

## Research Article

# Hydrogen Production by Supercritical Water Gasification of Biomass with Homogeneous and Heterogeneous Catalyst

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Biomass gasification in supercritical water is a clean and efficient way to convert biomass to hydrogen-rich gaseous products. Appropriate catalyst can lower the reaction temperature to guarantee the technological and economic feasibility. This paper selects  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{LiOH}$ , and  $\text{ZnCl}_2$  as typical homogeneous catalysts and three kinds of Raney-Ni, dolomite, and olivine as typical heterogeneous catalysts. The catalyst effects are investigated in the process of biomass gasification in supercritical water with the temperature of  $400^\circ\text{C}$ , pressure of  $22 \sim 24$  MPa, and residence time of 20 min. The experimental results show that Raney-Ni has the best hydrogen selectivity and hydrogen yield. The mixture of  $\text{NaOH}$  with Raney-Ni was investigated in order to research the synergistic effect of different catalysts. The experimental results show that Raney-Ni and  $\text{NaOH}$  have a synergistic effect in the biomass gasification in supercritical water.

## 1. Introduction

Biomass has the potential to provide the increasing energy demand of the world due to the large world-wide resource potential and the optimistic long-term contribution [1]. The clean and efficient utilization of biomass is the object of growing attention due to the environmental and economic reasons [2].

Supercritical water gasification has recently received significant attention as a potential alternative to energy conversion method [3–6]. It has an obvious advantage in converting biomass directly without high energy-consuming drying process to obtain high energy efficiency [7]. Due to the unique physical properties of water above its critical conditions (i.e.,  $374.15^\circ\text{C}$  and 22.1 MPa), most of hydrogen bonds break [8–10] and offer a controlling mechanism depending on operating parameter and have an excellent transport properties based on their high diffusion ability, low viscosity, and new reaction alternatives for hydrolysis or oxidation [11, 12]. Organic compounds have complete miscibility in supercritical water, and chemical reactions have high efficiency due to the absence of interfacial transport limitations [4, 12]. Air-polluting species containing N and S are not produced because supercritical water gasification

conducts in relatively low temperature [13].  $\text{CO}_2$  can easily be enriched and separated owing to the difference in solubility between  $\text{CO}_2$  and other gaseous products [14]. The energy of fluid after reaction can be easily recovered by steam turbine [6].

Catalyst can decrease the reaction temperature and accelerate the reaction to guarantee the technological and economic feasibility of supercritical water gasification and conduct the reaction toward the desired products [15], so catalytic gasification of biomass in supercritical water has received much attention, and the catalyst investigated can roughly be divided into homogenous and heterogenous catalysts [16, 17].

As for homogenous catalyst, it is easy to be mixed with feedstock and is easy to operate for the gasification system. Researchers mainly focus on the alkaline metal catalyst such as  $\text{KOH}$  [18, 19],  $\text{NaOH}$  [20–22],  $\text{K}_2\text{CO}_3$  [23–27],  $\text{Ca}(\text{OH})_2$  [28, 29], and  $\text{KHCO}_3$  [30]. It is generally accepted that the water-gas shift reaction is accelerated by alkaline metal. Formic acid is assumed to be the intermediate product in the reaction process, and  $\text{H}_2$  and  $\text{CO}_2$  are produced through the pathway of formic acid decomposition. Alkali can also absorb  $\text{CO}_2$  so that water-gas shift reaction can conduct toward the

hydrogen production direction. However, the solubility of inorganic salt in supercritical water is significantly lower than the ambient condition and the eutectic melting of inorganic salt is observed, which may cause trouble in the continuous operation of the gasification system [28].

As for the heterogeneous catalyst, researchers have done extensive job in the screening of the active metal and supporting material to find a catalyst with high activity, hydrothermal stability, and resistance to carbon deposition [31]. Ni-based catalyst is frequently studied due to its relatively low price and high activity. However, hydrothermal instability and carbon deposition are still two big problems for the Ni-based catalyst development [32–34]. Activated carbon gained attention as a potential catalyst for hydrothermal gasification because activated carbon has high activity and does not introduce any pollution to the reaction system. But activated carbon is apt to have deactivation problems [8, 35, 36]. Expensive metal also gained attention due to the extremely high catalytic effects; however, the high price restricts its large-scale industrial application [37–39].

It can be observed that neither homogeneous catalyst nor heterogeneous catalyst is provided with all the advantages. Several typical homogeneous and heterogeneous catalysts are investigated in this paper to study the biomass gasification characteristics of biomass in order that optimal catalyst selection method can be obtained. Minowa and Ogi [40] studied the catalytic effect of mixture of Ni and  $\text{Na}_2\text{CO}_3$  in a autoclave at the temperature of  $350^\circ\text{C}$  and pressure range of 18–20 MPa in the process of thermochemical conversion of cellulose and the synergistic effect was found. This paper will investigate the synergistic effect of homogeneous catalyst and heterogeneous catalyst in supercritical water gasification condition.

## 2. Experimental Section

**2.1. Material.** Peanut shell is selected as typical real biomass which is produced in the city of Huanggang, Hubei Province. It is ground until the size of biomass particle is smaller than  $180\ \mu\text{m}$ . The ultimate analysis and proximate analysis of real biomass can be seen in Table 1. A small quantity of Carboxy methylated cellulose (CMC) is added into the slurry to make a uniform solution. Different types of Raney-Ni are prepared by Dalian general chemical Co., LTD, and the metal element analysis of Raney nickel catalyst (RTH-3110, RTH-4110, RTH-5110) can be seen in Table 2. LiOH, KOH, NaOH,  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{CO}_3$  are analytic reagent. Olivine and dolomite are provided by the Yingkou Hepingsanhua Mineral Co., Ltd. They are ground until the particle size is smaller,  $106\ \mu\text{m}$  and  $55\ \mu\text{m}$ , respectively.

**2.2. Experimental Apparatus and Procedure.** Gasification of biomass is carried out in a 140 mL, 316 L stainless steel, high-pressure autoclave. Detailed description of the experimental apparatus was published before [41]. Firstly, 11 g solution of 9.09 wt% glucose and 0.2 g catalyst is added to the reactor for these experiments. The reactor was heated from ambient temperature to the reaction temperature with a heating rate

of about 17 K/min. After gasification reaction, the reactor is cooled down below 473 K in 1 min and then below 373 K in 2.5 min.

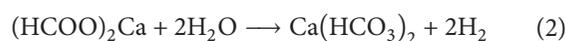
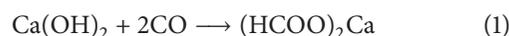
**2.3. Analytical Method.** The sampled gases were analyzed by a Hewlett-Packard model 6890 gas chromatograph (GC) with a thermal conductivity detector. A Carbon-2000 capillary column was used ( $\Phi\ 0.53\ \text{mm} \times 25\ \text{m}$ ), operating at 333 K for 7 min.  $\text{N}_2$  was adopted as the carrier gas with the flow rate of 10 mL/min. A standard gas mixture with 6 kinds of species ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ ) is employed for calibration and bought from and compounded by Nanjing Special Gas Co., Ltd. in China.

## 3. Homogeneous and Heterogeneous Catalyst

**3.1. Homogeneous Catalysts.** The experimental balance and enhancement of the addition of homogeneous catalyst upon the biomass gasification are seen in Tables 3 and 4, respectively. The yield of hydrogen is 2.86 mmol/g with no catalyst added. The presence of the catalyst increased the yield of hydrogen. KOH has the best catalytic effect and the amplification of hydrogen yield is 144.76%.  $\text{Ca}(\text{OH})_2$  takes the second place. The amplification is 132.87%.  $\text{NaCO}_3$  has the worst catalytic effect and the amplification is only 9.79%. Meanwhile, the fraction of hydrogen increases at the same time. When  $\text{Ca}(\text{OH})_2$  is added, the fraction of hydrogen is 48.54%. The order of catalytic effect on hydrogen yield of biomass gasification is as follows:  $\text{KOH} > \text{Ca}(\text{OH})_2 > \text{K}_2\text{CO}_3 > \text{LiOH} > \text{NaOH} > \text{Na}_2\text{CO}_3$ . The order of catalytic effect on hydrogen fraction of biomass gasification is as follows:  $\text{LiOH} > \text{Ca}(\text{OH})_2 > \text{KOH} > \text{K}_2\text{CO}_3 > \text{NaOH} > \text{Na}_2\text{CO}_3$ .

As for the comparison of hydrogen yield between the alkali carbonate and alkali hydroxide, the influence of alkali metal cation ( $\text{Na}^+$ ,  $\text{K}^+$ ) is far more than that of anion ( $\text{CO}_3^{2-}$ ,  $\text{OH}^-$ ). Comparison between LiOH, NaOH, and KOH shows that the stronger the alkalinity is, the weaker the catalytic effect is for hydrogen production.

It can be seen that when basic catalysts are added, the yield of CO decreases sharply, that is probably due to catalytic effect of basic catalyst upon the water-gas shift reaction. The amount of  $\text{CO}_2$  decreases compared with the reaction situation without catalyst because  $\text{CO}_2$  is absorbed by the basic catalysts (especially LiOH, NaOH, KOH, and  $\text{Ca}(\text{OH})_2$ ) as carbonates. For example,  $\text{Ca}(\text{OH})_2$  is used in HyPr-RING by Lin et al. [28] to absorb  $\text{CO}_2$  and to integrate water-gas shift reaction and  $\text{CO}_2$  absorption reaction in one reactor. The reactions are as follows:



It can be seen that although the presence of basic catalyst increases the yield of hydrogen and methane, carbon gasification efficiency increases. Basic catalyst has catalytic

TABLE 1: Elemental and proximate analysis of peanut shell.

Biomass	Elemental analysis (wt%)					Proximate analysis (wt%)			
	C	H	N	S	O	M	A	V	FC
Peanut shell	43.80	4.92	1.52	0.17	34.10	7.99	7.50	65.85	18.66

TABLE 2: Metal element analysis of Raney nickel catalyst.

Type	Active metal	Promoter	Al	Particle size/ $\mu\text{m}$
RTH-3110	~90 wt% Ni	1 wt% Mo	4–10 wt%	50
RTH-4110	~85 wt% Ni	2 wt% Fe, 2.5 wt% Cr	8–12 wt%	50
RTH-5110	~75 wt% Ni	15 wt% Fe	4–10 wt%	32

effect on water-gas shift reaction, and its catalytic effects are reported in earlier publication [18].

On the other hand, basic effect has an important effect in the process of biomass hydrolysis. Sinađ et al. studied the function of  $\text{K}_2\text{CO}_3$  in the process of glucose gasification in supercritical water. It is found that  $\text{K}_2\text{CO}_3$  is in favor for the decomposition of glucose to formic acid and restrained furfurals formation. And formic acid is regarded as an intermediate of gas formation. Furfurals can be converted to be phenols and produce tar and coke. Therefore, the presence of  $\text{K}_2\text{CO}_3$  increases the yield of gas and restrained tar and coke production [26, 42].

Encinar et al. [43] reported that metal chloride such as  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ , and  $\text{ZnCl}_2$  has a catalytic effect in the process of bagasse gasification.  $\text{ZnCl}_2$  has an obvious promotion in the process of hydrogen production especially. When  $\text{ZnCl}_2$  is used as catalyst, a great amount of char particles are produced, and viscous black tarry substance is produced as well, which is a typical phenomenon of incomplete gasification. Although the carbon gasification efficiency remains constant, the hydrogen selectivity increases sharply and the yield of hydrogen increases by 82.5% because  $\text{ZnCl}_2$  has the function of swelling and dissolution and can permeate into the inner place of feedstock so as to form a small opening to increase the contact area of the catalyst and biomass matrix.

**3.2. Heterogeneous Catalysts.** The experimental balance and enhancement of the addition of heterogeneous catalyst upon the biomass gasification are seen in Tables 5 and 6, respectively. Three kinds of Raney-Ni (RTH-3110, RTH-4110, and RTH-5110) are selected as typical Raney-Ni. They obtained carbon gasification efficiency of 66.73%, 59.66%, and 53.07%, respectively, among which RTH-3110 holds the highest carbon gasification efficiency. The three kinds of Raney-Ni have the hydrogen yield of 9.57, 8.34, and 10.78 mmol/g gas yield compared with 2.86 mmol/g without catalyst.

Raney-Ni is mainly [44, 45] a fine-ground solid composed mostly of nickel derived from a nickel-aluminum alloy, and there are trace elements spread in nickel-aluminum. The lattice defects in the metallic surface and the trace elements increase catalytic effects. The metal analyses for the three catalysts are shown in Table 2. It can be seen from Table 5 that different trace elements have distinct catalytic effects. RTH-5110 doping with Fe has the highest hydrogen yield,

because Fe is in the eighth main group in the periodic table of the elements, and the Ru, Rh, Pd, and Ni have been proved to be an effective catalyst for biomass gasification in supercritical water. Elements in the eighth main group have strong chemical absorption for reactant, so that elements in this main group show catalytic ability in relatively low temperature. Compared with RTH-4110, RTH-3110 has better catalytic effect in hydrogen production. It can be seen that addition of Mo favors hydrogen production from biomass more obviously than Cr. It can provide useful information for home-made catalysts development.

As for the gasification of coal in a pipe flow continuous experimental device operated by Li et al. [23], gasification efficiency, carbon gasification efficiency, and hydrogen gasification efficiency with  $\text{K}_2\text{CO}_3$  are higher than those with Raney-Ni, because Raney-Ni powder is not well distributed as particles, and  $\text{K}_2\text{CO}_3$  dissolves in water to form a uniform solution.

It can be seen from Table 6 that olivine and dolomite have a catalytic effect on biomass gasification. They increase hydrogen yield by 46.2% and 37.8%, respectively, compared with the reaction condition without catalyst. Although their catalytic effects are not as high as  $\text{KOH}$  and  $\text{Ca}(\text{OH})_2$ , they are still higher than that of  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$ . The fraction of hydrogen increases with the addition of dolomite and olivine. Complex of  $\text{CaO-MgO}$  is generated by calcinations and it is a mixed oxide acid-base type catalyst with polar active sites. These active sites can absorb hydrocarbon and break the C–C and C–H bond to obtain gas and liquid product in small molecular in the hydrogen production reaction of biomass gasification in supercritical water. Dolomite also has a catalytic effect on the decomposition of tar and coke with large molecular. Because tar contains a great amount of condensed ring with electronegative  $\pi$ -electron system so they can be absorbed in the  $\pi$ -shaped electron cloud and lose stability and make C–C bond and C–H bond broken easily, so as to lower the activation energy of pyrolysis. Olivine also has good catalytic effect in biomass gasification and is commonly used in traditional biomass gasification process. What is more, olivine has good wear-resisting property and is especially useful in fluidized bed reactor for biomass gasification, which can get rid of the problem of the fragments of the catalyst by friction when catalyst is used as bed material [16, 40, 46–49].

TABLE 3: Mass balance for homogeneous catalyst investigation.

Catalyst	$W_R/g$	$W_G/g$	$W_L/g$	$W_S/g$	$(W_G + W_L + W_S - W_R)/g$	Mass balance <sup>a</sup> coefficient $Q_m/\%$
Noncatalytic	11.3	0.49	9.94	0.54	0.33	97.09
LiOH	12.3	0.24	10.98	0.71	0.37	96.99
Na <sub>2</sub> CO <sub>3</sub>	12.3	0.40	10.92	0.71	0.27	97.82
NaOH	12.3	0.34	10.15	0.87	0.94	92.36
K <sub>2</sub> CO <sub>3</sub>	12.3	0.39	10.06	0.99	0.86	93.04
KOH	12.3	0.36	10.48	0.77	0.69	94.39
Ca(OH) <sub>2</sub>	12.3	0.31	9.32	1.39	1.29	89.52
ZnCl <sub>2</sub>	12.3	0.53	9.91	0.84	1.02	91.74

<sup>a</sup>In the reaction situation with catalyst, all catalyst mass is included in the mass of solid product.

TABLE 4: Experimental results for different homogeneous catalysts.

Catalyst	Gas yield (mmol/g feedstock)				CGE (%)	Gas composition (%)			
	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>		H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>
Noncatalytic	2.86	2.19	1.71	6.48	23.16	21.60	16.54	12.92	48.94
LiOH	5.23	1.30	1.34	2.72	11.96	49.39	12.28	12.65	25.68
Na <sub>2</sub> CO <sub>3</sub>	3.14	1.43	1.42	5.42	18.46	27.52	12.53	12.45	47.50
NaOH	3.51	0.78	1.63	4.82	16.13	32.68	7.26	15.18	44.88
K <sub>2</sub> CO <sub>3</sub>	5.64	1.08	2.55	5.09	19.44	39.28	7.52	17.76	35.45
KOH	7.00	0.92	2.98	4.22	18.12	46.30	6.08	19.71	27.91
Ca(OH) <sub>2</sub>	6.66	1.88	1.81	3.37	15.75	48.54	13.70	13.19	24.56
ZnCl <sub>2</sub>	5.22	1.06	2.13	7.72	24.33	32.36	6.57	13.21	47.86

Catalyst, 1 g; feedstock, 1 g peanut shell + 0.3 g CMC; water density, 0.071 g/cm<sup>3</sup>; reaction time, 20 min; pressure, 22~24.0 MPa.

## 4. Synergistic Effect of Homogeneous and Heterogeneous Catalyst

**4.1. Influence of the Amount of NaOH.** In the process of hydrogen production by biomass gasification in supercritical water when Raney-Ni (RTH-5110 type) is used as catalyst in 400°C, the liquid obtained is transparent without the smell of tar. When the mixture of Raney-Ni and NaOH is used as catalyst, the liquid product amount and composition have a great relationship with the amount of NaOH. When the amount of NaOH is low, the residual liquid is transparent and no char is produced. As the amount of NaOH increases, the color of residual liquid becomes yellowish-brown and then brown and the smell of tar becomes stronger. It can be seen that the appropriate amount of NaOH favors biomass gasification and excessive amount of NaOH has restraining effect.

Mass balance of reactions for peanut shell gasification in supercritical water when 1 g RTH-5110 type Raney-Ni (in water slurry state) and 0.0~0.75 g NaOH are used as catalyst in 400°C. The yield of gas increases first and then decreases, and the solid product has increasing trend. The mass balance is within the range of 94.51%~99.60%.

In the temperature of 400°C, initial pressure of 4 MPa, the pressure of 24~28 MPa, residence time of 20 min, with the concentration of 10 wt%, and the mixture of 1 g RTH-5110 type Raney-Ni (in water slurry state) and 0.0~0.75 g NaOH are used as catalyst. The gasification characteristics

of peanut shell in supercritical water can be seen in Figure 1 and the mass balance can be seen in Table 7. It can be seen that as the amount of NaOH increases, gasification efficiency, carbon gasification efficiency, and hydrogen yield all increase first and then decrease and peak when the amount of NaOH equals 0.25 g. The gasification efficiency, carbon gasification efficiency, and hydrogen fraction are 110.95%, 86.57%, and 172.02%, respectively. Compared with the reaction condition without NaOH, the amplification is 8.48%, 15.87%, and 52.37%, respectively. As the amount of NaOH increases to 0.75 g, the gasification efficiency, carbon gasification efficiency, and hydrogen fraction are 69.11%, 50.64%, and 143.32%. Compared with the reaction condition without NaOH, the decline is 33.36%, 20.06%, and 23.67%, respectively.

NaOH is a catalyst with strong alkaline, and it can enhance hydrogen production by biomass gasification. Meanwhile, when NaOH and Raney-Ni are mixed, good catalytic effect is obtained. However, the amount of NaOH has an optimum value and it is speculated that excessive amount of NaOH has restraining effect on the effect of Raney-Ni.

It can be seen from Figure 2 that catalytic effect of different amount of NaOH is investigated at the reaction temperature of 400°C, initial pressure of 4 MPa, reaction pressure of 24~28 MPa, residence time of 20 min, concentration of feedstock 10 wt%, and 1 g RTH-5110 Raney-Ni (in water slurry state). It can be observed that as the amount of NaOH

TABLE 5: Mass balance for heterogeneous catalyst investigation.

Catalyst	$W_R/g$	$W_G/g$	$W_L/g$	$W_S/g$	$(W_G + W_L + W_S - W_R)/g$	Mass balance coefficient $Q_m/\%$
Noncatalytic	11.3	0.49	9.94	0.54	0.33	97.09
R-Ni, RH3110	12.3	0.24	10.98	0.71	0.37	96.99
R-Ni, RH4110	12.3	0.40	10.92	0.71	0.27	97.82
R-Ni, RH5110	12.3	0.34	10.15	0.87	0.94	92.36
Olivine	12.3	0.39	10.06	0.99	0.86	93.04
Dolomite	12.3	0.36	10.48	0.77	0.69	94.39

TABLE 6: Experimental results for different heterogeneous catalysts.

Catalyst	Gas yield (mmol/g feedstock)				CGE (%)	Gas composition (%)			
	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>		H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>
Noncatalytic	2.86	2.19	1.71	6.48	23.16	21.60	16.54	12.92	48.94
R-Ni, RH3110	9.57	1.63	12.11	16.18	66.73	23.92	4.07	30.26	40.43
R-Ni, RH4110	8.34	1.04	10.61	15.10	59.66	23.55	2.94	29.95	42.64
R-Ni, RH5110	10.78	1.38	9.41	13.00	53.07	31.18	3.99	27.22	37.60
Olivine	4.18	0.88	1.94	7.61	23.25	28.61	6.02	13.28	52.09
Dolomite	3.94	1.33	1.96	3.62	15.42	36.31	12.26	18.06	33.36

Catalyst, 1 g; feedstock, 1 g peanut shell + 0.3 g CMC; water density, 0.071 g/cm<sup>3</sup>; reaction time, 20 min; pressure, 22~24.0 MPa.

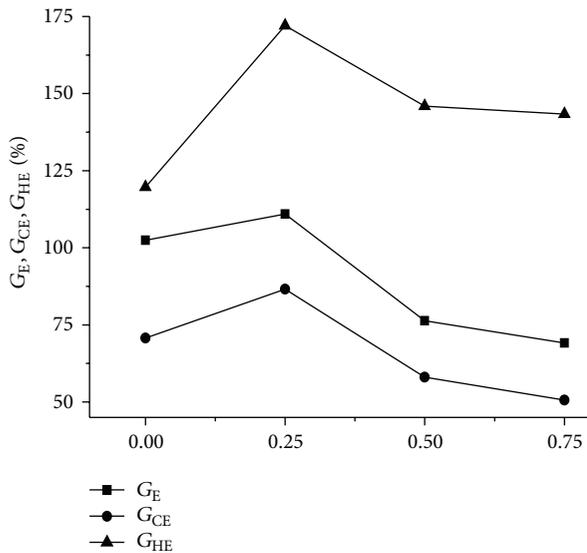


FIGURE 1: The effect of amount of NaOH upon the hydrogen yield and potential hydrogen yield (water : CMC : feedstock : Raney-Ni = 10 g : 0.3 g : 1 g : 1 g, temperature: 400°C, and residence time: 20 min).

increases, the hydrogen fraction increases first and then decreases. The fractions of methane and carbon dioxide have decreasing trend, and the fraction of CO increases slightly and then remains constant. The hydrogen fraction is 59.23% when the amount of NaOH is 0.5 g, and the amplification of hydrogen fraction is 28.35% when the amount of NaOH is 0.75 g. The fraction of carbon dioxide is 37.23% with no NaOH added, while the fraction of carbon dioxide is 23.99% when the amount of NaOH is 0.75 g. The fraction of methane

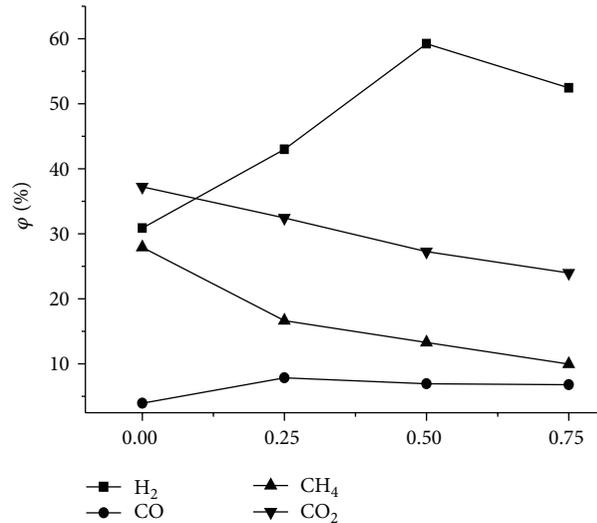


FIGURE 2: The influence of NaOH on the gas fraction (%) (water : CMC : biomass : Raney-Ni = 10 g : 0.3 g : 0.1 g : 1 g, temperature: 400°C, and residence time: 20 min).

decreases from 27.93% to 9.97% when the amount of NaOH increases from 0 to 0.75 g. It can be seen that the addition of NaOH can restrain the formation of methane. As a typical basic catalyst, NaOH can absorb carbon dioxide and promote the water-gas shift reaction toward the direction of hydrogen formation.

Figure 3 shows the hydrogen yield and hydrogen yield potential by supercritical water gasification of peanut shell versus the amount of NaOH. As the amount of NaOH increases, hydrogen yield and hydrogen yield potential [50]

TABLE 7: Mass balance for the mixture of NaOH and Raney-Ni as catalyst.

Mass of NaOH/g	$W_R/g$	$W_G/g$	$W_L/g$	$W_S/g$	$(W_G + W_L + W_S - W_R)/g$	Mass balance coefficient $Q_m/\%$
0.00	12.30	1.02	10.25	0.84	0.19	98.44
0.25	12.55	1.11	10.46	0.93	0.05	99.60
0.50	12.80	0.76	10.51	1.04	0.49	96.15
0.75	13.05	0.69	10.43	1.21	0.72	94.51

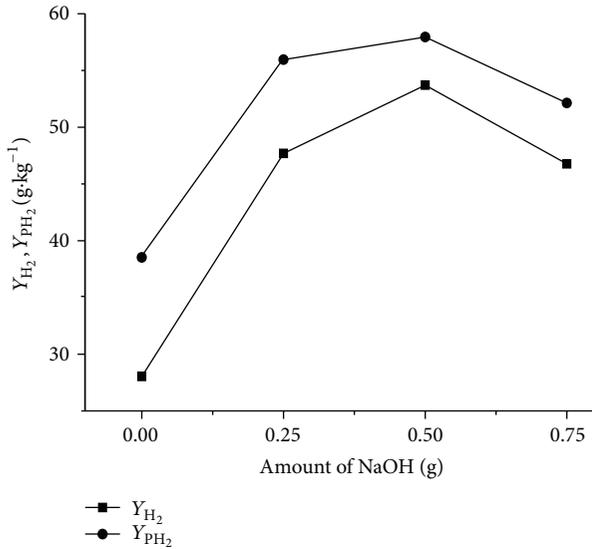


FIGURE 3: The hydrogen yield and hydrogen yield potential by supercritical water gasification of peanut shell versus the amount of NaOH (water:CMC:biomass:Raney-Ni = 10 g:0.3 g:1 g:1 g, temperature: 400°C, and residence time: 20 min).

by supercritical water gasification of peanut shell increase first and then decrease. When the amount of NaOH is 0.5 g, they obtained the maximum value. When NaOH is not present, the hydrogen yield and hydrogen yield potential are  $28.02 \text{ g} \cdot \text{kg}^{-1}$  and  $38.53 \text{ g} \cdot \text{kg}^{-1}$ , respectively. As the amount of NaOH increases to 0.25 g, the hydrogen yield and hydrogen yield potential are  $47.69 \text{ g} \cdot \text{kg}^{-1}$  and  $55.95 \text{ g} \cdot \text{kg}^{-1}$ , respectively, and the increments are  $25.68 \text{ g} \cdot \text{kg}^{-1}$  and  $19.41 \text{ g} \cdot \text{kg}^{-1}$ , respectively. However, when the amount of NaOH increases further, the hydrogen yield and hydrogen yield potential decrease. When the amount of NaOH equals 0.75 g, the hydrogen yield and hydrogen yield potential are  $46.77 \text{ g} \cdot \text{kg}^{-1}$  and  $52.14 \text{ g} \cdot \text{kg}^{-1}$ , respectively. It is presumed that excess amount of NaOH prevents the contact of the active center and the biomass particle and results in the lower gasification efficiency, carbon gasification efficiency, and hydrogen yield.

**4.2. Synergistic Effect of Catalyst.** The synergistic effect of Raney-Ni and NaOH can be seen in Figure 4. The yield of hydrogen by peanut shell supercritical water gasification is  $7.44 \text{ g} \cdot \text{kg}^{-1}$  without catalyst. The yield of hydrogen is

$11.43 \text{ g} \cdot \text{kg}^{-1}$  with NaOH as catalyst and  $11.43 \text{ g} \cdot \text{kg}^{-1}$  with RTH-5110 Raney-Ni as catalyst. The yield of hydrogen is as high as  $53.71 \text{ g} \cdot \text{kg}^{-1}$  when both NaOH and Raney-Ni are used as catalyst. It can be deduced that the mixing effect of Raney-Ni and NaOH is as follows:

$$(53.71 - 7.44) - ((11.43 - 7.44) + (28.03 - 7.44)) = 21.69 \text{ g} \cdot \text{kg}^{-1}. \quad (4)$$

The reason for the synergistic effect of Raney-Ni and NaOH is analyzed. The process of biomass gasification in supercritical water is a typical multiphase chemical reaction. NaOH can dissolve in supercritical water to form a uniform slurry, and it can react with biomass particle and leads to the formation of formats, which subsequently degrades to hydrogen and carbon dioxide [18]. Char formation was considerably suppressed. NaOH could also accelerate the gasification of phenols [20] and reinforce the hydrogenation of phenol to form benzene and further to cyclohexane for hydrogen production [22]. Raney-Ni is a kind of particle catalyst that can react with liquid and gas intermediate. It favors breaking the C-C bond and C-H bonds to obtain gas and liquid product in small molecular to enhance the carbon conversion at relatively low temperature [40]. Raney-Ni can also future adjust the gas fraction by water-gas shift reaction and methanation reaction. So the Raney-Ni and NaOH have a synergistic effect in the biomass gasification in supercritical water.

## 5. Conclusion

Peanut shell is selected as typical biomass to investigate the catalytic gasification result of biomass in supercritical water at the temperature of 400°C, pressure of 22~24 MPa, and residence time of 20 min. The order of catalytic effect on hydrogen yield of biomass gasification is as follows: KOH > Ca(OH)<sub>2</sub> > K<sub>2</sub>CO<sub>3</sub> > LiOH > NaOH > Na<sub>2</sub>CO<sub>3</sub>. The order of catalytic effect on hydrogen yield of biomass gasification is as follows: LiOH > Ca(OH)<sub>2</sub> > KOH > K<sub>2</sub>CO<sub>3</sub> > NaOH > Na<sub>2</sub>CO<sub>3</sub>. As for Raney-Ni, RTH-3110 has the highest carbon gasification efficiency and RTH-5110 has the highest hydrogen yield. The mixture of Raney-Ni and NaOH shows great synergistic effect in the process of biomass gasification in supercritical water.

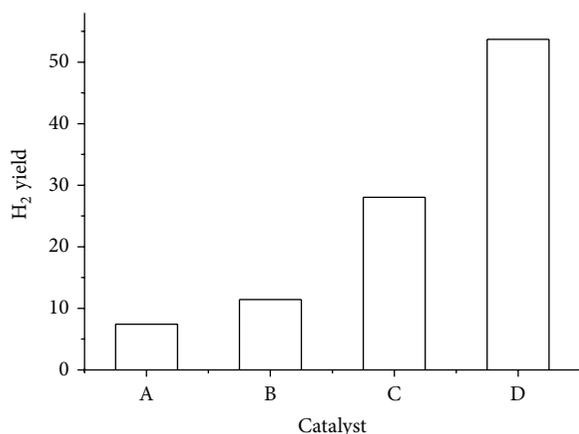


FIGURE 4: The mixed effect of Raney-Ni and NaOH/g·kg<sup>-1</sup>. Reaction temperature: 400°C, reaction pressure: 24~28 MPa, initial pressure: 4 MPa, residence time: 20 min, and concentration of feedstock: 10% (A: none; B: 0.5 g NaOH; C: 1.0 g Raney-Ni; D: 0.5 g NaOH + 1.0 g Raney-Ni).

## Nomenclature

- $G_{CE}$ : Carbon gasification efficiency, the mass of carbon element in gaseous product/the mass of carbon in dry matter in the water-coal-slurry
- $G_E$ : Gasification efficiency, the mass of gaseous product/the mass of dry matter in the water-coal-slurry
- $G_{HE}$ : Hydrogen gasification efficiency, the mass of hydrogen gas/the mass of hydrogen in dry matter in the water-coal-slurry
- $W_G$ : Sum mass of gas product
- $W_L$ : Sum mass of liquid product
- $W_R$ : Sum mass of reactant
- $W_S$ : Sum mass of solid product
- $Y_{H_2}$ : Yield of hydrogen, the mass of certain gas product divided by the mass of dry matter in feedstock
- $Y_{PH_2}$ : Hydrogen yield potential, defined as the sum of measured hydrogen and the hydrogen which could theoretically be formed by completely shifting carbon monoxide and completely reforming hydrocarbon species.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgments

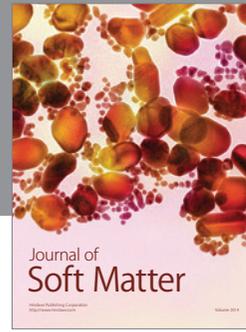
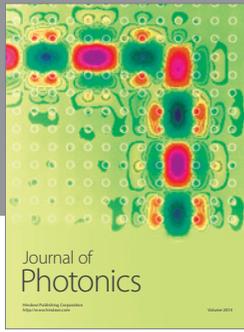
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