

# Hydrogen production by supercritical water gasification of food waste using nickel and alkali catalysts

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## Abstract

Supercritical water gasification (SCWG) of food waste was carried out with nickel and alkali catalysts (NaOH, KOH,  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and  $\text{K}_2\text{CO}_3$ ). The food waste was comprised of a variety of food items. The experiment was performed in a batch reactor at supercritical water (SCW) conditions of 400°C and 22.1MPa for 10mins. Hydrogen ( $\text{H}_2$ ) gas yield regarding the use of the catalysts was in the sequence;  $\text{Ni-K}_2\text{CO}_3 > \text{Ni-NaOH} > \text{Ni-KOH} > \text{Ni-NaHCO}_3 > \text{Ni} > \text{Ca}(\text{OH})_2 > \text{Ni-Na}_2\text{CO}_3 > \text{No catalyst}$ . The results of this study indicate that using Ni was effective to support the steam reforming reaction. However its effects on the water gas shift reaction (WGSR) was little. Also carbon dioxide ( $\text{CO}_2$ ) was the predominant gas product in the presence of metal carbonates and bicarbonate. As a result,  $\text{H}_2$  selectivity was in the sequence,  $\text{Ni-NaOH} > \text{Ni-KOH} > \text{Ni-K}_2\text{CO}_3 > \text{Ni-Ca}(\text{OH})_2 > \text{Ni} > \text{Ni-Na}_2\text{CO}_3 > \text{Ni-NaHCO}_3 > \text{No catalyst}$ . Furthermore, using 4g of NaOH was effective to shift the WGSR forward to produce a higher  $\text{H}_2$  yield and selectivity than when 4g of Ni was used. However, when equal amounts of Ni and NaOH were used, the conversion of food waste into gaseous products was necessary to produce more  $\text{H}_2$  during the WGSR.

*Keywords: hydrogen, food waste, nickel, alkali catalysts, water gas shift reaction, carbon dioxide, NaOH, selectivity, supercritical water, gaseous products.*

## 1 Introduction

Biomass (energy crops, agricultural residue, forest waste and residue and municipal solid waste) is one of the most abundant renewable energy resources.



Biomass's energy potential is addressed to be the most promising among the renewable energy sources due to its wide spread and availability worldwide [1]. Producing  $H_2$  from biomass is considered to be sustainable and carbon-neutral since the  $CO_2$  generated is consumed during photosynthesis [2–9].

Over the past decade, SCWG has proven to be the most suitable method to produce higher  $H_2$  yields [10] from biomass with moisture content greater than 75% [11]. That is, the cost incurred in the drying of feedstock (biomass) in other methods such as pyrolysis is avoided [2]. During SCWG, organic compounds are converted into gases containing  $H_2$ , methane ( $CH_4$ ), carbon monoxide (CO) and  $CO_2$  [11, 12]. Water at this point has a low density and a low dielectric constant therefore increasing the solubility of organic molecules at this stage [11–17]. The C-H covalent bonds are broken down to form carbon oxides and  $H_2$  [11] in a process referred to as steam reforming [2, 17–19]. However, the carbon monoxide (CO) in the reactor further reacts with water to produce  $CO_2$  and more  $H_2$  [2, 15, 16, 20–22]. This reaction is known as the water gas shift reaction (WGSR). Due to the difference in C-H bond in organic compounds, their solubility and liberation of  $H_2$  varies at SCW conditions. Moreover, at the same temperature and pressure, some organic compounds release more  $H_2$  than others.

The chemical structure of food waste is an important factor in influencing the resistance or otherwise of samples to convert into intermediates relevant for  $H_2$  gas production [23]. Food waste [24, 25] and other biomass feedstock [26, 27] have complex compositions that typically comprise of carbohydrates, proteins and fats and oils [28]. Thus, there is a ton of literature on the hydrothermal (subcritical and supercritical) gasification of model compounds (cellulose, glucose, xylan, glycerol, p-cresol and phenol) to simulate the conversion of real food waste for  $H_2$  production [29]. It is worth knowing that there are catalysts that influence the formation of certain product gas components [30] and also inhibit the formation of tar and char at considerably low temperatures [30, 31].

Transition metals such as Ni, Pt, Ru and Rh accelerate the steam reforming and the cleavage of C-O and C-C bonds during SCWG of biomass [15, 29]. These catalysts are therefore used to overcome energy barriers for low temperature SCWG. However, Ni is widely used due to its affordability. Also at SCW conditions,  $H^+$  and  $OH^-$  ions are liberated at high concentrations which creates a perfect condition favorable to acid-base catalysts during the WGSR [32–34]. Therefore, alkaline homogeneous catalysts such as KOH, NaOH,  $K_2CO_3$  and  $Na_2CO_3$  can promote biomass gasification for effective  $H_2$  production [15]. For instance, the addition of KOH increases the  $H_2$  and  $CO_2$  yield [15]. In the absence of a catalyst, the WGSR has been demonstrated to be accelerated by system pressure [35].

This study seeks to discriminate the combined effects of Ni and alkali catalysts (NaOH, KOH,  $Ca(OH)_2$ ,  $Na_2CO_3$ ,  $NaHCO_3$  and  $K_2CO_3$ ) on  $H_2$  yield during the SCWG of real food waste at 400°C and 22.1 MPA for 10mins. Therefore the objective of this study is to find the best Ni and alkali catalyst combination there is and the right proportion that will produce the highest  $H_2$ -rich gas from this type of food waste. It is important to note that this literature only focuses on  $H_2$  yield and does not highlight details of liquid and solid residue.

Also this study will serve as a baseline for further studies regarding food waste of multiple constituents to juxtapose other studies that use one food waste item under similar conditions.

## 2 Materials and method

### 2.1 Raw materials

The food waste used in this study was provided by the Hohai University's student's cafeteria, Nanjing, China. It was stored in a refrigerator at 4°C prior to use. The constituents of the food waste are shown in Table 1. Ni, NaOH, KOH, Ca(OH)<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> catalysts were supplied by Sinopharm Chemical Reagent Co. Ltd. All of these reagents were analytically pure. The water content and proximate and ultimate analysis are shown in Table 2. Carbon (C), H<sub>2</sub> and Nitrogen (N) were detected using the Vario MICRO Elementar. To determine the water content 10g of the food waste was placed in an oven at 105°C for 24hrs and weighed afterwards to calculate the water loss.

Water content

$$WC = \frac{Mw - Md}{Mw} * 100\% \quad (1)$$

where, WC is water content, Mw is mass of wet food waste, Md is mass of dry food waste.

Table 1: Constituents of food waste.

Grains/tubers	Vegetables	Protein/fats	Others
Rice	Onions	Pork	dumplings
Corn	Green pepper	Chicken	Fried egg
Sweet potato	Red pepper	Beef	Bean sprout
Potato	Green leaves	Cooking oil	Dried bean curd
Vermicelli	Red radish		Bean curd puff
	White radish		Pork sausage
	Kelp		Rice noodles
	Shiitake mushroom		
	Enoki mushroom		
	Agaric		
	Cabbage		
	Broccoli		
	celery		

### 2.2 Reactor system and experimental procedure

Food waste was pretreated by blending five times in a food waste disposer supplied by Diao Gong mao Gongs Co. Ltd. It was further sieved with a 0.5mm mesh in order to facilitate efficient gasification. SCWG of food waste was performed by using a 316 L stainless steel batch reactor that was obtained from the Songling Chemical Instrument Co., Yantai, Shandong, China. The schematic

Table 2: Proximate and ultimate analysis for food waste sample.

Sample	Moisture content	Proximate analysis <sup>a</sup>			Ultimate analysis <sup>a</sup>			
		Volatile Matter	Fixed Carbon <sup>b</sup>	Ash	C	H	N	O <sup>b</sup>
Food waste	81.5	93	1.5	5.5	46.36	6.98	1.86	39.3

<sup>a</sup> Weight percent of dry basis.<sup>b</sup> By difference.

of the reactor is illustrated in Figure. 1. The reactor has a 100 mL capacity and a maximum operating temperature and pressure of 650°C and 35MPa, respectively. The reactor was heated by a salt-bath furnace that was fit with a PID temperature control unit with a K-type thermocouple.

The reaction pressure (which was not adjusted manually) was read from a pressure gauge (fitted to the top of the reactor) and depended on the reaction temperature and the water loading in the reactor. In this experiment, the reactor pressure was above 22.1MPa at 400°C when 33 mL of water was in the reactor, which indicated that the water achieved supercritical conditions at this temperature. At the head of the reactor is fitted a gas sampling tube with two high-pressure valves. This is used for gas sampling at the end of the reaction.

40.5g of food waste and a total of 4g of catalysts were placed in the reactor. After the reactor was sealed, it was dipped into a 400°C salt-bath furnace that had an average heating rate of 10.6°C/min. Once the reaction temperature was reached, the temperature was maintained for 10mins. At the end of each experiment, heating was stopped and the reactor was removed from the salt-bath before rapidly cooling to room temperature with cooling water and fans. The reactor was subsequently allowed to stand for 60 min to allow the gas to stabilize. After cooling, the final ambient temperature and pressure were noted. The gas outlet valve was opened to collect the gas sample.

### 2.3 Gas analysis

Effluent gas was sampled through a syringe (20 mL) with a three-way stop. These gas samples were analyzed with a gas chromatograph (GC5890) that was equipped with a thermal conductivity detector (TDX-01 packed column) and a flame ionization detector (PLOT Al<sub>2</sub>O<sub>3</sub>/S column) to determine H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub>. The generated gas volume was measured by the displacement amount of the saturated sodium hydrogen carbonate (see Fig. 1).

## 3 Results

From Fig. 2, H<sub>2</sub> yield from the various reactions was in the sequence, Ni-K<sub>2</sub>CO<sub>3</sub> > Ni-NaOH > Ni-KOH > Ni- NaHCO<sub>3</sub> > Ni > Ca(OH)<sub>2</sub> > Ni-Na<sub>2</sub>CO<sub>3</sub> > No catalyst. The effects of combining Ni and K<sub>2</sub>CO<sub>3</sub> gave the highest H<sub>2</sub> yield of



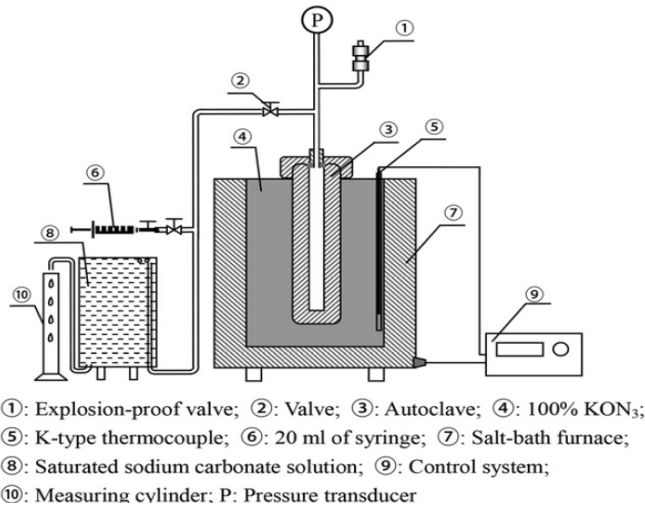


Figure 1: Experimental apparatus.

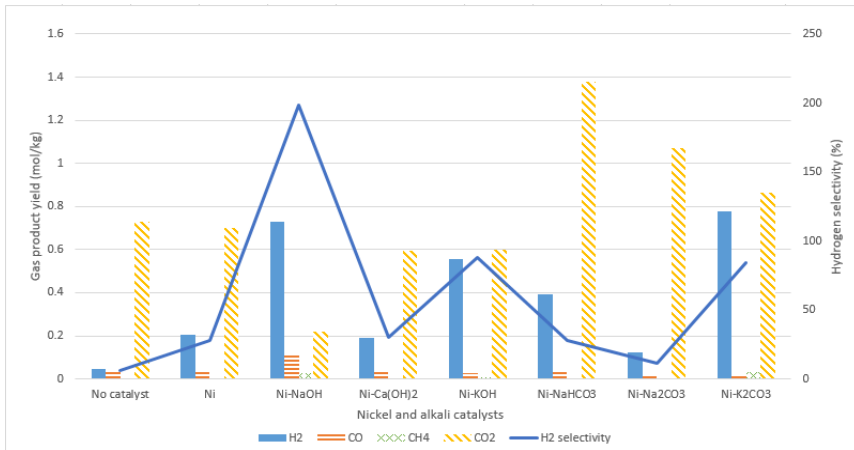


Figure 2: Gas product yield and hydrogen selectivity when 40.5g of food waste was gasified for 10mins at 400°C and 22.1MPa using Ni and alkali catalysts.

0.77mol/kg, which is about 4 times more than the H<sub>2</sub> yield when only Ni catalyst was used. SCWG of only food waste produced the least H<sub>2</sub> gas yield (0.04mol/kg) recorded. Furthermore, the effects of Ni-Na<sub>2</sub>CO<sub>3</sub> and Ni-Ca(OH)<sub>2</sub> on H<sub>2</sub> yield were relatively low. From Fig. 2, there is not a significant distinction between hydroxides and carbonates regarding H<sub>2</sub> yield. However higher CO<sub>2</sub> yields (> 0.8mol/kg) were produced when Ni and carbonates/bicarbonate

catalysts were used. Whereas combining Ni and hydroxides catalysts showed relatively lower yields of  $\text{CO}_2$  gas. Using equal amounts of Ni and NaOH produced the lowest  $\text{CO}_2$  gas of 0.22mol/kg. This observation showed that the gas produced by Ni-NaOH catalysts was rich in  $\text{H}_2$  although Ni- $\text{K}_2\text{CO}_3$  ( $\text{CO}_2$  yield was 0.87mol/kg) recorded a slightly higher  $\text{H}_2$  yield. The CO content of the gases produced from this experiment was very low and was in the range of 0.01–0.06mol/kg. Also  $\text{CH}_4$  gas was the least detected in this study.  $\text{CH}_4$  gases detected were in the range of 0.001–0.027mol/kg.

Furthermore, the amounts of Ni and NaOH were varied in the reactor to determine the right amounts of the two catalysts that will produce the best  $\text{H}_2$  rich gas. From Fig. 3, decrease in the amounts of Ni in the reactor showed significant increase in the  $\text{H}_2$  yield. However decreasing the amounts of Ni did not show any pattern regarding the  $\text{H}_2$  yield, in that, at a Ni to NaOH ratio of 1:3, there was a decline in the  $\text{H}_2$  yield as compared to the steady increase from reactions with 100%, 75% and 50% Ni. Moreover, the highest  $\text{H}_2$  yield (0.9mol/kg) was recorded when food waste was gasified with 100% NaOH. This reaction also recorded the lowest  $\text{CO}_2$  content signifying the most efficient reaction for  $\text{H}_2$  production in this study. Also the inhibition of  $\text{CO}_2$  production did not show a definite pattern with the different amounts of Ni and NaOH in the reactions but generally  $\text{CO}_2$  production was significantly inhibited with a more than 50% decrease in the amounts of Ni loaded in the reactor. However, a 25% decrease in the amounts of Ni recorded the highest  $\text{CO}_2$  yield of 0.88mol/kg. Furthermore, methane production was very low, (0.004–0.027mol/kg). SCWG of food waste with 4g of only Ni recorded the lowest methane gas yield of 0.004mol/kg. Also gasifying food waste with equal amounts of Ni and NaOH recorded the highest CO yield (0.118mol/kg).

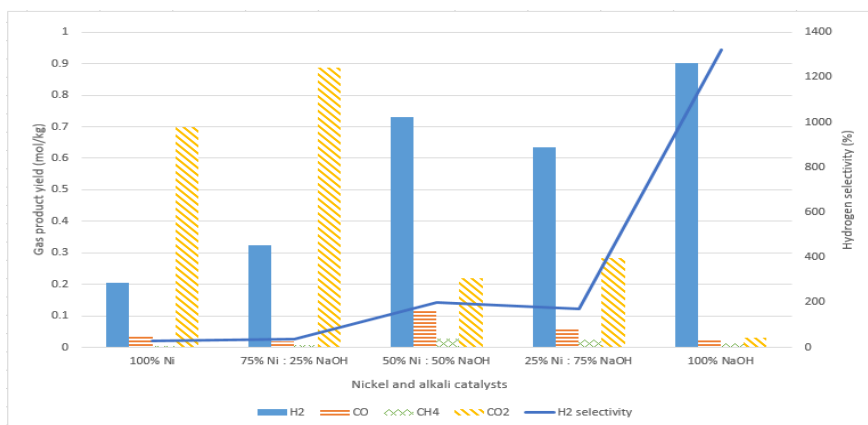
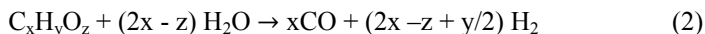


Figure 3: Gas product yield and hydrogen selectivity when 40.5g of food waste was gasified for 10mins at 400°C and 22.1MPa using different amounts of Ni and NaOH catalysts.

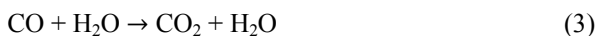
## 4 Discussion

This experiment basically investigates the effects of alkali catalysts in the presence of Ni on H<sub>2</sub> production from food waste of multiple constituents. The feedstock containing lignin, cellulose and hemicellulose, carbohydrates, proteins and other species was expected to undergo a complex chemical reaction. However the three major reactions that can occur in the process of catalytic gasification of biomass in supercritical water are as follows;

Steam reforming



Water gas shift reaction



Methanation



### 4.1 Effects of Ni and alkali catalysts on H<sub>2</sub> yield

A closer look at the results presented in this study gives a clear implication of the combined effects of Ni and alkali catalysts on the conversion of organic matter to gaseous products and also the WGSR in order to produce more H<sub>2</sub>. In this study, Ni was able to enhance the steam reforming reaction in converting the food waste into gaseous products. As a result, there was a significant increase in the H<sub>2</sub> yield as compared to when only food waste was gasified in the absence of a catalyst. However, Ni may have a little impact on the WGSR as carbon oxides were not captured and also H<sub>2</sub> yield was less compared to results from the addition of NaOH, NaHCO<sub>3</sub>, KOH and K<sub>2</sub>CO<sub>3</sub>. Also, the addition of Ca(OH)<sub>2</sub> to Ni could not shift the WGSR forward to increase H<sub>2</sub> yield because of the unavailability of Ca<sup>+</sup> to capture CO<sub>2</sub>. This deficiency is as a result of low decomposition of calcium formates at low supercritical temperatures [36]. The effects of the addition of Ni and K<sub>2</sub>CO<sub>3</sub> on the H<sub>2</sub> yield is interesting as it differs from results in recent studies by Muangrat *et al.* [36] when only alkali catalysts were used to gasify glucose at 330°C and 13.5MPa. Also in their study, hydroxide alkalis produced more H<sub>2</sub> than carbonates/bicarbonate alkalis. The complex constituent of the feed stock and the reaction time in this study could be the reason for the discrepancies in the results between these two studies.

Also, the variation of the amounts of Ni and NaOH catalysts in this study highlights the relevance of the WGSR in the SCWG of biomass. From Fig 3, the addition of 1g of NaOH facilitated the conversion of food waste to produce more gaseous products (CO<sub>2</sub>). The initiation of the WGSR also resulted in a significant increase in the H<sub>2</sub> yield. Also it is important to note that using equal amount of Ni and NaOH produced a higher H<sub>2</sub> yield than when 1g of Ni and 3g of NaOH were used. This observation is best explained as a result of the existence of more CO to react with the abundant H<sub>2</sub>O (81.5%) in the system (50%Ni - 50%NaOH) during the WGSR to produce more H<sub>2</sub>. That is, although, more than 50% of H<sub>2</sub>

produced during the SCWG of biomass is from the WGSR [9], conversion into gaseous products during the steam reforming reaction is also vital to increase the  $H_2$  yield especially when little amounts of NaOH is used. Furthermore, using 4g of NaOH catalyst produced 4.5 times more  $H_2$  gas than when 4g of Ni catalyst was used. This further implies that the WGSR is responsible for the increase in  $H_2$  yield in this study and NaOH was effective to support that.

#### 4.2 Effects of Ni and alkali catalysts on $H_2$ selectivity

Poor  $H_2$  selectivity has been identified as a factor that hinders  $H_2$  production from biomass [14].  $H_2$  selectivity basically indicates a comparison between the amount of  $H_2$  produced and the amount of carbon atoms produced.  $H_2$  selectivity is therefore calculated by the expression;

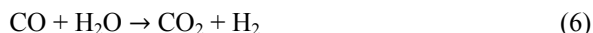
$H_2$  selectivity

$$\%H_2 \text{ selectivity} = \frac{\text{moles of } H}{\text{carbon atoms}} \left( \frac{1}{RR} \right) 100 \quad (5)$$

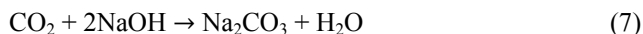
where RR is reforming ratio of feed stock.

In this study, due to the nature of the feed stock, we assumed an RR of 1 since this factor (RR) does not affect the analysis.  $H_2$  selectivity was in the sequence, Ni-NaOH > Ni-KOH > Ni- $K_2CO_3$  > Ni- $Ca(OH)_2$  > Ni > Ni- $Na_2CO_3$  > Ni -  $NaHCO_3$  > No catalyst. In this study, the predominance of  $CO_2$  was a major contributor to the low  $H_2$  selectivity in the product gases when Ni and alkali carbonates/bicarbonates were used. The inability for  $CO_2$  to be captured in these reactions is speculated by Muangrat *et al.* [36] to be a  $CO_2$ -exchange rather than a  $CO_2$ -removal process. This hypothesis then implies that the activity of using only Ni catalyst was able to capture  $CO_2$  as compared to when  $Na_2CO_3$  and  $NaHCO_3$  were added. It also signifies that using Ni may have an influence on the WGSR but minimal as compared to NaOH. A closer look at Fig. 2 shows that the addition of  $K_2CO_3$  to Ni in the reaction could increase the  $H_2$  yield during the WGSR but showed a  $H_2$  selectivity 2.4 times lesser than when NaOH and Ni were used (fig. 2). Furthermore, increasing the amount NaOH in the reactor showed a decrease in  $CO_2$ , hence higher  $H_2$  selectivity. This observation may be due to the following reactions;

Water gas shift reaction.



$CO_2$ -capture reaction for NaOH



Decarbonylation tends to favor  $H_2$  production via the WGSR, especially when NaOH is used. This is parallel to Le Chatelier's Principle which implies that the removal of the carbon oxides, in particular  $CO_2$ , is largely responsible for the increased production of  $H_2$  gas [37]. Figs 2 and 3 tend to show the extent of decarbonylation in the various reactions. That is,  $H_2$  selectivity could be seen as



a good indicator to measure the ability of the catalysts to shift the WGSR to the right in order to increase the purity of  $H_2$  in the effluent gas.

## 5 Conclusion

SCWG of food waste was carried out using Ni and alkali catalysts; NaOH, KOH,  $Ca(OH)_2$ ,  $Na_2CO_3$ ,  $NaHCO_3$  and  $K_2CO_3$ . The addition of the alkali catalysts to Ni influenced the gas yield however no significant distinction was observed between hydroxide catalysts and carbonates/bicarbonate regarding the  $H_2$  yield. Furthermore, although the SCWG of food waste in the presence of Ni and  $K_2CO_3$  produced the highest  $H_2$  yield, using Ni and NaOH gave a 2.4 times higher  $H_2$  selectivity. We further gasified food waste using Ni and NaOH at different loading ratios. Increase in the amounts of NaOH in the reactor showed a significant increase in  $H_2$  yield and selectivity. However using equal amounts of Ni and NaOH produced a higher  $H_2$  yield than when 1g of Ni and 3g of NaOH were used. We suspected this observation to be as a result of the Ni catalyst supporting the steam reforming reaction in order to produce more CO to facilitate the WGSR.

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