Novel Approach to Hydrogen Production with Suppressed CO\textsubscript{x}
Generation from a Model Biomass Feedstock

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Supporting Information

ABSTRACT: The alkaline thermal treatment of biomass has recently been proposed as a novel method for producing high purity H\textsubscript{2} with suppressed CO\textsubscript{x} formation under moderate reaction conditions (i.e., 523 K and ambient pressure). This technology has a great potential for sustainable bioenergy production because it can handle a wide range of feedstocks including biomass and biogenic wastes with high water content. Unfortunately, due to the complexity of the reactions involved, the alkaline thermal treatment of biomass is still poorly understood. In this study, using a model biomass system of glucose, a series of noncatalytic kinetic and mechanistic studies was performed to investigate the effects of reaction temperature and reactant ratios in terms of H\textsubscript{2} conversion, purity, and formation rates of H\textsubscript{2} as well as gaseous products such as CH\textsubscript{4}, CO, and CO\textsubscript{2}. The CO concentration is one of the important factors for the utilization of the product gas because CO is generally poisonous to catalytic systems such as those found in proton exchange membrane (PEM) fuel cells. Thus, high CO concentration would require additional gas cleanup processes. This study found that NaOH does play an important role in suppressing CO and CO\textsubscript{2} formation while facilitating H\textsubscript{2} production and promoting CH\textsubscript{4} formation. The noncatalytic alkaline thermal treatment of glucose resulted in a maximum H\textsubscript{2} conversion of about 27% at 523 K with a stoichiometric mixture of NaOH and glucose. While the H\textsubscript{2} conversion was limited in the absence of catalyst, the moderate reaction conditions, low CO\textsubscript{2} concentration, and solid—solid reaction scheme give advantages over conventional biomass conversion technologies. The solids analysis confirmed the presence of Na\textsubscript{2}CO\textsubscript{3} in the solid product, indicating the inherent carbon management potential of the alkaline thermal treatment process.

1. INTRODUCTION

In 2010, it was reported that fossil fuels accounted for 80–90% of global energy consumption,\textsuperscript{1} and they will continue to be the predominant source of energy for the foreseeable future, considering that they are still the most abundant and affordable source of energy. Rapid economic growth in developing countries such as China and India will further amplify the increasing demand for fossil fuels. Unfortunately, fossil fuel resources are not uniformly distributed in the world, and thus many nations depend on importation for much of their fuel supply. The utilization of fossil fuels also results in the emission of many environmentally detrimental byproducts, including greenhouse gases. Therefore, the issues of energy security and imbalances in the global carbon cycle brought about by anthropogenic carbon emissions have prompted much investigation into new sustainable fuel and energy generation paradigms. Achieving a sustainable energy pathway requires both a multifaceted technological solution and the use of various energy sources. In particular, the development of efficient energy conversion schemes is desired for alternative feedstocks, rather than simply applying conventional fossil energy conversion technologies to them.

As an alternative energy resource, biomass is a feedstock that is renewable, carbon neutral, diverse, and diffusely spread throughout the world. In the United States, the U.S. Energy Information Administration (EIA) predicts that energy consumption from biomass will increase 2.9% annually from the period of 2009 to 2035, comprising 4.6% of U.S. energy consumption by 2035.\textsuperscript{2} For the developing world, which the EIA is projecting to have an 84% increase in energy demand versus a 14% increase for the developed world by 2035,\textsuperscript{2} biomass is a crucial energy resource. In 2001, nearly 50% of Africa’s total primary energy supply was from biomass and waste.\textsuperscript{3} Biomass will therefore be an important energy feedstock for decades to come; however, it must be utilized in a sustainable and efficient manner.

As biomass is a very low energy density feedstock, thermochemical pathways have been developed to increase its energy density. One pathway is through the conversion of biomass to biocrude via pyrolysis.\textsuperscript{4–7} Biomass feedstocks can also be converted into a synthesis gas (i.e., CO and H\textsubscript{2}) through conventional or supercritical gasification processes, the latter being more well-suited to biomass feedstocks with greater than 35 wt % moisture content.\textsuperscript{8–10} Fischer–Tropsch synthesis can then be employed to make hydrocarbon fuels from the synthesis gas. Most of these thermochemical processes can be made to be highly flexible, allowing for a range of fuels to be made from a wide variety of biomass feedstocks. However, there has been less investigation into processes where biomass can be utilized as a feedstock in a local, distributed generation scheme, one that does not require increasing the energy density of the feedstock through fuel conversion to make fuel transportation feasible. Distributed biomass conversion is particularly attractive for the developing world and...
rural communities, as many of these regions lack the infrastructure necessary for a large scale grid. The aforementioned thermochemical conversion technologies, such as gasification and pyrolysis, can also be scaled down into small units, but due to their high operating temperatures and pressures the main difficulties of their distributed small-scale deployment will lie in the need for skilled operators and the issue of safety. Therefore, the development of a biomass conversion scheme that can safely be operated at lower temperature and pressure is desired.

Several studies have been conducted to investigate one-step H2 production methods from biomass primarily through the addition of alkaline and alkaline earth hydroxides, which transfer the carbon in the biomass to a stable, solid carbonate while producing H2. Thus, unlike gasification and pyrolysis where both carbon and hydrogen remain in the fuel streams, this technology allows for inherent carbon management by fixing carbon in a solid carbonate matrix while maximizing H2 production. Saxena proposed this concept in 2003, applying it to the reaction of carbon with NaOH and water vapor:

\[
C(s) + 2NaOH(s) + H_2O(g) = 2H_2(g) + Na_2CO_3(s)
\]  

(1)

Subsequently, alkaline thermal treatment of carbonaceous materials to produce H2 has been applied to a number of biogenic feedstocks.12−20 With regard to biomass, Ishida et al. carried out a number of interesting studies on its alkaline hydrothermal treatment using Ni-based catalysts to produce CO- and CO2-free H2 under relatively low temperature and atmospheric pressure conditions, while producing solid product, Na2CO3 which is an environmentally benign, potentially value-added product.21,22 The produced H2 can be used to generate electricity using a number of energy conversion systems including fuel cells. The fuel cell technology offers a highly adaptable and efficient way to generate energy in a local, distributed framework. Specifically, the polymer electrolyte membrane (PEM) fuel cell confers a number of benefits, which include low operating temperature, quick startup time, high energy density, and water vapor as the only source of emission.23 However, the catalyst in a PEM fuel cell can be irreversibly poisoned by CO with concentrations as low as 5–10 ppm.24 Thus, the alkaline thermal treatment of biomass offers the potential to produce H2 from biomass that can be directly fed into a PEM fuel cell without the need for reforming or gas cleanup processes to lower the CO concentration. Also, because the alkaline thermal reaction of biomass occurs at low temperature (thermodynamically and kinetically favorable at less than 573 K) and atmospheric pressure, a simplified and compact reactor design becomes possible. The overall reactions of glucose (eq 2) and cellulose (eq 3) with NaOH in the absence of oxygen can be written as:

\[
C_6H_{12}O_6(s) + 12NaOH(s) = 6Na_2CO_3(s) + 12H_2(g)
\]  

(2)

\[
C_{6n}H_{10}O_5(s) + 12NaOH(s) + H_2O(g) = 6Na_2CO_3(s) + 12H_2(g)
\]  

(3)

As shown in the above reactions, this scheme of bioconversion requires water, particularly for the systems using cellulosic biomass. Thus, alkaline thermal treatment can be readily used for a wide range of biomass feedstocks including the ones with high water content, whereas most of conventional thermal biomass conversion technologies such as gasification and pyrolysis prefer dry feedstocks.

With the addition of Ni-catalysts, Ishida et al. found cellulose conversions to H2 close to 100%.22 Unfortunately, their process involved an energy-intensive pretreatment process to improve mass transfer during the reaction, which entailed the impregnation of the aqueous NaOH solution onto biomass, followed by the evaporation of excess water. Therefore, the overall energetics of the biomass conversion would not be sustainable. Since this work, Su et al. have investigated H2 conversion from cellulose using a novel Al2O3·Na2O·xH2O/NaOH/Al(OH)3 ionic catalyst containing the base. Their solid−solid cellulose systems achieved as high as 60% H2 conversion; however, with this approach, CO concentration in the gaseous product stream was as high as 700 ppm under similar reaction conditions. This scheme did not require the need for the aqueous NaOH solution-based pretreatment process, but their catalyst preparation step did necessitate the removal of water. It was reported that greater conversions to H2 are observed as the sodium content in the catalyst was increased.15−17 None of the prior studies provided detailed analyses of gaseous and solid products during the alkaline thermal treatment of biomass, and thus the reaction mechanisms are still poorly understood.

Therefore, this study focused on a systematic kinetic and mechanistic investigation of the noncatalytic alkaline thermal treatment of glucose, a surrogate for biomass. One of the important differences in this study from those conducted previously was the use of solid NaOH powder mixed in with glucose as opposed to pretreated glucose using NaOH solution. The motivation for this was to avoid the energy penalty associated with the evaporation of the solvent, water, used in NaOH solution. The effects of the reaction temperature and the NaOH:glucose reactant ratios on H2 conversion, purity, and formation rates of gaseous products including CH4, CO, and CO2 were quantitatively investigated, while the compositions of solid products were determined to further probe the reaction mechanisms.

2. MATERIALS AND METHODS

2.1. Experimental Setup and Procedure. The schematic of the experimental setup used in this study is shown in Figure 1. To maximize mass transfer during the solid−solid reaction, NaOH (Acros) pellets were ground together with procured D- (+)-glucose powder using a mortar and pestle. For the majority of experiments, 3.35 g of mixed sample was added to a 10 mL ceramic boat, which was placed inside a quartz tube reactor (2.54 cm O.D. × 91.44 cm length) operated at ambient pressure. In the case of experiments involving variation in reactant ratios, different total amounts of sample were used, whose amounts are given in section 2.2. The reactor was then
sealed with ultra-torr fittings (Swagelok) and placed inside a three-zone horizontal split-tube furnace (Mellen Co., SC12R). Once the reactor was secured, N2 carrier gas was introduced through the reactor zone horizontal split-tube furnace (Mellen Co., SC12R). Once the investigated in terms of the H2 conversion and the formation rate of each gaseous product. A stoichiometric mixture of D-(+)-glucose and NaOH was prepared on the basis of reaction 2 (total sample weight = 0.14 g to maintain CO concentrations within the detectable range of the GC. The extent and kinetics of the reaction were determined on this type of batch experiment. The amount of glucose was kept above the melting temperature of NaOH:glucose. The ratio of 0:1 represents the glucose pyrolysis case and 10:1, where 1:1 corresponds to the stoichiometric ratio of 12:1 given in reaction 2. Both ratios lower and higher than the alkaline thermal treatment of glucose. The molar ratios of NaOH:glucose. The ratio of 0:1 represents the glucose pyrolysis case and 10:1, where 1:1 corresponds to the stoichiometric ratio of 12:1 given in reaction 2. Both ratios lower and higher than that of the Agilent GC. However, the Agilent GC’s detection limits were significantly lower for carbonaceous compounds. Thus, the Micro GC was used only for the fast kinetic studies discussed in section 3.3.

2.2. Investigations of Reaction Parameters. The effect of reaction temperatures on the alkaline thermal treatment of glucose was investigated in terms of the H2 conversion and the formation rate of each gaseous product. A stoichiometric mixture of D-(+)-glucose and NaOH was prepared on the basis of reaction 2 (total sample weight = 2.35 g). A wide range of reaction temperatures, 373, 423, 473, 523, and 573 K, were selected as the final reaction temperature, with the highest reaction temperature being limited by the melting temperature of NaOH (591 K). During each run, the reaction progress was monitored by sampling the gaseous product stream via the GC.

The molar ratios of the two solid reactants, D-(+)-glucose and NaOH, were also varied to investigate the role of NaOH during the alkaline thermal treatment of glucose. The molar ratios of NaOH:glucose were normalized on the basis of the stoichiometric ratio of 12:1 given in reaction 2. Both ratios lower and higher than the stoichiometric ratio were considered for the study: 0:1, 0.2:1, 1:1, 2:1, and 10:1, where 1:1 corresponds to the stoichiometric ratio of 12:1 NaOH:glucose. The ratio of 0:1 represents the glucose pyrolysis case in the absence of NaOH. The total sample weights used were 0.64 g (0:1 case), 0.98 g (0:2:1 case), 2.35 g (1:1 case), 3.44 g (2:1 case), and 3.90 g (10:1 case), respectively. On the basis of preliminary results performed using different thicknesses of NaOH/glucose mixture layers, there was no significant mass transfer limitation observed for this type of batch experiment. The amount of glucose was kept above 0.14 g to maintain CO concentrations within the detectable range of the GC. The extent and kinetics of the reaction were determined on the basis of the online GC measurements as described earlier.

2.3. Solid Product Characterization. At the end of each run, the remaining solids were collected and analyzed using Raman and 13C nuclear magnetic resonance (NMR) spectroscopies. Raman data were collected at room temperature using a LabRAM ARAMIS spectrometer (Horiba JobinYvon) equipped with a microscope and a 40X objective, employing a 325 nm UV laser and 1200 grooves/mm grating. Measurements were performed on a glass slide with an exposure time of 20 s. Five scans were collected for each sample to improve the signal-to-noise ratio. The 13C spectra of the solid products were also obtained using a 300 MHz NMR spectrometer (DPX 300, Bruker Bio Spin Co.). This was done to confirm and quantify the formation of Na2CO3 resulting from the reaction of D-(+)-glucose and NaOH. A sample of pyrolyzed glucose and standards of Na2CO3 and unpyrolyzed D-(+)-glucose were also analyzed via the same solid analyses methods for comparison. For the NMR measurements, products were dissolved in D2O, with acetonitrile-d3 added as an internal reference except in the cases of the D-(+)-glucose and Na2CO3 standards. The diluted solid product was then added to 5 mm diameter NMR tubes (Wilmad), and the analyses were performed overnight to enhance the signal-to-noise ratio.

3. RESULTS AND DISCUSSION

Most of the prior work performed on alkaline thermal treatment reported high H2 conversions and very low concentrations of COx while collecting very limited information on gaseous products other than H2, CO, CO2, and CH4. Thus, an extensive gas analysis was performed to identify all of the gaseous products using the Agilent 7890A GC/5975C MS based on the NIST MS Search 2.0 library. The total gaseous products were collected in a 40 L Tedlar bag, manufactured by Grace, and at the end of the experiment the bag was well mixed prior to gas sampling to obtain the average concentration of gaseous products. As shown in the GC spectrum given in the Supporting Information, there were peaks associated with gases other than those four reported by prior work. The identified gases include H2, CH4, C2H6, C2H4, CO, and other tracer gases (possibly C3 and C4 hydrocarbons as well as benzene and toluene). Some of these gases were quantified to evaluate their impact on the purity of H2 produced. It was found that, although larger gaseous molecules such as C2H6 and C2H4 were formed during the alkaline thermal treatment of glucose, as shown in Table 1, which lists typical compositions of gaseous products, their amounts were significantly lower than those of both H2 and CH4. Therefore, for the kinetic experiments, the gas analysis was focused on the two major gaseous products, H2 and CH4, which accounted for >98% of gaseous products, to increase the online gas sampling frequency. The formation of CO and CO2 was also monitored throughout the experiments because CO is the primary poison to the catalyst in a PEM fuel cell and CO2 is a greenhouse gas. As the Agilent 7890A GC method was designed to only measure these four gases to increase the online sampling frequency, spikes in concentration of other gaseous side products may have been undetected during data acquisition.

Table 1. Average Concentration of Each Gaseous Product from the Alkaline Thermal Treatment of Glucose*  
<table>
<thead>
<tr>
<th>gaseous product</th>
<th>concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>82.22</td>
</tr>
<tr>
<td>CH4</td>
<td>16.00</td>
</tr>
<tr>
<td>CO</td>
<td>0.06</td>
</tr>
<tr>
<td>CO2</td>
<td>0.00</td>
</tr>
<tr>
<td>C2H6</td>
<td>0.94</td>
</tr>
<tr>
<td>C2H4</td>
<td>0.23</td>
</tr>
<tr>
<td>others*</td>
<td>0.58</td>
</tr>
</tbody>
</table>

*The final reaction temperature of 523 K, stoichiometric ratio of NaOH and glucose. For example, C2H6, C2H4, benzene, toluene.
Figure 2 shows a typical output of the alkaline thermal treatment of glucose in terms of the formation rates of the four gaseous products: H₂, CO, CH₄, and CO₂. This particular result was obtained for a stoichiometric mixture of NaOH and glucose reacted at the final temperature of 573 K with a ramping rate of 1 K/min. The upper operating temperature was chosen to be 573 K for the temperature scan study because the melting temperature of NaOH is 591 K and the prior work has reported that the best kinetics for H₂ formation occur below 573 K. The molar formation rates were obtained on the basis of the concentrations measured by the GC and the given flow rate of the inert carrier gas, N₂. The detection limits of the GC for H₂ and carbonaceous species were 3.7 and 3.7 × 10⁻³ μmol/min, respectively. As shown in Figure 2, H₂ starts to form at around 390 K, and its formation was sustained during the temperature ramping with a maximum formation rate around 537 K. As the reaction progressed isothermally, there was a slow decrease in the H₂ formation rate due to the depletion of reactants in the batch reactor. The experimental run was stopped as the H₂ concentration fell below the GC's detection limit, which is marked as a dotted line in Figure 2. The formation rate of CH₄ followed a trend similar to that of H₂, with a slight delay in the onset formation temperature, and achieved the maximum rate at around 550 K. Its formation rate was significantly lower than H₂ until 537 K. Thus, to maximize the H₂ formation rate in the product gas stream while minimizing carbonaceous gaseous side products, it is suggested to maintain the reaction temperature lower than 537 K. Despite the high CH₄ formation at this temperature, PEM fuel cells can operate with CH₄ concentrations as high as 30%, which is higher than the concentration of CH₄ observed here. CO₂ was not detected throughout the temperature scan experiments from 298 to 573 K for a stoichiometric ratio of NaOH and glucose, while there was a small amount of CO formation between 480 and 573 K. Even at their maximum formation rates, the CO generation rate was about 3 orders of magnitude below the H₂ production rate, illustrating suppressed CO₂ generation during the alkaline thermal treatment of glucose. Similar trends in the gaseous product formation rates were observed for the rest of the study investigating the effects of the final reaction temperature and the reactant ratios; however, the actual temperature ranges associated with the formation of each gaseous species were slightly varied. Particularly, the onset temperature for the CO formation was not as reproducible as it was for H₂ because the CO concentrations were always very close to the GC's detection limit of 1 ppm and the kinetics of the solid–solid reaction was complicated by mass and heat transfer throughout the system. However, the integrated amount of gas production obtained by integrating the GC's online measurements was relatively consistent throughout the study. Therefore, most of the experimental results were discussed in terms of H₂ conversion and the total amounts of gaseous products formed, both obtained on the basis of the integration of the GC data.

3.1. Effect of Final Reaction Temperature. The first parameter explored in the alkaline thermal treatment reaction of glucose was the reaction temperature. On the basis of the temperature scan experiment shown in Figure 2, it was suspected that the optimum reaction temperature would be around 540 K, where the maximum H₂ production occurred. To systematically analyze the effect of the reaction temperature, a series of experiments was performed setting the final isothermal reaction temperature as 373, 423, 473, 523, and 573 K. To obtain the total molar production of gaseous products for each experiment, the molar formation rate versus time curves obtained using the GC, typified in Figure 2, were integrated via the Newman–Cotes method. The H₂ conversion was then calculated on the basis of the stoichiometric ratio given in reaction 2, where H₂ conversion of 100% was defined as 12 mol of H₂ produced for every mole of glucose present at the start of the experiment. Note that in all experimental results given in the study, error bars represent the range of values observed in repeated experiments. As shown in Figure 3, from 373 to 523 K the H₂ conversion steadily increased from 0.6% to 27.1% due to improved kinetics with increasing temperature. However, the H₂ conversion did not change significantly from 523 to 573 K, with a slight increase from 27.1% to 29.5%. Because the alkaline thermal treatment of glucose is an exothermic reaction (ΔH = -1220 kJ/mol-glucose (573 K)), there was an optimal reaction temperature of 523 K in this study that was chosen to balance between the kinetics and thermodynamics of the reaction. The maximum H₂ conversions achieved were comparable to those found in the literature. Ishida et al. reported about 40% H₂ conversion for the noncatalytic alkaline thermal treatment of glucose. The difference between this study and Ishida et al.'s study was due to their higher final reaction temperature of 773 K. They observed a small secondary peak of H₂ formation.
between 650 and 773 K, which accounted for the remaining 10% of H2 conversion.

In addition to enhanced H2 production, the development of the alkaline thermal treatment of biomass requires suppressed CO formation to minimize the subsequent gas cleanup steps. Thus, the total generation of CO, as well as CO2 and CH4, all gases that were not reported in the previous study of the noncatalytic alkaline thermal treatment of glucose,21 was investigated at each reaction temperature and compared to H2 production. As discussed in the experimental section, it was not possible to measure the concentrations of all of the gaseous products during the kinetic studies due to the GC sampling time. Thus, instead of reporting the results in terms of concentrations, the molar ratios of each gaseous product to initial moles of glucose were reported to represent the extent of their formation during each experiment. As shown in Figure 4, the production of both H2 and CH4 increased with increasing temperature to 523 K, and stayed roughly constant upon further temperature increase to 573 K. On the basis of the analysis of the total gaseous products, it was found that the selectivity toward H2 increased at lower reaction temperatures. For the highest overall H2 generation, which occurred at 573 K, the CH4 concentration was about 1/4 of H2, which is still under the range of the CH4 limit of PEM fuel cells. In case of CO2 species, CO2 was never detected throughout the experiments. Their data points are located at 10−5 mol-product/mol-glucose in Figure 4, which corresponds to the GC’s detection limit for CO2 compounds. The zero formation of CO2 suggests that one of the roles of NaOH in the alkaline thermal treatment of glucose is CO2 capture via a carbonation reaction.

CO showed a trend of increased production from negligible values to 4.4 × 10−4 mol/mol-glucose at 573 K. However, even at the maximum values at 523 and 573 K, the molar ratio of CO was well over 3 orders of magnitude lower than those of H2 and CH4 for the same initial amount of glucose. The variability observed in the CO values was most likely due to operating near the GC’s detection limit for CO of 1 ppm. It is important to report these values of CO because most of the prior work could not report low concentration values due to their GC’s high detection limit of 30 ppm.

Considering both H2 production and CO generation shown in Figures 3 and 4, 523 K was suggested to be the optimum reaction temperature for the alkaline thermal treatment reaction of glucose with suppressed CO2 generation. Therefore, the rest of the study was performed at 523 K.

3.2. Effect of Reactant Ratios. To further examine the role of NaOH in the alkaline thermal treatment of glucose, varying concentrations of NaOH with glucose were tested: the normalized NaOH:glucose ratios of 0:1, 0.2:1, 1:1, 5:1, and 10:1, where 1:1 corresponds to the stoichiometric ratio of 12:1 NaOH:glucose. The temperature ramping rate was kept at 1 K/min with a final isothermal reaction temperature of 523 K. The ratio of 0:1 represents the glucose pyrolysis case in the absence of NaOH.

As shown in Figure 5, NaOH-lean cases of 0:1 and 0.2:1 resulted in significantly less H2 conversion; in fact, no H2 was produced in the absence of NaOH as was also reported in many studies performed on glucose pyrolysis at low temperatures.27–29 The pyrolysis of glucose does produce H2, but this generally occurs at much higher temperatures around 775–1025 K.30 Considering the given reaction temperature of 523 K, this demonstrates the importance of NaOH in altering the decomposition reactions of glucose employed in this study. The maximum H2 conversion of 27% was observed for the 1:1 case. For the NaOH-rich cases, the H2 production slightly decreased from its maximum value. This may be due to heat and mass transfer issues within this complex solid—solid reactive system. Because there are a number of parallel or competing reactions occurring (e.g., glucose decomposition with possible reaction with NaOH, CO2 carbonation, and pyrolysis), the excess NaOH may have played a different role in glucose conversion to H2.

In addition to H2 conversion, the normalized concentrations of other gaseous products as a function of the reactant ratio were investigated, with the results presented in Figure 6. The minimum value of the y-axis for H2 was 10−2 mol-H2/mol-glucose, whereas that for the carbonaceous species was 10−5 mol-product/mol-glucose due to their different GC detection limits. The most important finding from these experiments was the sharp increase in H2 and CH4 production, coupled with the sharp decrease in CO and CO2 production, with increased NaOH concentration in the system from 0:1 to 1:1. The improvement in H2 production and CO2 suppression was sustained but not improved as the amount of NaOH was further increased to the normalized NaOH:glucose ratio of 10:1. Therefore, in terms of balancing high H2 production with

Figure 4. Comparison of the total amount of each gaseous product formed, per mole of glucose, for a stoichiometric mixture of NaOH and glucose (12:1 NaOH to glucose on molar basis) as a function of the final reactor temperature. Reaction temperature programming: 298 K → given final temperature at 1 K/min and isothermal at final temperature until [H2] fell below the GC’s H2 detection limit of 0.1%.

Figure 5. Conversion to H2 for varying normalized NaOH:glucose ratios (1:1 normalized NaOH:glucose ratio corresponds to the stoichiometric ratio, which is 12:1 NaOH to glucose on molar basis). Reaction temperature programming: 298 → 523 at 1 K/min and isothermal at 523 K until [H2] fell below the GC’s H2 detection limit of 0.1%. The NaOH:glucose ratio of 0:1 represents glucose pyrolysis conditions.
the minimization of CO and CO₂ formation, it was concluded that the optimum normalized ratio of NaOH to glucose for the alkaline thermal treatment system was 1:1, which corresponds to the stoichiometric ratio, which is 12:1 NaOH to glucose on molar basis. Because no CO₂ was detected in the case of the stoichiometric system as well as all systems NaOH-rich of stoichiometric, this was again indicative of the carbonation of CO₂ by NaOH, forming a solid carbonate product. The CO production per mole of glucose had a slight increase of about 4 times from the 1:1 case to the 10:1 case; however, the increase was not significant as it was within the error range.

Because the effect of the reactant ratios was most predominant between the normalized NaOH:glucose ratios of 0:1 and 1:1, those cases were further investigated in terms of the formation rates of gaseous products to gain further insight into the role of NaOH and the potential reactions that may be occurring in the alkaline thermal treatment system. The three cases selected for this part of the study were: two cases of alkaline thermal treatment (i.e., the normalized NaOH:glucose ratios of 0.2:1 and 1:1), and glucose pyrolysis (i.e., the normalized NaOH:glucose ratio of 0:1). As described in Figure 7, in all cases, the reactant(s) were first heated from room temperature to the final temperature of 523 K at a constant rate of 1 K/min, where the reaction was performed isothermally until the H₂ concentration fell below the GC’s H₂ detection limit of 0.1%.

Several immediate differences were noted. First, as shown in Figure 7a, the H₂ production was a strong function of the amount of NaOH added. H₂ was not produced through glucose pyrolysis, but significant amounts of H₂ were produced during the alkaline thermal treatment of glucose. For the 0.2:1 case,
the formation rate peaked at 50 μmol/min just as the reactor temperature reached 523 K. In the 1:1 case, the peak H₂ formation rate occurred at the same temperature of 523 K, reaching 138 μmol/min; however, the onset temperature of H₂ formation was lower than that of 0:2:1 case. Comparing the 0:2:1 and 1:1 cases, both started by following very similar production trends. In the 1:1 case, though, the H₂ production was sustained for longer, resulting in greater overall production of H₂ for the same initial amount of glucose. This confirmed that NaOH played an important role in producing H₂ from solid materials containing C, H, and O such as glucose.

In case of the CH₄ formation, it was found that the maximum CH₄ formation rate was 4 orders of magnitude lower in glucose pyrolysis than in the 1:1 case of alkaline thermal treatment (Figure 7b). In glucose pyrolysis, the onset of CH₄ formation was not seen until well after the reactor temperature had reached 523 K, and its production was short-lived as well as minimal, reaching a maximum molar flow rate of 4.6 × 10⁻³ μmol/min. In fact, the temperatures associated with the onset production of gaseous products and the maximum formation rates did not vary significantly with the addition of NaOH, except for the case of CH₄. The formation of CH₄ was accelerated to lower temperatures as greater concentrations of NaOH were added to glucose. With the addition of NaOH in the 0:2:1 case, the onset temperature for CH₄ production was significantly lowered by nearly 100 K, and the overall CH₄ formation dramatically increased, reaching a maximum molar formation rate of 1.7 μmol/min at 523 K. As in the case of H₂, further increase in NaOH content in the reactants to 1:1 caused a greater maximum CH₄ formation rate, reaching a maximum rate of 64 μmol/min at 523 K. Thus, it was quite clear that NaOH enhanced the production of CH₄ in the thermal conversion of glucose, pointing to an altered reaction mechanism from glucose pyrolysis, one that may be coupled to H₂.

Next, both CO and CO₂ formation rates were investigated for the same experimental sets. As shown in Figure 7c and d, in glucose pyrolysis (0:1 case), the significant gaseous products formed were CO and CO₂. The maximum CO formation rate was lowest for the 1:1 alkaline thermal treatment case, at 3.1 × 10⁻² μmol/min, which was over a magnitude lower than that for the 0:2:1 case and nearly 2 orders of magnitude lower than that for the glucose pyrolysis case. In the 1:1 case, that of the highest NaOH content, CO formation was terminated before H₂ formation was completed; however, in the 0:2:1 case of lower NaOH content, CO formation continued even after the termination of H₂ formation.

In terms of the CO₂ formation, it was nonexistent for the 1:1 alkaline thermal treatment case, whereas lower or zero NaOH content in the reactant(s) resulted in significant formation of CO₂ during the thermal conversion of glucose. The onset temperatures of the CO₂ formation were similar in the 0:1 and 0:2:1 cases; however, the peak CO₂ formation rate was about an order of magnitude higher in the case of glucose pyrolysis (3.7 μmol/min) than in the 0:2:1 case (0.28 μmol/min). As was previously discussed, the absence of CO₂ in the product gas in the 1:1 case of the alkaline thermal treatment of glucose was likely due to the carbonation reaction. Thus, it was concluded that NaOH suppresses the formation of CO₂ compounds during the thermal conversion of glucose.

There have been significant efforts to identify the reaction mechanisms of the pyrolysis of biomass (e.g., cellulose and glucose), and due to the complexity of the reactions, many reaction pathways have been suggested. Although many of the pyrolysis studies in the literature were performed at significantly higher temperatures than those investigated this study (0:1 case), the formation of CO₃ compounds and the absence of H₂ in the product gas at lower temperatures were analogous in many of the studies. In terms of H₂ production, fast pyrolysis processes performed at higher temperatures are more favorable.31 Regarding the gaseous products formed during low temperature pyrolysis, Bassilakis et al. performed interesting TG-FTIR tests on the pyrolysis products of biomasses, including glucose. They reported the trends of the formation rates as a function of the reaction temperature, which were very similar to those shown in Figure 7.27 Some have suggested that the predominance of CO and CO₂ in the product gas of glucose pyrolysis may be explained by pathways that lead to decarboxylation and decarboxylation, respectively.28

The chemistry of biomass undergoing pyrolytic heat treatment is already complex, and with the addition of additives such as NaOH, different reaction pathways become available. There are a number of possible reactions that could explain the observed trends of increased H₂ and CH₄ formation with decreased CO and CO₂ formation in the presence of NaOH. One of the potential sets of reaction pathways could involve the reaction between NaOH and the CO₃ compounds produced via glucose pyrolysis. As glucose pyrolysis occurs, the generated CO and CO₂ could be consumed by NaOH through reactions 4 and 5:

\[
CO_2(g) + 2NaOH(s) = Na_2CO_3(s) + H_2O(g) \tag{4}
\]

\[
CO(g) + 2NaOH(s) = Na_2CO_3(s) + H_2(g) \tag{5}
\]

These reaction schemes would account for the observed H₂ formation and decreased CO and CO₂ generation during the thermal conversion of glucose in the presence of NaOH. Considering the carbonation by NaOH is a fast reaction, it is expected that NaOH likely played an important role in the absence of CO₂ during the alkaline thermal treatment of glucose.

Two other possible reaction pathways that would enhance H₂ and CH₄ formations during the alkaline thermal treatment of glucose are the dehydrogenation of glucose as well as its decomposition into alkylated and hydroxylated carbonyl compounds in the presence of a strong base such as NaOH. Su et al. claimed dehydrogenation as the main reaction mechanism of cellulose decomposition over a combined gasification and water–gas shift reaction when the alkaline thermal treatment reaction was performed using their novel NaOH-containing ionic catalyst, because H₂ production is not favored at low temperatures (403–473 K) in the case of the endothermic gasification reaction.16 Onwudili and Williams suggested glucose decomposition into alkylated and hydroxylated carbonyl compounds as a possibility after studying the effect of NaOH on the hydrothermal gasification of glucose, as opposed to the dehydration and polymerization pathway observed in glucose pyrolysis in the absence of NaOH. The H₂ production can be explained by the high concentration of water in their system, which may have led to water–gas shift reaction when the smaller carbonyl and hydroxylated carbonyl compounds reacted with water.32 Another study also reported that NaOH increased yields of carbonyl compounds and carboxylic acids during glucose pyrolysis at 548 K, while in the absence of NaOH the major pyrolysis products were furan and...
sugar derivatives. The subsequent decomposition pathways for the furan and sugar derivatives are likely different from those for the NaOH-induced alkylated and carboxylic acid compounds, which may also explain the composition of the gaseous products generated from the alkaline thermal treatment of glucose.

The drop in the CO formation with the rise in the CH₄ generation in the presence of NaOH, particularly at high NaOH content, could also be contributed by the methanation reaction given in reactions 6 and 7:

\[
2\text{CO}(g) + 2\text{H}_2(g) = \text{CH}_4(g) + \text{CO}_2(g) \quad (6)
\]

\[
\text{C}(s) + 2\text{H}_2(g) = \text{CH}_4(g) \quad (7)
\]

These possible reactions may have also lowered the overall estimated H₂ conversion based on the stoichiometric ratio given in reaction 2, as both consume H₂. Ishida et al. reported that for the case of cellulose, with the proper catalyst, CH₄ formation was suppressed and the overall H₂ conversion was improved. Further investigation is desired to fully understand the reaction mechanisms that produce high purity H₂ via the catalytic alkaline thermal treatment of glucose.

**3.3. Production Rate versus H₂ Purity.** Because the alkaline thermal treatment of glucose produces H₂ with suppressed CO formation, the gaseous product could be a good candidate as a fuel for fuel cell applications such as in the PEM fuel cell. The fuel requirement for a PEM fuel cell primarily includes the CO concentration to be below 10 ppm. This should be achieved while producing H₂ at a sufficient formation rate. Thus, for the optimized reaction temperature of 523 K and the stoichiometric ratio of NaOH and glucose, a fast kinetic study was performed while monitoring online gas compositions and the formation rate of total gaseous products. For this particular online analysis, the Inficon 3000 Micro GC was used, as it extended the gas quantification out to C₆H₆ with minimal run times of 4 min. As this study included C₆H₆, the third most significant overall gas product at nearly 1% concentration, shown in Table 1, the Micro GC was able to quantify gases that made up over 99% of the overall gaseous product. Thus, online concentrations can be reported more accurately; however, as in the other studies conducted with the Agilent 7890A GC, it is still possible that spikes of other larger hydrocarbons may have gone undetected, making the reported concentrations here upper limits. Again, the experiment was terminated once the H₂ concentration fell below the detection limit of the Micro GC of 0.1%.

As shown in Figure 8a, low concentrations of CO ranging from 270 to 578 ppm were detected at high temperature conditions close to the final reaction temperature of 523 K. These values corresponded very closely to the detection limit of the Micro GC of 10 ppm when considering the presence of the large amounts of the N₂ carrier gas in the product stream, which was not included in the concentration calculation. Although the actual concentrations of CO were above the 10 ppm threshold for a PEM fuel cell, these concentrations were still relatively low as compared to that of other biomass conversion reactions such as gasification and pyrolysis. Without the additional processes, the fuel streams produced by these technologies contain significant amounts of carbon, which challenges their utilization in PEM fuel cell technologies. To further reduce the CO formation during the alkaline thermal treatment of glucose, faster ramping rates could be employed, because a preliminary study has shown that negligible CO formation was observed in the experiments described herein conducted at ramping rates of 10 and 20 K/min instead of 1 K/min, while hydrogen formation remained constant among various ramping rates. The final reaction temperature could be lowered or water could also be added to perform in situ water–gas shift reaction to further reduce the CO concentration in the product gas. Nevertheless, these measures should be applied only when the overall H₂ production rates can be maintained. For instance, the highest purity of H₂ was seen at lower reaction temperatures; however, the reaction kinetics limited the total formation rate of the gaseous products. Therefore, the optimization between the production rate and the H₂ purity would be an important factor for the optimization of the proposed alkaline thermal conversion of biomass.

As shown in Figure 8b, at higher reaction temperatures, the reaction kinetics allowed for much greater total gaseous product formation; however, side products began to significantly impact H₂ purity. The primary diluent for H₂ was CH₄, peaking at 42%, but fortunately occurring well after the reactor had reached 523 K. Although not a poison to the PEM fuel cell at lower concentrations (<30%), CH₄ may need to be removed prior to the use of the product gas in a PEM fuel cell to achieve a higher H₂ concentration in the fuel stream. The reduction of CH₄ during the alkaline thermal treatment of biomass (e.g., glucose, cellulose) can be accomplished through Ni-based catalysis. This will allow for the operation of the alkaline thermal treatment process at the kinetically favorable temperature of 523 K. Regarding C₆H₆, it peaked at nearly 8% concentration, again well after the reactor reached isothermal
conditions. Its formation was not detected until after the reactor had been operated isothermally at 523 K for 24 min. This indicates that the formation of C2H6 may be related to reactions of the lighter gases with the charred solid products, rather than being directly related to the alkaline thermal treatment process. Thus, in a continuous reactor system where the gaseous and solid products can be continuously removed, the production of C2H6 could be significantly reduced or avoided.

3.4. Solid Product Characterization. Unfortunately, there have been only limited analyses done on the solid products of the alkaline thermal treatment of biomass. Some reported that when cellulose was prepared via a pretreatment using NaOH solution, the final solid products were mainly Na2CO3. However, this may not be true for the case of solid–solid reactions proposed in this study. Thus, a series of experiments including Raman and 13C NMR analyses were performed to characterize and identify the composition of the solid products. The Raman spectrum of the solid product obtained from the optimal case, which was for a stoichiometric ratio of NaOH:Glucose mixture and reaction temperature of 523 K with ramping rate of 1 K/min, was compared to those of pyrolyzed glucose, pure Na2CO3, and pure D-(+)-glucose. As shown in Figure 9, the solid product from the alkaline thermal treatment experiment named “1:1 sample” exhibited quite different peak patterns as compared to D-(+)-glucose, indicating that glucose was definitely chemically converted. The formation of Na2CO3 in the alkaline thermal treatment sample was confirmed with the band at 1076 cm-1. Although Na2CO3 should be the only product in the 1:1 sample based on reaction 2, the formation of side-products was also evidenced by the presence of additional Raman bands at 1601 and 1371 cm-1. The exact assignment of those bands to specific vibrations is very challenging without the aid of other analytical techniques. It is likely that they are related to C-H, C-O-C, and C≡C stretching from carbonaceous side-products.

To further confirm the presence of Na2CO3 and quantify its content in the solid product, 13C NMR analysis was performed on three alkaline thermal treatment samples, each with a different normalized NaOH:glucose ratio, 0.2:1, 1:1, and 5:1 cases, as well as pyrolyzed glucose, pure Na2CO3, and pure D-(+)-glucose. Figure 10 shows six spectra, with the top being that of Na2CO3, followed by unpyrolyzed D-(+)-glucose, pyrolyzed glucose, the 0.2:1 sample, then the 1:1 sample, and finally the 5:1 sample. Like in the Raman results, the formation of Na2CO3 was confirmed for all alkaline thermal treatment samples by the presence of the carbonate peak, here at ~170 ppm. The carbonate peaks were integrated and compared against the area of the internal reference acetonitrile-d3 peak at ~120 ppm to obtain the molar quantity of Na2CO3 in the analyzed solid samples. The conversion in terms of the carbonate formation was then calculated by taking the ratio of Na2CO3 present in the sample to the theoretical moles of Na2CO3 given by reaction 2. On the basis of this method, the conversions were estimated to be 14.4%, 30.5%, and 15.4% for the normalized NaOH:glucose ratios of 0.2:1, 1:1, and 5:1, respectively, while the conversions calculated on the basis of the H2 formation (derived from the data presented in Figure 5) were 10.0%, 29.8%, and 27.0%, respectively. Interestingly, the conversions estimated in terms of H2 and Na2CO3 formations match well for the case of the stoichiometric mixture of reactants, while particularly the glucose-rich case of the 0.2:1 sample resulted in a greater conversion when it was estimated on the basis of the Na2CO3 formation. Regarding the lower conversion observed on the basis of the Na2CO3 formation method as compared to the H2 formation method for the 5:1 case, the difference observed between two methods of estimating conversions may have been due to incomplete dissolution of the solid products in D2O. Because liquid-state NMR was used to quantify Na2CO3 content in solid samples, the accuracy of the measurement was highly dependent on the complete dissolution of the solid samples. Unfortunately, some of the solid byproducts of the alkaline thermal treatment of glucose were insoluble carbonaceous materials, and those may have formed around the Na2CO3 particles, potentially locking in the carbonate and rendering it undetectable in the liquid sample by the 13C NMR, thus leading to a lower estimate of conversion when compared to the H2 formation method. The partial conversion of glucose to these insoluble carbonaceous materials may have also contributed to the incomplete conversion to H2 in stoichiometric and NaOH-rich cases. Therefore, a solid-state NMR method has been
suggested to be an alternative choice for the Na₂CO₃ quantification in solid samples, and it is now a part of ongoing effort.

In addition to the carbonate peak, additional peaks were observed in the spectrum of the 0.2:1 sample and to lesser extents in the 5:1 and 1:1 samples. These peaks were different from those observed for pure glucose and indicated the presence of other carbonaceous materials, which were most pronounced in the glucose-rich 0.2:1 case. The pyrolyzed D-(+)-glucose sample was difficult to dissolve in D₂O, and its spectrum did not show any peaks associated with carbonaceous compounds. This also indirectly supports the earlier discussion on the role of NaOH during the thermal conversion of glucose, suppressing dehydration and polymerization pathways. The presence of carbonyl-containing (C=O) species. Again, the precise assignments of these peaks to specific compounds remain challenging given the complexity of the reactions.

4. CONCLUSIONS

The alkaline thermal treatment of biomass is one of the novel biomass conversion technologies that has recently been proposed. Some have studied the effect of catalysts on the H₂ production; however, the reactions involved in the alkaline thermal treatment process are still poorly understood. In this study, the noncatalytic solid–solid alkaline thermal treatment reaction was investigated to produce H₂ with suppressed CO formation. A series of experiments involving online gas analysis and solid characterization was conducted to provide insight into the reaction kinetics and mechanisms. In particular, the effects of reaction temperature and reactant ratios were studied in terms of H₂ conversion and formation rates of the major gaseous products. It was found that higher temperatures promoted increased H₂ production through better kinetics, while there was an optimal reaction temperature based on both the thermodynamics of the reaction as well as the melting temperature of NaOH. The hydroxide, NaOH, was found to facilitate H₂ production, promote CH₄ formation, and suppress CO and CO₂ production. In fact, CO₂ was almost nonexistent in most of the gaseous products. The amount of NaOH also impacted the quality and the formation rates of H₂ in the product stream. The 1:1 stoichiometric NaOH/glucose ratio exhibited the best performance, while both glucose-rich and NaOH-rich cases suffered from possible mass and heat transfer issues and possible undesirable side reactions. For glucose-rich cases, a significant degree of pyrolysis may have occurred resulting in increased CO formation. The solids analyses using Raman and ¹³C NMR confirmed the formation of Na₂CO₃ during the alkaline thermal treatment of glucose, but more in-depth study on the solids is desired to fully understand the complex reaction mechanisms. Insight gained from this work will be applied to future studies with cellulose as well as to the incorporation of novel catalysts.

# ASSOCIATED CONTENT

Supporting Information

Full GC/TCD/FID spectrum of the gaseous products formed from the alkaline thermal treatment of glucose. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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