

Investigation of the synergistic mechanism during biomass and coal gangue co-gasification

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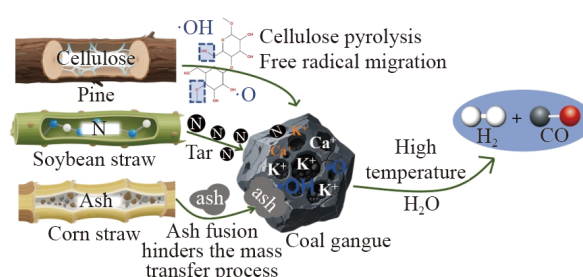
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Abstract: Biomass is considered as a sustainable green coal alternative, and its thermochemical conversion—particularly hydrogen-rich gasification technology—represents an effective pathway for achieving high-value utilization. Co-gasification of biomass with coal gangue enables synergistic utilization of carbon resources, offering significant potential for emission reduction and efficiency enhancement. To elucidate how typical biomass components govern the gasification process, three feedstocks with distinct, dominant characteristics were selected: pine stick (high cellulose content, representing highly reactive volatiles), soybean straw (high nitrogen, exemplifying feedstock prone to nitrogenous tar formation), and corn stover (high ash with abundant K^+ , reflecting catalytically active inorganics). Under fixed conditions (850 °C, steam flow rate of 2 mL/min, N_2 flow rate of 75 mL/min), their co-gasification with coal gangue was investigated. Results indicated that the compositional differences led to distinct synergistic patterns and product distributions. All systems achieved the highest hydrogen yield in the syngas at a 5:5 raw material mass ratio. The high-cellulose pine stick system yielded the most H_2 (9.06 mmol/g) and H_2+CO yield (15.25 mmol/g), exhibiting a “three high, three low” advantage due to efficient volatile reforming. In contrast, the high-ash/ K^+ corn stover system showed the strongest synergy for CO (SI = 1.22, where the Synergy Index (SI) > 0 indicates a synergistic promoting effect), promoted by the catalytic Boudouard reaction. The high-nitrogen soybean straw system, while achieving an optimal H_2/CO ratio (2.00), suffered from suppressed syngas yield due to the inhibitory effect of nitrogenous tars. This study confirms that biomass composition—specifically cellulose, ash/ K^+ , and nitrogen content—differentially regulates syngas production and synergy by steering dominant reaction pathways, providing a theoretical basis for the targeted conversion of waste resources.

Key words: biomass; coal gangue; co-gasification; synergistic effect; synthesis gas



In the context of China’s “dual carbon” strategic goals, the development of clean and renewable energy technologies has become imperative. Biomass, as the sole renewable carbon resource capable of being converted into gaseous, liquid and solid fuels^[1], holds significant potential. The Blue Book released by the Bioenergy Industry Branch

of the China Industrial Promotion Association shows that China’s main biomass resources have an annual output of about 34.94 billion tons, and the amount of biomass resources used for energy is about 46.1 million tons^[2], however, the utilization rate remains below 20%, indicating substantial room for improvement. At the same time, the

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coal industry generates massive amounts of solid waste, with coal gangue (CG) being a prominent example. Its annual emission exceeds 700 million tons, leading to a cumulative stockpile of over 4.5 billion tons, posing severe environmental challenges^[3–4]. The co-gasification of biomass and coal gangue presents a promising pathway for the synergistic and high-value utilization of these two solid carbon-containing resources, enabling the simultaneous reduction of waste and production of clean energy.

The physicochemical properties of the feedstocks have a profound influence on the distribution and quality of gasification products. Existing research has demonstrated that key biomass characteristics, such as cellulose/lignin content, ash composition, and nitrogen content are critical factors affecting gas yield and composition^[5–6]. For instance, Zhang et al.^[7] reported a significant synergy during the co-gasification of low-ash coal and potassium-rich biomass, attributing to the catalytic effects of alkali metals. Gong et al.^[8] found that the high volatile of soybean straw provided reactive intermediates during co-gasification, enhancing carbon conversion and syngas yield. Furthermore, Li et al.^[9] observed that both corn stover and soybean straw significantly promoted the gasification reactivity of biochar. Our previous work^[10] also revealed that alkali and alkaline earth metals (AAEMs) in pine wood can catalyze the gasification of CG, while the high-temperature environment sustained by the gasification of fixed carbon in CG facilitates the cracking of biomass-derived tars, creating a mutual synergistic enhancement. Despite these valuable insights, systematic comparative studies on the co-gasification of coal gangue with biomass feedstocks possessing distinctly different representative components remain scarce. The specific regulatory roles and synergistic mechanisms of biomass components—such

as the catalytic effects of cellulose-derived volatile, the inhibiting influence of nitrogen-containing compounds, and the dual role of ash (as both a catalyst and an inhibitor)—are not yet fully understood. In particular, a comparative analysis of how these distinct biomass types regulate syngas composition and hydrogen production efficiency within the same co-gasification system is lacking.

To address this research gap, this study strategically selected three representative biomass: pine wood (characterized by high cellulose content), soybean straw (characterized by high nitrogen content), and corn stover (characterized by high ash content). The objective is to systematically investigate their co-gasification with coal gangue, focusing on the differences in syngas yield, hydrogen selectivity, and synergistic effects. This work aims to elucidate the underlying regulatory mechanisms governed by biomass characteristics, thereby providing a theoretical foundation for the targeted and efficient conversion of waste resources.

1 Materials and methods

1.1 Raw materials

Experimental raw materials pine stick (labeled as PS) was sourced from Baotou City, Inner Mongolia; Soybean straw (SS) and corn stover (CS) were sourced from Songyuan City, Jilin Province; CG was obtained from Taiyuan City, Shanxi Province. All samples were crushed using a jaw crusher, and screened through a 200 mesh sieve. Tables 1 and 2 present the ultimate analysis, proximate analysis, and compositional analysis of each experimental feedstock, respectively.

Table 1 Ultimate analysis and proximate analysis of raw materials

Sample	Ultimate analysis $w_{ad}/\%$					Proximate analysis $w_{ad}/\%$			
	C	H	O [*]	N	S	FC	V	M	A
PS	46.64	6.99	43.76	0.13	0.03	16.67	81.97	0.30	1.06
SS	48.00	6.10	42.15	1.43	0.12	13.39	76.30	3.68	6.63
CS	42.43	5.59	39.05	1.22	0.91	16.90	70.77	2.21	10.12
CG	21.02	2.06	11.35	0.32	0.27	22.47	14.21	1.22	62.10

Note: ad: air-dried basis; O^{*}: calculated by difference.

Table 2 Compositional analysis of raw material

Sample	Ash composition/%							
	SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Fe ₂ O ₃	others
PS	1.20	0.50	30.50	22.00	0.04	0.05	0.10	45.61
SS	13.84	0.94	17.21	20.19	28.02	1.98	0.72	17.10
CS	41.20	7.55	12.01	6.96	7.32	2.15	5.80	17.01
CG	56.21	32.10	1.59	0.24	3.6	0.11	2.90	3.25

1.2 Gasification process

As shown in Figure 1, the gasification experiment employed a custom-built two-stage fixed-bed reactor. The reactor was heated from room temperature to the target temperature of 850 °C at a heating rate of 25 °C/min and maintained at this temperature for the duration of the experiment. The experiment employed high-purity N₂ as the carrier gas at a flow rate of 75 mL/min. Deionized water was injected using a syringe pump at a flow rate of 2 mL/min, vaporized in a pre-heating zone, and served as the gasifying agent.

Before each experiment, the airtightness of the experimental apparatus was verified by pressurizing the system with N₂ and monitoring for pressure drop. The biomass and coal gangue were thoroughly mixed at predetermined mass ratios of 10:0, 7:3, 5:5, 3:7 and 0:10. For each run, a total mass of 5.0 g of the mixture was accurately weighed and loaded into a quartz boat. The quartz boat was then rapidly inserted into the constant-temperature zone of the reactor once the target temperature was stable. Rapid devolatilization of the feedstock occurred, producing volatile matter and syngas. The gaseous products passed through a series of condensers and a gas scrubber filled with color-changing silica gel to remove condensable tars and moisture. The resulting non-condensable dry gases were collected in a gas sampling bag over a period of 10 min for subsequent composition analysis.

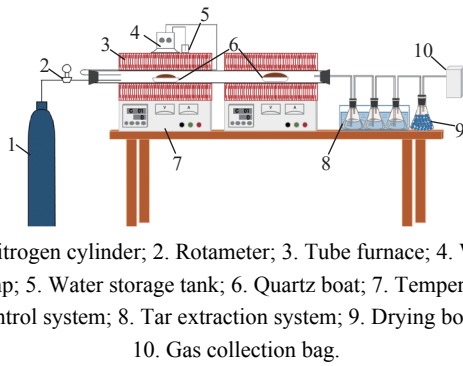


Fig. 1 Experimental setup diagram

1.3 Data analysis

Gaseous products were analyzed using an Agilent 8890B gas chromatograph (GC) equipped with TCD and FID detectors for H₂, CO, CO₂, N₂ and hydrocarbons. Experimental analysis of biomass-coal gangue co-gasification primarily includes syngas yield (Y_{syngas}), syngas ratio (H₂/CO), higher heating value (HHV), carbon conversion efficiency (CCE) and synergy index (SI). Calculation formulas are as follows^[11]:

$$Y_{\text{syngas}} = (1 - C_{\text{N}_2}) \times V_{\text{N}_2} \times t / (C_{\text{N}_2} \times m) \times 10^{-3} \quad (1)$$

In equation (1), Y_{syngas} denotes the synthesis gas yield in m³/kg; C_{N_2} represents the volume fraction of N₂ in the gas bag in %; V_{N_2} denotes the N₂ flow rate at 75 mL/min; t

indicates the gas collection time at 10 min; m represents the mass of raw material used per experiment at 5.0 g.

$$\text{H}_2/\text{CO} = C_{\text{H}_2}/C_{\text{CO}} \quad (2)$$

In equation (2), H₂/CO denotes the synthesis gas ratio, and C_i represents the volume fraction of gas i , expressed in %.

$$\text{HHV} = 12.63 \times C_{\text{CO}} + 12.75 \times C_{\text{H}_2} + 39.82 \times C_{\text{CH}_4} + 80 \times C_{\text{C}_n\text{H}_m} \quad (3)$$

In equation (3), HHV denotes the higher heating value of the gas, expressed in MJ/m³. Since the concentration of C_nH_m is relatively low, the calorific value of a typical hydrocarbon (ethane or propane) is used as an approximate value (80 MJ/m³).

$$\text{CCE} = \frac{(Y_{\text{CO}} + Y_{\text{CO}_2} + Y_{\text{CH}_4} + Y_{\text{C}_n\text{H}_m}) \times 10^{-3} \times 12}{C} \quad (4)$$

In equation (4), CCE denotes carbon conversion rate, expressed in percent; Y_i denotes the yield of gas i , expressed in mmol/g.

$$X_{\text{Calculated}} = (1 - \alpha) X_{\text{CG}} + \alpha X_i \quad (5)$$

$$\text{SI} = \frac{X_{\text{Experimental}} - X_{\text{Calculated}}}{X_{\text{Calculated}}} \quad (6)$$

In equations (5) and (6), $X_{\text{Calculated}}$ denotes the theoretical gas yield during co-gasification, $X_{\text{Experimental}}$ represents the actual gas yield from co-gasification, α is the biomass mass fraction in the CG-biomass mixture expressed as a percentage, while X_{CG} and X_i denote the gas yields from gangue and biomass gasification, respectively. SI denotes the synergistic effect index for the co-gasification of CG and biomass. SI > 0 indicates that co-gasification promotes the production of the gas, while SI < 0 indicates that it inhibits the gas production. A larger absolute value of SI signifies a stronger influence.

2 Results and discussion

Under the established reaction conditions, this study systematically conducted co-gasification experiments of three typical biomass types (PS, SS and CS) with CG at different blending ratios, and conducted an in-depth analysis of their synergistic reaction mechanisms.

2.1 Co-gasification of PS and CG

PS is rich in cellulose and rapidly releases hydrogen-rich volatiles within the low-temperature pyrolysis range (300–500 °C)^[12], supplying reactive oxygen species to CG. The fixed carbon in CG undergoes steam reforming with pine volatile under high-temperature steam conditions^[13]. Concurrently, mineral components such as Fe, K and Ca in CG catalyze tar reforming^[12], significantly reducing coke formation and enhancing overall syngas yield^[14]. Figures 2 and 3 illustrate the composition and yield variations of gaseous components in the co-gasification products of PS

and CG as a function of their mass ratio. The high oxygen content in PS consumes potential hydrogen sources, forming H_2O . Its high volatile matter requires substantial steam for reforming to effectively convert into H_2 , hence the H_2 volume fraction decreases with increasing PS proportion. However, the H_2 yield exhibits a non-monotonic trend, first increasing then decreasing, and reaching a maximum at the mass ratio of 5:5. Both the CO volume fraction and yield significantly increase with rising PS proportion, rising from 12% to 34% and from 0.41 to 7.22 mmol/g, respectively. This phenomenon stems from the suppression of the water-gas shift reaction within the co-gasification system^[15]. CO_2 yield reached its lowest point at a mass ratio of 5:5, where synergistic effects effectively reduced carbon loss. This outcome stems from the catalytic effect of minerals in CG on tar cracking^[16] and the promoting effect of PS volatiles on coal gasification^[17].

Experimental results indicate that the total syngas yield from CG gasification was 2.16 mmol/g, with a hydrogen yield of 1.75 mmol/g. When PS was gasified alone, the H_2+CO yield reached 13.18 mmol/g, with a hydrogen yield of 5.96 mmol/g. Notably, when PS and CG were co-gasified at a 5:5 mass ratio, the total syngas yield reached a maximum of 15.25 mmol/g, with the H_2 yield significantly increased to 9.06 mmol/g. Compared to single CG gasification, the co-gasification system achieved a 593% increase in total syngas yield and a 417% increase in H_2 yield. Compared to PS gasification alone, the co-gasification system increased the total syngas yield by 15% and the H_2 yield by 52%. This series of data clearly demonstrates that the co-gasification process of PS and CG produces a significant synergistic effect on both H_2 and total syngas yields.

Figure 4 shows various gasification performance parameters for co-gasification of PS and CG at different mass ratios, including gas yield, syngas ratio, gross calorific value, and carbon conversion rate. Experimental results indicate: As the PS proportion increases, the Y_{syngas} initially increases and then decreases, peaking at 0.54 m^3/kg at a PS:CG mass ratio of 7:3, CO volume fraction significantly improves, and syngas ratio demonstrates a monotonically decreasing characteristic, the value decreased from 4.31 to 0.83. The gross calorific value peaks of 9.24 MJ/m^3 at a mass ratio of 3:7, attributable to the synergistic effect between the carbon-rich matrix provided by the high proportion of CG and the active volatile matter introduced by PS. This synergistic effect promotes increased CO production and elevates the overall volume fraction of combustible gases. At this ratio, the H_2/CO yield was only 9.65 mmol/g, significantly lower than the peak yield of 15.25 mmol/g at the 5:5 mixture ratio (Figure 3), indicating a non-synchronous optimization phenomenon between HHV and yield. Carbon conversion rate data further revealed the synergistic mechanism: pure pine gasification (PS:CG=0:10), lacking mineral catalysis, underwent tar polymerization reactions forming carbon deposits, resulting in a low CCE of 6.66%; In contrast, within the 5:5 co-gasification system, minerals in CG effectively catalyze tar cracking, while PS volatile promote the pore development

in coal coke. This synergistic interaction drives efficient conversion of carbon elements into gaseous products^[18], the CCE was maximally increased to 43.92%, significantly enhancing the carbon conversion in syngas.

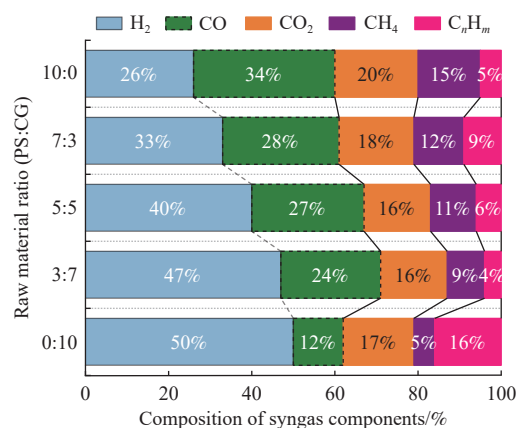


Fig. 2 Gas composition from co-gasification of PS and CG at different mass ratios

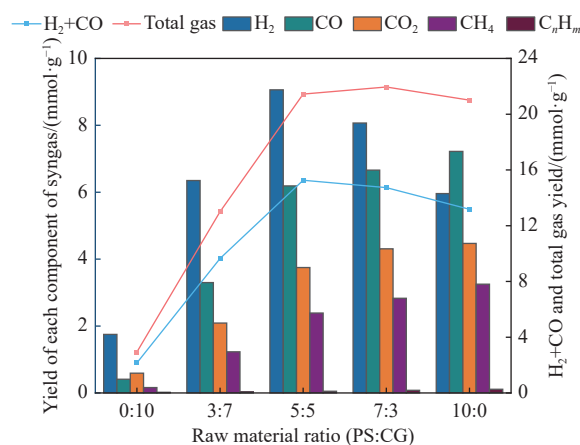


Fig. 3 Variation in gas yield from co-gasification of PS and CG at different mass ratios

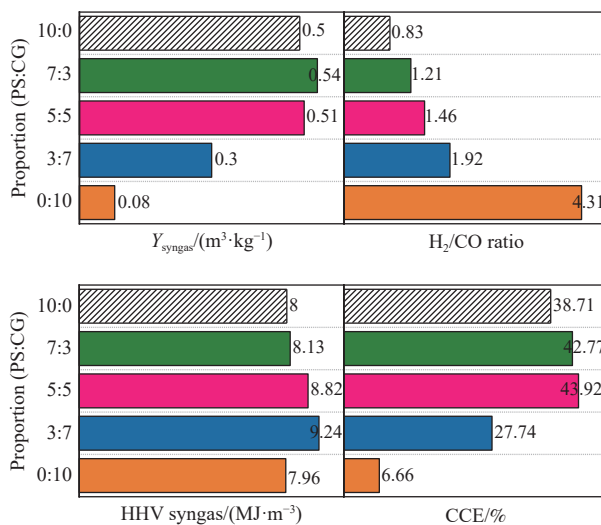


Fig. 4 Performance parameters of PS and CG co-gasification

As shown in Figure 5, the co-gasification of PS and CG produces positive synergistic effects on all gases, with the most pronounced effect observed for hydrogen. The synergistic effect indices for H_2 and CO both peaked at 1.75 and 0.91, respectively, when the mass ratio of PS to CG was 5:5. This aligns with the earlier conclusion that the total syngas yield reached its maximum at this ratio. At a mass ratio of 3:7 for PS and CG, the C_nH_m synergistic index was only 0.2. The co-gasification of PS and CG promoted the cracking of tar^[19], effectively suppressing C_nH_m production and converting it into syngas. In summary, the optimal feedstock ratio for producing syngas via the co-gasification of PS and CG is 5:5.

2.2 Co-gasification of SS and CG

Figures 6 and 7, respectively, reveal the influence patterns of different mass ratios of SS and CG on the volume fractions and yields of co-gasification products. Experimental results indicate that as the SS proportion increases, the H_2 volume fraction exhibits a non-monotonic change pattern of first rising, then decreasing. The volume fractions of CO and CH_4 show an overall downward trend. Key product yield peaks exhibit distinct distributions: the H_2 yield peak (8.66 mmol/g) occurs at a mass ratio of 5:5, while the yield peaks for CO, CO_2 and CH_4 simultaneously appear at a mass ratio of 7:3. The simultaneous peak in multi-component yields at the 7:3 ratio is attributed to the dual effect triggered by excess oxygen introduced at high SS ratios. This promotes gasification oxidation reactions, enhancing CO and CO_2 production, while increasing hydrogen consumption in the methanation reaction ($CO + 3H_2 \rightarrow CH_4 + H_2O$), thereby indirectly inhibiting H_2 accumulation^[18].

Experimental results indicate: The syngas yield from CG gasification alone is 2.16 mmol/g, with H_2 yield at 1.75 mmol/g. The syngas yield from SS gasification alone is 8.69 mmol/g, with H_2 yield at 4.99 mmol/g. When SS and CG were co-gasified at a 5:5 mass ratio, the total syngas yield significantly increased to 12.99 mmol/g, with an H_2 yield of 8.66 mmol/g. Compared to single CG gasification, the co-gasification system achieved a 490% increase in total syngas yield and a 394% increase in H_2 yield. Compared to pure SS gasification, the total syngas yield increased by 49% and the H_2 yield increased by 73%. These results confirm that co-gasification of SS and CG exhibits a significant synergistic enhancement effect on both syngas and H_2 yields.

Figure 8 presents the comprehensive performance parameters of co-gasification with varying mass ratios of SS and CG, including syngas yield, syngas ratio, gross calorific value, and carbon conversion rate. Experimental results indicate that as the SS proportion increases, the CO volume fraction continuously rises, while the Y_{syngas} first increases and then decreases, rising from 0.35 m³/kg for SS alone and 0.08 m³/kg for CG alone to 0.49 m³/kg at a 5:5 mass ratio

and peaking at 0.54 m³/kg at a 7:3 ratio. The oxygen-enriched characteristics of biomass promote oxidation reactions, leading to a monotonically decreasing H_2/CO ratio (with CO increasing at a higher rate than H_2), the H_2/CO ratio decreased from 4.31 to 1.55, which is primarily due to the high fixed carbon content in CG promoting the occurrence of the Boudouard and water-gas reactions, while the high ash content in SS leads to deterioration of the mass transfer process.

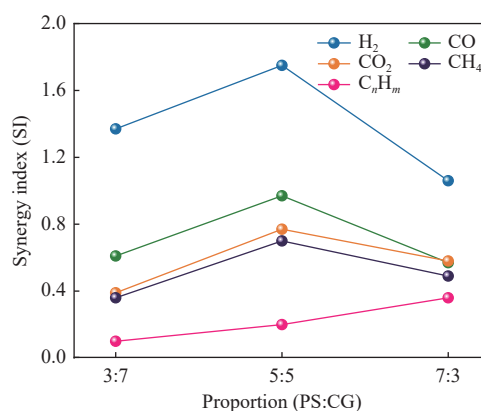


Fig. 5 Synergy effect index of co-gasification with different mass ratios of PS and CG

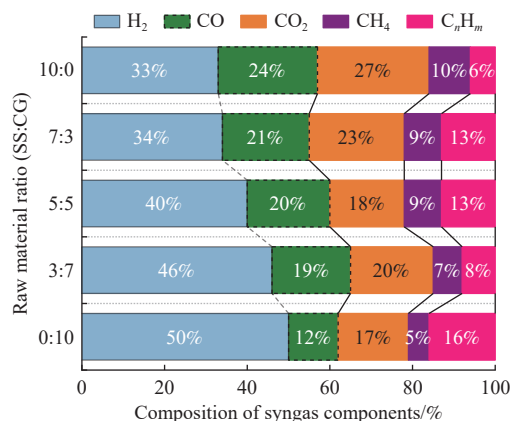


Fig. 6 Gas composition from co-gasification of SS and CG at different mass ratios

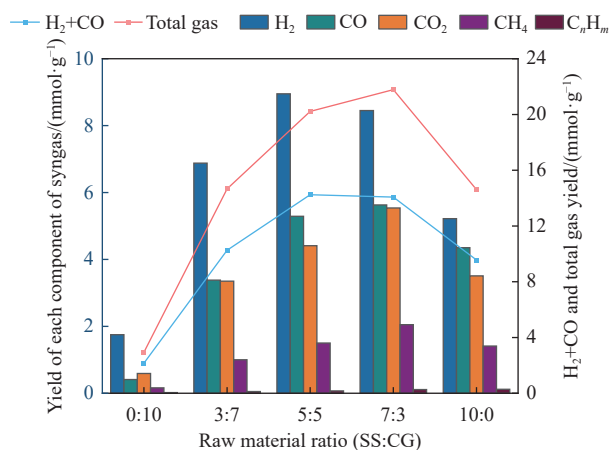


Fig. 7 Variation in gas yield from co-gasification of SS and CG at different mass ratios

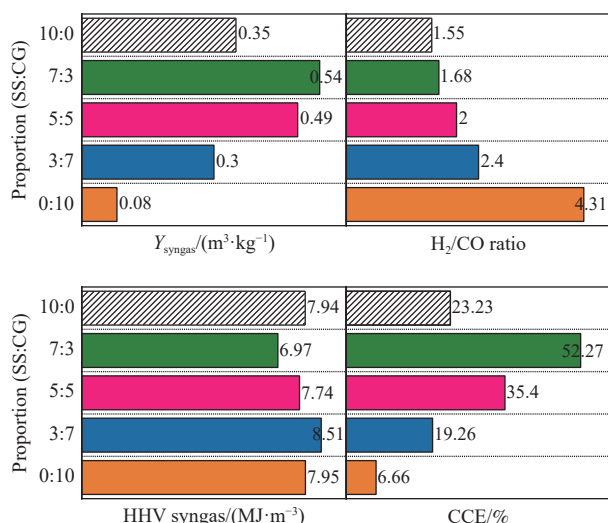


Fig. 8 Gasification performance parameters of SS and CG

HHV peaked at 8.51 MJ/m³ at a 3:7 mass ratio, this indicates that at this SS:CG ratio, the mixed utilization efficiency of the two feedstocks is the highest, and the synergistic promoting effect is the strongest at this point. The carbon-rich matrix of CG synergistically enhanced combustible gas concentration with SS volatiles, though H₂+CO yield reached only 8.93 mmol/g at this ratio. The CCE peaked at the 7:3 ratio. However, the high-oxygen environment promoted the Boudouard reaction^[19], diverting carbon toward CO₂ formation. Consequently, both H₂+CO and H₂ yield were lower than the optimized values achieved at the 5:5 ratio ($Y_{\text{syngas}} = 12.99$ mmol/g, H₂=8.66 mmol/g, Figure 7).

Figure 9 displays the distribution of synergistic effect indices for the co-gasification of SS and CG. The study confirms that all gas components exhibit positive synergistic effects, with hydrogen (H₂) demonstrating the most pronounced synergistic intensity. The synergy indices for H₂ and CO peaked at a 5:5 mass ratio of SS to CG, reaching 1.56 and 1.11, respectively. This phenomenon directly corroborates the earlier conclusion regarding the peak syngas yield. The synergistic effect of light hydrocarbons C_nH_m continuously increased with rising CG proportion, peaking at 1.22 at a 7:3 ratio.

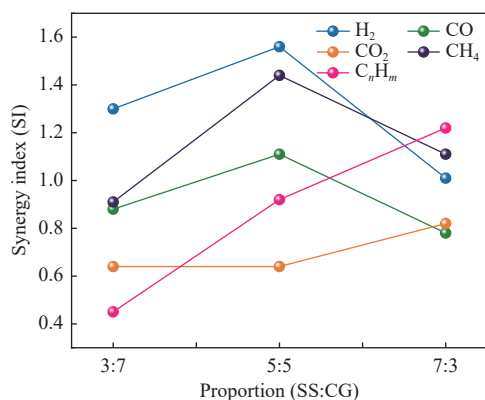


Fig. 9 Synergistic effect index of co-gasification with different mass ratios of SS and CG

This primarily resulted from minerals in CG effectively catalyzing the cracking of light hydrocarbons derived from SS hemicellulose tar. However, the high ash content of SS tends to cover catalytically active sites, hindering mass transfer processes^[20]. Its inherently high nitrogen content promotes the formation of pyridine-containing nitrogenous tars, thereby inhibiting the depth of gasification reactions^[21–22]. Considering gas yield, H₂ selectivity and synergistic effect intensity comprehensively, a 5:5 mass ratio of SS to CG was established as the optimal co-gasification mixture.

2.3 Co-gasification of CS and CG

Figures 10 and 11 systematically reveal the influence patterns of different mass ratios of CS and CG co-gasification on the volume fractions and yields of gas components. The study indicates that the H₂ volume fraction exhibits a continuous decreasing trend with increasing corn stover proportion, dropping from 50% to 33%. However, the H₂ yield demonstrates a nonlinear characteristic of first increasing and then decreasing, reaching a peak of 8.75 mmol/g at a mass ratio of 5:5.

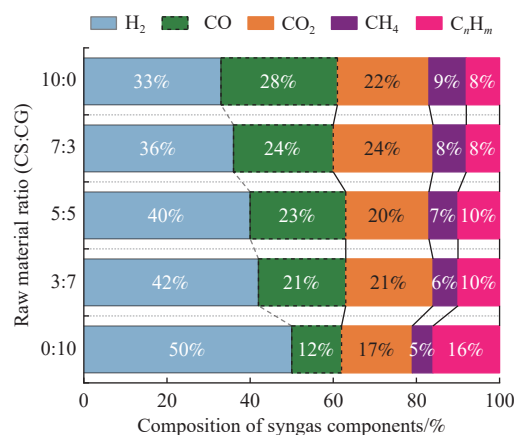


Fig. 10 Gas composition from co-gasification of CS and CG at different mass ratios

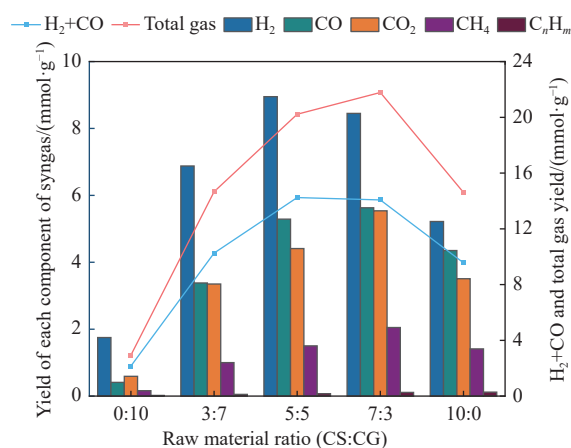


Fig. 11 Variation in gas yield from co-gasification of CS and CG at different mass ratios

The significant increase in total syngas volume dilutes the H_2 concentration but substantially enhances the H_2 yield. Concurrently, the CO volume fraction increased from 12% to 28% with rising corn stover proportion. Its yield peaked at 5.63 mmol/g at a mass ratio of 7:3 and exhibited a secondary peak of 5.29 mmol/g at 5:5, reflecting the sustained promotion of oxidation reactions by biomass's oxygen-rich characteristics.

Experimental data indicate that the syngas yield from CG gasification alone is 2.16 mmol/g, with an H_2 yield of 1.75 mmol/g; while CS gasification yielded 9.56 mmol/g of synthesis gas and 5.22 mmol/g of H_2 .

When CS and CG were co-gasified at a 5:5 mass ratio, synthesis gas yield peaked at 14.24 mmol/g, with H_2 yield reaching 8.75 mmol/g. Compared to CG gasification alone, this co-gasification system significantly increased syngas yield by 559% and H_2 yield by 400%. Compared to CS gasification alone, it increased syngas yield by 48% and H_2 yield by 67%. These results confirm that co-gasification of CS and CG exhibits significant synergistic effects on hydrogen and syngas production.

Figure 12 shows the gasification performance parameters for co-gasification of CS and CG at different mass ratios, including gas yield, syngas ratio, gross calorific value, and carbon conversion rate. As shown in Figure 12, Y_{syngas} from individual gasification of CS is 0.35 m^3/kg . As the CS proportion increases, Y_{syngas} increases up to a 7:3 mass ratio and then declines, peaking at 0.53 m^3/kg at a 7:3 ratio. The nitrogen gas yield during co-gasification of CS and CG is higher than when each is gasified separately. However, as the corn stover proportion increases, CO production rises, the H_2/CO ratio decreased from 4.31 to 1.29, leading to a monotonically decreasing $H_2+\text{CO}$ yield. The gross calorific value peaks at a 5:5 mass ratio of CS to CG. The maximum value is 8.41 MJ/m^3 , indicating the highest fuel efficiency at this point. In Figure 12, the carbon conversion rate, reached its maximum at a mass ratio of 7:3, with a peak value of 58.29%. However, the $H_2+\text{CO}$ yield at this ratio was lower than that at a 5:5 ratio. This occurs because the 7:3 ratio produces more CO and CO_2 ; yet the hydrogen yield is lower than at the 5:5 ratio. Considering all performance parameters, the gasification performance was optimal when the CS:CG ratio was 5:5.

Figure 13 shows the synergistic effect index diagram for the co-gasification of CS and CG. The figure indicates that the co-gasification of CS and CG produces positive synergistic effects on all gases, with the most significant positive synergistic effect observed for H_2 . The synergy indices for H_2 and CO both peaked at 1.43 and 1.22, respectively, when the mass ratio of CS to CG was 5:5. This aligns with the earlier conclusion that the total syngas yield reached its maximum at this ratio. Simultaneously, the synergistic effect on CO_2 production is strong during co-gasification, peaking at 1.15 when the CS to CG mass ratio is 5:5. This occurs because K^+ in CS ash catalyzes the Boudouard reaction^[23–24], but ash sintering inhibits secondary reactions^[20] while simultaneously increasing

carbon loss^[25–26]. The synergistic effect of C_nH_m increases with higher CG ratios, peaking at 1.04 when the CS to CG mass ratio is 7:3. In summary, the optimal feedstock ratio for co-gasification of CS and CG to produce synthesis gas is 5:5.

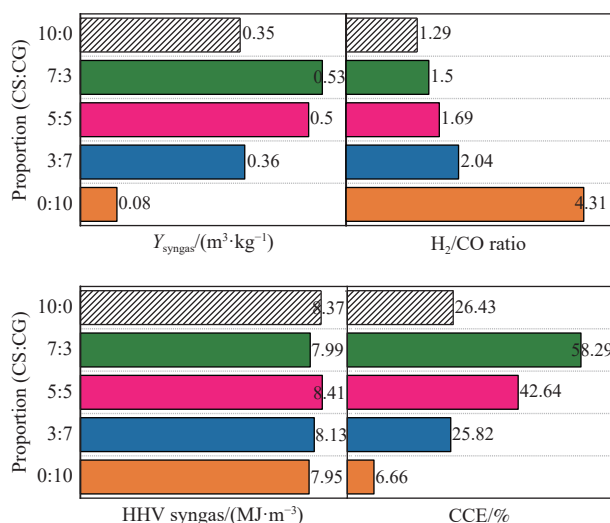


Fig. 12 Gasification performance parameters of CS and CG

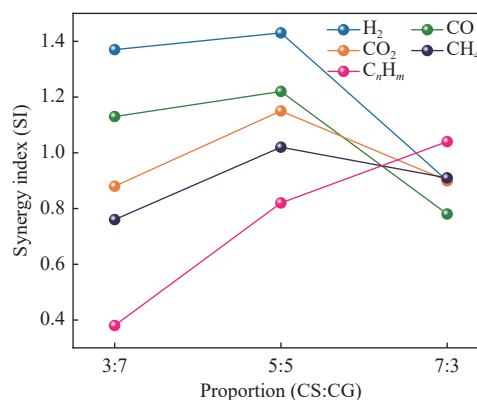


Fig. 13 Synergistic effect index of co-gasification with different mass ratios of CS and CG

3 Comparative analysis

As shown in Table 3, CS exhibits high ash content and demonstrates the strongest promotion effect on CO production during co-gasification with CG, making it suitable for blending in industrial applications requiring low synthesis gas ratios. SS exhibits high nitrogen and protein content. During pyrolysis, proteins generate nitrogen-containing radicals^[27], which are synergistically amplified by minerals in CG during co-gasification. Consequently, soybean straw possesses high C_nH_m characteristics, which are unfavorable for syngas production. However, it is suitable for replacing chemical feedstocks^[28] and exhibits the highest H_2/CO ratio, making it suitable for blending in industrial applications requiring high syngas ratios. co-gasification of PS and CG exhibits “three highs” and “three lows.”

Table 3 Comparison of co-gasification performance of three types of biomass at optimal proportions

Indicator	PS:CG(5:5)	SS:CG(5:5)	CS:CG(5:5)
$Y_{\text{syngas}}/(\text{mmol}\cdot\text{g}^{-1})$	15.25	13.00	14.24
H_2 yield/ $(\text{mmol}\cdot\text{g}^{-1})$	9.06	8.66	8.95
CO yield/ $(\text{mmol}\cdot\text{g}^{-1})$	6.19	4.34	5.29
CH_4 yield/ $(\text{mmol}\cdot\text{g}^{-1})$	2.39	1.95	1.50
CCE/%	43.92	35.40	42.64
H_2/CO ratio	1.46	2.00	1.69
HHV/ $(\text{MJ}\cdot\text{m}^{-3})$	8.82	7.74	8.41
SI(H_2)	1.75	1.56	1.43
SI(CO)	0.97	1.11	1.22
SI(CO_2)	0.77	0.64	1.15
SI(CH_4)	0.70	1.44	1.02
SI(C_nH_m)	0.20	0.92	0.82

The “three highs” refer to the highest syngas yield, strongest synergistic effect on H_2 and highest carbon conversion rate. The “three lows” denote the lowest synergistic effect on C_nH_m , the lowest synergistic effect on methane, and the lowest CO_2 yield. This is attributed to PS’s high cellulose content. During gasification, cellulose hydrolysis produces light oxygenated intermediates that efficiently generate H_2 via steam reforming^[29]. Simultaneously, lignin in PS releases phenolic radicals that quench tar condensation chain reactions, suppressing tar formation. This makes it suitable for syngas production and

clean hydrogen energy generation.

Figure 14 illustrates the synergistic mechanism of co-gasification between biomass and CG, which originates from the complementary physicochemical properties of both materials and the synergistic effects of multi-step reactions. Specifically, highly reactive free radicals ($\cdot\text{H}$, $\cdot\text{OH}$) generated from cellulose pyrolysis in biomass^[30] diffuse through the gas phase to the CG surface. These radicals attack and break their inert Si–O and Al–O bonds^[31], creating active sites. The newly formed radical sites significantly enhance surface reactivity, promoting oxidation, hydrolysis, and ion exchange reactions to activate the CG. Concurrently, minerals like K and Ca in CG catalyze tar reforming reactions^[32], synergizing with biomass volatiles to enhance coal-coke gasification and effectively reduce coking. In reaction pathways, K^+ preferentially catalyzes the Boudouard reaction to promote CO production, while Ca^{2+} tends to catalyze the water-gas shift reaction to enhance H_2 generation, enabling targeted regulation of syngas composition. However, synergistic effects are constrained by biomass properties: nitrogen-rich tar from high-nitrogen biomass pyrolysis readily coats active sites^[33], while ash melting in high-ash biomass impedes mass transfer, collectively inhibiting gasification reactions. The co-gasification synergistic mechanism arises from the coordinated action of multiple pathways, including radical activation, targeted metal ion catalysis, and tar cracking. Different biomass characteristics exert differential control over the gasification process by influencing active site availability and mass transfer efficiency.

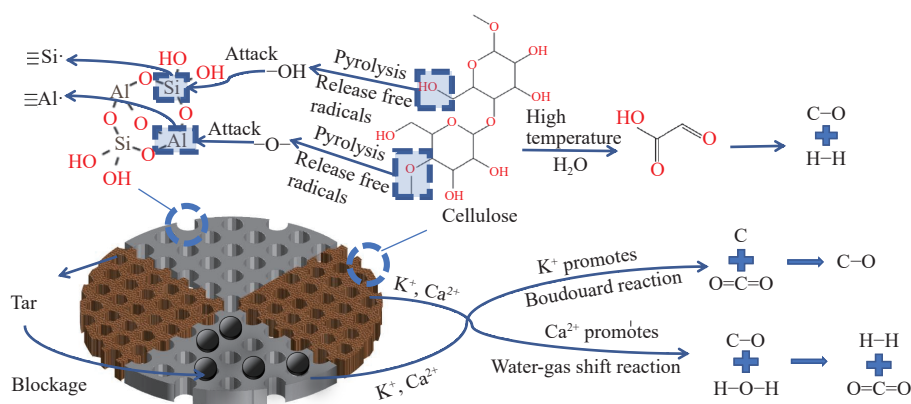


Fig. 14 Synergistic mechanism of biomass and coal gangue co-gasification

4 Conclusion

This study systematically investigated the co-gasification of three representative biomass types—PS (high cellulose), SS (high nitrogen), and CS (high ash)—with CG, revealing the regulatory mechanisms of biomass characteristics on syngas production and synergistic effects. The main conclusions are as follows:

co-gasification demonstrates significant synergy, with optimal product distribution being precisely directed by

feedstock composition. All three systems achieved peak syngas yields at a 5:5 mass ratio. However, their optimal products differed substantially due to distinct key components: The PS (high cellulose) system achieved the highest hydrogen yield (9.06 mmol/g), H_2/CO yield (15.25 mmol/g) and H_2 synergy index ($\text{SI}=1.75$), exhibiting a “three highs and three lows” advantage. The CS (high ash/ K^+) system showed the strongest synergy for CO production ($\text{SI}=1.22$), making it an ideal source for CO-rich syngas. The SS (high nitrogen) system achieved an ideal H_2/CO ratio (2.00), although its high nitrogen content led to

nitrogen-containing tar that suppressed the overall yield.

The synergistic mechanism originates from the complementarity of physicochemical properties and competition among reaction pathways. The synergy is governed by multiple pathways: radical activation (biomass pyrolysis radicals cleaving inert bonds in CG); directed catalysis by AAEMs (K^+ preferentially catalyzing the Boudouard reaction, while Ca^{2+} promotes the water-gas shift reaction); and catalytic tar cracking and its inhibition (CG minerals cracking tars, while by-products from high-nitrogen or high-ash biomass weaken this effect). The key components of the biomass determine which of these pathways becomes dominant.

This research clarifies the mechanism by which key biomass components (cellulose, nitrogen, ash and AAEMs) govern the distribution of products and the intensity of synergy by regulating the dominant reaction pathways during co-gasification, providing a theoretical basis for the targeted conversion of waste resources.

Declaration of Competing Interest

The authors declare no conflict of interest.

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生物质与煤矸石共气化及协同机制研究

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摘 要: 生物质被誉为可持续利用的绿色煤炭, 其热化学转化特别是富氢气化技术, 是实现生物质高值化利用的有效途径。将生物质与煤矸石共气化, 可实现碳资源的协同利用, 具有显著的减排增效潜力。本研究为阐明关键生物质组分对气化过程的调控作用, 选取了三种具有鲜明组成特征的典型原料——松木(高纤维素, 代表高反应性挥发分)、大豆秸秆(高氮, 体现含氮组分影响)和玉米秸秆(高灰分且富含 K^+ , 反映灰分催化特性), 与煤矸石进行共气化实验。在固定水蒸气流量(2 mL/min)、温度(850 $^{\circ}\text{C}$)及氮气流量(75 mL/min)的条件下, 研究了不同生物质与煤矸石共气化的协同效应。结果表明, 三种生物质体系均在生物质与煤矸石质量比为 5:5 时合成气产率达到峰值。其中, 高纤维素的松木体系 H_2 与 CO 产率最高, 达 15.25 mmol/g, 其氢气产率为 9.06 mmol/g, 相较于纯煤矸石提高 417%, 较纯松木提高 52%, 表现出“三高三低”优势: 即高产气率、高 H_2 协同指数、高碳转化率; 低 C_nH_m 生成、低 CH_4 协同效应和低 CO_2 排放。高灰分的玉米秸秆体系对 CO 生成的协同效应最强(协同指数 $\text{SI}=1.22$), 而高氮的大豆秸秆体系则获得最佳的合成气组成比例(H_2/CO 比=2.00), 但其含氮组分在一定程度上抑制了合成气总产率。研究表明, 生物质类型通过其关键组分(纤维素、氮、灰分及金属元素)调控共气化反应路径, 实现对合成气产量与组成的差异化导向。本研究揭示了生物质与煤矸石共气化的协同机制, 为废弃资源的高值化转化与清洁能源生产提供了理论依据和技术支撑。

关键词: 生物质; 煤矸石; 共气化; 协同效应; 合成气

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