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Comparative study on microwave-assisted co-pyrolysis of tissue paper and polyethylene: Effects of zeolite, metal oxide, and carbon-based additives on syngas production

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Comparative study on microwave-assisted co-pyrolysis of tissue paper and polyethylene: Effects of zeolite, metal oxide, and carbon-based additives on syngas production

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Abstract: Microwave-assisted pyrolysis for syngas production represents a promising technology for the resource utilization of solid waste. Due to the selective heating nature of microwaves, the introduction of microwave absorbers or catalysts is a prevalent strategy to enhance the process. This study investigated the effects of 3 representative categories of microwave absorbers/catalysts—zeolites (HZSM-5), metal oxides (CaO), and carbon-based materials (biochar)—on gas evolution and product characteristics during the co-pyrolysis of tissue paper and polyethylene (PE). The results indicated that HZSM-5 exhibited the most pronounced catalytic performance, notably intensifying the synergistic interaction between the feedstocks. CaO functioned effectively as both a CO_2 sorbent and a microwave absorber, while biochar significantly improved the heating rate and temperature throughout the reaction stage. The optimal loading for all 3 additives was determined to be 20 wt.%. The effect of the additives in promoting gas production followed the order: HZSM-5 > CaO > biochar. Specifically, with the addition of 20% HZSM-5, the gas yield and volume increased from 26.1% and

247 mL/g to 48.5% and 465 mL/g, respectively.

Keywords: Microwave-assisted heating; Co-pyrolysis; syngas production; Microwave absorber

1 Background

China's energy structure has long been dominated by coal, with natural gas accounting for a relatively low share. In 2024, China's apparent natural gas consumption reached 420 billion m^3, while domestic production was only 240 billion m^3, resulting in a high external dependency of 43% [1]. Under the "dual carbon" goals, the State Council's Action Plan for Carbon Peaking Before 2030 explicitly calls for "orderly guidance of natural gas consumption and optimization of utilization structure," projecting that the share of natural gas in primary energy consumption will increase from the current 8.5% to approximately 15% by 2030[2, 3]. However, the widening supply-demand gap poses significant challenges to national energy security, necessitating the development of distributed, low-carbon, and cost-effective alternative gas sources. This imperative has directed attention toward the thermochemical conversion of combustible solid waste, which represents both an environmental burden and an underutilized energy resource. China generates approximately 300 million tons of municipal solid waste (MSW) annually[4]. If the combustible components (estimated at 60%) were fully converted via pyrolysis, the theoretical gas yield could reach 60–90 billion m^3/year[5], equivalent to 14%–21% of current natural gas consumption. Nevertheless, realizing this potential requires conversion technologies capable of efficiently processing high-moisture,

heterogeneous waste streams while delivering gas products of sufficient quality for end-use applications.

Two primary thermochemical routes exist for waste-to-gas conversion: pyrolysis and gasification. Conventional gasification typically employs air as the gasifying agent. Although cost-effective, this approach inevitably introduces atmospheric nitrogen into the product gas. This dilution results in low-calorific-value syngas (4–7 MJ/m^3) [6], and subsequent purification to obtain high-purity components entails substantial energy penalties. In contrast, pyrolysis operates in oxygen-deficient or inert atmospheres, fundamentally avoiding nitrogen dilution. Besides, municipal solid waste (MSW) is characterized by high moisture content, complex composition, significant heterogeneity, and often coupled with large particle sizes. Consequently, a higher excess air coefficient is frequently required to achieve complete gasification, which inevitably further dilutes the producer gas and lowers its heating value, resulting in products with limited economic value. In contrast, the pyrolysis of unsorted combustible MSW can yield gas with an average heating value of 15 MJ/Nm^3 [7], making it suitable for direct application as civil or industrial boiler fuel gas.

However, conventional pyrolysis of MSW faces critical limitations that have restricted its commercial viability: high moisture content, large particle sizes, and extreme compositional heterogeneity result in low thermal conversion efficiency and limited gas yields, typically below 1 Nm^3/kg even at 900°C [7]. Unlike conventional conductive heating that relies on surface-to-core heat transfer, microwave energy penetrates directly to the material center, generating volumetric heating with "hotspot"

effects[8].

This rapid, uniform heating improves energy efficiency and eliminates the need for extensive feedstock size reduction[9]. It was demonstrated that, under identical heating conditions, compared with conventional pyrolysis, both the gas production rate and gas quality are significantly improved in microwave pyrolysis. Notably, the proportions of hydrogen (H_2) and carbon monoxide (CO) in the gas composition increase remarkably (even exceeding 80%). Similar results have been observed by different researchers in pyrolysis experiments involving lignocellulosic biomass[10] , straw[11], rice husk[12], bamboo[13] , algae [14, 15] , lignite coal [16] , and plastic[17]. However, microwaves are not heat sources and cannot directly heat solid materials. When microwave radiation acts on solid materials containing polar molecules, dipole polarization is the dominant factor in the conversion of microwave electromagnetic energy into thermal energy. Consequently, microwave heating exhibits a distinct characteristic: selectivity. The microwave absorption capabilities of different material components vary drastically. The main components of municipal solid waste, such as paper and plastics, generally possess poor microwave absorption capabilities[18] [19]. Therefore, the addition of microwave absorbers is usually required. These absorbers instantaneously capture microwave energy, converting it to localized high temperatures that are transferred to the waste, inducing and accelerating catalytic cracking reactions[20]. While numerous microwave absorbers exist, green, low-cost, high-activity, and long-lifetime materials are essential for scale-up. Currently, three additive categories dominate research attention: metal oxides[21, 22], zeolites, and carbon-

based materials [23, 24].

As a cost-effective and abundant metal oxide, calcium oxide (CaO) functions as both a typical microwave absorber and a catalyst. Its dual functionality—acting as a CO_2 sorbent and catalyst—significantly enhances syngas production quality[25, 26]. For instance, Magoua Mbeugang et al. [27] reported a volatile carbon conversion rate of approximately 90 wt.% using CaO. Similarly, Wei et al. [28] developed a high-performance CaO-based dual-functional material that achieved a CH_4 yield of 17.2 mmol/g with 97% selectivity in integrated CO_2 capture and methanation. Ma et al. [29] further identified CaO as a superior catalyst compared to Fe_2O_3 for improving biogas yield and quality. Moreover, both CaO and its carbonation product ($CaCO_3$) possess favorable dielectric loss properties, enabling the efficient conversion of microwave energy into heat[30].

Distinct from metal oxides, zeolites operate through distinct catalytic mechanisms wherein physical structure and pore dimensions play dominant roles, as described by Shafizadeh et al. [31]. Their regular microporous structures selectively catalyze the conversion of oxygenated compounds to hydrocarbons via dehydration and decarbonylation, significantly reducing bio-oil oxygen content and increasing heating value. For instance, Rahman et al. [32] showed that zeolites with varying pore sizes and acidic active sites enhance deoxygenation reactions, thereby improving aromatic yields. Li et al. also demonstrated that hierarchical HZSM-5 significantly enhances aromatic yields during rice husk pyrolysis compared to standard catalysts [33, 34]. Similarly, Dong et al. found that Zn-modified hierarchical zeolites optimize hydrocarbon

112 production from biomass-plastic co-pyrolysis[35]. Furthermore, Tian et al. found that
113 HZSM-5 favors monocyclic aromatics from polyethylene, whereas other structures
114 catalysts yield different byproducts[36].

115 Carbon-based materials function as both catalysts and microwave absorbers in
116 microwave-assisted pyrolysis. Dong et al. [37] investigated biochar-catalyzed
117 microwave pyrolysis of the same biomass source, demonstrating that biochar
118 significantly enhanced bio-oil conversion to gaseous products through efficient
119 cracking activity. Wang et al. [38] employed biochar as a catalyst for biomass and
120 plastic waste co-pyrolysis, enhancing aromatic and syngas production. Among carbon
121 materials, pyrolytic char—derived from the process itself—has attracted increasing
122 attention due to its excellent microwave absorption performance, economic viability,
123 ready availability, and inherent compatibility with the reaction system.

124 In summary, while the 3 primary categories of catalysts used in microwave
125 pyrolysis—metal oxides, zeolites, and carbon-based materials—have been the subject
126 of extensive research, existing studies have largely examined them in isolation.
127 Consequently, there is a notable lack of comparisons conducted under identical
128 microwave power, temperature, and reactor configurations. This gap makes it difficult
129 to objectively evaluate the differential effects of these additives on pyrolysis gas
130 characteristics. Furthermore, the variations in how these 3 types of additives influence
131 biomass/plastic co-pyrolysis gas evolution process have not been adequately explored.

132 Hence, this study focuses on paper and polyethylene (PE) plastic, the primary
133 components of combustible municipal solid waste. Under consistent microwave heating

conditions (700 W, 800 °C), calcium oxide, zeolite, and pyrolytic char were employed as catalysts to investigate the effects of catalyst type and loading on the heating characteristics, gas evolution process, gas properties, and product distribution during the microwave co-pyrolysis of paper/plastic mixtures.

2 Experimental Materials and Methods

2.1 Materials

In this study, tissue paper (Vinda, China) and 30-mesh polyethylene (PE) plastic granules (Hongyun Polymer Materials Co., Ltd., China) were selected as the experimental feedstocks with a mass ratio of 4:1. Prior to the experiments, both the tissue paper and plastic granules were dried. Their proximate and ultimate analyses are presented in Table 1. Calcium oxide, HZSM-5 zeolite, and pyrolytic char were selected as representative microwave absorbers and catalysts for the 3 categories of metal oxides, zeolites, and carbon-based materials, respectively. Specifically, high-purity, ultrafine 800-mesh calcium oxide was supplied by Guangzhou Metal Metallurgy Co., Ltd, China. The zeolite used was a hydrogen-form HZSM-5 with a silica-to-alumina ratio of 20–25, obtained from Hebei Yuanying New Materials Co., Ltd. (Hebei, China). The pyrolytic char was the solid residue collected from the pyrolysis of pure tissue paper.

Table 1 Proximate and ultimate analysis of waste paper and plastic PE

	Proximate analysis（%）				Ultimate analysis（%）				
	Aad	*Mad*	*Vad*	*FCad*	*Cad*	*Had*	*Nad*	*Sad*	*Oad*
Paper	0.03	7.38	84.35	8.24	41.41	6.71	1.72	0.08	42.68
PE	0	0.20	99.80	0	81.77	16.34	1.62	0.07	0

2.2 Experimental Apparatus and Method

The experimental apparatus, consistent with that described in the literature[39], primarily comprised a gas supply system, a microwave pyrolysis furnace, a power and temperature acquisition control system, a product condensation and filtration unit, and a gas collection system. A silicon carbide (SiC) reactor was employed to enhance the microwave absorption capability of the materials during the reaction. Nitrogen was used as the carrier gas at a flow rate of 100 ± 5 mL/min. Prior to each experiment, nitrogen was purged through the system for 10 min to remove residual air from the reactor.

Upon the commencement of the reaction, the pyrolysis vapors passed through a condensation and dedusting unit, and was collected in a 50 L gas bag. The gas production rate was measured using a mass flow meter. The process was held at the final pyrolysis temperature of 800 °C for 5 min. To monitor the gas evolution process, gas sampling was conducted at 100 °C intervals within the 200–800 °C temperature range. The gas composition was analyzed using an Agilent 7890 gas chromatograph. Finally, the char remaining after the experiment was collected and weighed.

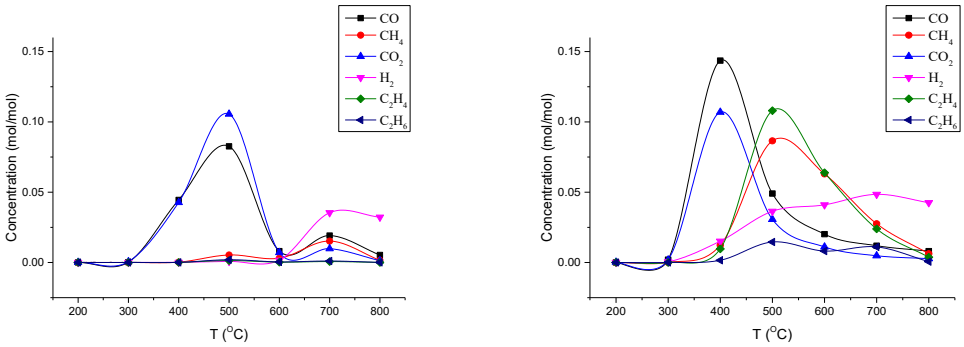
2.3 Product Yield Analysis

The mass yield of the gas phase was calculated based on the total volume of gas produced and the component concentrations. The solid yield was determined by direct weighing, while the liquid yield was obtained by difference.

3 Results and Discussion

3.1 Comparative Analysis of Gas Production Between Paper and Paper/PE Co-

pyrolysis



(a)Microwave Pyrolysis Gas Evolution Process of Tissue Paper (b)Microwave Co-pyrolysis Gas Evolution Process of Tissue Paper/PE

Fig.1 Comparative analysis of gas evolution process between paper and paper/PE co-pyrolysis

As shown in Fig. 1(a), the pyrolysis of pure tissue paper occurs in two distinct stages. During the 300-600℃ range, gas production is primarily dominated by CO and CO_2. In contrast, hydrogen-containing gases (H_2, CH_4, C_2H_4, and C_2H_6) are produced in very small amounts during this phase, with their main release occurring between 600-800 °C. In the primary pyrolysis stage (300-600 °C), heat mainly breaks down the cellulose backbone and cleaves oxygen-containing functional groups. Specifically, the cleavage of carbonyl (C=O) and ether (C–O–C) bonds, along with the decomposition of aldehyde (–CHO) intermediates, generates most of the CO. Meanwhile, the decarboxylation of carboxyl groups (–COOH) serves as the main pathway for CO_2 formation. Consequently, this stage is characterized by deoxygenation, making CO and CO_2 the dominant gaseous products.

Following the primary stage, the process transitions to a secondary reaction phase at 600–800 °C, where the carbon-rich char becomes the main reactant. Under the high temperature, the char undergoes significant aromatization and condensation. The

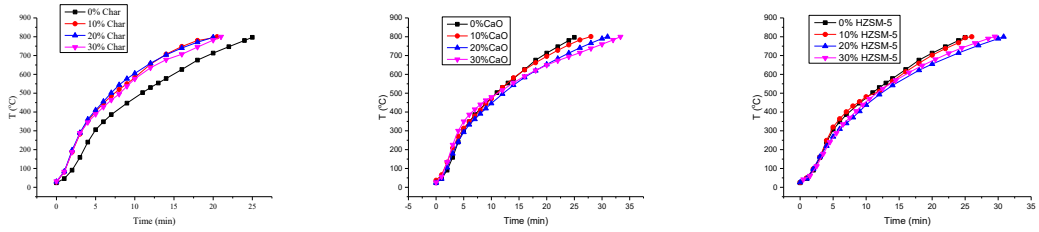
192 aromatic ring systems release H_2 via dehydrogenation to form more stable structures.
193 Simultaneously, the deep cracking of residual aliphatic structures and heavy tar
194 contributes to the generation of hydrocarbon gases such as CH_4, C_2H_4, and C_2H_6.
195 Essentially, this stage represents a process of dehydrogenation and structural ordering
196 of the solid residue.
197 During the co-pyrolysis of tissue paper and polyethylene (PE), the peak CO
198 concentration significantly increases to nearly 0.14 mol/mol (compared to ~0.08
199 mol/mol for paper alone), with the peak temperature shifting forward from 500 °C to
200 approximately 400 °C. A similar advance occurs for CO_2. This behavior indicates a
201 strong synergistic effect driven by PE acting as a "hydrogen donor." Hydrogen radicals
202 and hydrogen-rich volatiles from PE stabilize oxygen-containing radicals generated
203 during cellulose pyrolysis, inhibit char condensation, and promote the low-temperature
204 cleavage of oxygenated functional groups (e.g., carbonyl, ether, and carboxyl groups).
205 Consequently, oxygen is selectively released as CO rather than CO_2 or solid char.
206 Specifically, the enhanced hydrodeoxygenation pathway shifts carboxyl conversion
207 toward aldehyde intermediates, which ultimately form CO, and decreased CO_2 yields.
208 Additionally, the co-pyrolysis significantly increases the yields of H_2, CH_4, and C_2H_4,
209 with their peak release temperatures advancing notably (e.g., H_2 and CH_4 shift from
210 700 °C to ~500 °C). This is primarily because PE becomes the dominant source of
211 small-molecule hydrocarbons. Between 400 °C and 500 °C, PE undergoes intense
212 random chain scission, generating abundant alkyl and hydrogen radicals. These active
213 species not only surge CH_4 and C_2H_4 production but also shift the gas release peaks to

PE's primary pyrolysis range, masking the higher-temperature gas evolution of paper. Furthermore, the rapid hydrogen transfer from PE stabilizes unstable macromolecular fragments, inhibiting char formation and promoting the early release of light gases like H_2 and CH_4.

Finally, the biochar produced from tissue paper possesses excellent microwave absorption properties, functioning as an in-situ "microwave hotspot." Within the experimental encapsulating structure, this creates a micro-reactor environment where primary volatiles undergo microwave heating, catalytic reforming, and secondary cracking over the biochar surface, thereby promoting their conversion into small-molecule gases such as H_2 and CH_4.

In summary, the addition of PE not only altered the gas distribution during the microwave pyrolysis of tissue paper—shifting it from being dominated by oxygenated organic compounds to being primarily composed of low-carbon hydrocarbon gases (H_2, CH_4, C_2H_4)—but also generated a synergistic effect by providing an abundant source of active radicals. This synergy achieved both a migration of the gas production process to lower temperature regions and an enhancement in gas yield.

3.2 Effects of Different Microwave Catalysts/Absorbers on the Heating Process of Microwave Co-Pyrolysis



(a) Char (b) CaO (c) HZSM-5

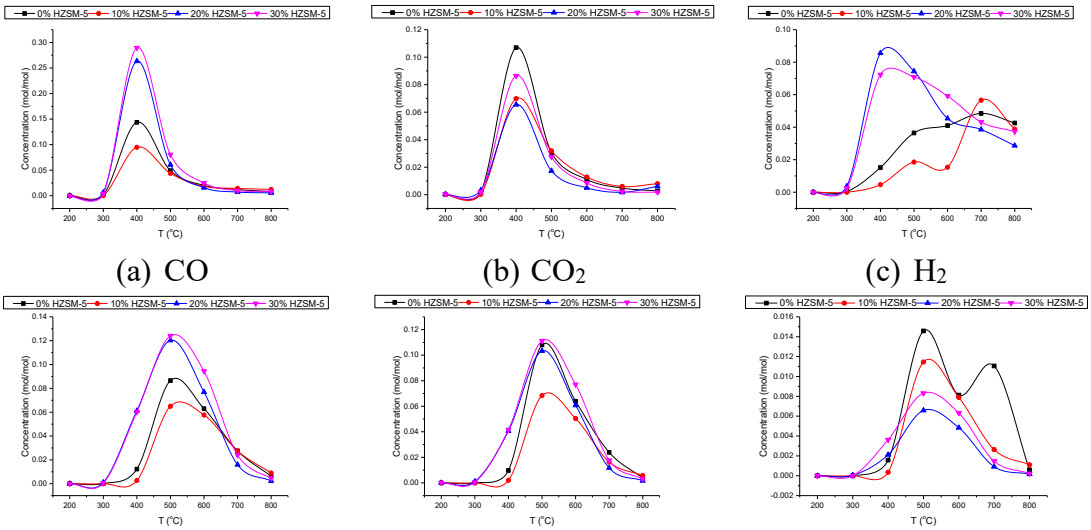
Fig.2 Comparative effect of 3 different microwave catalysts/absorbers on the heating process of microwave pyrolysis

As shown in the Fig.2, char is an excellent microwave absorber[40]. At different addition ratios, it significantly increases the reaction temperature throughout the entire co-pyrolysis process of tissue paper and PE. Prior to 300 °C (before the onset of pyrolysis), variations in char addition have a negligible effect on the heating temperature. However, above 300 °C, no distinct correlation is observed between char content and temperature. This irregularity is attributed to the endothermic nature of the pyrolysis reaction; the heat consumption associated with decomposition alters the system's thermal balance, thereby obscuring the heating trends typically induced by different char loadings.

CaO helps raise the temperature of the mixture before 500°C, but its effect is not as strong as that of char. This matches the findings in related studies, which show that metal oxides are weaker at absorbing microwaves than carbon materials[41]. In the later stage of the reaction, the temperatures under different CaO additions are lower than those in the blank group (with no CaO). This is directly linked to CaO's catalytic effect on the pyrolysis reaction. The catalyst speeds up the heat-absorbing pyrolysis process, which means the system absorbs more net heat, ultimately leading to a drop in the overall reaction temperature.

For the HZSM-5 zeolite catalyst, its effect on the heating process happens in two stages. Before 200°C, it has almost no effect on the temperature, mainly because HZSM-5 itself is not very good at absorbing microwaves[42]. After 200°C, however, HZSM-5 uses catalytic cracking to break down the long PE molecular chains faster. This strengthens the interaction between PE and tissue paper during co-pyrolysis. Because this combined reaction absorbs a lot of heat, the overall temperature of the system ends up lower than when no catalyst is added.

3.3 Effects of Different Microwave Catalysts/Absorbers on the Gas Evolution Process of Microwave Co-Pyrolysis



(a) CO (b) CO_2 (c) H_2

(d) CH_4 (e) C_2H_4 (f) C_2H_6

Fig.3 Effect of HZSM-5 Addition on Gas Evolution Process of Tissue Paper and PE Co-Pyrolysis

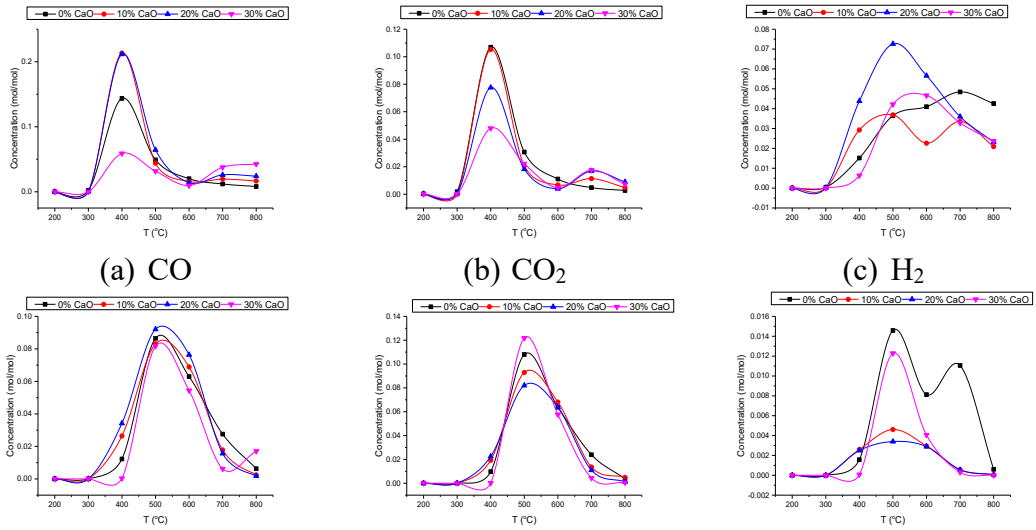
As shown in the Fig.3, the addition of HZSM-5 significantly alters the evolution behavior and yield distribution of gas-phase products during the co-pyrolysis of tissue

paper and PE. When the catalyst addition ratio is increased to the 20%–30% range, although the peak temperatures for the release of CO and CO_2 remain basically stable, their yields exhibit distinctly different trends: the production of CO increases significantly, while the generation of CO_2 is suppressed. Meanwhile, the yields of hydrocarbon gases such as H_2, CH_4, C_2H_4, and C_2H_6 all increase substantially, and their peak release temperatures shift noticeably toward the lower temperature region.

This phenomenon is primarily attributed to the regulatory effect of HZSM-5's unique acidic pore structure on pyrolysis kinetics, which is specifically reflected in two aspects. On the one hand, as a strongly acidic zeolite molecular sieve, HZSM-5 can effectively reduce the activation energy required for the scission of long PE chains. This causes the initial pyrolysis temperature of PE to shift forward significantly from the original 400–500 °C to 300–400 °C. This temperature range highly overlaps with the active pyrolysis zone of the cellulose component in tissue paper. This "overlap of temperature windows" creates favorable conditions for free radical interactions between the two components, thereby strengthening the synergistic effect during the co-pyrolysis process. On the other hand, a large number of highly active hydrogen-rich free radicals (such as alkyl radicals) are generated during the pyrolysis of PE. Under the action of the acidic sites of HZSM-5, these active hydrogen species are more likely to migrate to the oxygen-containing intermediates or hydrogen-deficient free radicals produced by the pyrolysis of tissue paper via hydrogen transfer reactions. The supply of active hydrogen promotes the hydrogenation and saturation of unsaturated hydrocarbons and the formation of small-molecule hydrocarbons, leading to a significant increase in the yields of H_2, CH_4,

and light olefins. Furthermore, the hydrogen transfer process accelerates deoxygenation reactions (such as decarboxylation and decarbonylation), resulting in an increased yield of CO. At the same time, because some oxygen-containing intermediates are hydrogenated and reduced into hydrocarbons or water rather than undergoing decarboxylation to form CO_2, the relative yield of CO_2 decreases.

In summary, HZSM-5 not only reduces the reaction energy barrier through catalytic cracking but also fundamentally reshapes the reaction network and product distribution of the co-pyrolysis process by promoting hydrogen transfer between the components.



(a) CO (b) CO_2 (c) H_2

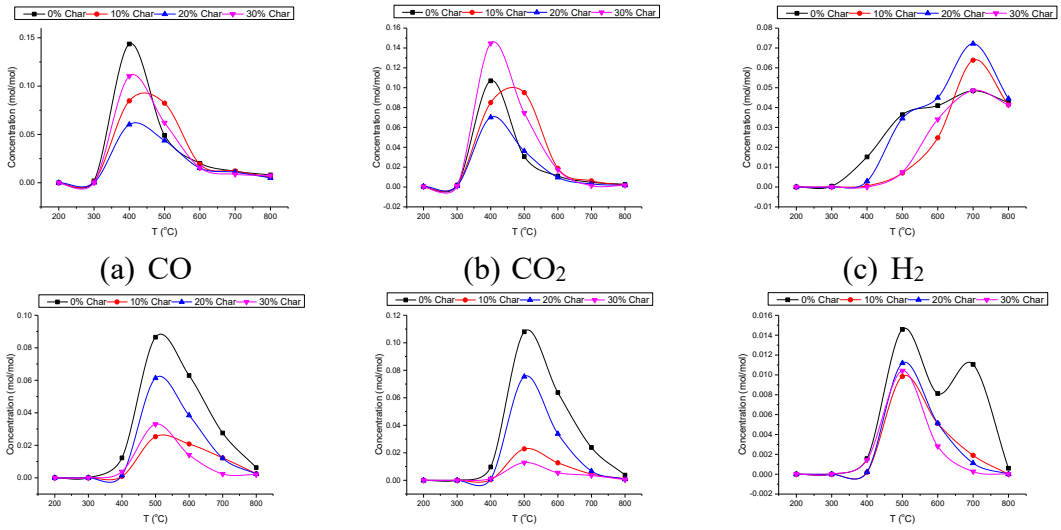
(d) CH_4 (e) C_2H_4 (f) C_2H_6

Fig.4 Effect of CaO Addition on Gas Evolution Process of Tissue Paper and PE Co-Pyrolysis

As shown in Fig.4, the addition of CaO significantly changed the distribution and release behavior of the gaseous products. In the medium temperature range of 300-500°C, the yield of CO increased obviously, while the yield of CO_2 was significantly suppressed. However, the peak release temperatures for both gases did not change much. When the temperature reached the high range of 600-800°C, the yields of both CO and

CO_2 increased. In addition, as the amount of CaO increased, the peak release temperature of H_2 moved to an earlier point, which indicates that the reaction activation energy was lowered. In contrast, the peak temperatures of other hydrocarbon gases remained relatively stable. It is worth noting that CaO showed different effects on different hydrocarbons: it generally increased the yield of C_2H_6, but its effect on C_2H_4 yield was irregular.

These phenomena can be explained by the multiple roles of CaO in the microwave pyrolysis system. First, as a basic oxide, CaO captures the CO_2 produced in the early stage of pyrolysis through an in-situ carbonation reaction ($CaO(s)+CO_2(g)\rightarrow CaCO_3(s)$). This chemical absorption directly reduces the CO_2 concentration in the gas. At the same time, it pushes the reaction balance to produce more CO. Second, in the high-temperature stage, CaO acts as both a microwave absorber to maintain high temperatures and a catalyst to promote the steam reforming of tar ($Tar+H_2O\rightarrow CaO$ $CO+H_2+CH_4$). This combined thermal and catalytic effect speeds up the breakdown of large tar molecules, leading to higher yields of H_2, CH_4, and CO at high temperatures. In summary, CaO functions as a CO_2 absorbent, a microwave absorber, and a tar reforming catalyst. Especially at an optimal addition amount of 10-20%, CaO can effectively improve the product distribution. It significantly increases the yields of syngas (CO, H_2) and CH_4 while reducing CO_2 emissions, thereby increasing the total gas yield and improving the overall gas quality.



(a) CO (b) CO_2 (c) H_2

(d) CH_4 (e) C_2H_4 (f) C_2H_6

Fig. 5 Effect of Char Addition on Gas Evolution Process of Tissue Paper and PE Co-Pyrolysis

As shown in the Fig. 5, the addition of char significantly affected the gas evolution behavior. Compared to the blank group, the yields of all gas components decreased significantly, except for CO_2. However, within the char-added groups, when the addition amount increased to 20%, although the yields of CO and CO_2 continued to decrease, the yields of hydrocarbon gases such as H_2 and CH_4 showed a significant rebound; yet, when the addition amount was further increased to 30%, while the yields of CO and CO_2 continued to increase, the yields of hydrocarbon gases like H_2 and CH_4 decreased again.

This phenomenon is mainly attributed to the unique physical properties of Char. Unlike dense CaO and HZSM-5, Char, as the solid residue of tissue pyrolysis, has a fluffy structure and low bulk density. Notably, the bulk volume of Char is comparable to that of the tissue paper feedstock, which is substantially greater than that of CaO and HZSM-5. During the experiment, when the paper was used to tightly wrap PE particles and char, the large volume of char occupied a significant amount of internal space,

preventing the paper from tightly binding the PE particles. This "structural expansion" created many macro-pores inside the reaction unit, destroying the close contact interface between raw materials. This loose structure produced two negative effects: on one hand, the air insulation layer formed between char particles hindered the effective transfer of microwave energy to the PE core, inhibiting deep cracking reactions. On the other hand, these macro-pores provided a low-resistance escape channel for volatiles, significantly shortening the residence time of oil and gas in the high-temperature zone. This caused primary pyrolysis products to escape rapidly without undergoing secondary cracking or reforming reactions. Consequently, this explains why the addition of char led to a reduction in gas production, despite the overall increase in the reaction zone temperature.

3.4 Effects of Different Microwave Catalysts/Absorbers on the Gas Distribution of Microwave Co-Pyrolysis

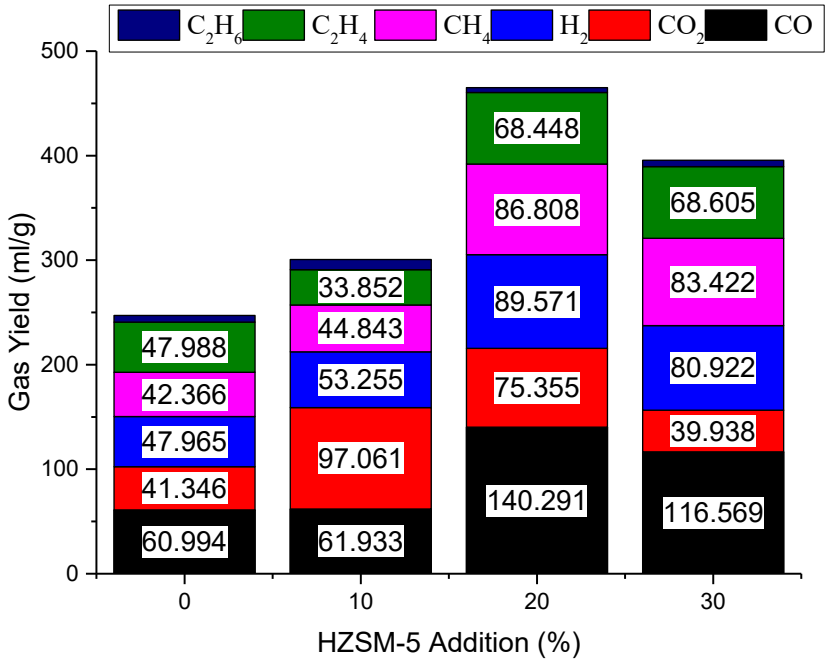


Fig. 6 Effect of HZSM-5 Addition on Gas yield of Tissue Paper and PE Co-Pyrolysis

As shown in Fig. 6, the addition of the molecular sieve HZSM-5 significantly enhances gas production during the microwave co-pyrolysis of paper and PE. The gas yield exhibits a trend of initially increasing and then decreasing with the amount of HZSM-5 added, reaching a peak at an addition ratio of 20%. Specifically, the total gas yield increased from 247 mL/g (without additive) to 465 mL/g. The yields of CO and CO_2 derived from the paper component also showed a marked increase. This phenomenon is attributed to two main mechanisms: First, HZSM-5 significantly advances the cracking temperature of PE, causing it to overlap with the pyrolysis temperature range of cellulose in the paper. This synchronization generates a large abundance of hydrogen radicals (H-), which promotes synergistic interactions between the paper and plastic phases and facilitates further cracking of the paper. The research results by Li et al. on the co-pyrolysis of pine sawdust (PS) and high-density polyethylene also indicate that

the introduction of HZSM-5 can significantly promoting the yield of pyrolysis gas and reducing the tar yield[43]. Consequently, the yields of oxygen-containing gases from the paper, such as CO and CO_2, increase substantially. Second, when the HZSM-5 addition ratio reaches 20–30%, the yields of H_2, CH_4, and C_2H_4 increase significantly. This is because the abundant long-chain hydrocarbon molecules produced from PE pyrolysis undergo deep catalytic cracking within the pores of the molecular sieve, directly breaking down into gaseous hydrocarbons ranging from C1 to C5. This process is the core reason for the surge in the yields of H_2, CH_4, C_2H_4, and C_2H_6 observed in the product gas.

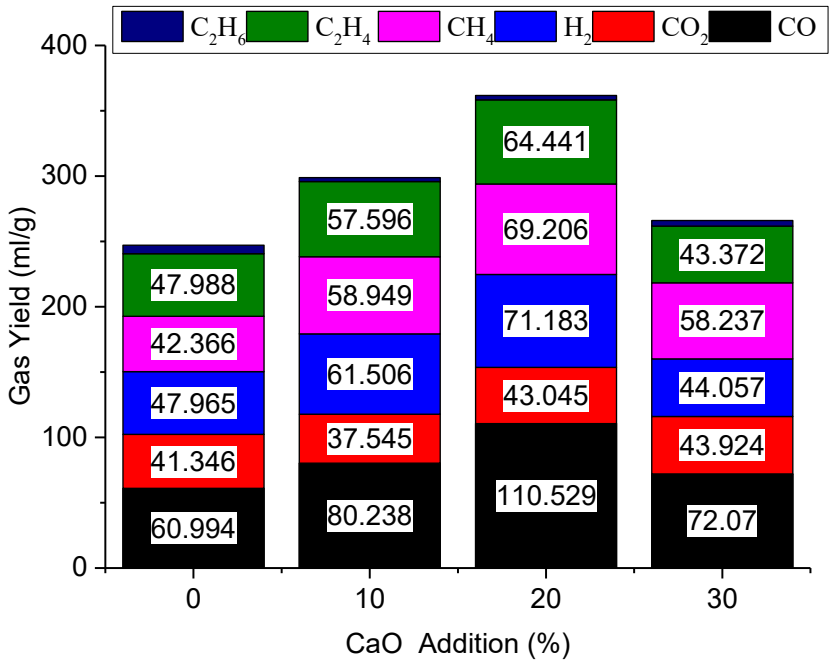


Fig. 7 Effect of CaO Addition on Gas yield of Tissue Paper and PE Co-Pyrolysis

As shown in Fig. 7, with increasing CaO loading, the pyrolytic gas yield follows a non-monotonic trend of initial enhancement followed by subsequent decline. Within the 10–

20% addition range, while CO_2 production remains relatively stable, the yields of CO, H_2, CH_4, and C_2H_4 are all markedly elevated; at 20% CaO loading, the total gas yield surges from 250 mL/g to a peak value of 350 mL/g. However, upon further increasing the CaO loading to 30%, both individual gas component yields and total gas production experience a pronounced decrease.

This trend is primarily governed by the dual functionality of CaO as both a CO_2 sorbent and a basic catalyst. The surface alkaline sites of CaO facilitate β-scission reactions and hydrogen transfer processes, effectively driving the directional cracking of heavy volatiles into light hydrocarbons (CH_4, C_2H_4) and H_2. This catalytic promotion significantly boosts the yields of combustible gases. Moreover, the enhanced cracking rate generates additional CO_2 as a byproduct, which compensates for the CO_2 captured by carbonation. Consequently, this dynamic balance allows for a substantial increase in total gas yield while keeping the net CO_2 emission relatively. Nevertheless, the decline gas yield observed at excessive CaO loadings (30%) is likely attributed to mass transfer limitations. An overabundance of CaO may increase diffusion resistance, hindering the release of volatiles and reducing the effective contact between the catalyst and reactants, which ultimately suppresses the overall gas evolution.

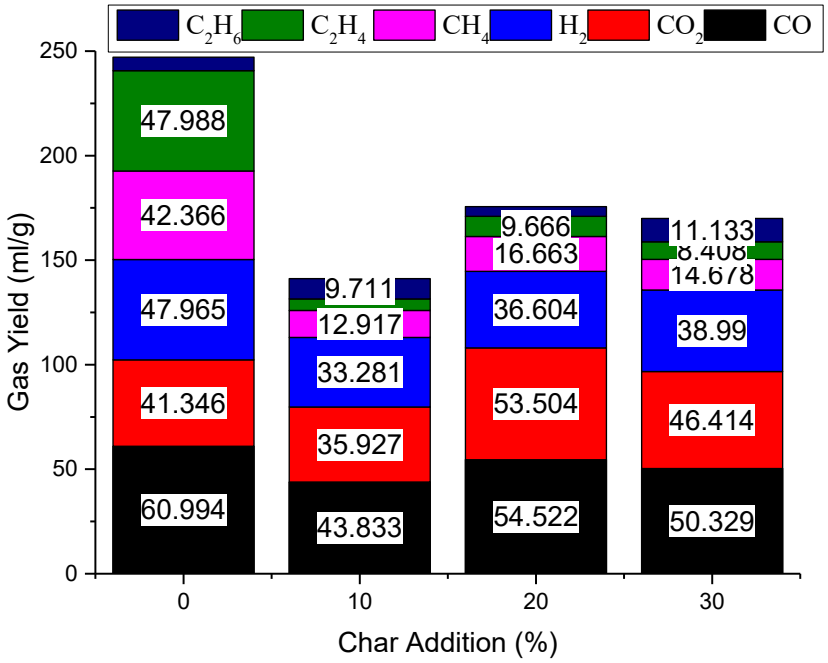


Fig. 8 Effect of Char Addition on Gas yield of Tissue Paper and PE Co-Pyrolysis

Fig.8 illustrates the influence of char addition (0–30 wt.%) on gas yield and composition during the co-pyrolysis of tissue paper and polyethylene (PE). Contrary to the promoting effects typically observed with HZSM-5 or CaO, the introduction of char resulted in a significant suppression of total gas production. The total gas volume decreased sharply from approximately 248 mL/g in the absence of char (0%) to roughly 140 mL/g at 10% char addition, before stabilizing at around 170 mL/g for higher dosages (20% and 30%). Among the individual gas species, ethylene and methane exhibited the most pronounced reductions, decreasing from 48 mL/g to below 10 mL/g and from 42.4 mL/g to below 16.7 mL/g, respectively, followed by hydrogen and carbon monoxide. This further corroborates that the decline in gas yield is primarily attributable to the diminished secondary cracking of primary pyrolysis products derived from PE. The reduction in the gas generation rate from PE secondary cracking, in turn,

alters the gas evolution pathway during tissue paper pyrolysis. The underlying reasons for the counterintuitive decrease in gas yield upon char addition have been discussed in Section 3.3 and are therefore not reiterated here. Moreover, among the char-amended groups, the 20% char loading exhibited the most favorable gas generation performance. In summary, while char facilitates rapid heating via microwave absorption, its catalytic inefficiency and the resulting short vapor residence time lead to reduced secondary gas-phase reactions, ultimately yielding less gas but potentially higher liquid fractions compared to uncatalyzed pyrolysis. The optimal balance for gas generation involving decarboxylation appears to be at 20% char loading, beyond which diminishing returns or competitive adsorption effects dominate.

3.5 Effect of different microwave catalysts/absorbers on the pyrolysis production distribution

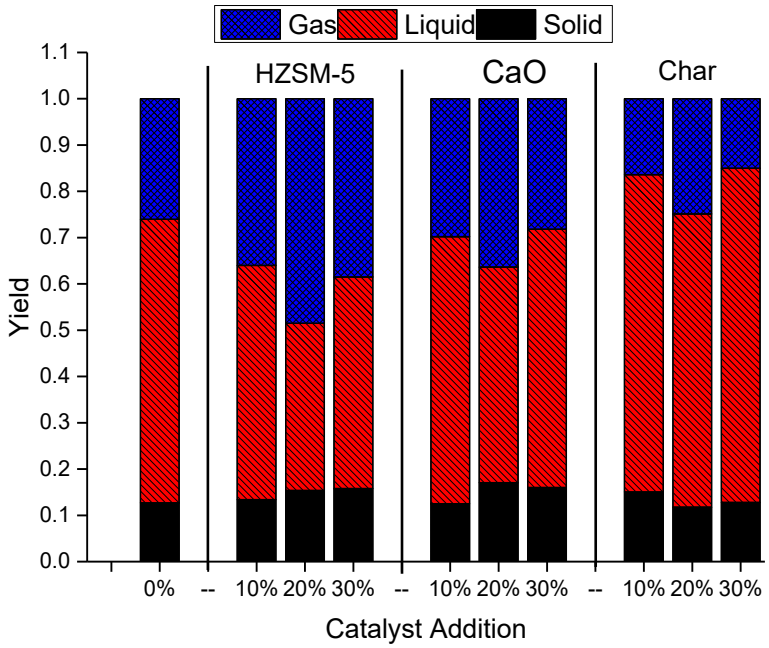


Fig.9 Effect of 3 different microwave catalysts/absorbers on the pyrolysis production distribution

Fig.9 shows that changing the amount of catalyst does not change the solid product

(char) much. However, it has a big effect on the gas and liquid products. HZSM-5 is the best at increasing the gas yield. This is because HZSM-5 easily breaks the C-C bonds in PE. This makes the reaction happen at a lower temperature and produces small gas molecules and hydrogen radicals. This also helps the tissue break down more, creating even more gas. CaO is the second best, and Char is the weakest. CaO catches acidic gases (like CO_2 and H_2S). This pushes the reaction to make more gas. Also, CaO helps break heavy tar into lighter gases.

Char mainly works by absorbing microwaves to heat the feedstock. Due to the loose structure of the pyrolysis char derived from tissue paper, it cannot maintain intimate contact with the feedstock, thereby hindering the effective transfer of absorbed microwave heat. Furthermore, combined with the rapid heating nature of microwave irradiation, the final pyrolysis products are predominantly liquid, with a relatively low gas yield.

For all 3 catalysts, 20% is the best amount to use. At this level, the gas yields are 48.51% for HZSM-5, 36.35% for CaO, and 24.87% for Char. If the amount is too low, there are not enough active sites for the reaction. If the amount is too high, the catalyst particles stick together and cause bad side reactions, which lowers the gas yield.

4 Conclusion

This study investigated the effects of 3 typical microwave absorbers/catalysts—HZSM-5, CaO, and Char—on the gas production characteristics during the co-pyrolysis of tissue paper and polyethylene (PE). The main conclusions are as follows:

1) HZSM-5 exhibited the most significant impact on gas production. While HZSM-5 had a negligible effect on microwave absorption heating, it primarily functioned through catalysis. It significantly lowered the pyrolysis temperature of PE, shifting it into the main pyrolysis range of the paper. This enhanced the synergistic interaction between the two materials, thereby improving both gas yield and quality.

2) CaO showed the second most significant effect. Acting as both a microwave absorber and a CO_2 sorbent, and facilitating tar gasification and reforming, CaO effectively enhanced gas yield and quality.

3) Char demonstrated the least promotion effect on gas production. Although char is an excellent microwave absorber capable of significantly increasing the pyrolysis temperature, its effect is limited. Derived from paper pyrolysis, char possesses a loose structure; therefore, achieving close contact with the primary pyrolysis products of PE to ensure effective heat transfer is the key factor determining its ability to promote gas production.

4) In summary, the 3 categories of additives exhibit distinct advantages and limitations in terms of catalytic activity, in-situ CO_2 capture, and microwave absorption efficiency. Future research should focus on developing multifunctional composite additive systems (e.g., metal oxide-modified zeolites or supported biochar). By constructing a synergistic "absorption-catalysis-adsorption" mechanism, it is expected to achieve the directional conversion and in-situ upgrading of pyrolysis volatiles while reducing microwave energy consumption, thereby maximizing both the yield and quality of syngas.

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Statements and Declarations

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Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

Xuebin Lin: Conceptualization, Methodology, Investigation, Writing - original draft, Supervision, Funding acquisition, Project administration. Jiangshan Qin: Methodology, Formal analysis, Investigation, Data curation, Writing - review & editing. Yuanbo Huang: Investigation, Resources, Writing - review & editing. Xiaodong Zhang:

Software, Validation, Investigation, Writing - review & editing. Hongzhou He: Investigation, Resources, Writing - review & editing. All authors read and approved the final manuscript.

Data Availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.