Influence of torrefaction pretreatment on biomass gasification technology

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Torrefaction is a slow pyrolysis process that is carried out in the relatively low temperature range of 220–300°C. The influence of torrefaction as a pretreatment on biomass gasification technology was investigated using a bench-scale torrefaction unit, a bench-scale laminar entrained-flow gasifier, and the analysis techniques TGA-FTIR and low temperature nitrogen adsorption. A series of experiments were performed to examine the characteristics of the torrefaction process, the properties of torrefaction products, and the effects of torrefaction on gas composition, cold gas efficiency and gasification efficiency. The results showed that during the torrefaction process the moisture content of biomass were reduced, and the wood fiber structure of the material was destroyed. This was beneficial to storage, transport and subsequent treatments of biomass in large scale. For solid products, torrefaction increased the energy density, decreased the oxygen/carbon ratio, and created a more complex pore structure. These improved the syngas quality and cold gas efficiency. Combustible gases accounted for about 50% of non-condensable gaseous torrefaction products. Effective use of the torrefaction gases can save energy and improve efficiency. Overall, biomass torrefaction technology has good application prospects in gasification processes.

biomass, torrefaction, pretreatment, gasification

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Energy is the most important basis for economic and social development. With large-scale industrial development, the total exploitable amount of fossil fuel is declining, and environmental pollution is increasing. With the advantages of being clean and CO₂ neutral, biomass is the only renewable energy source that can fix carbon, and biomass has gradually won worldwide attention. However, as a result of its dispersion, low energy density, low bulk density and high moisture content, the costs of logistics and transport are increased. Those factors make large-scale utilization of biomass for bioenergy production inefficient and uneconomic. Consequently, it is necessary to enhance the characteristics of biomass feedstocks through pretreatment.

At present, biomass pretreatments include drying, pelletisation, pyrolysis and torrefaction. While drying is a relatively mature conventional technology, the moisture content of biomass is as high as typically about 10 wt% after drying [1]. Dried biomass will re-absorb water and start to decompose. In addition, drying has little benefit for the improvement on the properties such as low energy density and bulk density, high oxygen content and grindability. As a slow pyrolysis process at moderate temperatures under atmospheric pressure, torrefaction can solve these problems. Using torrefaction technology, the energy density and bulk density of biomass are increased, and the costs of transportation and storage reduced. Moreover, because of its high process efficiency (94%) compared with pelletisation (84%) and pyrolysis (64%), torrefaction is potentially the best method for improving the economics of the overall production chain for bioenergy [2].

Most research has been focused on the mechanism, feedstock and products of torrefaction. At the operating tem-
perature (220–300°C), the main process of torrefaction is hemicellulose pyrolysis. The feedstocks include mainly herbaceous and ligneous plants. The results show that under the same torrefaction conditions, the conversion of agricultural residues is higher than that of the latter because of the high content of volatile matter and hemicellulose in agricultural residues. A comparison between wood and agricultural residues in gas composition indicates that the latter is characterized by higher CO₂ production [3], whereas wood samples yield a higher proportion of solid products [4]. Deciduous trees are more active than coniferous trees. This may be explained because the hemicellulose fraction in deciduous wood contains mainly xylan, which is much more reactive than the mannan found in coniferous wood [1]. Because of the fibrous structure and the tenacity of ligneous plants, the power consumption for grinding is higher [5] but the grindability can be improved through torrefaction [6]. Prins et al. [7] analyzed the torrefaction products of four kinds of biomass. Bridgeman et al. [8] used three kinds of biomass to investigate the effects of torrefaction on solid fuel qualities and combustion properties.

Compared with combustion and pyrolysis, gasification technology has higher efficiency and more environment-friendly performance, and is considered to be a very important route to large-scale utilization of biomass. However, little attention has been paid to the influence of torrefaction on the performance of the biomass gasification process. Hence, based on entrained flow gasification technology, the aim of the present study was to investigate the combination of torrefaction technology and the gasification process. A series of experiments were carried out to examine the characteristics of the torrefaction process, the properties of torrefaction products, and the effects of torrefaction on syngas quality and gasification efficiency. Gasification technology is widely used in China for centralized gas supply, and much attention has been paid to the straw resources of the country. In the future, gasification technology will be extensively applied for power generation, combined heat and power generation and indirect liquefaction for liquid fuel production to relieve the energy crisis. And there are abundant resources of forestry and wood processing waste. In the experiments reported herein sawdust was chosen as the feedstock for torrefaction and gasification. The experimental results provide a practical and theoretical basis for large-scale use of bioenergy.

1 Experimental

(i) Materials. Sawdust was pulverized and screened to obtain particles with size in the range 20–30 mesh. Proximate and ultimate analyses of the biomass sample are shown in Table 1.

(ii) Biomass torrefaction. The bench-scale torrefaction unit is shown schematically in Figure 1. The diameter of the reactor was 30 mm. During torrefaction about 10 g of sawdust was heated under a continuous N₂ flow to the desired temperature (230, 250, 270 or 290°C) at a heating rate of 10°C min⁻¹, and maintained at this temperature for 20 or 30 min. The non-condensable gaseous products were collected after cooling and cleaning, then the solid and gaseous products were analyzed.

(iii) Entrained flow gasification. Gasification tests for the torrefied solid products were carried out using a bench-scale high-temperature entrained flow gasification system, shown schematically in Figure 2. A corundum pipe with effective height 1500 mm and inner diameter 60 mm was used as the gasifier. The biomass throughput for this reactor was 5 g min⁻¹. The gasification temperature was controlled at 1200°C with an oxygen/biomass ratio of 0.3. This gasification system had the advantages of short residence time and high gasification rate.

(iv) TG-FTIR analysis. The mechanism of the torrefaction process was investigated using a thermogravimetric analyzer (Mettler-Toledo TGA/SDTA851e) and a Fourier transform infrared spectrometer (Nicolet NEXTUS 670). An inert atmosphere was maintained using nitrogen (purity>99.99%) as a carrier gas with flow rate 50 mL min⁻¹. The sample was heated at 10°C min⁻¹ from 25°C to the desired temperature (230, 250, 270 or 290°C), and maintained at that temperature for 30 min. To analyze the relative concentrations of the volatile pyrolysis products based on the intensity of absorption peaks, an accurately weighed 5.6 mg wood sample was used for each test.

(v) Pore structure analysis. The pore structures of sawdust and torrefied sawdust particles were determined by the low-temperature nitrogen adsorption method. Isothermal

![Figure 1](image_url)  
**Figure 1** Schematic diagram of the torrefaction unit. 1, N₂; 2, tube furnace; 3, temperature control system; 4, quartz glass reactor; 5, condenser; 6, filter; 7, gas analysis system.

| Material  | Ultimate analysis (air-dried, wt%) | Proximate analysis (air-dried, wt%) | Heating value (kJ kg⁻¹) |
|-----------|----------------------------------|----------------------------------|-------------------------|
|           | C      | H    | O     | N     | S     | Moisture | Ash     | Volatile | FC     | LHV   |
| Sawdust   | 40.85  | 6.17 | 39.07 | 0.03  | 0.05  | 13.45    | 0.38    | 73.15    | 13.02  | 17096 |
adsorption and desorption were conducted at the saturation temperature of liquid nitrogen (−196°C), using nitrogen (purity>99.99%) as the adsorption medium, at relative pressure ($P/P_0$) between 0.01 and 0.995 ($P$ and $P_0$ are low-temperature adsorption equilibrium pressure and saturation pressure, respectively). The adsorption-desorption isotherms obtained were used to determine the pore structures of samples through Brunauer-Emmett-Teller (BET) theory and Barrett-Joyner-Halenda (BJH) theory.

2 Results and discussion

2.1 Characteristics of torrefaction

Figures 3 and 4 illustrate the influence of torrefaction temperature and residence time on the final mass yield of solid residue. After water evaporation in the initial 0–6 min, sawdust seldom showed weight loss. During the isothermal period, the weight loss became apparent as a result of the large quantity of volatiles that were produced. Judging from the peak heights and areas in the DTG curves, increasing temperature had a marked effect on the decomposition of the sample: the maximum mass loss rate occurred at higher temperatures for samples that had undergone torrefaction at higher temperatures. This was the main stage of the torrefaction process. Finally, the tendency for weight to be lost gradually disappeared, and the remaining material decomposed slowly until the end of pyrolysis.

Figure 5 shows FTIR spectra obtained during sawdust torrefaction at 290°C, and indicates the effect of residence time on the torrefaction process. According to the DTG curve at 290°C, eight representative time/temperature points were selected: before, at and after the first peak; between the two peaks; before, at and after the second peak; and at the stage of the slow decomposition, as follows. 1.337 min, 38.4°C; 2.406 min, 49.1°C; 6.082 min, 85.8°C; 14.036 min, 165.4°C; 22.373 min, 248.7°C; 25.695 min, 282.0°C; 28.739 min, 290°C; 52.599 min, 290°C. During the heating stage at low temperature (1.337, 2.406 and 6.082 min) only the characteristic H$_2$O peak appeared, and became gradually more intense as the temperature increased. This peak was associated with the evolution of free water. At the stage of slight weight loss (14.036 min), the characteristic peak of CO$_2$ appeared together with weak peaks of carbonyl compounds and aromatics. These observations can be explained by the release of small molecular compounds such as H$_2$O, CO and CO$_2$, caused by depolymerization, recombination and modification of samples [9]. At the main stage of the torrefaction process (22.373, 25.695 and 28.739 min), in addition to the characteristic peaks of H$_2$O and CO$_2$ there were strong absorption peaks that were assigned to C–H stretching vibration (3000–2650 cm$^{-1}$), the carbonyl C=O double bond stretching vibration (1850–1600 cm$^{-1}$), C–H in-plane bending vibration, and C–O and C–C skeletal vibrations (1500–900 cm$^{-1}$). Those bands are attributed to alkanes, carbonyl compounds, aromatics and phenols asso-
ciated with the production of tar and other substances, and damage and fracture of the fiber structure. Because H₂O was fully evaporated in the previous stages, the intensity of characteristic peaks except for H₂O increased and then decreased with increasing residence time. At the decomposition stage of residue (52.599 min), CO₂ was the main gaseous product. These results were in accordance with the DTG data.

Because the main process of torrefaction occurred in the isothermal stage, the time points corresponding to the maximum mass loss rates in this stage at different torrefaction temperatures were selected to analyze the effect of temperature on the torrefaction process. From the results shown in Figure 6, it seemed that the volatile constituents were mainly H₂O and CO₂ at low temperatures. As the temperature increased, the intensity of characteristic peaks of alkanes, carbonyl compounds, aromatics and phenols were gradually enhanced, indicating that increasing temperature could accelerate decomposition of fiber structures.

Torrefaction is a slow pyrolysis process, during which biomass experiences dehydration, devolatilization, depolymerization and carbonization. The experimental results discussed above showed that H₂O was one of the main products generated by drying at low temperature and by dehydration reactions between organic molecules at high temperature [3]. The dehydration reaction results in the destruction of hydroxide radicals, which causes the loss of capacity to form hydrogen bonds with water. Furthermore, formation of non-polar unsaturated structures also occurs [10], making the torrefied biomass more hydrophobic and reducing its tendency to weathering, cracking or self-combusting, which is advantageous for storage and transportation. In addition, the fibrous structure of biomass was destroyed because of decomposition to alkanes, aldehydes, ketones, carboxylic acids, alcohols and other macromolecules. Consequently, the grindability and feeding properties, especially for entrained flow gasification, can also be improved.

2.2 Effect of torrefied solid product on gasification

(i) Properties of torrefied solid product. Experiments were carried out to study the effect of the torrefaction temperature (230, 250, 270 or 290°C) and residence time (20 or 30 min) on the solid product. According to the TG data, the changes in weight loss were small when the residence time was more than 30 min. Hence it was thought that a residence time of more than 30 min would not have a significant effect on torrefaction.

Proximate and ultimate analyses of solid products are shown in Table 2. Compared with raw sawdust, the moisture and volatiles content of torrefied fuels decreased greatly with increasing temperature and residence time, whilst large increases were observed in the ash and fixed carbon content. The sulfur and nitrogen contents remained almost constant. The hydrogen content decreased rapidly at higher temperatures (270 and 290°C) because of the volatilization of water and release of hydrocarbons (such as CH₄ and C₂H₆) only at high temperature. The increase of carbon was as high as 27.8% compared with raw sawdust, and the largest percentage decrease of oxygen was 29.1%. This was because the oxygen-containing functional groups with high activity and low activation energy were easy to crack or recombine to release CO and CO₂ [11]. The increased calorific value illustrated the effect of these changes on the energy content. The above information together with the TG and DTG data suggested that torrefaction could significantly improve the physical density, energy density and bulk density of biomass feedstock to effectively use storage space and reduce costs of transportation [12].

The pore structures of torrefied sawdust at different temperatures with residence time 30 min were measured by the low-temperature nitrogen adsorption method. The data in Table 3 show that because of the release of gaseous and volatile products, the total pore volumes of torrefied fuels were higher than that of raw sawdust. Figure 7 displays the influence of torrefaction temperature on the specific surface area and average pore diameter of samples. When the temperature was relatively low (230°C), the specific surface area and pore diameter of torrefied fuel changed little compared with raw sawdust. It can be inferred that the release of H₂O and CO₂ as the main products at lower temperature has
Table 2 Ultimate and proximate analysis of torrefied fuels

| Residence time (min) | Temperature (°C) | Ultimate analysis (air-dried, wt%) | Proximate analysis (air-dried, wt%) | Heating value (kJ kg⁻¹) |
|----------------------|------------------|------------------------------------|-------------------------------------|------------------------|
|                      |                  | C  | H  | O  | N  | S  | Moisture | Ash | Volatile | FC  | LHV   |
| 20                   | 230              | 44.89 | 5.08 | 37.23 | 0.65 | 0.27 | 3.54 | 8.34 | 69.24 | 18.88 | 19089 |
| 250                  | 46.52            | 4.99 | 35.74 | 0.69 | 0.28 | 3.15 | 8.63 | 66.69 | 21.53 | 19453 |
| 270                  | 48.74            | 4.78 | 33.32 | 0.74 | 0.31 | 2.77 | 9.34 | 61.54 | 26.35 | 20435 |
| 290                  | 51.47            | 4.62 | 29.21 | 0.76 | 0.32 | 2.35 | 11.27 | 55.21 | 31.17 | 20881 |
| 30                   | 230              | 45.92 | 5.20 | 37.01 | 0.53 | 0.28 | 2.44 | 8.62 | 69.1 | 19.84 | 19366 |
| 250                  | 47.16            | 5.01 | 35.52 | 0.55 | 0.29 | 2.26 | 9.21 | 64.79 | 23.74 | 19496 |
| 270                  | 50.67            | 4.77 | 30.81 | 0.65 | 0.32 | 2.15 | 10.63 | 57.07 | 30.15 | 21065 |
| 290                  | 52.22            | 4.41 | 27.72 | 0.71 | 0.33 | 2.07 | 12.54 | 49.68 | 35.71 | 21384 |

Table 3 Total pore volume of raw sawdust and torrefied sawdust

|                        | Raw sawdust | 230°C | 250°C | 270°C | 290°C |
|------------------------|-------------|-------|-------|-------|-------|
| Total pore volume (cm³ g⁻¹) | 2.92×10⁻² | 3.57×10⁻² | 3.35×10⁻² | 3.51×10⁻² | 3.51×10⁻² |

Figure 7 Dependence of specific surface area and average pore diameter on torrefaction temperature.

Figure 8 Pore size distribution.

Little effect on the pore structure. At 250°C the pores were enlarged and more open pores were generated as a result of the increased speed of volatilization of gaseous products. At the same time volatile tar in semi-precipitated state may plug some pores to form new pores. That effect complicated the pore structure and led to the decreased average pore size and the increased specific surface area. When the temperature reached 270 or 290°C, carbonyl compounds, aromatics, phenols and other tar substances cracked further and released some light compounds. Simultaneously, some pores were closed and restructured resulting in increased average pore size and reduced specific surface area. That was attributed to softening, deformation and carbonization of the particles and the plastic deformation of the pores. In addition, the decrease of specific surface area was partly related to the higher ash content of solid products [13]. Figure 8 shows that the pore size distribution curves of raw sawdust and torrefied sawdust produced under different torrefaction temperatures were similar. However, the volume of pores with diameter 20–100 nm was higher for torrefied particles than for raw samples. These results suggested that torrefaction can improve the pore structure of feedstocks. Torrefied particles with the largest specific surface area and smallest pore size were produced by torrefaction at 250°C.

(ii) Effect of torrefied solid product on the gasification. Gasification is a typical heterogeneous reaction. Through external and internal diffusion, the reactant gases are absorbed on the surface of solid particles to react with biomass. The above analysis indicated that the torrefied sawdust had improved physical and chemical characteristics compared with raw sawdust. Hence the gasification characteristics of the torrefied fuels were investigated under conditions of high heating rate and high temperature. The results are shown in Figures 9 and 10.

The non-condensable gaseous products were mainly CO, H₂ and CO₂. CH₄ content was negligible. Torrefaction lowered the moisture and oxygen content to reduce the oxygen/carbon ratio. Hence, compared to gasification of raw sawdust, the H₂ and CO content increased, whilst CO₂ decreased. The H₂ content at 270 or 290°C was lower than at 250°C. It was known that H₂ content depended on the oxygen
content as well as on the hydrogen content of torrefied fuels. The release of H$_2$O during torrefaction led to hydrogen loss. In general, different torrefaction temperatures and residence times had limited effects on the syngas composition.

Cold gas efficiency was improved by torrefaction, and it increased slightly with increasing residence time. Higher gasification efficiencies can be achieved for torrefied fuels with low O/C ratios. The highest cold gasification efficiency was found for sawdust torrefied at 250°C. This result was in accordance with the measured pore structure of torrefied sawdust, which indicated that the torrefied fuel produced at 250°C had the largest specific surface area and smallest pore size.

The cold gas efficiency is given by

$$\eta = \frac{Q_{\text{syngas}}}{Q_{\text{torrefied fuel}}} = \frac{(Q_{\text{H}_2}y_{\text{H}_2} + Q_{\text{CO}_2}y_{\text{CO}_2} + \sum Q_{\text{i}}y_{\text{i}}) \times V / 22.4}{Q_{\text{torrefied fuel}}},$$

where $Q$ is the heating value, $y$ is the gas volume fraction, $i$ represents hydrocarbons and $V$ is the total volume of syngas.

### 2.3 Effect of torrefaction gases on gasification

(i) Composition of torrefaction gases. Based on the qualitative FTIR analysis, the composition of torrefaction gases was determined quantitatively using gas chromatography.

Figure 11 shows that the non-condensable torrefaction gases included CO$_2$, CO, C$_3$H$_8$ and trace amounts of H$_2$ and C$_2$H$_6$. The combustible gases accounted for about 50% of the non-condensable gases. As the torrefaction temperature increased, CO$_2$ and CO concentration increased; the CO$_2$ content was higher than that of CO. As the most active of the three lignocellulose components in biomass, hemicellulose decomposes at temperatures ranging from 200 to 250°C. The decomposition of cellulose occurs at 240–350°C, and lignin is the last component to decompose at still higher temperatures (280–500°C) \[3\]. Hence the main thermal decomposition process during torrefaction is the pyrolysis of hemicellulose because of its poor heat stability. Xylan is the predominant hemicellulose found in biomass, and contains a large number of furfural acid side chains, from which the removal of a carboxyl group occurred to release a large amount of CO$_2$ during the pyrolysis process \[14\]. The concentration of CH$_4$, which originates mainly gasification efficiencies can be achieved for torrefied fuels with low O/C ratios. The highest cold gasification efficiency was found for sawdust torrefied at 250°C. This result was in accordance with the measured pore structure of torrefied sawdust, which indicated that the torrefied fuel produced at 250°C had the largest specific surface area and smallest pore size.

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$$\eta = \frac{Q_{\text{syngas}}}{Q_{\text{torrefied fuel}}} = \frac{(Q_{\text{H}_2}y_{\text{H}_2} + Q_{\text{CO}_2}y_{\text{CO}_2} + \sum Q_{\text{i}}y_{\text{i}}) \times V / 22.4}{Q_{\text{torrefied fuel}}},$$

where $Q$ is the heating value, $y$ is the gas volume fraction, $i$ represents hydrocarbons and $V$ is the total volume of syngas.
from the large number of methoxy groups in lignin [15], was too low to be detected. The H₂ content was also close to zero, indicating the release of hydrogen in the form of water and hydrocarbons.

(ii) Effect of torrefaction gases on the gasification efficiency. The gasification efficiency is given by

\[ \eta = \frac{Q_{\text{syngas}}}{Q_{\text{biomass}}} = \left( Q_{\text{H}_2}y_{\text{H}_2} + Q_{\text{CO}}y_{\text{CO}} + \sum Q_i y_i \right) \times V / 22.4 \]  

Figure 12 shows that the gasification efficiency of torrefied sawdust was lower than that of raw sawdust. This difference was mainly because of the energy loss caused by the release of gaseous and volatile products during torrefaction; those products were not used in the gasification experiments. Furthermore, the devolatilization was strengthened by increasing torrefaction temperature and residence time. Hence, in practical applications of torrefaction, to improve the overall gasification efficiency the carbon and the energy in the torrefaction gases should be utilized effectively.

As discussed above, there are positive and negative influences of torrefaction on the gasification process. Compared with other pretreatments, torrefaction has strong advantages and very promising market potential. The combination of torrefaction and gasification process is equal to two-stage pyrolysis and gasification technology, but the energy consumption of torrefaction is lower than that of high-temperature pyrolysis [16]. And the power required for grinding wood can be saved as high as 50%–85% [17]. Because of the diversity and seasonality of biomass, fuel flexibility is required for biomass utilization technology for sustainable development. It was found that torrefaction process can make different types of biomass, including commercial timber, agricultural waste and energy crops, have quite similar physical and chemical properties. Seasonal influences on the properties of feedstocks are also reduced [10].

### 3 Conclusions

Based on the idea of the combination of torrefaction and gasification, experiments were carried out to show that the torrefaction process had a strong competitive advantage and good application prospects in gasification processes.

(1) Torrefaction can completely dry raw biomass, destroy the fibrous structure, and release torrefaction gases. Increased temperature and residence time enhances the decomposition of fiber structures, and facilitates storage, transportation, grinding, briquetting and pneumatic feeding.

(2) Torrefaction can increase the energy density and reduce the oxygen/carbon ratio of sawdust, and form porous structures. Sawdust particles torrefied at 250°C have the largest specific surface area and smallest pore size. In the gasification of torrefied fuels, syngas quality and cold gas efficiency are improved compared with raw sawdust.

Gasification of sawdust torrefied at 250°C gives the best results.

(3) The non-condensable torrefaction gases include mainly CO₂, CO and C₃H₆, which are the predominant pyrolytic products of hemicellulose. Flammable gas accounts for about 50% of the total non-condensable gases. As a result of the energy loss caused by the unused torrefaction gases, the total gasification efficiencies of torrefied fuels are lower than that of raw sawdust. In practical applications of torrefaction, the torrefaction gases should be used effectively to improve the gasification efficiency.

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