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Effect of Temperature and Steam-to-Carbon Monoxide (CO) Ratio on Hydrogen Production in Water-Gas Shift Reaction using Cu-ZnO-Al_2O_3 Catalyst

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Abstract

This study investigates the effect of steam-to-CO molar ratio and temperature on hydrogen production in a water gas shift reaction using a Cu-ZnO-Al_2O_3 catalyst. Herein, different steam-to-CO molar ratios (1:1, 2:1, and 3:1) and temperatures (200 °C, 250 °C, and 300 °C) were applied to investigate their impact on the reaction and H_2 production. The Cu-ZnO-Al_2O_3 catalyst was characterized by its surface area, pore size distribution, and chemical composition. Moreover, the experimental setup enabled the control of temperature and steam-to-CO molar ratio while monitoring the product gas composition. The results revealed a considerable influence of temperature and steam-to-CO molar ratio on CO conversion efficiency. Notably, the majority of the experiment variations exhibited CO conversion exceeding 90% within 1 min throughout the reaction. Additionally, the highest H_2 composition of 53.10% was reached at 250 °C with the steam-to-CO molar ratio of 3:1.

Keywords: *Cu-Zn-Al catalyst, CO conversion time, hydrogen production, steam-to-CO molar ratio, water gas shift reaction*

Introduction

Although Indonesia has a high potential for biomass utilization, as an energy source, this area still needs improvement. According to the data from the Indonesian Ministry of Energy and Mineral Resources, the potency of biomass in Indonesia can reach 443000 MW, while its utilization in 2022 has only reached 1.9%. Biomass can be used as an energy source through thermochemical conversions, such as gasification and pyrolysis [1]. These processes produce synthetic gas or syngas, i.e. mainly hydrogen (H_2) and carbon monoxide (CO).

With the increasing of H_2 as a clean energy source, the development of its production process has received growing interest. H_2 is a material that has multiple uses, such as fuel for fuel cells and a supporting material in making substitute fuels, including hydrodeoxygenation and hydrogenation. H_2 can be used directly as a fuel or chemical for the petrochemical industry [2–4]. One of the ways to produce H_2 is by using syngas from thermochemical conversion products. Syngas can be subjected to downstream processes to produce pure H_2 using water-gas-shift (WGS) reaction [2]. The WGS reaction is crucial in generating H_2 from carbon-based fuel [3]. The main advantages of the WGS reaction are the simultaneous CO removal and H_2 production [4]. This aspect is very useful, especially when applying pure H_2 in fuel cells. In fuel cells, using polymer electrolyte membranes, the WGS reaction can be employed to avoid the toxic adsorption of CO onto the Pt active sites [5]. Therefore, the WGS reaction that converts carbon monoxide to produce H_2 is needed.

The composition of synthetic gas from thermochemical conversion varies based on the feedstock and conversion process. In general, syngas comprises 30%–60% CO, 25%–30% H_2, and small amounts of methane, carbon dioxide, and other trace contaminants. For increased H_2 production, the CO gas from syngas can react with steam through the WGS reaction as follows:

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad \Delta H\ 298K = -41.4\ kJ/mol \quad (1)$$

The WGS reaction is an exothermic equilibrium reaction. An equilibrium reaction product can be shifted either to the product or to the reactant itself depending on several factors, such as temperature, pressure, volume, molar ratio of the feed, and the presence of a catalyst [6]. Hence, obtaining the optimum conditions of the WGS reaction that can produce the highest amount of H_2 gas is crucial.

In industrial processes, the WGS reaction can be performed in high-temperature Shift (HTS) at 300 °C–450 °C and low- temperature shift (LTS) at 200 °C–250 °C. Given that the WGS reaction is exothermic, high CO conversions are favored at low temperatures. However, high temperatures increase the reaction rate [6]. With the use of an The LTS reactor, over a commercial Cu-ZnO-Al_2O_3 catalyst, CO can be converted up to a concentration of 0.10% [7]. Furthermore, the LTS reactor requires less energy than the HTS reactor, making the former more appropriate for use on a laboratory scale. In addition to temperature, the WGS reaction rate is influenced by feed composition. Increasing the steam-to-CO molar ratio can improve CO conversion by shifting the reaction toward product formation [6]; however, a large amount of energy is being used to vaporize water. Therefore, this study aimed to determine the optimum steam-to-CO molar ratio and operating temperature for the WGS reaction.

In this study, CO gas is reacted with steam through the WGS reaction in a microactivity reactor over a Cu-ZnO-Al_2O_3 catalyst, which is suitable for the LTS. Steam-to-CO molar ratio of 1:1, 2:1, and 3:1 and temperatures of 200 °C, 250 °C, and 300 °C are employed to determine the most optimum ratio and operating temperature for the highest H_2 production. The information gathered from this study might be utilized to support the large-scale H_2 production from Indonesian biomass.

Experiment

The WGS reaction is vital in H_2 production. CO reacts with H_2O as steam to generate H_2 gas and CO_2. This reaction can be accelerated using a catalyst. In this study, a Cu-ZnO-Al_2O_3 catalyst was prepared and characterized before being used in the microactivity reactor equipped with a system that provides real-time data. The gas produced from the reactor was then analyzed to determine its composition.

Catalyst material. The use of a Cu-ZnO-Al_2O_3-based catalyst in the WGS reaction is common and has shown promising results for H_2 production. Cu-ZnO-Al_2O_3 catalysts are typically composed of Cu, Zn, Al, and additional promoters or modifiers as required. This study used 2 g of Cu-Zn-Al_2O_3 catalyst (MDC-3) from Sud Chemie, Japan. Before being loaded into the reactor, the catalyst pellets were ground using a ball mill and screened using a test sieve to obtain a uniform particle size of 150–250 mm.

Catalyst characterization. Prior to its use in the reactor, the characteristics of the catalyst that can influence the reaction, such as catalyst composition and pore volume must be determined. The catalyst's compositions were characterized by the X-ray fluorescence (XRF) method using the Niton XL3t 500 Portable. Its pore volume and diameter were determined by the Braunauer–Emmet–Teller (BET) method using the Novatouch 2 LX instrument.

Microactivity measurement. The microactivity flow reactor system is vital in measuring and controlling the catalytic activity during the WGS reaction. Gas flow, reactor temperature, and pressure were measured and regulated. Figure 1 displays the experimental setup in this study.

The experiment consists of several key steps: preheating 1, reduction, preheating 2, reaction, nitrogen flush, and cooling. The preheating 1 step involved gradually increasing the reactor's temperature to 200 °C for the catalyst reduction stage. The system was flushed using 100 mL/min nitrogen gas for 40 min to clean the system

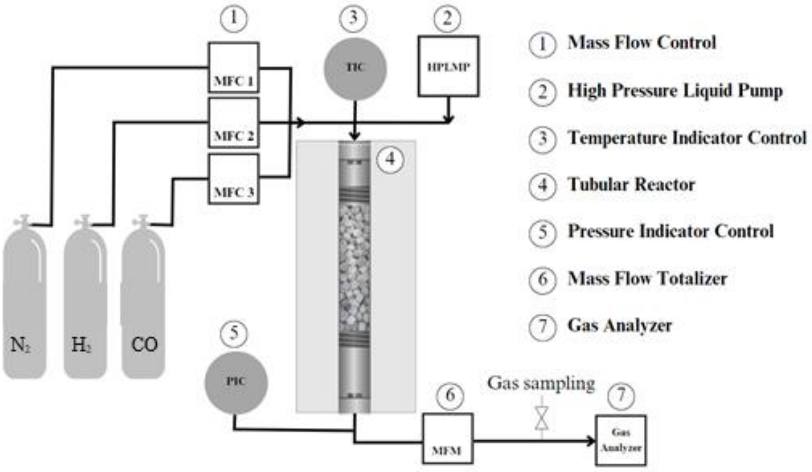

Figure 1. Tubular Flow Reactor Systems

from any impurities and prevent unwanted reactions. For the reduction step, a reducing agent using H_2 30 mL/min was introduced to the reactor for 30 min. This process aimed to activate the catalyst or to form active metal species in the catalyst by dispersing the Cu all over a large surface area [8, 9]. The reactor was flushed again with 150 mL/min nitrogen gas while preheating 2 was performed to clear out the H_2 gas used in the catalyst reduction step. H_2 can influence the WGS reaction and therefore must be flushed using nitrogen gas before the reaction starts. Preheat 2 involved further heating the reactor to high temperatures (200 °C, 250 °C, and 300 °C). CO with 200 mL/min flow and H_2O with desired steam-to-CO molar ratio (1:1, 2:1, and 3:1) were introduced into the reactor at controlled flow rates and proportions during the reaction phase. In addition, the CO conversion rate was determined as follows:

$$X_{CO}\ (\%) = \frac{F_{COin} - F_{COout}}{F_{COin}} x100\% \qquad (2)$$

where X_{CO} represents the CO conversion, and F_{COin} and F_{COout} represent the CO molar flow rates (mL/min) at the reactor's input and exit, respectively.

Gas composition characterization. The gas composition during the reaction was measured using the Dashboard 3100p gas analyzer and characterized using Gas Chromatograph Bruker Scion 456 with a thermal conductivity detector.

Results and Discussion

Catalyst characterization result. The catalyst for the WGS reaction must be designed according to the reaction temperature range [4]. Cu-ZnO-Al_2O_3 catalysts from Sud Chemie (MDC-3) used in this study are widely applied in the WGS reaction at the LTS range. Group B elements strengthen the redox characteristics and support structural stability [9]. Among transition metals, Cu-based catalysts are frequently utilized because they are more reasonably priced, possess higher catalytic activity, and exhibit better selectivity than other metals [10]. The traditional support for Cu-based WGS catalysts is Al_2O_3 with added ZnO.

Cu-based catalysts are vulnerable to temperature, air, sulfur, and other substances [1]. In the low-temperature region, Cu-based catalysts exhibit excellent activity but are also prone to thermal sintering and chemical poisoning. Therefore, Cu-based catalysts with different compositions are developed to improve their activity, stability, toxicity, and sintering performance [11, 12]. Consequently, Cu must be doped with other materials to protect and reinforce its characteristics. Al_2O_3 is usually added as a modifier that does not alter Cu's catalytic activity. Meanwhile, introducing ZnO stabilizes the Cu-Al composite and extends its lifespan. ZnO acts as a H_2 reservoir and a sulfur poison scavenger, and Cu-Zn has a synergic effect on various reaction mechanisms [13]. However, the effectiveness of ZnO relies on the type of oxidizing support [2]. The composition of the Cu-Zn-Al_2O_3 catalyst used in this study was characterized using the XRF method, and the results are summarized in Table 1.

The most crucial component in the Sud Chemie catalyst is Zn, followed by Cu and Al at 48.42%, 42.52%, and 7.05%, respectively. This result is concordant with the data from the manufacturer, that is the catalyst comprises 42% CuO, 47% ZnO, and 10% Al_2O_3. Commercial LT-WGS (Low Temperature-Water Gas Shift) catalysts commonly consist of 50%–60% Cu, and 30%–40% ZnO, with the rest of the composition being Al. Despite being produced under distinct conditions, the formulation of LT-WGS catalysts is similar to that of methanol synthesis catalysts [14].

In addition to the catalyst's composition, the pore diameter and volume of the catalyst were measured using the BET method. Pore volume is one of the essential parameters influencing the catalyst's activity. A large pore volume means a high surface area, which results in a high catalyst activity. The BET surface areas and pore volumes are shown in Table 2. The Cu-Zn-Al_2O_3 catalysts used for the WGS reaction vary widely based on the treatment method and sources. Generally, a Cu-Zn-based catalyst has a surface area of 30–200 m^2/g and a pore volume of 0.10–0.70 cc/g [3, 4, 15].

Analysis of reaction time and CO conversion during H_2 production. Figure 2 depicts the CO conversion profile observed during the WGS reaction. The desired temperatures were set at 200 °C, 250 °C, and 300 °C, and the steam-to-CO molar ratios were set as 1:1, 2:1, and 3:1. The majority of the experimental runs achieve CO conversion exceeding 90% throughout the reaction. The CO conversion rises with elevated temperatures until it reaches a particular equilibrium owing to thermodynamic restrictions [16].

Table 1. Elemental Analysis of Sud Chemie Catalyst with Energy-Dispersive X-ray Fluorescence

Components	Percentage (%)
Zn	48.42
Cu	42.52
Al	7.05

Table 2. Sud Chemie Catalyst Characterization

Parameter	Value
Surface Area (m^2/g) BET	50.74
Pore Volume (cc/g) BJH	0.16

The average CO conversion of each reaction condition is presented in Table 3. The average CO conversion increased with the increasing temperature, from 200 °C to 250 °C. Therefore, the reaction rate increased with the temperature. This finding indicated that the optimum equilibrium CO conversion was rapidly attained, thereby generating additional products at a given time. However, the CO conversion decreased when the temperature was 300 °C. The WGS reaction is exothermic and reversible; therefore, it is favorable at low temperatures, particularly for CO conversion. The Gibbs free energy of the WGS reaction rises with temperature and gradually becomes positive at around 825 °C, implying that the reaction becomes thermodynamically unfavorable at elevated temperatures [6]. Furthermore, considering the equilibrium constant's equation as a function of temperature (denominator), a high temperature coincides with a low equilibrium constant, implying a backward reaction to the reactant [8].

In the reactions at 250 °C, the increase in steam-to-CO molar ratio resulted in high CO conversion. Increasing the steam-to-CO molar ratio can shift the reaction to the product side based on the equilibrium reaction, however, the energy needed to increase the steam-to-CO molar ratio must be considered [17]. As listed in Table 3, the highest CO conversion of 99.81% was attained from the reaction at 250 °C with steam-to-CO molar ratio of 3:1. The WGS reaction can decrease the CO concentration to 0.10% [7, 15]. Thus, the WGS reaction in this study performed well because it could reach the maximum CO conversion. According to the CO conversion rates, performing the reaction at 250 °C with a steam-to-CO molar ratio of 3:1 is preferable to reach the highest CO conversion.

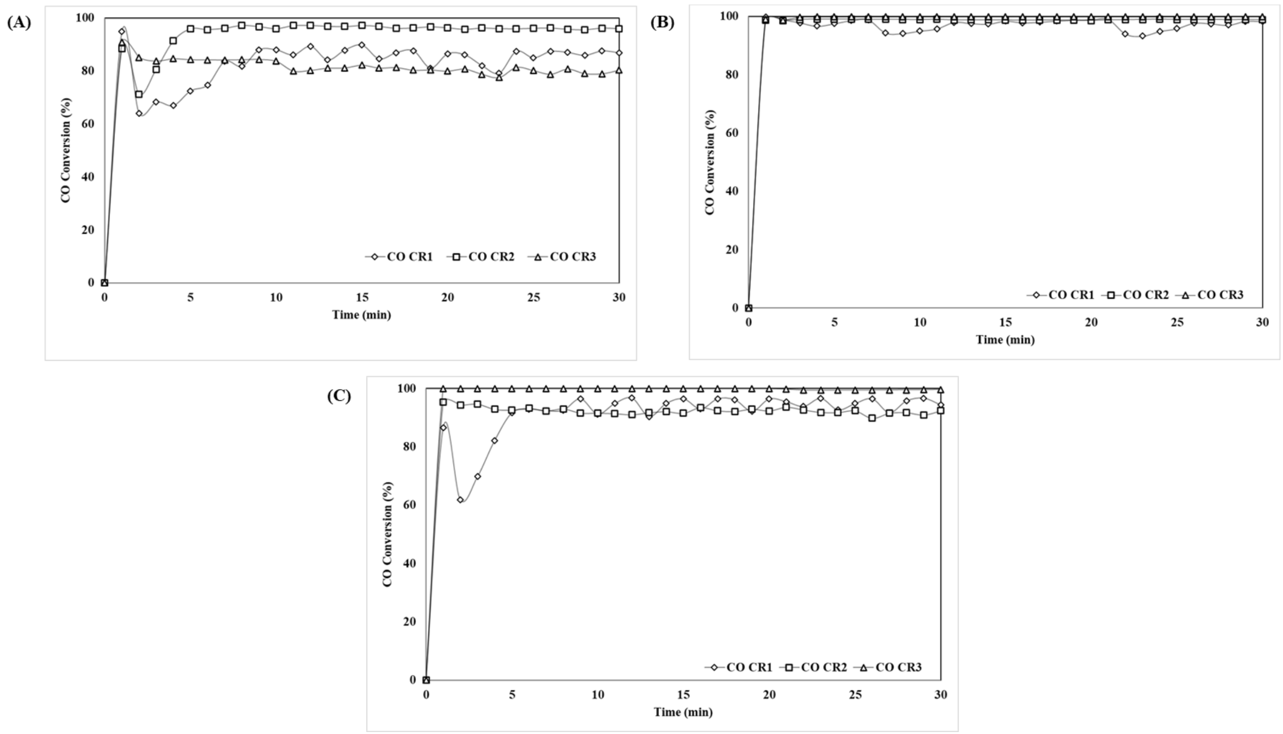

Figure 2. CO Conversion Profile for Steam to CO molar Ratios of 1:1 (CO CR1), 2:1 (CO CR2), and 3:1 (CO CR3) at Temperatures of (a) 200 ºC, (b) 250 ºC, and (c) 300 ºC

Table 3. Average CO Conversion and Time to Reach Stable State for Each Condition

Temperature (°C)	CO Conversion (%)			Time to reach a stable state (minutes)		
	Steam: CO molar ratio					
	1:1	2:1	3:1	1:1	2:1	3:1
200	83.34	94.55	81.79	9	5	3
250	97.23	98.87	99.81	1	1	1
300	94.02	92.26	99.71	6	1	1

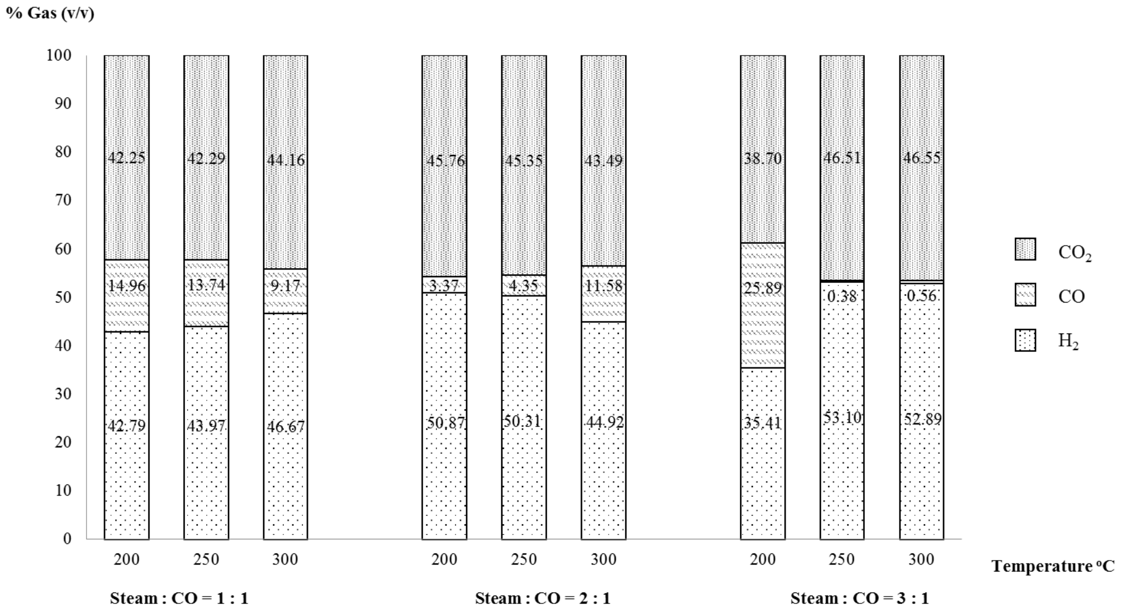

Figure 3. Average Gas Output Concentration

According to Table 3, the reaction at 250 °C was the fastest to reach stability in 1 min. This finding is consistent with other reports demonstrating the optimum LT-WGS reaction at around 200 °C–280 °C [6]. The reaction reached a stable state approximately 5 minutes into the reaction. The consistent attainment of CO conversions above 90% during most of the experiments reflected the effectiveness of the catalyst and reaction conditions.

The most stable CO conversion profile over time was obtained at 250 °C, making it the most favorable working condition. The temperature of 250 °C gives sufficient energy to reach maximum equilibrium CO conversion (Figure 2 and Table 3). It also efficiently accommodates kinetic and thermodynamic limitations. On the contrary, the relatively unsteady CO conversion profile was found in high temperatures (300 °C) and low temperatures (200 °C). At 200 °C, the reaction is the slowest, preventing the peak equilibrium CO conversion from occurring under such conditions [18]. At 300 °C, the fluctuating profile is due to its exothermic reactions potentially causing a backward reaction to the reactant and reducing its equilibrium constant. Another reason is Cu's sensitivity toward the temperature system, but this behavior is still unclear [19]. Nevertheless, 300 °C gives an overall better CO conversion profile than 200 °C because the high temperature increases the reaction rate. Consequently, the optimum equilibrium CO conversion can be rapidly achieved.

Effect of operating temperature and steam-to-CO molar ratio on H_2 production. This study applied three different temperatures (200 °C, 250 °C, and 300 °C) and three different steam-to-CO molar ratios (1:1, 2:1, and 3:1). Figure 3 shows the average concentrations of gas output consisting of H_2, CO_2, and the remaining CO. The H_2 production rate varied for each ratio: 42.79%–46.67% for the steam-to-CO molar ratio of 1:1; 44.92%–50.87% for the steam-to-CO molar ratio of 2:1; and 35.41%–52.89% for the steam-to-CO molar ratio of 3:1. Overall, a higher steam-to-CO molar ratio produced a high amount of H_2 in almost all of the applied temperature. This phenomenon follows Le Chatelier's principle, where the excess steam or increased steam-to-CO molar ratio, shifts the reaction towarsd the products [8]. In addition, the amount of CO_2 generated in each experiment exhibited a similar pattern to the amount of H_2 in the final product. This trend followed the WGS reaction equation theory, where H_2 and CO_2 have equal reaction coefficients, leading to a comparable concentration.

Some of the CO from the feed remained at the end of the reaction. Figure 3 shows that with the increase in the steam-to-CO molar ratio, the percentage of CO decreased and the H_2 concentration increased. A critical rate of steam flow can produce a maximum H_2 yield, but an excessively high steam input may result in a decline in H_2 yield [20]. The low CO percentage in the gas products means a high CO conversion. This finding was aligned with the data from Table 3, which showed that the highest conversion (99.81%) was achieved in the reaction at 250 °C with the steam-to-CO molar ratio of 3:1. Meanwhile, Figure 3 shows that these conditions left behind the smallest CO amount (0.38%). This satisfactory result was better than those recently reported for Cu-Zn-Al-based catalysts, whose CO conversion is almost above 90 % (Table 4). The LTS catalyst has a significant level of selectivity, enabling a high CO conversion ratio and effective performance even under low intake concentrations [21]. Cu has the highest activity level among the catalysts examined in the literature. It displays optimal adsorption energies for interactions involving O and CO [9].

The mechanism of the LT-WGS reaction is complex and remains unclear; however, the two most presumed mechanisms of LT-WGS reaction over Cu-based catalysts are the associated or surface intermediate [19] and redox or regeneration [5]. Various contradicting results on the rate-controlling mechanism have been reported due to variations in specific experimental circumstances, such as catalyst compositions, synthesis type and measurement methods. Most of the evidence supports the general idea that the associative mechanism is a dominant pathway in the LT-WGS reaction by utilizing Cu-based catalyst via intermediate formations (formate, carbonate, or carboxylate) through water dissociation, leading to CO_2 and H_2 generations [6, 8, 19, 26].

Nevertheless, a redox mechanism is possibly to be found in high temperature zones (300 °C–400 °C) [5, 8] and under practical conditions where H_2-rich gas is involved in the reactant [5]. The carboxyl breakdown is assumed to be rate-determining at low temperatures and CO_2-rich environments. At moderate temperatures and under excessive water, the low CO_2 concentration leads to formate decomposition, which becomes a rate-determining step [6]. Hence, this study presumed the involvement of an associate surface mechanism in the reaction at 200 °C to 250 °C via the formate intermediate, and then the redox and associative mechanism at 300 °C. However, the associative pathway seemed to play a major role in most of the temperatures applied in this study.

Fluctuating results were recorded for the reactions with a steam-to-CO molar ratio of 2:1 at 300 °C and 3:1 at 200 °C. The steam-to-CO molar ratio of 2:1 had the lowest H_2 production (44.92%) at 300 °C compared with that under the other temperatures. This phenomenon contradicted the fundamental idea and maybe because of a slight sintering at the 300 °C zone caused by the sensitive nature of Cu, as indicated by its low Hüttig and Tammam temperature correlating with a low melting point [24, 27]. The lower the Hüttig and Tammam temperature, the more susceptible the material is to deactivate via sintering because of surface migration [28]. Therefore, the Cu-based catalyst exhibits an upper operation limit at around 300 °C because the CO conversion and H_2 production rates start to decrease. This finding also emphasized the possibility of a reversible reaction to the reactant because almost all the CO was already converted during the 250 °C regime. The excess energy (high temperature) may shift the reaction to the reactant and potentially start deactivating the catalyst. Additionally, the lowest H_2 level and CO conversion of 35.41% and 81.79%, respectively, were found in the reaction at 200 °C with the steam-to-CO molar ratio of 3:1. A low temperature zone typically favors a low amount of reactant [18] and a high steam-to-CO molar ratio requires additional energy to run the WGS reaction. Hence, a high temperature is suitable for this reaction.

Table 5 shows the summary of H_2 production throughout all nine experiments. The reactions at 200 °C and 300 °C in all steam-to-CO molar ratios produced H_2 at a reasonably good rate of 52–112 mL/min, and the reaction at 250 °C in all steam-to-CO molar ratios produced H_2 at a considerably low rate at 24–35 mL/min. Despite having low H_2 rates, all the reactions at 250 °C achieved good CO conversion, of more than 97% as shown in Table 3. The H_2 production rate fluctuated with the increasing reaction temperature for any of the molar ratios. The highest H_2 production rate of 111.95 ± 7.40 mL/min was obtained from the reaction at 200 °C with the steam-to-CO molar ratio of 2:1. Therefore, a mild temperature and a relatively high steam-to-CO ratio are the best conditions for running a WGS reaction [6, 8].

Table 4. Overview of CO Conversion Using Various Catalyst Compositions

No	Cu/Zn/Al Catalyst Composition	Reactor	Temp (ºC)	Pressure (atm)	Feed ratio	CO conversion (%v/v)	Note	Reference
1	22.3% Cu, 44.4% Zn, 33.3% Al	plug flow reactor	250	1.5	0.55 ^{a}	~ 95	$^{a)}$ steam / ($CO + H_2 + CO_2 + CH_4$)	[22]
2	65% Cu, 25% Zn, 10% Al	fixed bed microtubular quartz reactor	210	1	2 ^{b}	93,8	$^{b)}$ steam / ($CO + CH_4 + CO_2$)	[23]
	70% Cu, 20% Zn, 10% Al	fixed bed microtubular quartz reactor	210	1	2 ^{b}	94,9		
3	30% Cu, 20% Zn, 50 % Al	fixed bed reactor	200	1	1 ^{c}	~ 86 % (Stability test 100 h)	$^{c)}$ vapor / ($CO + H_2 + CO_2 + N_2$)	[24]
4	65% Cu, 25% Zn, 10% Al	quartz type reactor	240	1	2 ^{d}	~ 95% (Stability test 200h)	$^{d)}$ steam / ($CO + CH_4 + CO_2$)	[25]
5	42% Cu, 47% Zn, 10% Al	fixed bed reactor	250	1	3 ^{e}	99.81 %	$^{e)}$ steam / CO	This experiment

Table 5. H_2 Production Rate in mL/min

Temperature (°C)	The mol ratio of Steam: CO		
	1:1	2:1	3:1
200	87.47 ± 12.28	111.95 ± 7.40	52.01 ± 3.14
250	24.34 ± 7.59	26.25 ± 1.94	35.77 ± 3.05
300	61.42 ± 2.81	60.92 ± 4.77	94.20 ± 9.44

Conclusions

The experiments on the WGS reaction using a Cu-Zn-Al_2O_3 catalyst have shed light on the crucial role of the steam-to-CO molar ratio and temperature in H_2 production. The findings underscore the potential impact of these variables on H_2 generation using Cu-Zn-Al_2O_3 catalysts. Across all the experiments, the average CO conversion time was 1 min, indicating the catalyst's rapid and efficient performance in converting carbon monoxide. The highest CO conversion of 99.81% and the highest H_2 composition of 53.10% were achieved at 250 °C with the steam-to-CO molar ratio of 3:1, suggesting that these conditions favor H_2 production in the WGS reaction. These findings provide valuable insights into the role of temperature and steam-to-CO molar ratio in the WGS reaction using a Cu-Zn-Al_2O_3 catalyst. The catalyst facilitated a swift CO conversion time and high H_2 composition and production rates. These results have substantial implications for advancing efficient and sustainable processes for H_2 production and CO removal.

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