Obtaining High Yield Hydrogen from Sewage Sludge by Two-Stage Gasification: Alkaline Pyrolysis Coupled with Catalytic Reforming

Fan Wang,* Jinyi Wang, Zhiyong Yu, Jingbin Ma, Liping Liu, Tao Wang, and Haijiao Guo

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ABSTRACT: Municipal sludge is a sizable byproduct of sewage treatment plants, and its treatment and disposal need to agree with both environmental protection and resource utilization policies. In this study, municipal sludge was treated to produce hydrogen as a resource. A two-stage reactor was employed, and alkaline pyrolysis was coupled with ex-situ catalytic gasification and optimized to promote hydrogen production from sludge. The gas production characteristics were analyzed under different gasification parameters, and the catalyst was characterized following the reaction. Optimal gasification conditions were found at a steam flow of 5 mL h\(^{-1}\) in which 34.23 mmol g\(^{-1}\) of hydrogen was produced from dry sludge. Results suggested that the increased amount of hydrogen produced was due to promoting the water gas shift reaction. A brief economic analysis showed that this process is feasible for use in future industrial applications and provides an effective process route for the resource treatment of sludge.

1. INTRODUCTION

Hydrogen (H\(_2\)) is a clean energy source, and its production and use are of great significance for reducing carbon emissions and achieving carbon neutrality. At present, 90% of H\(_2\) is obtained from a natural gas reformation reaction; however, biomass energy, which is renewable and abundant, can also be used to produce H\(_2\) and replace the use of fossil fuels. Municipal sludge is a type of biomass waste that is difficult to treat, and it has a negative effect on the environment. With the increase in urbanization and the associated population, the amount of sludge produced has also increased. The safe disposal of this sludge is considered in China’s Action Plan for Water Pollution Prevention and Control, and the production of H\(_2\) from sludge thermochemistry is a widely used resource.

The production of H\(_2\) from the pyrolysis gasification of sludge requires a high temperature (>700 °C), and the associated energy consumption affects the economic benefits of using the technology. However, alkaline pyrolysis technology has the advantages of enhancing H\(_2\) production at a low-temperature and enabling the in situ capture of carbon. For example, NaOH promotes the low-temperature production of H\(_2\) while achieving negative carbon emissions when producing H\(_2\) during biomass alkaline pyrolysis reactions. The reduction in the reaction temperature during alkaline pyrolysis also means that certain volatiles cannot be completely degraded, which means ex-situ catalytic reaction downstream of alkaline pyrolysis that effectively increases H\(_2\) production is necessary. Ni/ZrO\(_2\) is one of the most widely used catalysts in this respect, Ni promotes the rearrangement of aromatic rings and dehydration of the decarboxylation reactions, ZrO\(_2\) inhibits the methanation reaction, and it can be derived from zirconium-based waste, which can achieve repeated use of solid waste. Therefore, the demand for an increase in H\(_2\) production can be met through the use of alkaline pyrolysis coupled with ex-situ catalytic gasification. H\(_2\) production has been increased from 2.81 mmol g\(^{-1}\) to 29.03 mmol g\(^{-1}\) sludge, dry basis, using this process.

Studies have shown that H\(_2\) production can be further improved by employing steam gasification. In the study of pyrolysis gas production from sludge in a fixed-bed reactor, the production of H\(_2\) was increased by approximately 60% when steam was added. In terms of industrial applications, gasification is also of practical significance. For example, a total 2260 kJ of energy is required to remove 1 kg of water during sludge dewatering, and if wet sludge could be used to produce H\(_2\), the amount of energy consumed by sludge dewatering would be reduced. Studies have shown that in the case of adding steam (external water), the generation of H\(_2\)
and the formation behavior of biomass that has not been dehydrated are very similar to those of dry biomass when using alkaline pyrolysis with steam. Therefore, a theoretical basis exists for simulating the pyrolysis process of actual sludge by using dry sludge with steam. In this respect, to further improve H2 production and provide theoretical support for practical applications, this study optimizes the process of alkaline pyrolysis coupled with ex-situ catalytic gasification to improve H2 production, with the aim of further increasing the production of H2 during the resource utilization of biomass waste.

2. MATERIALS AND METHODS

2.1. Materials Used in Experiment. Sludge samples were obtained from the Sixth Sewage Treatment Plant of Yunnan Province. The results of proximate analysis and ultimate analysis of sludge can be found in a previous study. The same Ni/DW catalysts employed in previous studies were used here, and a catalyst with a theoretical Ni loading of 10% was selected for conducting the reaction in this study.

2.2. Experimental Methods. An injection pump device (HK-400, China) was added to a two-stage reactor to provide steam required for the reaction (Figure 1). The two-way connector upper ventilation port of the two-stage reactor was changed to a three-way connector to enable the steam and nitrogen carriers from the injection pump to simultaneously enter the reactor. The lower steam outlet of the injection pump was located 15 mm above the catalytic layer to allow the steam and nitrogen carrier to mix evenly before passing through the catalytic bed.

In the alkaline pyrolysis stage, the mass of sludge and NaOH (Xilong Chemical Industry, China) was fixed at 0.2 and 0.4 g, respectively. The alkaline pyrolysis stage was heated from 20 to 500 °C at a rate of 10 °C min⁻¹ and then maintained at 500 °C for 72 min. The 10 wt % Ni/DW mass weighed 0.2 g during the catalytic gasification stage, and the temperature was 800 °C. The steam flow parameters were 0 mL h⁻¹, 3 mL h⁻¹, 4 mL h⁻¹, 5 mL h⁻¹, 6 mL h⁻¹, 7 mL h⁻¹, and 10 mL h⁻¹, respectively.

2.3. Analytical Methods. The phase properties of the catalysts after gasification were compared using X-ray diffraction (XRD) (Rigaku D/Max 2500 V+/PC, Cu Kα, scan 2θ = 10–90°, Bruker, Germany), and the XRD patterns were analyzed using a standard pattern database from the International Diffraction Data Center (ICDD).

The microstructure of the catalyst was observed using scanning electron microscopy (SEM) with an accelerating voltage of 10.00 kV (MERLIN VP Compact). Prior to conducting the test, the sample was sprayed with gold at a thickness of approximately 8 nm. The morphology of the catalyst was investigated by SEM and energy dispersive X-ray spectroscopy (SEM-EDS).

The gas flow at the outlet of the tubular furnace was measured using a soap film flowmeter, and the gas composition was analyzed using a micro-gas-chromatograph (3000 Micro GC, INFICON, USA). Gas production was obtained by the curve integral of the generation rate and associated timing of the gas components. Repeatability tests were conducted under optimum reaction conditions, and the error was less than 2%. H2, CH4, CO, and CO2 were the main components of biomass pyrolysis gas and investigated in this study. The analysis method was the same as in a previous study.

3. RESULTS AND DISCUSSION

3.1. Effect of Different Gasification Flow Rates on Hydrogen Production. Figure 2 shows the effect of different steam flow rates on the H2 production rate. The addition of steam significantly increased the H2 production rate, and the maximum H2 production rate was increased by approximately

![Figure 1. Schematic diagram of two-stage reactor.](https://pubs.acs.org/acsomega/article-figs/2022/acsomega.2c00345_01c.png)

![Figure 2. Effect of different steam flow rate on H2 generation rate.](https://pubs.acs.org/acsomega/article-figs/2022/acsomega.2c00345_02c.png)
0.3 mmol min⁻¹ g⁻¹ (5 mL h⁻¹ vs 0 mL h⁻¹). However, with a continuous increase in the steam flow rate, the instantaneous H₂ production rate began to decline. The maximum instantaneous hydrogen production rate was lower at 10 mL h⁻¹ than at 5 mL h⁻¹, and this might have occurred because the high steam flow rate reduced the local reaction temperature. As the catalytic reaction of the Ni catalyst is endothermic, a high temperature is more conducive to the reaction.

Figure 3 shows the effects of different steam flow rates on the production of the four gases. With an increase in the flow rate, the production of H₂ and CO₂ first increased and then decreased, while the production of CO decreased and that of CH₄ first increased, then decreased, and then increased.

The reasons for the gas production changes were further analyzed using the main reaction equations relating to the catalytic section.17,18

\[
\begin{align*}
C_nH_m + mH_2O &\rightarrow mCO + \frac{1}{2}(m+n)H_2 \\
CH_4 + H_2O &\rightarrow CO + 3H_2 \\
C + H_2O &\rightarrow CO + H_2 \\
CH_4 + CO_2 &\rightarrow 2CO + 2H_2 \\
CO + H_2O &\rightarrow CO_2 + H_2 \\
2CO &\rightleftharpoons C + CO_2 \\
C + H_2 &\rightleftharpoons CH_4
\end{align*}
\]

As evident from the above reaction equations, eqs 1–5 are mostly associated with H₂ generation and most of them require the participation of steam. The reactants in these equations include H₂, CO, and CO₂. Equations 1–3 and 5 can be used to describe the reaction that occurs when the steam flow rate increases. When the steam flow rate was less than or equal to 5 mL h⁻¹, H₂ production continued to increase, but when the flow rate was greater than 5 mL h⁻¹, it was not conducive to the progress of the endothermic reaction. Equations 1–4 are all endothermic. The production of H₂ significantly decreased at 10 mL h⁻¹, and this may have been associated with the excessive steam flow and the high-water-content of the carrier gas, which resulted in large numbers of hydroxyl groups on the surface of the catalyst. Hydroxyl groups may have covered part of the active sites of the catalyst, which resulted in a suboptimal catalytic effect. Another reason for this result could be that with an increase in the flow rate, the residence time of steam in the catalytic bed decreased, which reduced the time of the pyrolysis gasification reaction and the H₂ generation reaction.

Some researchers have proposed that an appropriate extension of time maximizes the efficiency of H₂ production by biomass steam reforming.19 Therefore, in this study, to maximize H₂ production, the optimal steam flow rate was set at 5 mL h⁻¹, which resulted in a H₂ production of 34.23 mmol g⁻¹, with an H₂ purity of 81.5%. If converted into the actual sludge moisture content, 5 mL h⁻¹ would be equivalent to sludge with a moisture content of 98%, which is the percentage water content of sludge in the sewage plant after centrifugal precipitation. Therefore, this result is highly significant for practical applications, and it shows that if the reaction conditions (such as the reaction temperature or reactor type) are changed, the optimal steam flow rate will also change. However, it is necessary to provide sufficient steam without reducing the residence time or reaction temperature.

Figure 3 also shows that the production of CO and CO₂ changed after the addition of steam. In this respect, the production of CO decreased significantly and the production of CO₂ increased significantly. However, there was no significant change in the production of CH₄, which shows that eq 5 plays a leading role in the gasification reaction.

When no steam was added, the main function of the catalyst was to promote the reforming of CH₄ to generate CO and H₂ (Figure 4). However, with the addition of steam, the concentration of CO decreased significantly, and the concentration of CO₂ increased significantly. Study has shown that when steam is added, the water gas shift reaction dominates the gasification process (eq 5).20 As evident from these results, with an increase in the flow rate, the concentrations of H₂ and CO in the gas products of sludge pyrolysis both increased and then slightly decreased, while the contents of CH₄ and CO decreased first and then slightly increased. These results indicate that in a certain flow range, an increase in the flow rate changes the balance of the water gas shift reaction in the direction of H₂ generation and promotes the steam reforming reaction of alkanes. With the increased steam flow rate, the slight rise in the contents of CH₄ and CO prior to reducing can also be attributed to a reduction in the
residence time, as this reduced the efficiency of the steam reforming reaction and the water gas shift reaction. The results of this study show that when the flow rate was greater than 5 mL h⁻¹, the effect of the increased steam concentration facilitating the reaction was lower than the effect of the shortened residence time hindering the reaction.

To further clarify the gas generation process during the reaction, the diagrams of the production rates of CH₄, CO, and CO₂ were also analyzed. Figure 5 shows the influence of different steam flow rates on the CH₄ production rate, where it is evident that the instantaneous production rate of CH₄ was very low. This result shows that Ni/DW had a good catalytic effect in CH₄ steam reforming reaction. The first small peak seen in the CH₄ production rate curve (between 400 and 500 °C) was not obvious in any of the cases except that of 5 mL h⁻¹, and the maximum amount of H₂ was produced in the 5 mL h⁻¹ case. H₂ can be produced via dry reforming (eq 4) and wet reforming (eq 2) of CH₄. Nickel-based catalysts have a good catalytic effect in these reactions. The two obvious peaks corresponding to 5 mL h⁻¹ may thus represent the reactions of CH₄ dry reforming (eq 5) and wet reforming (eq 2), respectively. It can be seen from Figure 2 that CO₂ production was at its maximum at this time, which also indicates that it was conducive to the occurrence of dry reforming. However, the CO content was not at its highest because of the occurrence of water gas shift reaction.

A comparison between the instantaneous production rates of CO and CO₂ (Figures 6 and 7) shows that when steam was added, the production rates of CO and CO₂ displayed waning and waxing trends. The addition of steam reduced the peak value of the instantaneous production rate of CO and production (Figure 6), while the peak value of the instantaneous production rate of CO₂ shifted to the right and production increased (Figure 7), which provides further evidence that the appearance of steam significantly enhanced the water gas shift reaction.

3.2. Characterization Analysis of Catalyst after Reaction. The XRD characterization of the catalyst after the gasification reaction (Figure 8) showed that the peak of Ni decreased significantly with the addition of steam. When the flow rate of steam was larger than 5 mL h⁻¹, there was almost no Ni peak, and only the case without steam (0 mL h⁻¹) showed an obvious Ni peak. The peak of NiO increased with an increase in steam flow rate, mainly due to the presence of H₂O, which reacted with Ni to form NiO. However, the catalytic effect of Ni was better than that of NiO, thus, when the steam increased, the content of Ni decreased. This may be another reason why H₂ production did not always increase with the steam flow rate; an increase in the NiO content meant that more H₂ was needed in the reaction to reduce NiO, and Ni played a catalytic role. However, the peaks of Zr₀.₉₂Y₀.₀₈O₁.₉₆
were almost unchanged, which indicates that the catalyst carrier was sufficiently stable.

Figure 9 shows the SEM results of catalyst (with and without steam). A comparison shows that the agglomeration of the catalyst morphology without steam was greater than that with steam, and this may have been due to the reaction between the steam and the carbon deposited on the catalyst (eq 3), which alleviated agglomeration.

Figure 10 shows a photograph of the color of the catalyst under different flow rates of steam. It is obvious that when the steam flow rate was greater than 5 mL h⁻¹, the color of the catalyst became lighter after the reaction, which further proves that the introduction of steam caused the removal of carbon deposited on the catalyst. However, the steam reacted with the carbon deposited and also with Ni; therefore, the excess steam did not necessarily have a favorable effect on the reaction.

As shown in Figure 10, the amount of carbon deposited on the catalyst differed at different flow rates. Raman characterization of the catalyst after different steam flow rates was conducted, and the results are shown in Figure 11.

The D and G peaks of graphite carbon are frequently observed in the Raman characterization of the pyrolysis catalysts. Figure 10 shows that there is no obvious carbon deposition peak (1200–1800 cm⁻¹), which indicates either that there was no obvious carbon deposition on the catalysts or that the amount of carbon deposited was too small to be characterized by Raman: the catalyst therefore provided a good anticarbon deposition performance. Such good resistance to carbon deposition may be associated with the carriers of yttrium-doped ZrO₂. Yttrium is a heavy rare-earth element; it was doped in ZrO₂, which improved the thermal stability of ZrO₂ and moving oxygen atoms were introduced into the crystal structure of ZrO₂. During the high temperature conversion of the biomass, moving oxygen can result in in-situ carbon gasification, which thus promotes the generation of H₂. ZrO₂ with additional doping elements attains a tetragonal phase where the trivalent rare-earth ions are replaced with tetragonal zirconium ions, which results in the formation of oxygen holes and improved ionic conductivity, and this may be one of the reasons for the reduction in the coking rate of the catalyst.²²

Two large peaks appeared near 450 cm⁻¹ and 1000 cm⁻¹, and the peak values increased gradually with an increase in steam flow rate. When the flow rate was 3 mL h⁻¹, 4 mL h⁻¹, and 5 mL h⁻¹, the peak values were not obvious, but when the flow rate was greater than 5 mL h⁻¹, two peaks, and their shoulder peaks nearby, became very prominent. One study showed that these two peaks are NiO peaks, and the Raman spectral peaks of conventional NiO samples are 531 cm⁻¹, 720 cm⁻¹, and 1086 cm⁻¹, respectively. In this respect, the spectral peak of 531 cm⁻¹ is the vibration peak of NiO, while the spectral peak of 720 cm⁻¹ and 1086 cm⁻¹ may be caused by the adsorption of CO₂ on the surface of NiO and the formation of adsorbed carbonate.²³ It is thus possible that with the increase in steam flow rate, the surface area carbon reacts with H₂O to generate CO₂ and the elemental Ni reduced by H₂ in the catalyst further generates NiO with H₂O. CO₂ is then further adsorbed on NiO, resulting in spectral peaks of 720 cm⁻¹ and 1086 cm⁻¹. In addition, under the conditions of 7 mL h⁻¹ and 10 mL h⁻¹, the spectral peak of 720 cm⁻¹ is more obvious. This may be one of the reasons why it is not easy for the catalyst to accumulate carbon. However, the generation of adsorbed carbonate also reduces the catalyst efficiency. Therefore, in the gasification process dominated by water gas shift gasification (exothermic reaction), the local reaction temperature decreases with an increase in steam flow rate; although this is conducive to an exothermic reaction, the production of H₂ does not continue to increase.

### 3.3. Strategies toward Cost Reduction

The process would involve high costs in relation to the cost of NaOH and the use of a nickel-based catalyst. One possible solution for reducing the NaOH costs would be to make reductions via the Ca–Na cycle (Figure 12), and this would also benefit the carbon capture effect. After the alkaline pyrolysis reaction, NaOH captures CO₂ and converts it into Na₂CO₃, and CaCO₃ is produced by the chemical reactions of Na₂CO₃ and Ca(OH)₂. Reaction ४ in Figure 12 can be facilitated by the formation of NaOH by removing the CaCO₃ precipitate from the reaction system. This is a caustizing reaction that is commonly used in the pulp and paper industries. NaOH can then be regenerated from Ca(OH)₂ through a double decomposition reaction, in which Ca(OH)₂ is formed from mineral and industrial alkaline residues. Some researchers have
studied the process of applying regenerated NaOH from a caustic reaction to the alkaline pyrolysis reaction of biomass. Results showed that the regenerated NaOH had a similar H2 production effect to the fresh NaOH, although Na2CO3 and Ca(OH)2 remained in the regenerated NaOH due to the limited solubility of Ca(OH)2. However, this did not affect the performance of Na2CO3 in the alkaline pyrolysis process, and the formation rule of CH4 and the carbon capture effect were not affected.24 These results show that it is feasible to recycle NaOH from Na2CO3 to reduce the cost of alkaline pyrolysis. The CaCO3 produced by the causticizing reaction is calcined to generate CaO and CO2, where CaO reacts with H2O to generate Ca(OH)2. By removing Ca(OH)2 precipitation from the reaction system, reaction ④ in Figure 11 can be facilitated to continuously generate Ca(OH)2. In addition, the CO2 generated by the calcination of CaCO3 can be combined with Ca(OH)2 to generate CaCO3. Theoretically, the economic costs relating to the use of NaOH can be effectively reduced through the Ca–Na cycle. Another idea would be to reduce the economic cost of NaOH by collecting Na2CO3 from the reactants. One ton of Na2CO3 from the Jinan Chaoyixing Chemical Co., Ltd. costs 1500 Yuan25 and one ton of NaOH costs 2000 Yuan.26 According to reaction ① in Figure 12, assuming that the conversion rate of NaOH into Na2CO3 is 80%, 1.06 tons of Na2CO3 can be generated by 1 ton of NaOH costs 2000 Yuan. According to reaction ① in Figure 12, assuming that the conversion rate of NaOH into Na2CO3 is 80%, 1.06 tons of Na2CO3 can be generated by 1 ton of NaOH. Therefore, the cost of using 1 ton of NaOH can be effectively reduced from 2000 Yuan to approximately 500 Yuan, and the economic costs from the use of NaOH can also be effectively reduced.

With respect to the high catalyst price, the carrier of zirconium-based waste is recyclable solid waste with a low separation cost. Although the price of Ni(NO3)2 is relatively high, catalysts in the catalytic stage can be recycled, and relevant studies have shown that nickel-based catalysts have good cycling stability.27,28 Therefore, applying the process in future applications is economically feasible.

4. CONCLUSIONS

Based on the two-stage reaction of alkaline pyrolysis coupled with catalytic reforming, steam was added by modifying the reactor, and the gas production and catalysis were analyzed. The results showed that when the steam was added, H2 production was further improved, and under an optimal steam flow rate of 5 mL h−1, the production of H2 was increased to 34.23 mmol g−1, thus showing an excellent H2 production performance. This study provides theoretical support for the industrial application of producing H2 via the direct thermochemical treatment of sludge with a high-water-content.

The study also shows that municipal sludge has a high H2 production potential under treatment with alkaline pyrolysis, and waste can thus be transformed into a valuable resource. If the material was replaced with biomass waste that has a more volatile content, such as straw or wood waste, the H2 production potential could be further increased. In addition, zirconium-based waste and other waste-based carriers could be used as catalyst carriers to further reduce the cost of the catalysts employed. The results of this study confirm that alkaline pyrolysis coupled with ex-situ catalytic gasification has the potential to be practically applied to produce H2 from municipal sludge.

N Notes

The authors declare no competing financial interest.

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