and as well as the larger number of Ni-defect sites associated with

the higher metal dispersion in Raney nickel catalyst. Therefore, if hydrogen production is the target of biomass gasification in SCW, using catalysts with lower nickel dispersions (i.e., larger crystallite sizes) may be beneficial.

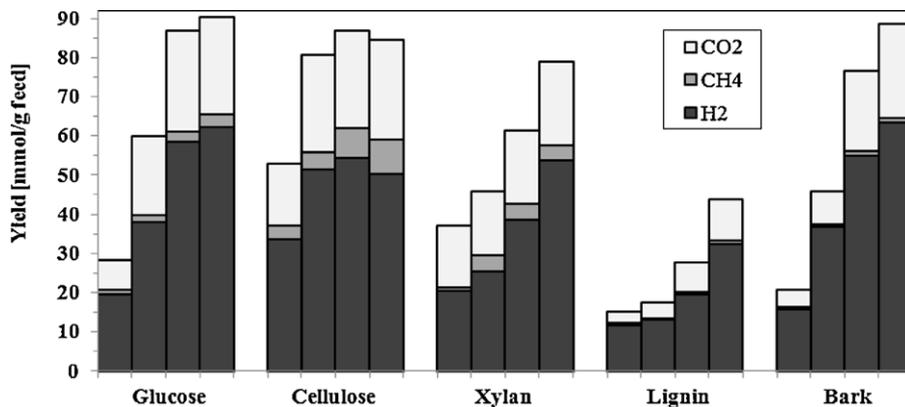


Fig. 6. SCWG of lignocellulosic feeds using Ni/Hydrotalcite. 380 °C, 2 wt% feed, 5, 15, 30 and 60 min (bars from left to right respectively), 120 mg Ni.

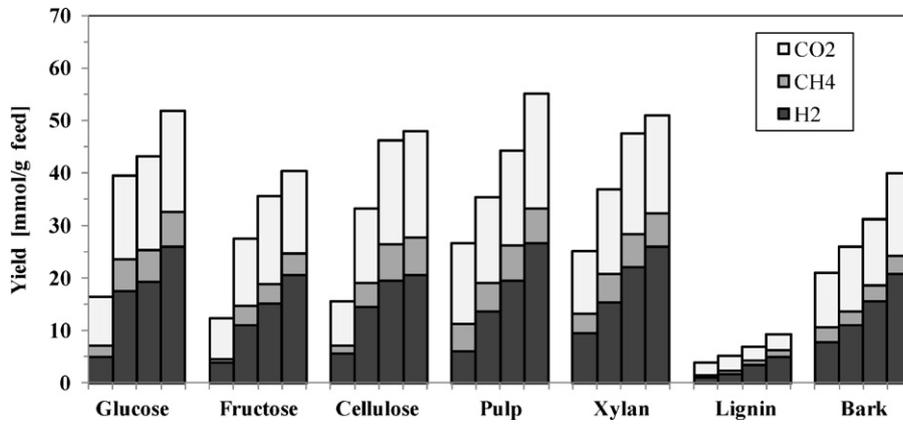


Fig. 7. SCWG of lignocellulosic feeds using Ru/C. 380 °C, 2 wt% feed, 5, 15, 30 and 60 min (bars from left to right respectively), 6 mg Ru.

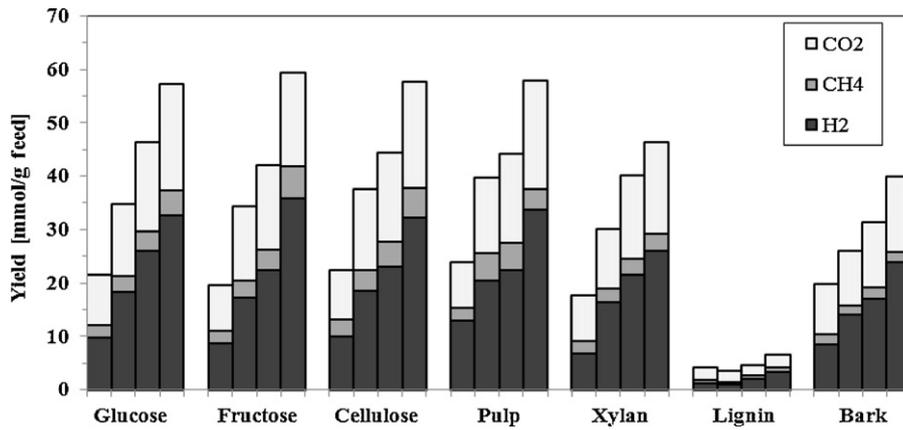


Fig. 8. SCWG of lignocellulosic feeds using Ru/γ-Al<sub>2</sub>O<sub>3</sub>. 380 °C, 2 wt% feed, 5, 15, 30 and 60 min (bars from left to right respectively), 6 mg Ru.

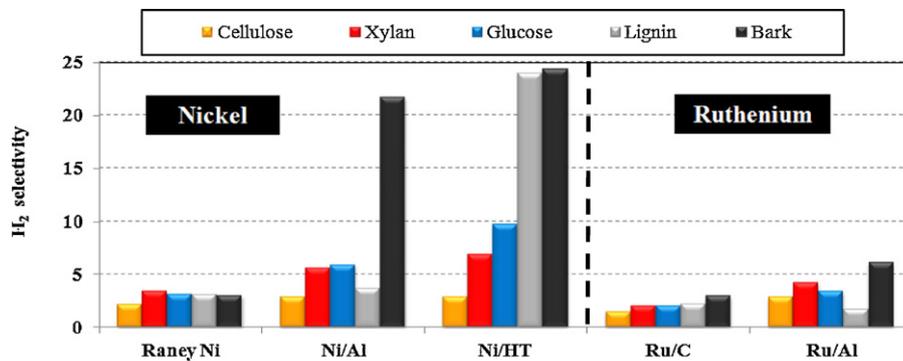


Fig. 9. Hydrogen selectivities obtained from SCWG using different catalysts. 380 °C, 2 wt% feed, 60 min, 120 mg Ni and 6 mg Ru.

Table 4 shows the ratio of the produced hydrogen gas to the amount of hydrogen available in the feed. It can be seen that utilization of Ni/α-Al<sub>2</sub>O<sub>3</sub> and Ni/hydrotalcite not only resulted in a higher hydrogen to alkane ratio but also offered a higher hydrogen production yield after 60 min reaction time compared to the other catalysts.

### 3.6. Carbon conversion

Figs. 10–14 illustrates the effects of the catalyst type and the reaction time on the carbon gasification ratio (CGR) of different compounds. Based on these figures, the following conclusions can be made regarding the catalyst's performances: (i) the

Table 4

Ratio of the produced H<sub>2</sub> gas to the amount of hydrogen available in the feed. 380 °C, 2 wt% feed, 60 min, 120 mg Ni and 6 mg Ru.

Feed	Raney Ni	Ni/α-Al <sub>2</sub> O <sub>3</sub>	Ni/Hydrotalcite	Ru/C	Ru/γ-Al <sub>2</sub> O <sub>3</sub>
Glucose	1.32	1.46	1.87	0.78	0.98
Cellulose	1.31	1.46	1.63	0.66	1.04
Xylan	1.34	1.52	1.61	0.78	0.78
Lignin	0.92	0.25	1.43	0.22	0.14
Bark	1.48	1.53	2.05	0.67	0.77

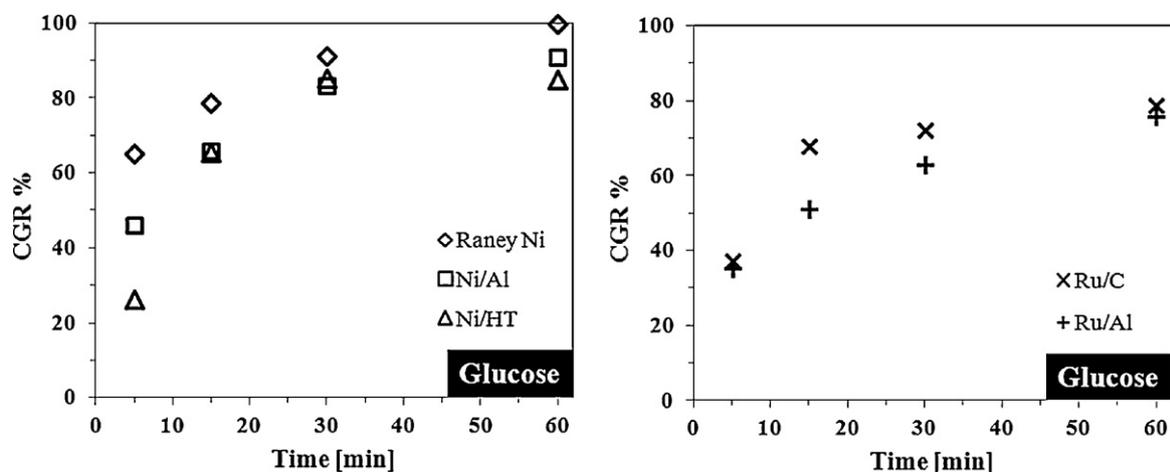


Fig. 10. Carbon gasification ratio of glucose as a function of time. 380 °C, 2 wt% feed, 120 mg Ni (left) and 6 mg Ru (right).

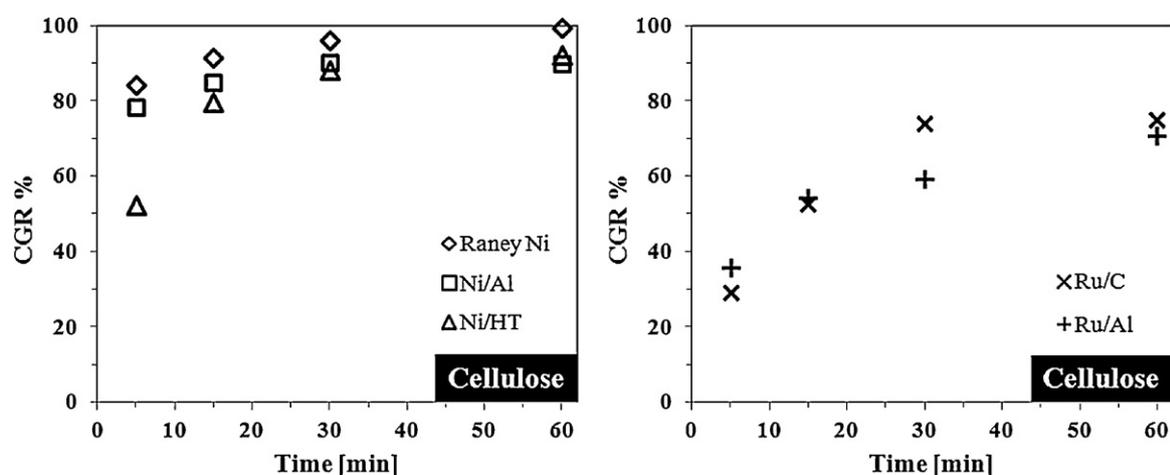


Fig. 11. Carbon gasification ratio of cellulose as a function of time. 380 °C, 2 wt% feed, 120 mg Ni (left) and 6 mg Ru (right).

order of activities for the nickel catalysts were as follow: Raney nickel > Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> > Ni/Hydrotalcite, (ii) higher activity of Raney nickel may be attributed to the higher metal dispersion and also the higher number of active sites on the outer surface of catalyst particles, (iii) high carbon conversion ratios associated with short batch experiments (e.g., <15 min) for cellulose, suggest that the gasification rates of the cellulose's hydrolysis intermediates were

faster than that of the glucose, (iv) Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Ru/C and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed low activity (e.g., CGR < 10%) for the SCWG of lignin at the conditions tested, and (v) Ru/C was found to be more active than Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, likely due to the higher dispersion of the active metal (see Table 1) and/or the adverse effects of phase transform of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>; as previously suggested in the literature [3], and the subsequent deactivation of the Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in SCW. This

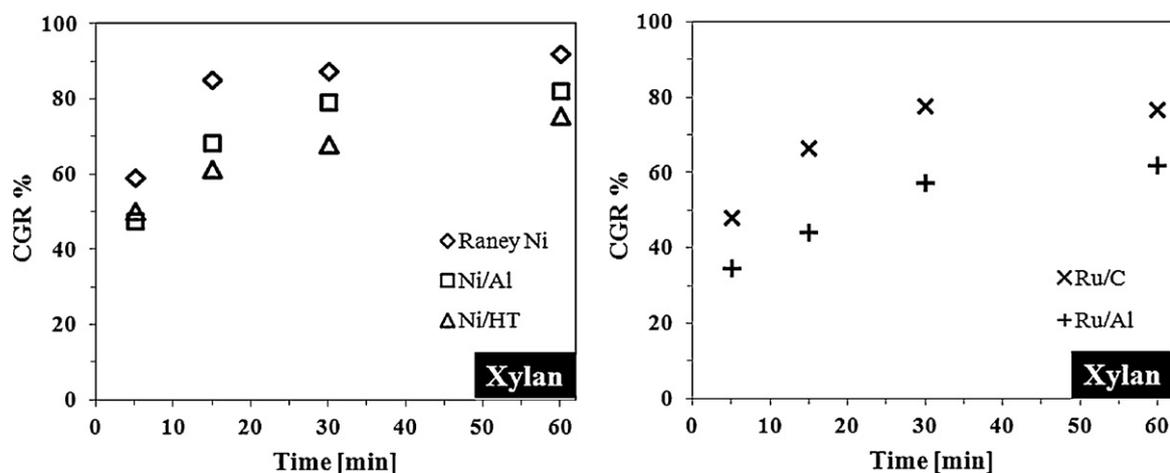


Fig. 12. Carbon gasification ratio of xylan as a function of time. 380 °C, 2 wt% feed, 120 mg Ni (left) and 6 mg Ru (right).

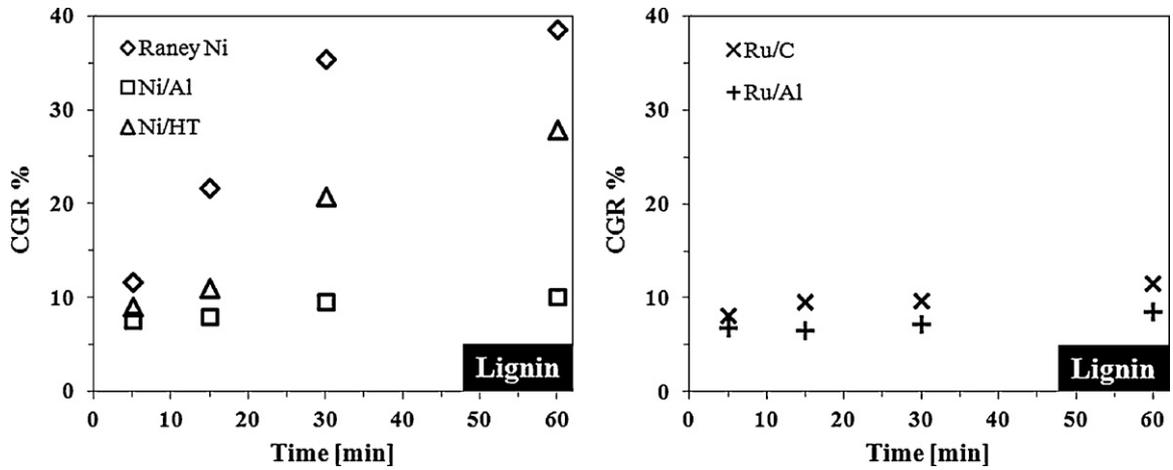


Fig. 13. Carbon gasification ratio of lignin as a function of time. 380 °C, 2 wt% feed, 120 mg Ni (left) and 6 mg Ru (right).

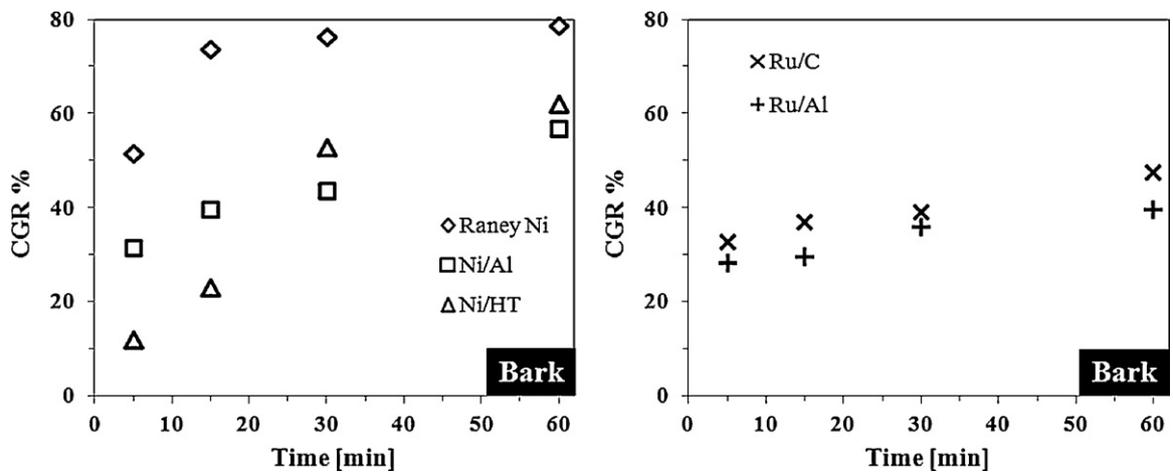


Fig. 14. Carbon gasification ratio of bark as a function of time. 380 °C, 2 wt% feed, 120 mg Ni (left) and 6 mg Ru (right).

phase change is associated with a significant loss of surface area and reduction in the number of catalytically active sites.

### 3.7. The relationship between carbon conversion and hydrogen selectivity

The reaction pathway for the nickel (or ruthenium) catalyzed supercritical water gasification of biomass is depicted in Fig. 15. Based on the proposed pathway, the methane formation occurs on the metal catalyst through the hydrogenation of CO<sub>2</sub> and CO. Therefore, it can be concluded that the methane yield is directly related to the partial pressure of reactants (i.e., H<sub>2</sub>, CO<sub>2</sub> and CO) as well as activity of the catalyst for dissociating hydrogen and cleaving the C–O bonds which will in turn, lead to the formation of methane. Considering that, the most appropriate way to compare the performances of different catalyst is to plot the hydrogen

selectivity versus carbon conversion which directly represents the partial pressure of carbon-containing gases (Fig. 16). According to this figure, at a given carbon conversion, the order of hydrogen selectivity for the studied catalysts was Ni/HT > Ni/α-Al<sub>2</sub>O<sub>3</sub> > Raney nickel > Ru/γ-Al<sub>2</sub>O<sub>3</sub> > Ru/C. For both nickel and ruthenium catalysts, the hydrogen selectivity seems to be inversely correlated with the metal dispersion (Table 1), implying that the catalytic methanation in the supercritical water medium may be a structural-sensitive reaction which preferably proceeds on the defect sites (e.g., edges and corners) of the metal crystallites. However, this hypothesis

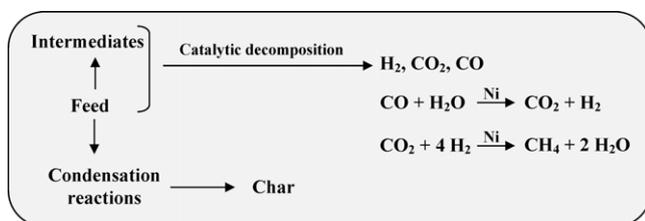


Fig. 15. The reaction pathway for the catalytic SCWG of biomass.

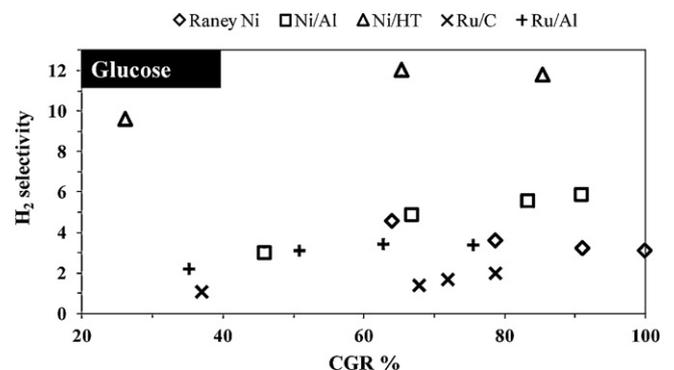


Fig. 16. Hydrogen selectivity vs. carbon CGR for SCWG of glucose using different catalysts.

should be further studied using catalysts with the same support material but different metal loadings. By varying the metal loading on the support, one is able to change the crystallite size and obtain different defect to facet site ratios.

#### 4. Concluding remarks

In this paper, results of the supercritical water gasification of several lignocellulosic materials using Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Ni/hydrotalcite, Raney nickel, Ru/C and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts have been presented. It was found that for a given catalyst, gasification of carbohydrates (i.e., glucose, fructose, cellulose, xylan and pulp) resulted in comparable gas yields ( $\pm 10\%$ ) after 60 min reaction time. However at short reaction times (e.g., 5 min) and in the presence of Ni-based catalysts, cellulose had consistently higher carbon conversion than glucose and xylan. Although lignin was substantially harder to gasify than cellulose, gasification yield of bark, which has high lignin content, was comparable to that of cellulose. Utilization of Raney nickel, Ru/C and Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> resulted in high methane yields. In spite of the low surface area of the laboratory-made Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ni/hydrotalcite catalysts, they exhibited high activities and superior hydrogen selectivities compared to those of the other catalysts tested in this work. More specifically, the amount of alkane formed upon supercritical water gasification of bark in the presence of Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ni/hydrotalcite catalysts was found to be very small (i.e. < 1.5 mmol/g after 60 min). Additional work is ongoing to examine the stability and possible deactivation of these catalysts under SCW conditions.

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