

Alkali-thermal gasification and hydrogen generation potential of biomass

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Abstract Generating hydrogen gas from biomass is one approach to lowering dependencies on fossil fuels for energy and chemical feedstock, as well as reducing greenhouse gas emissions. Using both equilibrium simulations and batch experiments with NaOH as a model alkaline, this study established the technical feasibility of converting various biomasses (e.g., glucose, cellulose, xylan and lignin) into H₂-rich gas via catalyst-free, alkali-thermal gasification at moderate temperatures (as low as 300 °C). This process could produce more H₂ with less carbon-containing gases in the product than other comparable methods. It was shown that alkali-thermal gasification follows $C_xH_yO_z + 2xNaOH + (x-z)H_2O = (2x + y/2 - z)H_2 + xNa_2CO_3$, with carbonate being the solid product which is different from the one suggested in the literature. Moreover, the concept of hydrogen generation potential (H₂-GP)—the maximum amount of H₂ that a biomass can yield, was introduced. For a given biomass C_xH_yO_z, the H₂-GP would be (2x + y/2 - z) moles of H₂. It was demonstrated experimentally that the H₂-GP was achievable by adjusting the amounts of H₂O and NaOH, temperature and pressure.

Keywords hydrogen generation potential, biomass, lignocellulose, alkali-thermal gasification, sodium hydroxide

1 Introduction

Many techniques for the production of hydrogen gas (H₂) as an environmentally friendly and economical energy carrier, as well as a valuable chemical synthesis feedstock, have been studied. Currently, approximately 95% of worldwide H₂ is produced from carbonaceous fossil resources, primarily natural gas [1]. While H₂ produced

from fossil fuels can be considered a clean fuel, a large amount of net greenhouse gases like CO₂ are emitted in hydrogen production from fossil fuel. Moreover, fuel processing typically involves a number of reaction steps to produce pure H₂, which can decrease efficiency and increase production costs [2].

One of the most promising alternatives to the current H₂ generation technique is biomass gasification. It offers a broad range of advantages, including reduction of net greenhouse gas emissions, reduced dependence on fossil fuels, use of renewable feedstock and more [3–5]. However, thermochemical conversion methods for the production of H₂ from biomass often suffer from low yields of H₂, char and tar formation, high energy demand, as well as concerns regarding the use of food crops for fuel production [3–5]. To overcome these obstacles various types of catalysts and additives have been examined and applied to the thermochemical processing of non-food crop or lignocellulosic biomass: the most abundant feedstock available for biomass gasification [3].

Specifically, alkaline additives have gained prominence and have been shown to be effective under hydrothermal conditions, where solid biomass is processed in liquid water at elevated temperatures and pressures [6]. Schmiender et al. reported that at 600 °C and 250 bar with the addition of KOH or K₂CO₃, natural biomass could be completely gasified under hydrothermal conditions into a H₂-rich gas, with CO₂ as the main carbon compound [7]. Muangrat et al. further compared the effects of several alkaline additives on the H₂ produced from biomass when reacted in a batch system. Their results showed that NaOH generated the highest amount of H₂, with no CO or CO₂, and small traces of hydrocarbon gases at 330 °C [8]. In other studies, Azadi et al. observed an significant increased activity of supported nickel catalysts with the addition of alkali promoters for the supercritical water gasification of biomass [9]. Similar results have been reported for the gasification of other biomass model compounds [10].

Although the above hydrothermal processes at elevated temperatures and pressures have shown promising results in terms of biomass conversion, operational issues and safety concerns surrounding this technology remain to be a major drawback for the application of such technologies [11].

Gas phase thermo-chemical processes are among alternative methods for biomass gasification. Ishida et al. studied the reaction between various biomass sources and NaOH in the presence of water vapor [12]. Unlike the work by Muangrat et al., gasification was conducted using a conventional mass-controlled gas flow system under atmospheric pressure. Using cellulose and a fixed amount of NaOH, H₂ was generated as the majority product, with a total yield of 62% [12]. Similar to Williams et al. this study showed that H₂ could be generated without forming CO or CO₂ at relatively low temperatures (< 300 °C), but with steam instead of supercritical water. However, once again, the amount of NaOH was not optimized and the system was far from achieving equilibrium, as gases continuously evolved and temperature continuously increased during the gasification process.

Previous work suggests that alkali metals are effective catalysts for biomass gasification through conversion and minimization of char. It has been reported that Group I metals, particularly potassium, are the best catalysts for the gasification of char not only through their inherent catalytic activity but also via volatilization and possibly formation of carbon/alkali meal complexes [13]. Alkali earth metals naturally present in biomass have been also found to improve the co-conversion of biomass and coal blends [14,15]. Using Raman spectroscopy and scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM-EDX), Liu et al. suggested that Na₂CO₃ (or K₂CO₃) were reduced to alkali metal and resulted in the cracking of aromatic ring systems, hence reducing char formation [16]. Alkali earth metals were found to also have a high activity for the reforming of tar formed during the biomass gasification processes [17].

Treating alkali-thermal biomass gasification as a generic system, this study attempts to better understand its behavior under a wide range of conditions, including temperature, water content, time and amount of NaOH. By conducting non-stoichiometric equilibrium simulations with FactSage-6.2, an advanced thermodynamic software package, the theoretical conditions to achieve the maximum H₂-production with minimal gaseous by-products, chars, tars and energy requirements for given generic biomass sources are explored. Moreover, to determine the maximum amount of H₂ that a biomass can yield, the concept of hydrogen generation potential (H₂-GP) is developed. It is hoped that this study may contribute to the development of more energy, material efficient and sustainable biomass gasification processes for H₂-production.

2 Materials and methods

2.1 Chemicals

The model compounds investigated in this study included: D-(+)-glucose (CAS 50-99-7), microcrystalline cellulose (CAS 9004-34-6), alkali lignin (CAS8068-05-1) and xylan from birch wood (CAS 9014-63-5). Sodium Hydroxide (CAS 1310-73-2) was used as the model alkali. All chemicals were obtained from Sigma–Aldrich, Canada.

2.2 Experiments

Inconel 600 pipe fittings purchased from Swagelok were used to construct a 25 mL reactor (see Fig. 1). This material was selected based on its corrosion resistance (Table S1). Experimental runs were conducted by first loading the desired amounts of biomass, NaOH and water into a Pyrex glass tube. The tube, used to prevent nickel from catalyzing the reaction and only test the effect of NaOH, was then inserted into the reactor. The system was purged with N₂, sealed and then immersed into a preheated furnace. After a fixed reaction time, the reactor was quenched to condense all water vapor. After quenching, the increase in pressure was measured using a pressure gauge and recorded to calculate the total gas yield. A gas chromatograph (Hewlett-Packard 5890 series) was used to calculate the composition of the gas produced.

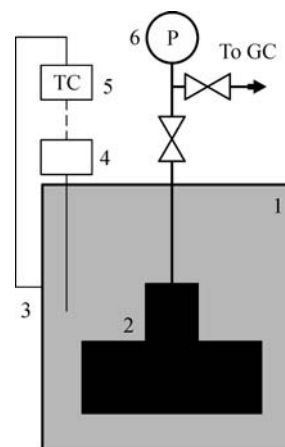


Fig. 1 Schematic of reactor (1) furnace; (2) reactor (pipe tee); (3) electrical heater; (4) thermocouple; (5) temperature controller; (6) pressure gauge

The measures used to quantify the performance of each experimental run were hydrogen yield and total gas yield, measured in mmol/g reactant. Also carbon gasification ratio (CGR), hydrogen gasification ratio (HGR) and hydrogen selectivity (HS) were calculated. The latter three parameters are defined as follows:

$$\text{HGR} = \frac{\text{Moles of hydrogen in gaseous product}}{\text{Moles of hydrogen in feed biomass}},$$

$$\text{CGR} = \frac{\text{Moles of carbon in gaseous product}}{\text{Moles of carbon in feed biomass}},$$

$$\text{HS} = \frac{\text{Moles hydrogen in gaseous product}}{2 \times (\text{Moles of methane in gaseous product})}.$$

Based on the total gas yield and the composition, the specific yield of each gas component, selectivity, HGR and CGR were calculated. Solid residue obtained after gasification was scanned for solid crystals with powder X-ray diffraction (PXRD) equipment. This was done using a Siemens D5000 conventional theta/2-theta diffractometer. The solid residue was also analyzed to determine the elemental composition and the amount of organic carbon remaining using an Exeter Analytical CE-440 elemental analyzer. Lastly, the composition of the product, as well as the impact of heating rate, was verified using Q500 Thermogravimetric Analyzer (TA Instruments).

2.3 Modelling

Non-stoichiometric thermodynamic modelling based on minimization of Gibbs free energy was performed using FactSage 6.2 (Thermfact and GTT-Technologies) chemical equilibrium software. Calculations were conducted with a range of biomass model compounds containing C, H and O. Since real biomass sources have been shown to form monomeric sugars during gasification [18], glucose was particularly relevant. Elements such as sulfur and nitrogen were ignored due to their very low concentrations in biomass [18].

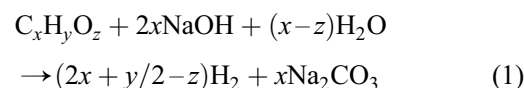
The software's Equilib module was used to test the heterogeneous equilibrium system and access compound databases. The module uses a non-stoichiometric methodology so, unlike stoichiometric approach, it does not require any knowledge of reaction mechanisms [19]. The simulation output included changes of enthalpy, entropy, and Gibbs free energy for the overall process, as well as concentrations of all main products (i.e., H₂, CH₄, CO₂, CO, H₂O, Na₂CO₃, NaOH and C) along with their respective states and molar fractions. To cross examine the model predicted, results obtained from FactSage 6.2 were compared to those of HSC 5.11 (Outotec Oyj, Finland), another chemical equilibrium software package.

3 Results and discussion

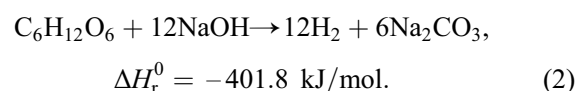
3.1 Thermodynamic analysis

For a model biomass with chemical composition C_xH_yO_z, the maximum amount of hydrogen generation, that is

referred to as the hydrogen generation potential or H₂-GP, is (2x-y/2-z) moles of H₂ per mole of biomass, corresponding to the following overall reaction:



However, to maximize hydrogen in the product gas and to minimize the formation of carbon containing by-products; or C-gases, such as CO₂, CO and CH₄, the relative amounts of H₂O and NaOH in the reaction medium must be carefully adjusted. The optimum amounts of these reactants depend on the chemical composition of biomass and particularly to its carbon content. As shown in Reaction 1, for a model biomass with composition C_xH_yO_z, the theoretical value for required amount of NaOH in moles; herein referred to as NaOH consumption potential or NaOH-CP, is two times the number of moles of carbon in the biomass, or simply 2x. Likewise, the H₂O consumption potential, or H₂O-CP, is equal to x - z. Therefore, depending on the relative amounts of oxygen and carbon in the biomass, H₂O-CP may be zero or even assume a negative value. Under such conditions, water addition would not be necessary since excess amounts H₂O will be produced during the gasification reaction. Reaction 1 also shows that achieving H₂-GP, results in the production of solid Na₂CO₃ as a by-product. The moles of Na₂CO₃ produced may be termed the Na₂CO₃ generation potential or Na₂CO₃-GP and is equal to x. For example, in the case of glucose, the hydrogen generation potential is 12:



The thermodynamic model showed a clear impact of increased temperature and water on the amount of H₂ and C-gases, or HGR and CGR, produced during gasification of biomass. Accordingly to Fig. 2, with no excess water, the theoretical amount of H₂ generated from alkali-thermal gasification of glucose exhibits a maximum at approximately 650 °C.

Moreover, both CO₂ and CO production increased with temperature, with CO increasing more appreciably (Figs. S1 and S2). Conversely, CH₄ was found to decrease with increased temperature, most noticeably at lower temperatures (Fig. S3). Accordingly, the total amount of C-gases produced from glucose gasification showed a minimum at approximately 650 °C (Fig. S4), coinciding with the maximum hydrogen production.

The relationship between maximum H₂ production and minimum C-gas production is likely due to competing reactions. The steam reforming of CH₄ (Reaction 3) is strongly endothermic and requires high temperatures to proceed. The gas shift reaction (Reaction 4) is mildly exothermic and occurs at lower temperatures. Other

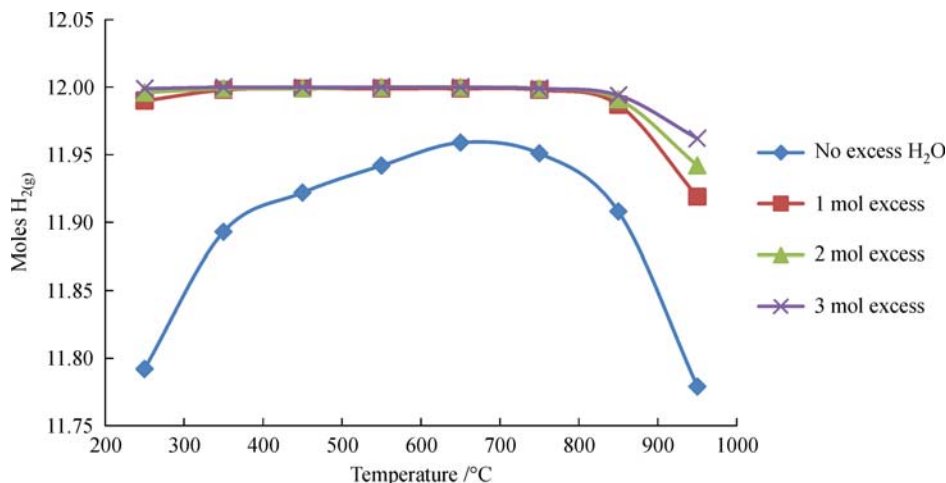
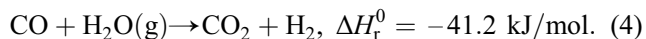
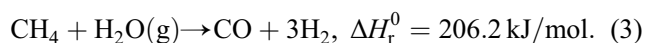
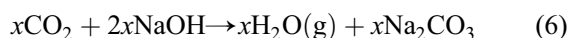
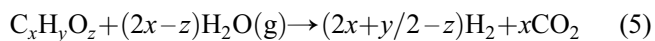


Fig. 2 Effect of temperature and excess H₂O on predicted H₂ production from glucose with stoichiometric amount of NaOH

competing side-reactions, such as the formation of larger hydrocarbons, were observed to be negligible and could be disregarded. This conclusion is supported by the experiments of Yan et al. [18] and Lee et al. [20].



Based on the thermodynamic model, CH₄ production increased at lower H₂O loadings, lower temperatures and higher pressures. This result is supported by Le Chatelier's principle (see Reaction 3) and is consistent with the findings of Azadi et al. [9]. Similarly, Reactions 3 and 4 explains why CO production increased at lower H₂O loadings and at higher temperatures, while CO₂ production increased with added H₂O and at higher temperatures (see Fig. 2 and Fig. S4). In addition, thermodynamic analysis showed that biomass gasification with excess steam may be modeled as the steam reformation process followed by the water gas shift reaction to form H₂ and CO₂ as its two main gaseous products (as shown in Reaction 5). The addition of NaOH to this system resulted in the exothermic sequestration or fixation of CO₂, which further increased H₂ production. By adding Reactions 5 and 6, the overall exothermic Reaction 1 for alkali-thermal gasification can be obtained.



3.2 Experimental results

While many researchers have suggested that the complete gasification of biomass into H₂ is impracticable due to competing side reactions [8], based on the thermodynamic

analysis presented earlier, the use of NaOH and H₂O could hinder H₂-consuming side reactions by sequestering C-gases as solid Na₂CO₃ and hence approaching H₂-GP. In the case of glucose, the optimum condition for hydrogen production could be theoretically achieved at NaOH-to-biomass molar ratios greater or equal to 2 and temperatures less than 500 °C. The validity of this analysis was examined by conducting batch experiments, and results are presented and discussed in this section.

3.3 Effect of NaOH loading

Figure 3 demonstrates the theoretical (or thermodynamic) and experimental results for alkali-thermal gasification of glucose, as measured by HGR, as a function of NaOH loading. The experimental results followed the same general trend as the one predicted by the model; namely, an increase in HGR and decrease in residual solid with increasing NaOH, followed by a plateau after the same stoichiometrically related amount. In the case of the experiments, the maximum HGR was reached at NaOH: glucose ratio of 3:1, corresponding to the molar ratio

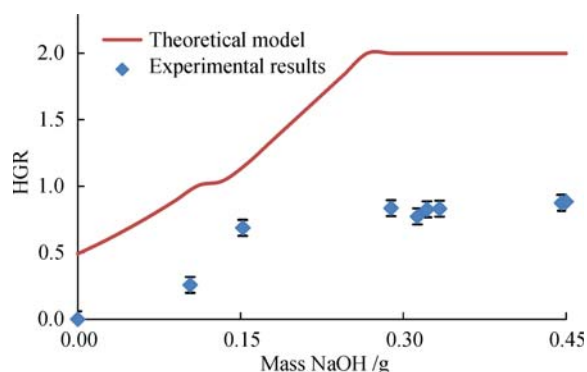
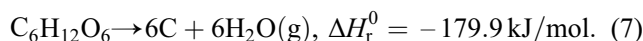


Fig. 3 HGR vs. mass of NaOH for 0.10 g glucose, 50 min at 350 °C

prescribed in Reaction 1. However, the experimental value for this plateau occurred at an HGR of about 0.87 or 45% of the ideal HGR value of 2.

Beyond the quantitative impact of added NaOH on HGR, qualitative observations were noted. Without NaOH clear signs of carbon-rich material like char and tar were observed, formed through dehydration and polymerization as opposed to gasification. This material was hydrophobic and non-polar in nature, resulting in reactor plugging and difficulty in reactor cleaning. Furthermore, it was noted that although negligible gases were generated after quenching the system in the no NaOH case, the pressure of the reactor did increase more significantly than expected due to temperature alone. The main reaction was therefore likely the carbonization of glucose, shown as Reaction 7, where all hydrogen and oxygen atoms are released as water vapor. This explains the formation of solid carbonaceous residue and the pressure increase (pre-quenching) in the absence of NaOH.



As NaOH loading increased, not only glucose gasification improved but also less char and/or tar was visually observed in the reactor and the solid residue became lighter in color and more soluble in water. Therefore, alkali addition had the added benefit of resolving problems associated with reactor plugging due to tar and char formation. It should be pointed out that some dark carbon residues were observed in the reactor even at high NaOH loadings that is evidence of an incomplete alkali-thermal gasification reaction. Overall, while these results confirmed the optimal ratio of NaOH-to-glucose for H_2 generation, optimization of other factors including H_2O content is critical to approach the ideal H_2 -GP value.

3.4 Effect of H_2O loading

Theoretically, water plays two distinct roles in the alkali-gasification of biomass; firstly it can act as a hydrogen supplier (see Reaction 5), and secondly excess H_2O added beyond the H_2O -CP can alter the equilibrium composition of the gasification products. As shown in Fig. 2, excess H_2O is expected to favor H_2 formation, consistent with Le Chatelier's principle.

The above thermodynamic consideration were examined experimentally and the results are shown in Fig. 4. In the first case, water was pre-mixed with NaOH and glucose before loading into the reactor while in the second case, steam was added to the reactor to avoid pre-mixing. As evidenced from the figure, contrary to the thermodynamic model, in both cases HGR decreased with increased water loading. However, the reduction in HGR was more pronounced when reactants were pre-mixed.

The above findings suggest that side reactions were the likely cause of deviation from the thermodynamically

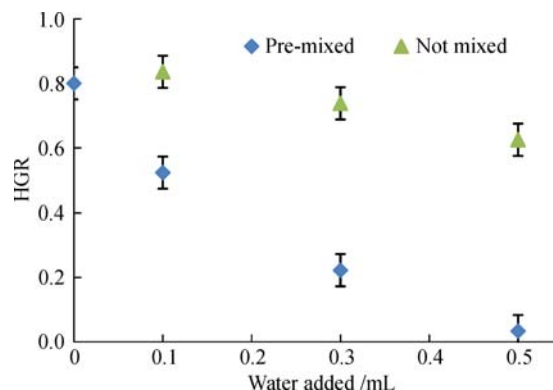


Fig. 4 HGR vs. amount water added (either pre-mixed with glucose and NaOH or reacted as steam) for 0.10 g glucose, 0.30 g NaOH, 50 min, 350 °C

predicted HGR values for glucose gasification. A possible explanation could be that side reactions initiated upon the exothermic mixing of NaOH in water with glucose. It has been reported that heating monosaccharides under acidic or basic aqueous conditions has led to degradation reactions, forming reactive intermediates such as 5-hydroxymethylfurfural (5-HMF) and 2-furfural (2-FA) that could undergo further condensation and polymerization reactions to form colored polymers [21]. As reported by Onwudili and Williams, formation of 5-HMF and 2-FA are precursors to the formation of tar and char and thus reduce the gasification yield [22]. The exothermic reaction of NaOH and water could supply enough heat to initiate the above side reactions and limit gasification yield even before external heat was supplied. Evidence of this process, known as caramelization, was observed with a color change from a transparent solution to opaque, caramel-colored syrup after mixing and heating at 100 °C.

It is important to note that the model was conducted at a constant pressure of 1 atm, while the pressure in the reactor increased with added water. The increased pressure resulting from the water as steam decreases gasification potential (i.e., opposes gasification of solid biomass) and could be masking any benefit of excess water shifting the gas phase reactions to favor H_2 formation. Consequently, temperature and pressure must too be optimized.

3.5 Effect of temperature

As shown by the thermodynamic model (Fig. 2), the H_2 -GP or maximum HGR value for glucose was accomplished at temperatures as low as 300 °C provided sufficient amounts of NaOH and H_2O . Increased temperature is expected to improve reaction kinetics by increasing mass transport through enhanced diffusivity. In addition, NaOH melts at around 320 °C significantly improving its contact with the gas phase [23].

Figure 5 shows comparison of the experimental and

theoretical HGR values as a function of temperature. According to this figure, at 300 °C the maximum experimental HGR was only about (32±5)% of the theoretical HGR value. By increasing the temperature, HGR also increased; however, this came at the expense of H₂ selectivity. At temperatures less than 400 °C, H₂ accounted for almost all of the gas phase products with a hydrogen selectivity of 38. As temperature increased, HGR approached its ideal value for glucose, reaching to approximately (90±5)% of its ideal value at 500 °C. In this case, gaseous products included both CH₄ and H₂ and hydrogen selectivity decreased to about 3.0±0.9 such that if only H₂ were considered in the HGR calculation, the HGR value would have been about 65% of its ideal value at 500 °C.

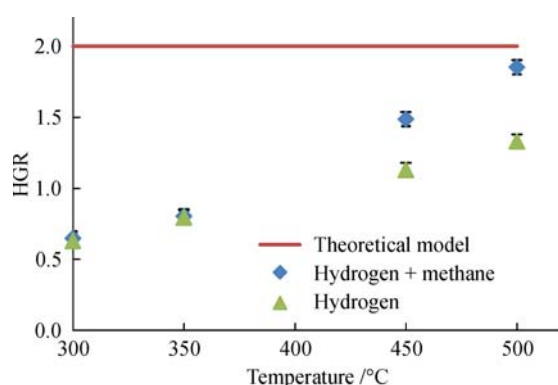
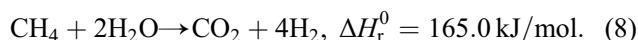


Fig. 5 HGR vs. temperature for 0.10 g glucose, 0.30 g NaOH, 50 min

The reason for CH₄ production is mostly due to the increased pressure associated with higher temperatures in the batch system, which favor CH₄ production according to Reaction 3. Furthermore, higher temperatures result in higher gas yields, which further increase system pressure. It has already been shown that at higher temperatures the discrepancy between the thermodynamic model and experimental results is reduced.

3.6 Effect of pressure

According to the thermodynamic model, varying pressure did not have as significant an effect on the equilibrium composition as temperature, NaOH or H₂O. The minimal effect of pressure has been similarly noted by Yan et al. [18]. The one case where pressure had a significant impact was on CH₄ and H₂ generation. High pressure favors CH₄ production, in the process consuming H₂ with increased pressure. This relationship between CH₄ and H₂ at high pressure is explained by Reaction 8 (the summation of Reactions 3 and 4) and by considering that the majority of the C-gas consumes H₂ to form CH₄ in high pressure and temperature systems (following Le Chatelier's principle).



Under these conditions, with increasing pressure H₂ would be consumed at 4 times the rate that CH₄ is generated as confirmed by the thermodynamic model (Fig. S5). This result provides insights into how to further improve the H₂ generation, for example by using a continuous reactor strategy to control pressure independently of temperature. Nevertheless, while it explains the decrease in H₂ selectivity, it does not explain the discrepancy in overall yield between the thermodynamic and experimental analysis when conducted at the same temperature. For this, kinetic considerations due to limitations from insufficient mixing and/or time in the batch system must be investigated.

3.7 Effect of mixing

To determine the extent of mixing, thermogravimetric analysis (TGA) was used on the solid residue to determine the proportion of NaOH reacted. Theoretically, at NaOH: glucose ratio of 3:1, all NaOH would be required to react in order to achieve the H₂-GP value. However, TGA analysis showed signs of residual NaOH and organic carbon in the form of a weight gain (Fig. 6). This weight gain is an indication of the fixation of the CO₂ generated during the TGA analysis as carbonate by the residual NaOH. TGA analysis (tabulated in Table 1) also demonstrated that about

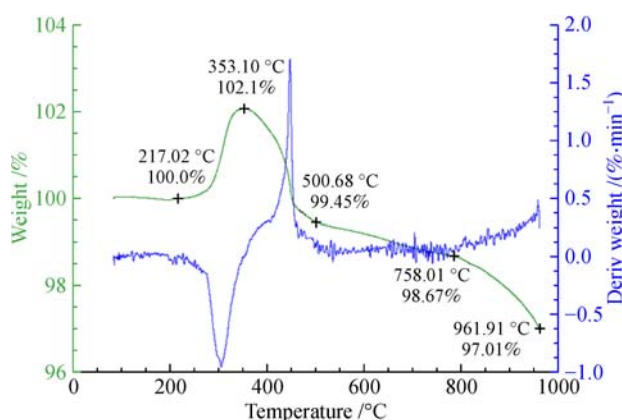


Fig. 6 Thermogravimetric analysis of solid product residue from alkali-thermal gasification, conducted in air with a heating rate of 20 °C/min

Table 1 Carbon analysis of the gasification product (from 0.10 g glucose, 0.30 g NaOH, 350 °C, 50 min) pre- and post-ashing at 500 °C for 4 h

Carbon content in products	%
Total carbon in gasification product (A)	15±2
Total inorganic carbon in ashed gasification product (B)	10±1
Total organic carbon (A-B)	5±2

around (50±2)% of carbon fed to the reactor as part of biomass was remained in the solid residue. This finding is consistent with the observed result for the biomass conversion to H₂ (40±5)% determined via gas chromatography.

3.8 Effect of reaction time

Experimental results show that the reaction system reached steady-state with respect to HGR after approximately 40 min that is less than the reaction time (50 min) used for these experiments. Incidentally, Kamo et al. reported that at 600 °C the gasification rate of activated carbon ($x = 1$) increased linearly with the NaOH:C ratio until a value of 2:1 was reached, where the rate became maximized with no further benefit of additional NaOH [24]. In other words, the NaOH-CP was, in this case, also related to the optimum rate of reaction.

While reaction time was not limiting, the rate of heating was a factor as it took about 20 min to reach within 10% of the target temperature of 350 °C. Thermogravimetric analysis was conducted for a mixture of NaOH and glucose (3:1) at two different heating profiles. The first heating profile involved heating at a rate of 20 °C/min until 400 °C and holding the sample at that temperature for 50 min (Fig. S6). The second profile involved a jump in temperature to 400 °C and holding the sample at that temperature for 50 min (Fig. S7). The slower heating rate resulted in a weight loss of approximately 14.4%, while the faster heating rate produced a weight loss of about 24%.

Research by Fushimi et al. showed a similar impact of heating rate for the steam gasification of cellulose. They found that a rapid heating rate significantly increased the evolution of H₂, CO and CH₄ by steam-reforming reactions of volatiles and char [25]. Alternatively, a slow heat-up period exposes the biomass to lower temperatures for longer time periods. These conditions favor the thermal dehydration and polymerization of biomass to form tars and chars instead of gasification [22].

3.9 Alkali-thermal versus other gasification methodologies

Figure 7(a) shows alkali-thermal gasification of glucose conducted in this study (gasification temperature: 350 °C, glucose loading: 0.10 g, NaOH loading: 0.30 g) along with the hydrothermal gasification of glucose for a catalyst-free system, as well as with Raney-nickel 4200, Ruthenium Carbon and Raney-Copper (gasification temperature: 370 °C, glucose loading 0.17 g, water loading: 3.00 g, catalyst loading: 0.05 g). The hydrothermal gasification experiments were conducted by Azadi et al. [26]. The comparison revealed that alkali-thermal gasification resulted in more than 5 times the H₂ yield and reduced the C-gas content by about 40 times. Furthermore, the alkali-thermal treatment reversed the trend of diminishing

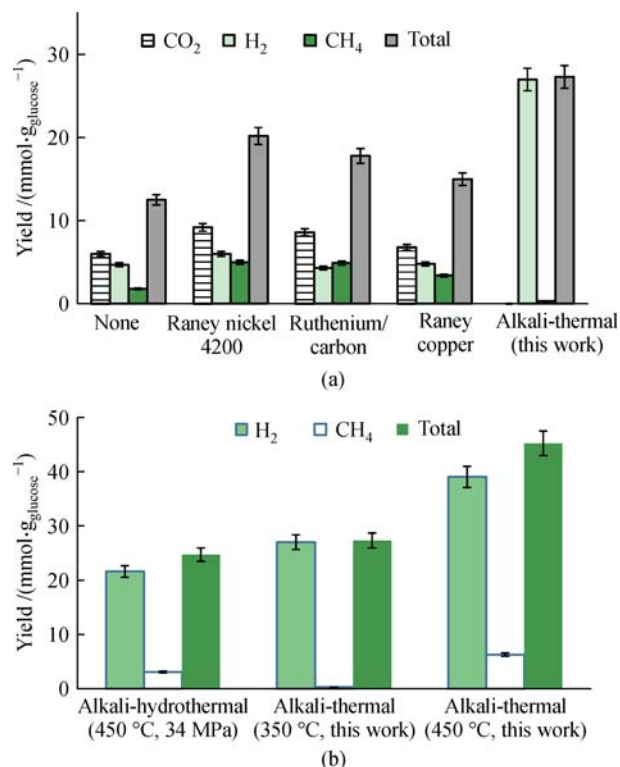


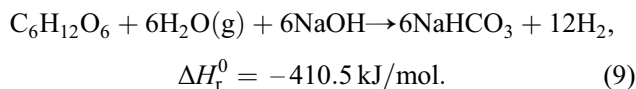
Fig. 7 Product yields of alkali-thermal gasification glucose compared to (a) gasification with and without metal catalysts [26], and (b) alkali-hydrothermal gasification [27]

hydrogen selectivity with yield, as well as enhanced the increasing trend of HGR with yield.

Alkali-hydrothermal gasification (conducted by Onwudili and Williams [22]) has also been compared with alkali-thermal gasification of glucose (shown in Fig. 7(b)). Both processes produced negligible amounts of CO and CO₂ due to their sequestration by alkali; however, the alkali-thermal procedure achieved comparable HGR values and higher hydrogen selectivity values at lower temperatures and pressures. At comparable temperatures, the HGR value of the alkali-thermal approach was almost double that of the hydrothermal approach with comparable selectivity.

3.10 Na₂CO₃ versus NaHCO₃

The thermodynamic model suggests that due to the connection between CO₂, CO and CH₄ it is necessary to supply enough NaOH to completely trap all the carbon as Na₂CO₃ to achieve the H₂-GP. Onwudili et al. have suggested a gasification scheme where less NaOH than the NaOH-CP might be required if NaHCO₃ is the final C-containing product, since upon cooling to < 60 °C more CO₂ could be captured in the process of NaHCO₃ formation [22]. This reaction, shown for glucose, may be written as follows:



Reaction 9 suggests that the H₂-GP for glucose (12 moles) may be achieved with 6 moles of H₂O and 50% less NaOH than recommended by Reaction 1. Nonetheless, further examination of the C-gas formation reactions shows that a complete Reaction 9 is thermodynamically improbable. With a limited amount of NaOH at high temperatures, there is a significant amount of free CO₂ which establishes equilibria with CO and CH₄. Upon cooling, not all C-gases would be in the CO₂ form to react with Na₂CO₃ and H₂O forming NaHCO₃, plus Reactions 3 and 4 to form CO₂ from CO or CH₄ would no longer occur under these conditions.

Moreover, the overall reaction proposed in this research (with Na₂CO₃) is more energetically favorable than the one proposed previously (with NaHCO₃) over a wide temperature range, particularly between 350 °C and 750 °C. For all biomass compounds modeled, Reaction 1 is more thermodynamically favorable than the previously proposed Reaction 9, judging by Gibbs free energies and enthalpies of reaction (see Fig. S8 for enthalpy data).

To verify this thermodynamic result solid residue sample was analyzed using PXRD. While accurate quantitative PXRD analysis could not be done due to the hygroscopicity of Na₂CO₃ and any residual NaOH, a semi-quantitative analysis of the intensity of peaks revealed that the sample was almost pure Na₂CO₃ and no NaHCO₃ was identified (Fig. S9). Accordingly, supplying a sufficient amount of NaOH, explicitly the NaOH-CP required to form Na₂CO₃, is likely essential in minimizing C-gas in the product stream and achieving the H₂-GP.

3.11 Various feedstock

Alkali-thermal gasification experiments were conducted for a variety of model biomass compounds to verify whether the alkali-thermal process could be applied to other feedstock. Gasification results for cellulose, lignin and hemicellulose (specifically xylan from birch wood), which are the main components of lignocellulosic materials, are shown in Fig. 8.

Both cellulose and xylan had larger HGR values for a given mass of biomass and NaOH than glucose, while lignin performed less effectively than glucose but comparable within an uncertainty of ±10%. Although cellulose and xylan are sugar polymers and may be expected to generate less gas than glucose due to their more complex structures, this ignores a number of key factors. The cellulose in these experiments was microcrystalline, produced by isolating the crystalline segment of cellulose to yield a high purity powder with particles of 20 μm. Polymerization appears less significant than the benefit of having the feedstock present as fine particles

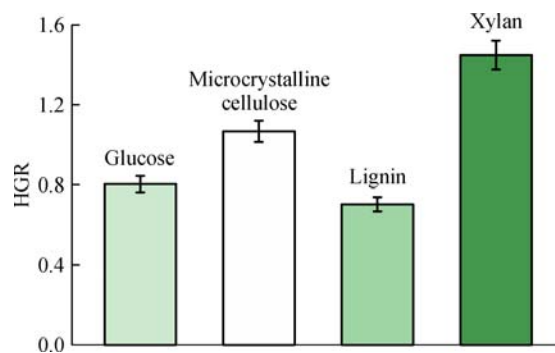


Fig. 8 Gasification of various feedstock (0.10 g biomass, 0.30 g NaOH, 350 °C, and 50 min)

with high surface area to increase mass transfer, as well as high crystallinity. This result has been verified by Wen et al., who demonstrated using Pt/C that the hydrogen selectivity and yield for cellulose gasification was significantly higher than for glucose. In particular, the hydrogen selectivity was found to be related to the degree of crystallinity and not the degree of polymerization [28]. A similar effect occurred for xylan; however, as reported by Widyawati et al., xylan has a greater reactivity towards alkalis, resulting in a greater increase in H₂ yield [27,28].

Overall it has been shown that the three major components of lignocellulosic biomass can be gasified separately to produce H₂. While more complex samples containing mixtures of the three components have not yet been investigated using alkali-thermal techniques, there is positive evidence that the model compound results may be extrapolated to real lignocellulosic feedstock. Yang et al. investigated the thermal degradation of cellulose, xylan and lignin, as well as the thermal processing of their mixtures and found negligible interaction among them [29].

While future work should include using real lignocellulosic plant matter and/or organic waste streams, this result in combination with the previous discussion suggests a practical and potentially cost-effective conversion technology to further promote sustainability in the energy sector as well as the many chemical industries which use hydrogen as a feedstock. It should be pointed out that NaOH is an expensive reagent and must be recovered. One way to recover NaOH is the chemical recovery process used by the pulp and paper industry where a slurry of lime (Ca(OH)₂) is used to convert Na₂CO₃ to NaOH. The resulting limestone (CaCO₃) is subsequently converted to lime in a lime kiln.

4 Conclusions

Based on both equilibrium simulations and batch experiments with NaOH as a model alkaline, this study

demonstrated the technical feasibility of converting various biomasses, including glucose, cellulose, xylan and lignin, into H₂-rich gas via alkali-thermal gasification at moderate temperatures (as low as 300 °C). This process was able to produce more H₂ with less carbon-containing gases (e.g., CO and CH₄) than other comparable methods. The overall reaction was found to be $C_xH_yO_z + 2xNaOH + (x-z)H_2O = (2x + y/2 - z)H_2 + xNa_2CO_3$, with carbonate being the solid product which is different from the one suggested in the literature. This overall reaction allowed the introduction of H₂-GP. For a given biomass of chemical composition C_xH_yO_z, the H₂-GP is found to be (2x + y/2 - z) moles of H₂. It was shown that the H₂-GP was achievable by adjusting the amounts of H₂O and NaOH, temperature and pressure.

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