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Hydrogen-Rich Gas Production from Two-Stage Catalytic Pyrolysis of Pine Sawdust with Nano-NiO/Al₂O₃ Catalyst

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Abstract: Hydrogen production from biomass pyrolysis is economically and technologically attractive from the perspectives of energy and the environment. The two-stage catalytic pyrolysis of pine sawdust for hydrogen-rich gas production is investigated using nano-NiO/Al₂O₃ as the catalyst at high temperatures. The influences of residence time (0–30 s) and catalytic temperature (500–800 °C) on pyrolysis performance are examined in the distribution of pyrolysis products, gas composition, and gas properties. The results show that increasing the residence time decreased the solid and liquid products but increased gas products. Longer residence times could promote tar cracking and gas-phase conversion reactions and improve the syngas yield, H₂/CO ratio, and carbon conversion. The nano-NiO/Al₂O₃ exhibits excellent catalytic activity for tar removal, with a tar conversion rate of 93% at 800 °C. The high catalytic temperature could significantly improve H₂ and CO yields by enhancing the decomposition of tar and gas-phase reactions between CO₂ and CH₄. The increasing catalytic temperature increases the dry gas yield and carbon conversion but decreases the H₂/CO ratio and low heating value.

Keywords: catalytic pyrolysis; biomass; hydrogen; nickel-based catalyst; temperature; residence time



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1. Introduction

Hydrogen is a promising alternative energy source for the future because of its abundant resources, high energy conversion, and clean application [1–3]. Biomass is one enormous and renewable source of hydrogen, as biomass is generated by natural photosynthesis and becomes the carrier of the hydrogen [4–7]. Hydrogen production from biomass is an attractive way to solve the energy shortage and environmental pollution problems. The two pathways for hydrogen-rich gas from renewable biomass are as follows: thermochemical conversion and biological conversion [8,9]. The thermochemical conversion is a feasible option in terms of economic and technological considerations. The main thermochemical processes include pyrolysis, gasification, supercritical water gasification, and chemical looping [10–12]. Pyrolysis is one of the most promising thermochemical processes that can co-produce high-value solid, liquid, and gas products, including hydrogen [13].

Pyrolysis is a process that can convert biomass into char, tar, and gas products (H₂, CO, CO₂, CH₄, etc.) under the heat and anoxic environment [14–16]. The pyrolysis process of biomass to hydrogen can be divided into a one-stage pyrolysis process and a two-stage pyrolysis process [17–19]. The one-stage pyrolysis process can directly produce hydrogen-rich gas from biomass pyrolysis in a reactor. Compared to the one-stage pyrolysis, the two-stage pyrolysis process adds another stage to produce hydrogen-rich gas through tar cracking or steam reforming of the products from the one-stage pyrolysis process. Therefore, the two-stage pyrolysis process can produce more hydrogen than the one-stage pyrolysis process due to the decomposition of heavy hydrocarbons [17,18]. In the two-stage pyrolysis process, the catalysts are commonly used for tar cracking, so the study of the catalyst for hydrogen production is of great significance.

The important factors, including biomass types, heating rate, and temperature, in the pyrolysis process have been studied by some researchers [20–23]. The fast pyrolysis of four different biomass types was examined by Eri et al. via detailed CFD modelling [23]. Their study showed that cellulose-rich biomass produced the highest bio-oil yield, and the generated char was mainly from the lignin and cellulose of the biomass. The effect of heating rate on pyrolysis products was investigated for 14 plant species by Safdari et al. [21]. Their results showed that a higher heating rate resulted in a higher tar yield, gas yield, and volatile yield. The effect of temperature on the biogas production from the pyrolysis of sewage sludge was investigated by Liu et al. [24]. It was found that high temperatures improved biogas production and especially increased the H_2 yield. The effect of temperature on pyrolysis characteristics was examined by Xu et al. for a single biomass particle using experimental and simulation methods [20]. They found that the increasing temperatures decreased the char yield and increased the shrinkage rate of the particles. The influence of temperature on the pyrolysis yield of hardwood residues was investigated by Mazlan et al. using a moving bed [22]. The results presented that with the temperature increase, the bio-oil and gas yields increased, while the char yield decreased. However, the current study of biomass pyrolysis is limited to medium temperatures $<600\text{ }^\circ\text{C}$ —the high-temperature pyrolysis behaviour of the biomass, especially for hardwood residue, such as pine sawdust, is still unclear.

The catalytic pyrolysis of biomass has been investigated by using different types of catalysts [13,25]. Different types of zeolites, including HZSM-5, β -zeolite, and Y-zeolite, are widely used in biomass pyrolysis because of their unique distribution of pores and surface acidic sites [26,27]. Catalytic pyrolysis of paddy husk was examined by Naqvi et al. using MCM-22 and ITQ zeolites [28]. It was found the pyrolysis oil decreased with the zeolite catalysts due to the catalytic cracking of oil, such as decarboxylation. Metal catalysts, including Ni-based catalysts, Al_2O_3 , $CaCO_3$, and $NaCO_3$, were also widely used in biomass pyrolysis [29]. The catalytic pyrolysis of municipal solid wastes was studied by Li et al. using Al_2O_3 as a catalyst in a fluidized bed reactor [30]. It was found that Al_2O_3 decreased the activation energy of the CO bond in the sample and improved the rate of decarboxylation, aromatization, and alkylation reactions. Six different Ni-based catalysts were studied by Liu et al. for syngas production from the pyrolysis of pine sawdust [31]. The results showed that Ni/magnesium slag achieved the best catalytic performance, which had a 95% tar conversion and a $1.46\text{ Nm}^3/\text{kg}$ gas yield. Although different types of catalysts have been studied, the application of nano $NiO/\gamma-Al_2O_3$ in biomass pyrolysis has not been studied to our knowledge.

The main objective of this study is to study the high-temperature catalytic pyrolysis performance of pine sawdust for hydrogen-rich gas production using nano $NiO/\gamma-Al_2O_3$ as a catalyst in a two-stage moving bed. The pyrolysis performance was examined in terms of pyrolysis products' distribution, gas composition, and gas properties. Firstly, the effects of residence time on pyrolysis performance were studied without catalysts. Moreover, the effect of catalytic temperature on pyrolysis performance was studied with nano $NiO/\gamma-Al_2O_3$.

2. Results and Discussion

2.1. Effect of Residence Time on Pyrolysis

The pyrolysis experiments of pine sawdust were performed at $850\text{ }^\circ\text{C}$ without using catalysts or a catalytic bed. The different residence times (12 s, 17 s, 22 s, and 30 s) in the pyrolysis bed were obtained by changing the secondary feeding speed (x_2). Their effects on pyrolysis performance are investigated in this section.

2.1.1. Effect of Residence Time on Pyrolysis Products Distribution

Figure 1 shows the influence of solid residence time (SRT) on the distribution of pyrolysis products. The proportion of gas yield increased rapidly from 61.79 wt% (SRT = 12 s) to 74.34 wt% (SRT = 30 s) with the prolonged residence time in the pyrolysis bed. However,

the trend of liquid and solid yield was just the opposite. When SRT was 12 s, liquid and solid yields were 16.9 wt% and 21.31 wt%, respectively. However, when SRT was increased to 30 s, liquid and solid yields were decreased to 7.71 wt% and 16.78 wt%, respectively. The experimental results showed that the longer the residence time, the less liquid and solid yields there were and the more gas yields there was at the same temperature and heating rate.

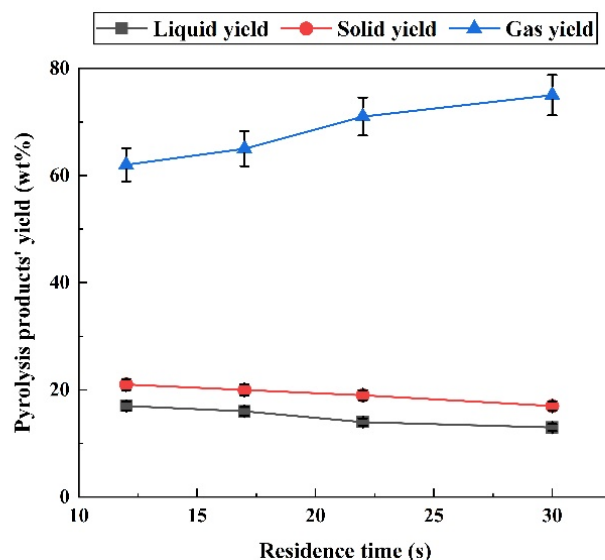
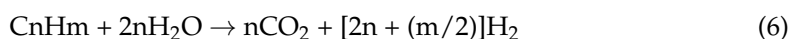
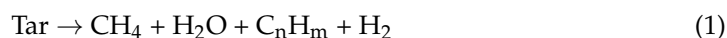


Figure 1. Effect of residence time on the distribution of pyrolysis products of pine sawdust at 850 °C without catalyst.

The pyrolysis process can be generally divided into the following two stages: primary pyrolysis and secondary pyrolysis. During the primary pyrolysis, the biomass particles are heated up and converted into char, tar, and light gases (such as H_2 , CO , CO_2 , CH_4 , H_2O , and other low hydrocarbons). With the increase in temperature, the secondary pyrolysis takes place. During the secondary pyrolysis, the tar is further thermally cracked into light gases, as seen in Equation (1). The gases released from the primary pyrolysis also undergo secondary gas-phase reactions (such as Equations (2) and (3)) and secondary solid-gas-phase reactions (such as Equation (2)). Hence, the increase in gas yield with residence time was mainly due to the thermal cracking of the tar and the secondary gas reactions.



2.1.2. Effect of Residence Time on Gas Composition

The influence of residence time (SRT) on pyrolysis gas composition is shown in Figure 2. The main gas products of pine sawdust pyrolysis were H_2 , CO , CO_2 , and CH_4 . No C_2 gas products or other hydrocarbons were measured in our experiments. With the increasing SRT, H_2 , CO , and CO_2 all increased significantly, but the concentration of CH_4 showed a downward trend. Specifically, as SRT increased from 12 s to 30 s, the CO_2 content increased from 17.33% to 24.17%. This may be due to the reaction of CO with H_2O (Equation (3)) and the heavy hydrocarbons cracking (Equation (6)), resulting in the formation of CO_2 .

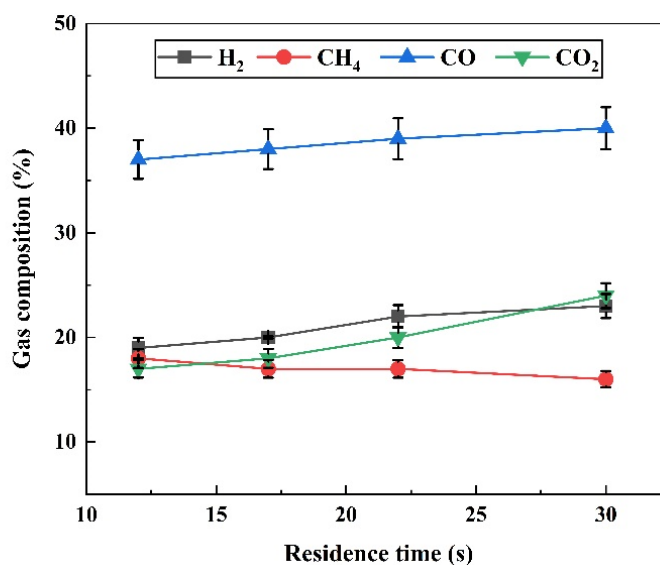


Figure 2. Effect of residence time on pyrolysis gas composition of pine sawdust at 850 °C without catalyst.

However, the CH₄ content decreased with the increase in SRT. When SRT was 12 s, the CH₄ content was 18.54%, and when SRT was 30 s, it decreased to 16.74%. This may be attributed to the tar cracking (Equation (1)) and the secondary gas reactions (Equations (4) and (5)).

The CO content increased by 5% with the increase of SRT from 12 s to 30 s. Similarly, the concentration of H₂ increased rapidly by 22% in the same range of SRT. The increase in H₂ and CO was due to the formation of more H₂ and CO by the tar cracking and the secondary gas reaction. Interestingly, the value of CO₂ concentration exceeded the value of H₂ concentration at 30 s. This could be a result of the secondary pyrolysis reactions using H₂ as reactants, such as the reverse of dry methane reforming (Equation (7)) and hydrogasification (Equation (8)) [10,32].



2.1.3. Effect of Residence Time on Gas Products Properties

The variation trend of the characteristic parameters of gas products with the residence time is shown in Table 1. The syngas (H₂ + CO) content and H₂/CO ratio increased by 11% and 16%, respectively, as SRT increased from 12 s to 30 s. In the SRT range of 12–30 s, the syngas content and H₂/CO ratio reached their maximum (62.27% and 0.5897, respectively) at 30 s. Experimental data revealed the influence of SRT on syngas yield and composition. At a constant temperature, the longer the SRT, the greater the syngas yield and H₂/CO ratio.

Table 1. Effect of residence time on properties of gas products.

Residence Time (s)	12	17	22	30
Syngas (H ₂ + CO) (%)	56.31	58.10	59.64	62.27
H ₂ /CO (–)	0.51	0.53	0.56	0.58
LHV (MJ/Nm ³)	13.40	13.29	13.53	13.43
Dry gas yield (Nm ³ /kg)	0.77	0.84	0.88	1.12
Carbon conversion (wt%)	65.48	72.57	78.03	85.25

The dry gas yield and carbon conversion also increased with the increase of SRT, from $0.774 \text{ Nm}^3/\text{kg}$ and 65.48% (SRT = 12 s) to $1.12 \text{ Nm}^3/\text{kg}$ and 85.25% (SRT = 30 s), respectively. According to the equation of the carbon conversion (Equation (13)), the value of the carbon conversion is determined by the dry gas yield and the total composition of CO, CO₂, and CH₄. Although the CH₄ composition decreased by 2 vol% with the residence time, the total composition of CO and CO₂ increased by 10 vol%. Therefore, the total composition of CO, CO₂, and CH₄ increased by 8 vol% at the residence time of 12–30 s. Meanwhile, the dry gas yield increased by $0.35 \text{ Nm}^3/\text{kg}$ with the residence time. Because of the increase in dry gas yield and total composition of CO, CO₂ and CH₄, the carbon conversion increased with the residence time. This result indicated that the increase in SRT improved pyrolysis reactions, resulting in a rise in the pyrolysis gas yield and carbon conversion. The low heating value (LHV) of pyrolysis gas fluctuated in the range of 13.29–13.53 MJ/Nm³ with the change of residence time, indicating no significant association between the LHV and residence time.

2.2. Catalytic Effect of Nano-NiO/ γ -Al₂O₃

In this section, the pyrolysis bed was performed at 800 °C, and nano-NiO/ γ -Al₂O₃ was used as the catalyst for the catalytic bed. The catalytic bed was conducted at 500–800 °C under a weighted hourly space velocity of 0.4 h^{-1} to study the catalytic effect of nano-NiO/ γ -Al₂O₃.

2.2.1. Effect of Catalyst on Pyrolysis Products Yield

Figure 3 shows the effect of catalytic temperature on the pyrolysis products' distribution of pine sawdust using nano-NiO/ γ -Al₂O₃. As seen, the gas yield with the catalyst at 500 °C significantly increased by 10.3 wt% compared to no catalyst. When the catalytic temperature rose from 500 °C to 800 °C, the gas yield increased from 75.4 wt% to 84.1 wt%. Meanwhile, the tar yield decreased with the increasing catalytic temperature. At 800 °C, the tar yield had decreased to 0.88 wt%, nearly zero. By contrast, the char almost kept stable at around 16 wt% regardless of catalyst and catalytic temperature. This is because the char yield was determined by the pyrolysis bed. In other words, the catalytic bed can only affect the tar and gas yield by the thermal decomposition of volatile organic gases and the catalytic reforming of gas products. The results showed that nano-NiO/ γ -Al₂O₃ had an excellent catalytic effect for tar removal, which can almost 100% remove tar at 800 °C. Under the catalytic effect of nano-NiO/ γ -Al₂O₃, the majority of the generated tar was converted into gas products.

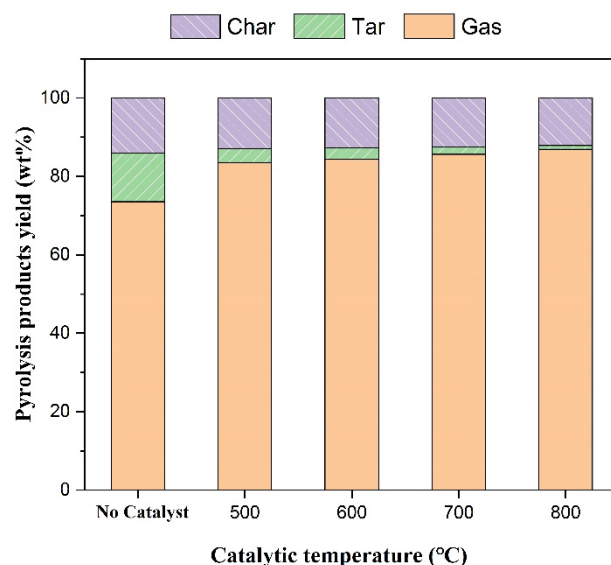


Figure 3. Effect of catalytic temperature on the distribution of pyrolysis products of pine sawdust.

2.2.2. Effect of Catalyst on Gas Composition

The effect of catalytic temperature on gas composition is presented in Figure 4. The generated gas products during catalytic pyrolysis were H_2 , CO, CH_4 and CO_2 . With the catalyst of nano $NiO/\gamma-Al_2O_3$, the content of H_2 and CO increased, but the content of CH_4 and CO_2 decreased. With the catalytic temperature increased, the constant increase of H_2 and CO and the decrease of CH_4 and CO_2 were observed at 500–800 °C. At 800 °C, the content of H_2 and CO reached a maximum value of 35.9% and 48.3%, respectively. The values nearly doubled those of no catalyst. By contrast, the value of CO_2 dramatically decreased from 34.3% (no catalyst) to 12.4% (500 °C), and further decreased to 9.1% (800 °C). The CH_4 showed a similar decrease trend with the catalyst and catalytic temperature. The increase in H_2 and CO can be attributed to the boosting of secondary decomposition of the tar (Equation (1)) and secondary gas reactions (Equations (4) and (5)) under the increasing catalytic temperature. Interestingly, the H_2 composition did not keep increasing but remained almost stable at 600–800 °C. The results indicated the consumption of H_2 occurred at a higher temperature, which may be a result of secondary pyrolysis reactions such as the reverse of dry methane reforming (Equation (7)) and hydrogasification (Equation (8)). The decrease in the CH_4 and CO_2 confirmed that secondary gas-phase reactions become more intensive with increasing catalytic temperature. The results revealed that nano $NiO/\gamma-Al_2O_3$ improved the secondary gas reactions and increased the content of H_2 and CO in gas products.

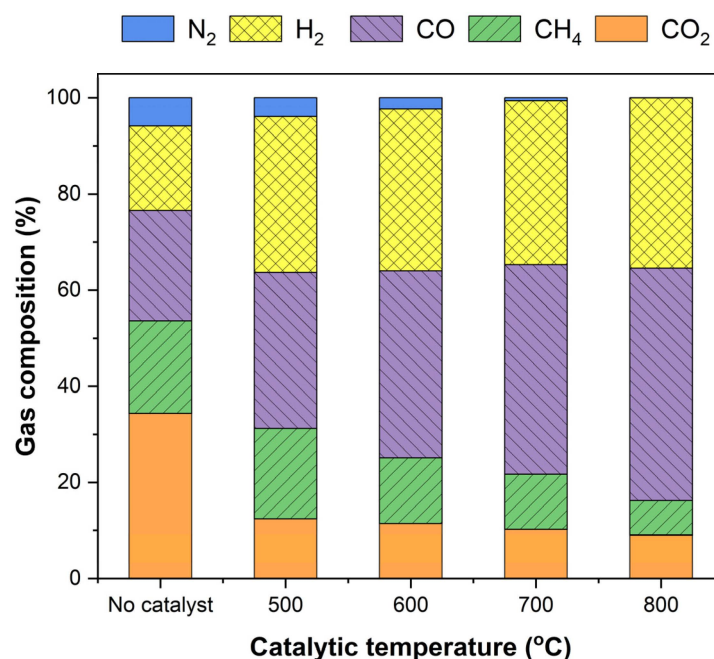


Figure 4. Effect of catalytic temperature on pyrolysis gas composition of pine sawdust.

2.2.3. Effect of Catalyst on Properties of Gas Products

The influence of catalytic temperature on gas properties is shown in Table 2. The ratio of H_2/CO under catalytic pyrolysis at 500 °C almost doubled to 1.00, compared to no catalyst. However, with the increasing catalytic temperature, the ratio of H_2/CO decreased from 1.00 (500 °C) to 0.74 (800 °C). This indicated that the increased rate of CO was greater than that of H_2 with catalytic temperature. Meanwhile, the syngas content in gas products significantly increased by 21.86%, with the catalyst at 500 °C. The value of syngas content steadily increased from 67.34% (500 °C) to 84.28% (800 °C) due to the tar cracking and gas-phase reactions. The dry gas yield and carbon conversion showed a similar trend. The numbers of dry gas yield and carbon conversion dramatically grew with the catalyst of nano- $NiO/\gamma-Al_2O_3$, and the values kept increasing with the catalytic temperature. The

results indicated that nano NiO/ γ -Al₂O₃ had an excellent catalytic effect for gas products, which improved syngas quality by changing the ratio of H₂/CO.

Table 2. Effect of catalytic temperature on properties of gas products.

Catalytic Temperature (°C)	No Catalyst	500	600	700	800
H ₂ /CO (–)	0.47	1.00	0.86	0.77	0.74
Syngas (H ₂ + CO) (%)	45.48	67.34	76.81	81.84	84.28
Dry gas yield (Nm ³ /kg)	0.36	0.58	0.62	0.78	0.97
Carbon conversion (wt%)	34.23	43.57	48.03	60.67	73.06
LHV (MJ/Nm ³)	12.4	14.59	14.20	13.73	12.70

3. Experimental Section

3.1. Sample Preparation

Pine sawdust was used as the feedstock in this study, which came from the furniture processing factory in Wuhan, China. The sawdust was air-dried and screened by a vibrating material screener, and it was sieved to a particle size of < 177 μ m. The proximate analysis of the pine sawdust was measured according to the Chinese standard-GB/T 28731-2012. Ultimate analysis of the sample was carried out by an elemental analyzer (Vario Micro Cube, Elementar, Langenselbold, Germany). These results of pine sawdust are shown in Table 3.

Table 3. The properties of pine sawdust (air-dry basis).

Sample	Proximate Analysis (wt%)				Ultimate Analysis (wt%)			
	Moisture	Volatile	Fixed Carbon	Ash	C	H	N	S
Pine sawdust	9.18	62.23	15.77	11.82	46.36	5.75	2.26	0.35

3.2. Catalyst Preparation and Characterization

Based on Li et al.'s study [33,34], the nano-NiO was prepared and then incorporated into the γ -Al₂O₃ support substrates by the deposition-precipitation method. Firstly, 0.08 mol of Ni(NO₃)₂·6H₂O and 0.24 mol of CO(NH₂)₂ was accurately weighed and then dissolved into 150 mL deionized water in a beaker. After that, 32.64 g γ -Al₂O₃ supports were transferred into the breaker with the mixture solution. The glass vessel was sealed and placed in a heater with a magnetic stirrer, where the mixture was heated in an oil bath at 115 °C for 5 h. With the process of the reaction, the nickel precursor of light green was precipitated on the γ -Al₂O₃ supports. After the completion of the reaction, the light green solid spheres were washed to colourless by using deionized water for removing possible absorbed chemicals. The γ -Al₂O₃ supports with the nickel precursor were then dried in an oven at 90 °C for 5 h. The dried samples were calcined in a muffle furnace at 400 °C for 4 h in the air, where the nickel precursor was decomposed into nickel oxide. The final catalyst products (nano NiO/ γ -Al₂O₃) were collected and obtained.

The crystalline structures of the catalyst samples were measured by a Bruker D8 Advance X-ray diffractometer. The surface area of the catalyst was examined by a surface area porosity analyzer (ASAP 2010, Micromeritics, Atlanta, GA, USA). Their XRD patterns are shown in Figure 5, and their surface properties are listed in Table 2. As shown in Figure 1, NiO was the main phase on the surface of the catalyst sample. The nanoparticles of NiO on the surface of the γ -Al₂O₃ were examined by a transmission electron microscopy (TEM). The TEM image of the nanoparticles of the NiO is presented in Figure 6. It can be seen from Figure 6 that the NiO particles had a small size at a range of 5–20 nm with spherical shapes. As seen in Table 4, the supported catalysts had a relatively high specific surface area. Compared to γ -Al₂O₃ supports, the BET surface area and pore volume of the catalyst were slightly smaller, possibly due to the blockage of the NiO particles on the surface of the support.

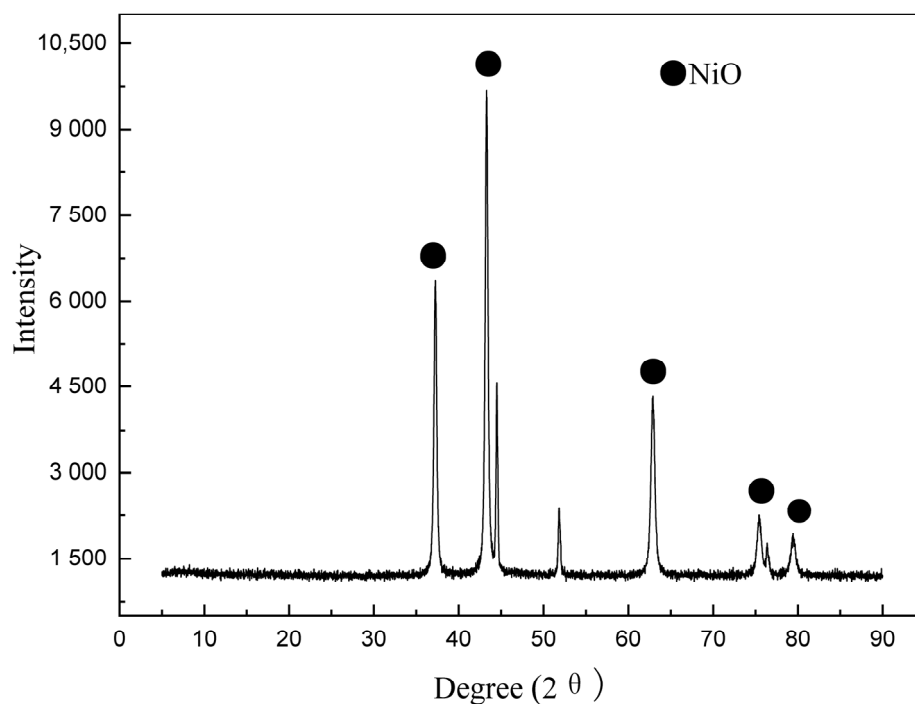


Figure 5. XRD patterns of nano-NiO/ γ -Al₂O₃.

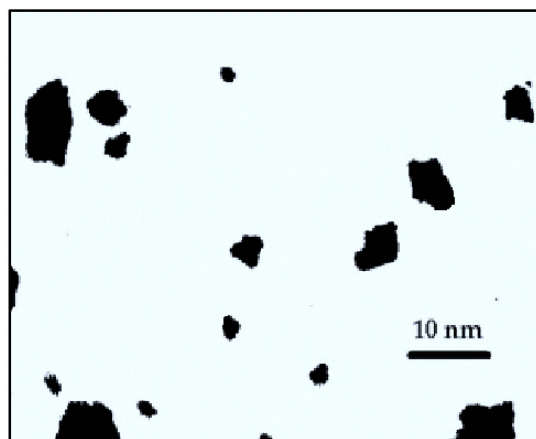


Figure 6. The TEM image of the nanoparticles of the NiO.

Table 4. The surface properties of γ -Al₂O₃ and nano-NiO/ γ -Al₂O₃.

Samples	BET Surface Area (m ² /g)	Micropore Surface Area (m ² /g)	External Surface Area (m ² /g)	Pore Volume (cm ³ /g)
Support, γ -Al ₂ O ₃	130.2	13.6	117.2	0.42
Nano-NiO/ γ -Al ₂ O ₃	125.2	10.3	114.9	0.39

3.3. Experimental Apparatus and Procedures

A self-designed two-stage catalytic pyrolysis reactor was used for catalytic pyrolysis experiments in our study. It was mainly composed of a two-stage screw feeder, a horizontal pyrolysis moving bed, a temperature control system, a vertical catalytic reforming moving bed, and a gas cleaning and tar collecting system. The schematic diagram of the apparatus is shown in Figure 7.

The two-stage screw feeder system consists of two screw feeders. The screw feeder mainly includes the screw, motor, and hopper. The motor drove the rotation of the screw

and then pushed the raw material forward. The primary screw feeder contained a hopper, and its end was connected to the pyrolysis reactor. A short distance was maintained between the screw end and the outlet of the feeder to achieve a good sealing performance by forming a material seal. According to the cold mode tests, the input mass of the feeder was determined by the speed of the primary screw feeder (x_1). The secondary screw feeder was located in the pyrolysis bed, and its rotational speed determined the biomass moving velocity within the reactor. According to the cold mode experiment (tests at room temperature), the feeding rate of biomass (Y , g/h) can be calculated, according to the speed of the primary screw feeder (x_1) and the secondary screw feeder (x_2) as follows:

$$Y = 11.6737x_1 + 0.6087x_2. \quad (9)$$

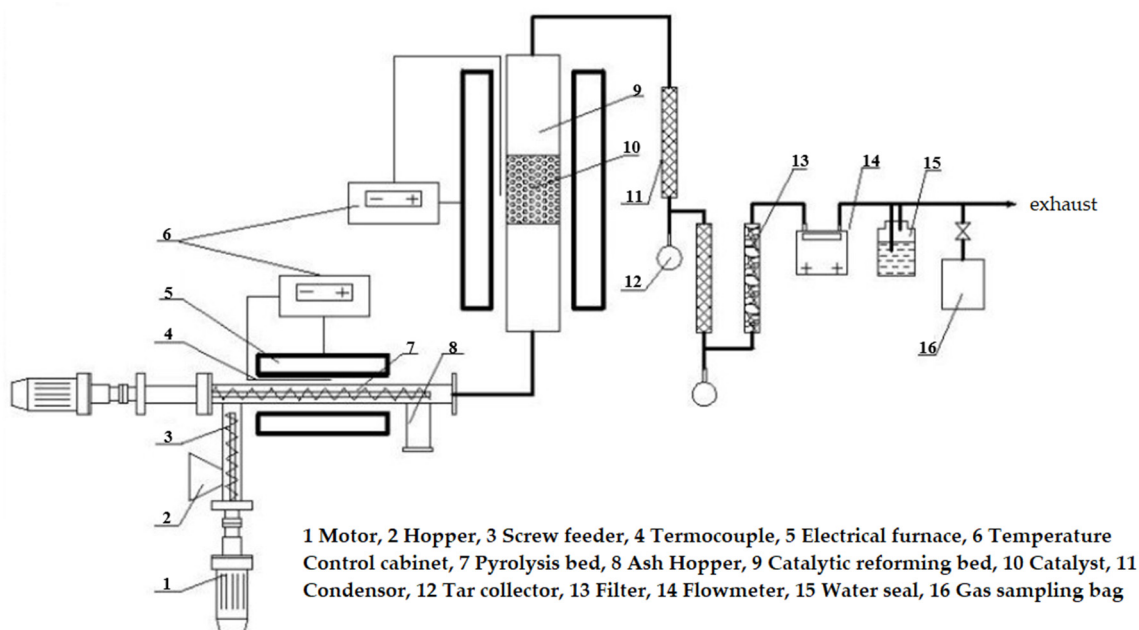


Figure 7. Schematic diagram of the two-stage catalytic pyrolysis reactor [35].

As shown in Figure 8, the moving velocity of biomass particles in the pyrolysis bed (V_{feed}) can be calculated by the speed of the secondary screw feeder (x_2) as follows:

$$V_{feed} = 0.03x_2 - 0.722 \quad (10)$$

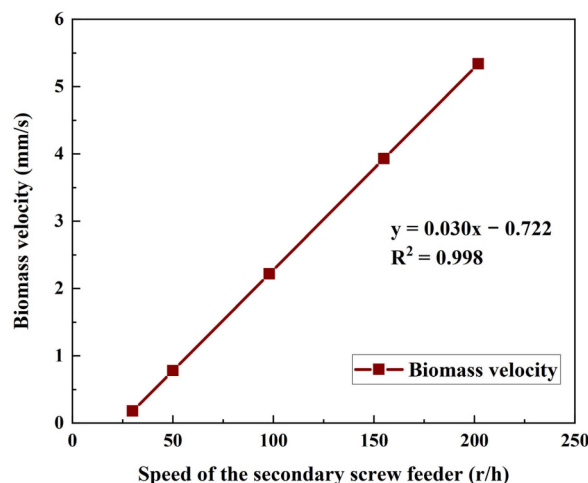


Figure 8. The relationship between biomass velocity and speed of the secondary screw feeder [35].

The electric horizontal pyrolysis bed reactor with electric heating was used in this study. The horizontal pyrolysis bed reactor mainly consisted of a motor, screw feeder, and ash hopper. The reactor was made of acid and alkali resistant, high-temperature resistant stainless-steel material. The highest temperature the reactor can reach is 1000 °C, the size of the internal reaction tube was $\varphi 80 \times 1100$ mm. The motor drove the rotation of the screw so that the biomass samples from the primary screw feeder moved forward and reacted in the pyrolysis reactor. Finally, the solid residue generated by the pyrolysis reactions fell into the ash hopper. An electric vertical tube reactor was used as the catalytic reforming bed. The reactor was made of high-temperature resistant stainless-steel material, with the designed highest temperature of 1000 °C, with an internal size of $\varphi 60 \times 1100$ mm. It was filled with the catalyst inside and had a gas outlet on the top.

In the catalytic pyrolysis experiments, the pyrolysis bed and catalytic reforming bed were preheated, and around 300 g pine sawdust was set in the hopper. When the two reactors were heated to the required temperature, N₂ was introduced for approximately half an hour to drain the oxygen from the system. After that, the two-stage screw feeder started feeding, at the primary feeding speed of 171 r/h and the secondary feeding speed of 300 r/h. The pyrolysis reactions of the pine sawdust took place in the pyrolysis bed at 700–900 °C. Then, the pyrolysis gas was inputted to the catalytic reforming reactor through the pipeline, and further cracked and reformed under the action of the catalyst. In the downstream, when the reformed gas passed the condensers under the ice water (~0 °C), most of the tar was condensed and collected by the collection impingers. The residual tar and impurities were absorbed and removed by the filters with quartz cotton. The output gas flow rate was recorded by the gas flowmeter. Finally, the gas passed through the water-sealed bottle and was then ignited and exhausted.

After the experiment ran for around 15 min in a steady state, the generated gas was collected by a gas sampling bag and analyzed by gas chromatography (GC 9800 T, Kechuang, Shanghai, China). The gas yield was counted by the gas flowmeter. After the experiment, the collected tar from the collection bottles was weighted. Solid residues were collected from the ash hopper for weighting and analysis. Each experiment was repeated three times, and the results were averaged and presented.

3.4. Data Analysis

- (1) Residence time, t (s), was calculated by the ratio of the length of the pyrolysis reaction zone (250 mm) to the biomass moving velocity (V_{feed}) in the reactor.

$$t = \frac{250}{0.03x_2 - 0.722} \quad (11)$$

- (2) Dry gas yield, G_Y (Nm³/kg), refers to the volume of gas that can be generated per kilogram of dried biomass, which was calculated by the following equation:

$$G_Y = \text{Produced gas volume (Nm}^3\text{)} \div \text{Dry biomass weight (kg)} \quad (12)$$

- (3) Carbon conversion rate, η_c (%), refers to the ratio of carbon content in gas products to the carbon content in biomass, which was calculated by the following equation:

$$\eta_c = \frac{\text{CO} + \text{CO}_2 + \text{CH}_4}{22.4 \times C} \times 12G_Y \times 100\% \quad (13)$$

where C means the mass percentage of carbon in the ultimate analysis of samples, G_Y is the dry gas yield, CO, CO₂, and CH₄ are the volume ratio of CO, CO₂, and CH₄ in gas products.

- (4) The lower heating value of gas products (LHV , MJ/Nm³) was calculated by the following equation [36]:

$$LHV = \text{CO} \times 12.63 + \text{H}_2 \times 10.78 + \text{CH}_4 \times 35.81 \quad (14)$$

where CO, H₂, and CH₄ are their corresponding gas composition by volume in gas products.

4. Conclusions

Catalytic pyrolysis of pine sawdust was investigated with nano-NiO/ γ -Al₂O₃ in a two-stage catalytic pyrolysis reactor. The effects of residence time and catalytic temperature on the pyrolysis performance of pine sawdust were examined. The main conclusions were summarized as follows:

- The longer residence time resulted in fewer solid and liquid products but more gas products. Longer residence time could promote tar cracking and gas-phase conversion reactions, improve the syngas yield, H₂/CO ratio, and improve carbon conversion.
- The catalyst of nano-NiO/ γ -Al₂O₃ had catalytic activity for tar removal, which could decrease tar yield to near zero at 800 °C.
- The increasing catalytic temperature of nano-NiO/ γ -Al₂O₃ could significantly increase H₂ and CO yields by improving the tar decomposition and the secondary gas reactions.
- Increasing catalytic temperature improved dry gas yield and carbon conversion but decreased the H₂/CO ratio and the low heating value.

However, the deactivation of the catalyst during the pyrolysis is key information for the catalyst, but it was not examined in this study. It will be further investigated in future work, particularly for catalyst evolution during the pyrolysis and its coking behaviour. Further investigation should also be undertaken using unmodified Al₂O₃ catalysts to compare with the catalyst of NiO/Al₂O₃.

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