

Article

Effects of Na and Na/CO₂ Synergism on Gas/Tar Production During Rapid Coal Pyrolysis

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Abstract

Coal pyrolysis and gasification are among the key technologies for the clean and efficient utilization of coal. This work examined the individual and synergistic effects of Na and CO₂ on gas/tar generation during rapid coal pyrolysis using a fixed-bed reactor integrated with gas chromatography–mass spectrometry (GC-MS) and a flue gas analyzer. Key findings reveal that Na, CO₂, and Na/CO₂ synergism increased total gas volume by 671 vol.%, 772 vol.%, and 667 vol.%, respectively, while reducing tar yields by 4.14%, 3.12%, and 7.15%. Light oil yields reached 27.18%, 27.93%, and 40.35% under corresponding conditions. Crucially, Na significantly enhanced CO and CH₄ release (dose-dependent), with low-concentration Na (1–3%) promoting light-component condensation versus high-concentration Na (5%) facilitating heavy-component cracking. Na/CO₂ synergism intensified heavy-component fragmentation (efficacy increasing with Na loading), while low-concentration Na (1–3%) substantially boosted CO yield, highlighting its potential for selective syngas modulation. This work plays a pivotal role in advancing the low-emission, high-efficiency utilization of coal energy, aligning with global carbon reduction strategies.

Keywords: Na/CO₂ synergism; gas/tar production; coal tar homogeneous transformation

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1. Introduction

The clean and efficient utilization of coal is a crucial foundation for carbon reduction, while coal pyrolysis and gasification are among the key technologies for achieving this goal [1]. Zhundong coal has a high alkali metal content, which exerts a significant influence on the products of pyrolysis and gasification [2,3].

Alkali metals, alkaline earth metals (AAEMs), and some transition metals possess catalytic activity [4,5]. Yan et al. [6] conducted studies on pyrolysis catalyzed by alkali metals and alkaline earth metals. The results showed that AAEMs significantly affect tar yield and composition distribution, and exhibit excellent catalytic activity for the decomposition of phenols and condensed aromatic hydrocarbons into light aromatic hydrocarbons. He et al. [7] investigated the effect of alkali metals on the catalytic cracking performance of tar during the co-pyrolysis of coal and biomass. It was found that alkali metals promote the enrichment of ketones and phenols in tar components and effectively reduce the aromatic components in tar.

Alkali metal Na in coal is one of the key factors affecting the reactivity of char pyrolysis and gasification, as well as product distribution. Coal pyrolysis is categorized

by temperature (low < 500 °C: high tar, low energy; high > 800 °C: high syngas, high energy) and heating rate (slow: high char, simple; fast: high bio-oil, precise control). We chose high-temperature fast pyrolysis to activate Na catalysts and avoid secondary reactions. During high-temperature pyrolysis and gasification, coal particles can instantly release a large number of condensable organic molecules. Alkali metal Na is one of the key factors limiting the reactivity of coal pyrolysis and gasification, affecting the product distribution of coal tar and the secondary cracking of heavy components [8–13]. Meanwhile, existing studies have confirmed that the alkali metal Na, as a catalyst, has a significant impact on tar cracking, primarily manifested in its acceleration of the catalytic conversion of polycyclic aromatic compounds to lighter tar species, resulting in an increase in the proportion of monocyclic aromatic compounds in the tar [14]. During the formation of light aromatic hydrocarbons from coal through slow pyrolysis, Na catalysis can increase the active sites on the coal surface, promote the decomposition of macromolecular fragments into small molecular fragments, and simultaneously facilitate the dissociation of C-C bonds in oxygen-containing functional groups, thereby promoting the generation of light aromatic hydrocarbons [15]. In addition, Na also has a significant impact on the microcrystalline structure of semi-coke: it can improve the gasification reactivity of char and significantly increase the yield of combustible gases. Alkali metal Na plays a catalytic role in the formation and transformation of coal tar [16]. During coal gasification reactions, the formation and thermal transformation of tar is a multi-step reaction process, mainly including the volatilization of gaseous components and the homogeneous transformation of tar fragments (e.g., heterogeneous cracking reactions and addition reactions). However, there is still a lack of quantitative studies on the effect of alkali metal Na on the composition of coal pyrolysis gas and tar products.

CO₂ can promote the cracking of pyrolytic volatiles and undergo reforming reactions with them. Reforming not only improves tar quality but also reduces coke deposition generated by tar cracking, making the entire process cleaner and environmentally friendly. In a study on coal pyrolysis, Lee et al. [17] found that CO₂ reacts with volatile organic compounds (VOCs) to generate more CO. Moreover, the CO₂ atmosphere promotes the cracking of VOCs. Oh et al. [18] found that CO₂ can promote the cracking of VOCs, reduce the yield of pyrolysis tar, and increase the yield of syngas. Luo et al. [19] carried out pyrolysis of a low-quality coal in a fixed-bed reactor and found that compared with an N₂ atmosphere, a CO₂ atmosphere has little effect on char yield. However, due to the catalytic reforming reaction of CO₂, it promotes the cracking of tar and the generation of syngas. GC-MS analysis of tar showed that CO₂ can promote the formation of phenols and inhibit the cracking of methyl side chains on aromatic rings. Bai et al. [20] conducted pyrolysis experiments on Yining coal in a fixed-bed reactor. The results showed that compared with an Ar atmosphere, a CO₂ atmosphere is more conducive to the release of water vapor; when the pressure is lower than 0.5 MPa, a CO₂ atmosphere can promote the release of CH₄. Studies have found that during coal rapid pyrolysis, with the addition of catalysts, the composition and distribution of products under different atmospheres are significantly affected by catalysts, and there are significant differences in tar components and gas composition under different atmospheres [5]. However, existing research mostly focuses on the qualitative effects of Na or individual atmospheres, lacking clear insights into how Na loading and atmosphere types jointly regulate the transformation of tar light/heavy fractions and key gas yields. Moreover, the interactive mechanism between Na and CO₂ atmospheres in tar catalytic conversion remains insufficiently clarified, limiting the in-depth understanding of product regulation rules. Therefore, studies on the effects of Na and atmospheres on char products and tar catalytic transformation processes need to be

continuously supplemented and updated, which is helpful for an in-depth understanding of the homogeneous transformation characteristics of coal tar.

During CO₂ gasification, the abundant porous structure formed by Na etching promotes the diffusion of CO₂ molecules, making the carbon matrix more susceptible to CO₂ attack. This accelerates the reaction rate, leading to the release and transformation of more light gas molecules and tar fragment molecules [21]. Therefore, this study will conduct research on the effects of different Na concentrations on tar generation and transformation, as well as the generation characteristics of gaseous products under the individual action of Na and the synergistic action of Na-CO₂. Coal pyrolysis feedstocks were prepared by loading Na into coal via the impregnation method. The effects of alkali metal Na content, volatile-char interaction reactions, and CO₂ as a gasifying agent on the yield of coal rapid pyrolysis products and the transformation law of pyrolysis tar under a CO₂ atmosphere were thoroughly investigated. Through multiple evaluation mechanisms, including char and tar conversion rates, tar components, and gas components, the gas-liquid-solid yields, as well as the generation and homogeneous transformation characteristics of tar and gas after the synergistic action of Na and CO₂, were in-depth explored. Additionally, the generation and transformation mechanisms and pathways of tar under different conditions were studied, providing data support for the homogeneous transformation of coal tar during rapid pyrolysis.

2. Experimental Apparatus and Methods

2.1. Experimental Raw Materials and Sample Preparation

Zhundong coal (denoted ZD) was selected as the raw material for char preparation. The ZD coal was first demineralized via acid washing: magnetically stirred at 60 °C for 24 h in an HCl-HF solution to remove inherent ash. The resulting sample was filtered, washed, and dried at 60 °C for 12 h to obtain HZD coal (acid-washed Zhundong coal). Proximate and ultimate analyses of both coals were conducted in accordance with the Chinese National Standard GB/T212-2008 [22], with the results presented in Table 1. The proximate analysis of coal samples uses a standard coal proximate analyzer, the ultimate analysis uses a coal elemental analyzer, and the ash composition analysis uses an X-ray Fluorescence Spectrometer (XRF). The acid-washed HZD coal was subsequently loaded with alkali metal Na using an impregnation method. Sodium carbonate (Na₂CO₃) solutions with concentrations of 1 wt%, 3 wt%, and 5 wt% were prepared. The choice of Na loadings (1%, 3%, 5%) was based on prior catalytic studies, allowing systematic investigation of concentration-dependent catalytic effects on pyrolysis products. Coal samples were immersed in the respective solutions until complete evaporation occurred in an oven. The Na-loaded coal samples were then dried at 105 °C for 24 h and denoted as 1%Na-HZD, 3%Na-HZD, and 5%Na-HZD. Figure 1 illustrates the preparation procedure. Reagents included concentrated sulfuric acid (99%), hydrofluoric acid, and solid sodium carbonate. Ash composition analysis (Table 2) indicated high alkali and alkaline earth metal content in Zhundong coal ash: Na₂O (5.57%), MgO (10.44%), and CaO (32.29%), with relatively low SiO₂ (1.02%) and Al₂O₃ (3.00%).

Table 1. Proximate analysis and ultimate analysis of Zhundong coal and cotton stalk.

Sample	Industrial Analysis					Elemental Analysis			
	M _{ad}	A _{ad}	V _{ad}	FC _{ad}	C _{ad}	H _{ad}	O _{ad}	N _{ad}	S _{ad}
ZD	25.92	4.22	19.75	50.10	67.66	3.58	27.4	0.74	0.62
HZD	24.25	1.54	16.44	57.77	73.45	3.48	21.18	1.24	0.65

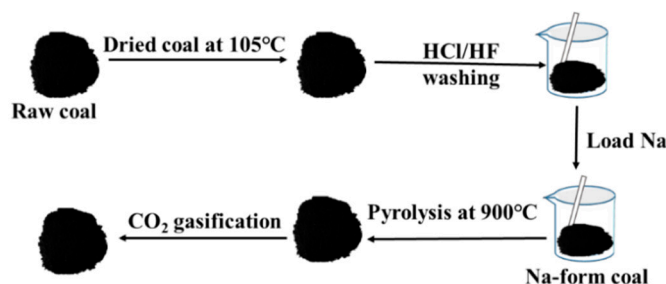


Figure 1. Sample preparation.

Table 2. Ash composition analysis of coal (wt.%).

Sample	Na ₂ O	K ₂ O	CaO	MgO	SiO ₂	SO ₃	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	TiO ₂
ZD	5.57	0.70	32.29	10.44	1.02	39.19	3.00	8.70	0.21	0.10

2.2. Preparation of Pyrolysis Tar and Online Analysis of Light Gases

Rapid pyrolysis experiments were performed using a horizontal tube furnace (Nanjing Boyuntong, Nanjing, China) coupled with a flue gas analyzer (Gaset, Fourier Transform Infrared Spectroscopy, FT-IR, Vantaa, Finland). The schematic diagram of a fixed-bed reactor system is shown in Figure 2. A sample boat containing 3.0 ± 0.1 g of coal was positioned at the reactor inlet. Nitrogen (N₂) was purged through the quartz reactor at 500 mL/min while heating from room temperature to 900 °C at 10 °C/min. Upon reaching 900 °C, the coal sample was rapidly introduced into the isothermal zone and held for 45 min. Post-reaction, the atmosphere was switched to N₂, and the reactor was removed to terminate the process. The reactor outlet was connected to the flue gas analyzer for quantitative determination of gas composition and yield. Tar was collected using absorbent cotton at the reactor outlet, combined with a cold trap; tar content was calculated by the weight difference in the cotton before and after adsorption. Char yield was determined by weighing the residual char. The collected tar was washed with a carbon disulfide (CS₂) solvent, filtered using calcium sulfate (CaSO₄), diluted to 10 mL in a volumetric flask, and then transferred to GC vials. GC-MS analysis was conducted on tar from all four coal samples. Char samples are denoted 0%NaC-N₂-1, 1%NaC-N₂-1, 3%NaC-N₂-1, and 5%NaC-N₂-1; tar samples are denoted 0%NaT-N₂, 1%NaT-N₂, 3%NaT-N₂, and 5%NaT-N₂.

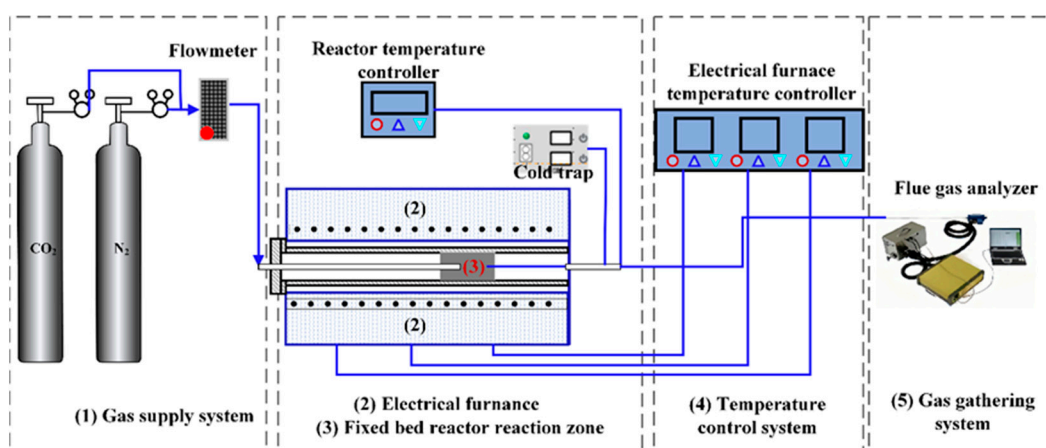


Figure 2. Schematic diagram of a fixed-bed reactor system.

2.3. Analysis of Homogeneous Conversion Characteristics of Pyrolysis Tar Under CO₂

Tar formation and homogeneous conversion under a CO₂ atmosphere at 900 °C were investigated using a fixed-bed reactor (TL1200-1200, Nanjing Boyuntong Instrument Tech-

nology Co. Ltd., Nanjing, China) The procedure followed Section 2.2, with the modification that upon reaching 900 °C, the atmosphere was switched to CO₂ (500 mL/min) and maintained for 45 min. Char samples are designated 0%NaC-CO₂-1, 1%NaC-CO₂-1, 3%NaC-CO₂-1, 5%NaC-CO₂-1; tar samples are designated 0%NaT-CO₂, 1%NaT-CO₂, 3%NaT-CO₂, 5%NaT-CO₂.

3. Results and Discussion

3.1. Influence of Alkali Metal Na on Pyrolysis Gas and Tar Generation Characteristics

3.1.1. Effect of Na on Pyrolysis Gas Products

The weight loss ratios of coal during rapid pyrolysis at 900 °C were determined by comparing mass changes before and after pyrolysis. Acid-washed coal (HZD) exhibited a weight loss ratio of 32.13%. Upon Na loading (1%, 3%, 5%), the ratios increased to 33.46%, 34.11%, and 35.57%, respectively. These results demonstrate that increasing Na content notably enhances coal weight loss. Within the coal macromolecular structure, Na acts as a cross-linking point, forming C-Na and C-O-Na bonds. The repetitive connection and disconnection of Na with the carbon matrix promote volatile release, thereby increasing char weight loss.

Gas release profiles during the pyrolysis of coals with varying Na content are shown in Figure 3, with the relative yields of light gas products presented in Figure 3a–d. Overall, the release trends for all samples were similar, exhibiting an initial increase followed by a decrease. Na content significantly influenced the profiles: higher Na loading correlated with increased gas evolution. Furthermore, Na addition promoted the premature release of H₂O, CO, CO₂, and CH₄, while extending the duration of gas release, consistent with the findings of Xiao et al. [23]. Increasing Na content also elevated the overall gas release curves, indicating higher maximum concentrations and total yields for H₂O, CO, CO₂, and CH₄. Notably, secondary release peaks for CO and H₂O emerged between 70 and 150 min, attributable to the presence of Na.

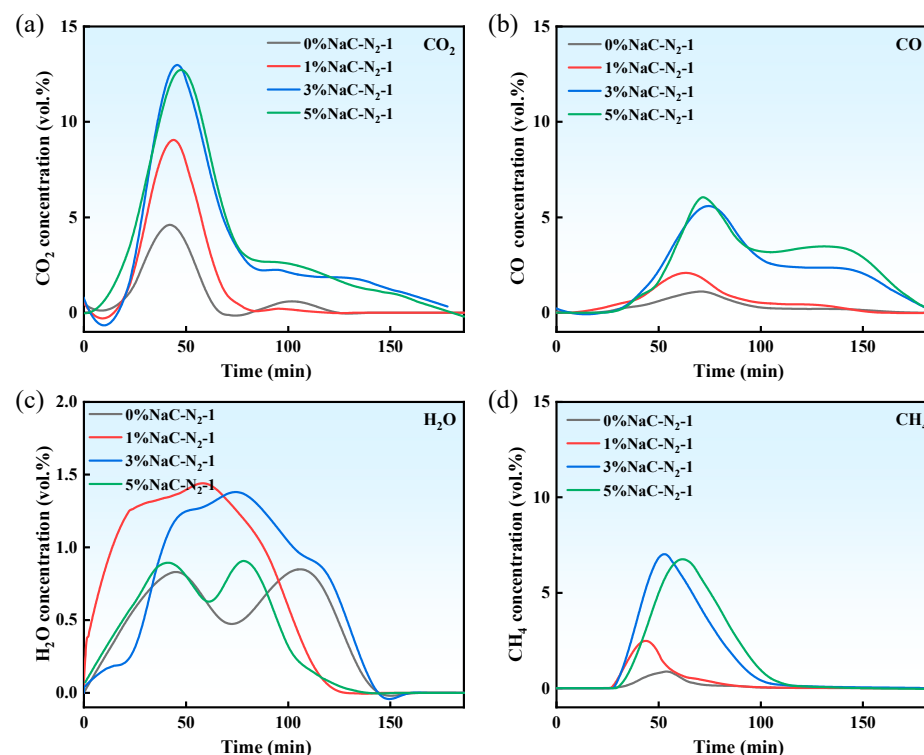


Figure 3. Gas release curve during pyrolysis: (a) CO₂; (b) CO; (c) H₂O; (d) CH₄.

For H₂O, yields increased significantly by approximately 40 vol.% at 1% and 3% Na, likely due to decarboxylation reactions where -OH from -COOH combines with adjacent H atoms. For CO₂, CO, and CH₄, a sharp yield increase occurred at 5% Na: approximately 49 vol.%, 382 vol.%, and 251 vol.%, respectively, indicating substantial promotion of their release. This is attributed to Na facilitating the cleavage of ether linkages and decomposition of oxygen-containing functional groups (e.g., carboxyl groups, oxygen heterocycles) at high temperatures, releasing CO₂. CH₄ primarily originates from the cleavage of -O-CH₃, -CH₃, and -CH₂- groups; Na likely promotes the cracking of alkyl side chains on aliphatic hydrocarbons, aromatic rings, and naphthenes, generating more CH₄. The increments for CO and CH₄ were markedly higher (approximately 8-fold and 3-fold, respectively) than those for CO₂ and H₂O, suggesting Na induces extensive decomposition of aliphatic structures and carboxyl groups in the char [24]. Concurrently, the significantly higher CO content compared to CO₂ may result from preferential adsorption of CO₂ within the system, reducing its concentration in the gas phase.

As shown in Figure 4, total gas production gradually increased with Na loading. Compared to 0%NaC, total gas volume increased by approximately 168%, 645%, and 613% for 1%NaC, 3%NaC, and 5%NaC, respectively. The maximum increase occurred at 3%NaC, demonstrating Na's significant role in enhancing gas yield. At 5% Na, the catalytic activity may diminish due to interactions between Na and coal minerals or radicals, which inhibit radical activation reactions with the carbon matrix and thereby reduce gas formation. These results indicate that moderate Na promotes gas release, while excessive Na may alter reaction pathways towards char or tar formation, suppressing gas generation.

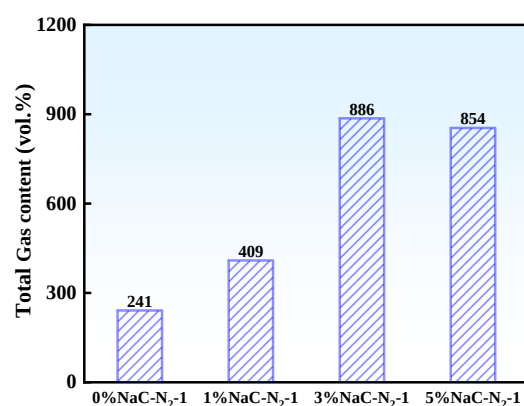


Figure 4. Total gas production during pyrolysis.

3.1.2. Effect of Na on Coal Tar Product Distribution

The formation of tar comes from the dissociation of weakly bonded structures in coal to form volatiles and subsequent volatile reactions [25,26]. To investigate the molecular weight (MW) distribution of pyrolysis tar, detailed analysis of component MW and relative content was performed (Figures S1 and S2). Pyrolysis tar components were concentrated within the 150–250 MW range for all samples (0%NaT, 1%NaT, 3%NaT, 5%NaT). Representative compounds in this range included phenolics, polycyclic aromatic hydrocarbons (PAHs), and oxygen-containing species. High-content components included fluorene, phenanthrene, 9-methylfluorene, 9-hydroxyfluorene, 1-methylphenanthrene, pyrene, and tetramethyldene. Notably, the relative content of these compounds was significantly higher in 1%NaT and 3%NaT compared to 0%NaT and 5%NaT.

Quantitative analysis of tar components at 900 °C (Table S1) revealed high relative contents (3%, often >10%) for phenol, m-cresol, cyclohexasiloxane, and phenanthrene. Increasing Na loading significantly reduced the relative content of m-cresol, 2-methylnaphthalene, 1,7-dimethylnaphthalene, 9-hydroxyfluorene, and 1,2-diphenylbenzene. Furthermore,

Na catalysis shifted the relative MW distribution of tar components towards lower values. GC-MS quantitation (from Table S1) showed: Phenol increased from 8.21% (0%NaT) to 18.57% (5%NaT, +126.2%); m-cresol dropped from 10.76% (0%NaT) to 6.83% (5%NaT, −36.5%); phenanthrene (PAH) rose by 11.8% at 3%NaT but fell by 2.1% at 5%NaT. The phenol/PAH ratio jumped from 1.09 (0%NaT) to 2.52 (5%NaT), confirming high Na boosts PAH-to-phenol conversion.

The relative content of light oil (fraction) and heavy oil is shown in Figure 5. Light oil content was 26.72% for 0%NaT, decreasing by 7.57% and 15.38% for 1%NaT and 3%NaT, respectively, while increasing by 0.46% for 5%NaT. Heavy oil exhibited the opposite trend. This indicates Na concentration significantly catalyzes the cracking and conversion processes of light and heavy tar fractions.

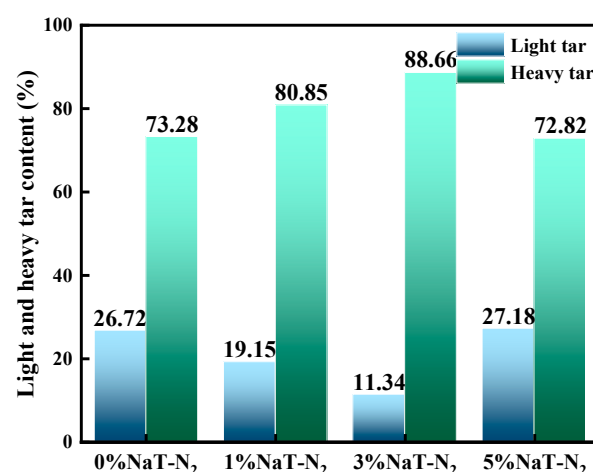


Figure 5. Distribution of light and light oil of tar products from coal pyrolysis.

At low Na concentrations (1%, 3%), Na acts as a catalyst, altering the direction and rate of free radical reactions. Radicals that might otherwise crack into light gases or small molecules instead tend to form larger molecular components with Na as a junction point. This suggests low-concentration Na promotes condensation reactions among light tar components. For instance, mono-aromatics and olefins recombine to form larger PAHs (heavy oil). Conversely, at high Na concentration (5%), light oil content increased significantly. Potential reasons include: (1) Abundant active sites from high Na concentration facilitate cracking of large tar molecules [27,28] (e.g., complex PAHs), breaking C-C and carbon-heteroatom bonds to form light components; (2) High Na alters the chemical equilibrium and reaction environment, suppressing polymerization [29]; (3) Na modifies tar surface tension and solubility, enhancing the separation of dissolved/associated light oil components. Thus, low Na promotes light-to-heavy oil conversion, while high Na favors heavy oil cracking.

Tar components were categorized as PAHs, phenolic compounds (P), cyclosiloxanes (D), oxygen-containing compounds (OOS), and nitrogen-containing compounds (ONS) (Figure 6). Non-ONS components constituted >95% of the tar. For 0%NaT-N₂, PAHs, phenolics, cyclosiloxanes, OOS, and ONS contents were 36.94%, 32.36%, 22.80%, 9.23%, and 0.00%, respectively. At low Na (1%, 3%), PAHs increased by 0.48% and 10.94%, while phenolics decreased by 10.40% and 12.64%. At high Na (5%), phenolics increased by 12.62% and PAHs by 7.19%. Cyclosiloxane content changed by +8.92%, −11.02%, and −16.26% for 1%NaT, 3%NaT, and 5%NaT relative to 0%NaT. OOS changed by −3.34%, +4.05%, and −4.25%; ONS changed by +3.01%, −1.42%, and −1.59%. This indicates low-concentration Na promotes PAHs and ONS formation while inhibiting phenolics, cyclosiloxanes, and OOS. High-concentration Na enhances phenolic formation.

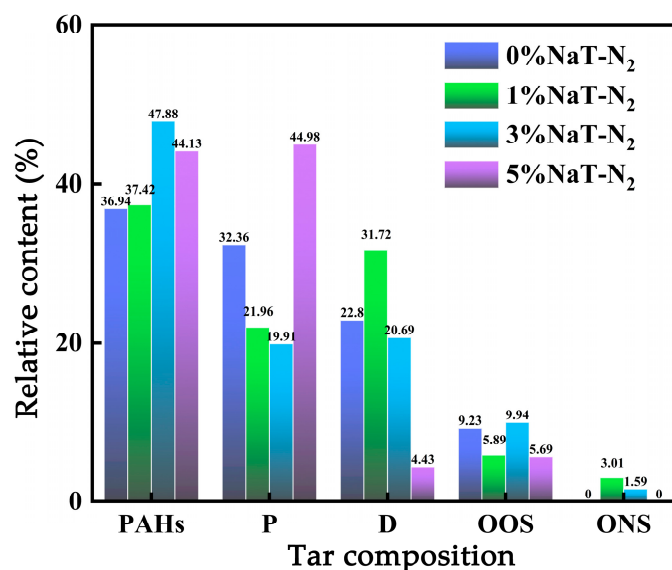


Figure 6. Distribution of tar components in coal pyrolysis.

These results demonstrate that Na significantly alters tar product distribution, exhibiting distinct reaction pathways and product selectivity depending on concentration [24,30]. Specifically, low Na may inhibit long-chain alkane and alkyl side-chain cracking while promoting polymerization of mono-aromatics, increasing PAHs. High Na's intense catalytic action accelerates the cleavage and rearrangement of oxygen-containing functional groups (e.g., hydroxyl, ether linkages), generating radical intermediates that recombine into stable phenolic compounds, significantly increasing their tar content.

3.2. Homogeneous Transformation Characteristics of Coal Tar Under Na/CO₂ Synergism

Pyrolysis tar undergoes a series of cracking and polymerization reactions under a CO₂ atmosphere [24]. To investigate the homogeneous transformation characteristics of tar during gasification, homogeneous conversion experiments of tar were conducted under a CO₂ atmosphere. Based on the tar analysis results in Section 3.1.2, which demonstrated the significant influence of Na concentration on tar yield and generation characteristics, this section explores the homogeneous transformation characteristics of tar under the synergistic effect of Na/CO₂.

3.2.1. Coal Tar Yields

The generation and transformation characteristics of coal tar under N₂ and CO₂ atmospheres are shown in Figure 7. Under an N₂ atmosphere, the collected tar yields from coals with different Na loadings showed significant differences due to primary cracking under high-temperature thermal action. The tar yield for 0%NaC was 17.18%, while yields for 1%NaC, 3%NaC, and 5%NaC decreased by 1.62%, 2.76%, and 4.14%, respectively. This indicates that alkali metal Na notably reduces tar yield, with higher Na content leading to lower yields.

Compared to the N₂ atmosphere, tar yields under the CO₂ atmosphere decreased by 3.12%, 2.72%, 2.41%, and 3.01% for the respective samples. As an active molecule, CO₂ reacts with tar fragments and other intermediates generated during coal pyrolysis, promoting further decomposition of tar precursors into small-molecule gases (e.g., CO, CH₄), thereby reducing tar yield [29]. Simultaneously, under the synergistic action of Na and CO₂, the tar yield for 0%NaC was 14.06%, while yields for 1%NaC, 3%NaC, and 5%NaC decreased significantly by 1.22%, 2.05%, and 4.03%, respectively. This demonstrates that the Na/CO₂ synergism further reduces tar yield.

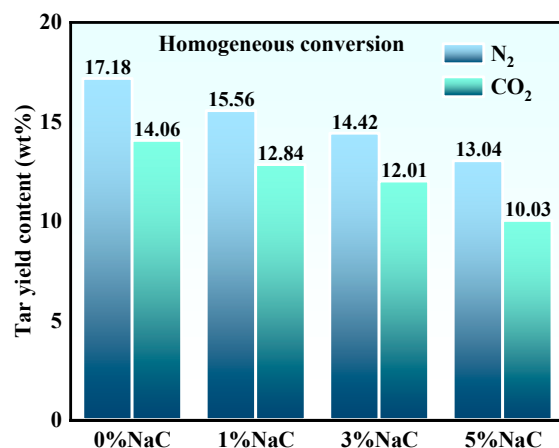


Figure 7. Coal tar yield in N₂ and CO₂ atmosphere.

3.2.2. Effect of Na/CO₂ Synergism on Gas Products

Gas release profiles during coal gasification are shown in Figure 8. The gasification of char under a CO₂ atmosphere primarily involves two steps: first, CO₂ diffuses and adsorbs onto the char matrix surface, reacting with carbon to generate active intermediates that decompose into gases; second, gas concentration increases initially and then decreases over time. The sequence of gas generation was CH₄, H₂O, and CO. As shown in Figure 7, Na catalyzed the char gasification reaction, increasing gas release.

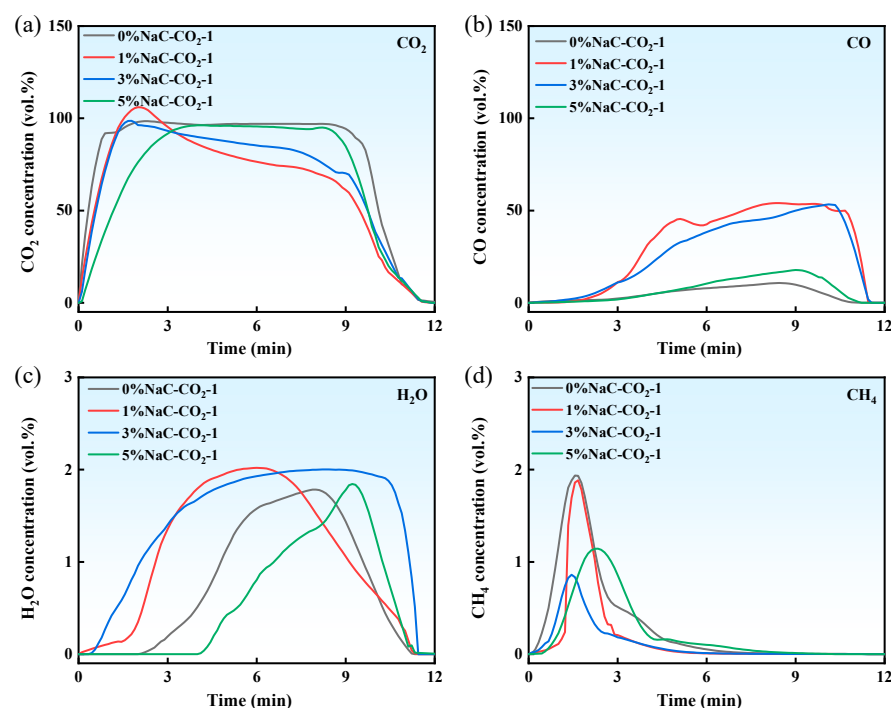


Figure 8. Gas release curve during CO₂ gasification: (a) CO₂; (b) CO; (c) H₂O; (d) CH₄.

Table 3 presents the conditions of this study and previous studies regarding tar yield and gas generation. Overall, this study exhibits more significant changes in tar yield and gas generation, and the synergistic effect of Na/CO₂ is more prominent in promoting gas release and inhibiting tar formation, which reflects the differences in the synergistic effect of Na/CO₂ under different experimental methods and conditions.

Under a stable CO₂ flow, the CO₂ concentration increased rapidly and then stabilized, indicating reaction equilibrium. However, after 9 min of gasification, the CO₂ concentration decreased significantly due to the ongoing reaction with char. During

gasification, the C=O bond in CO₂ breaks, reacting with the carbon matrix to form CO ($C + CO_2 \rightarrow 2CO$). Subsequent reactions include $CO + 3H_2 \rightarrow CH_4 + H_2O$ and $C + H_2 \rightarrow CH_4$. The CO concentration initially increased slowly, then gradually decreased. H₂O and CH₄ generation primarily stemmed from the decomposition and cleavage of hydroxyl (-OH), carboxyl (-COOH), and methoxy (-OCH₃) groups within the char, with their concentrations being low and showing an initial increase followed by a decrease. Notably, CH₄ release occurred predominantly within the first 3 min.

Table 3. The conditions of this study and previous studies regarding tar yield and gas generation.

Study	Tar Yield Reduction	Gas Composition (Key Gases)	Methodology/ Conditions	Main Findings and Notes
Current Study (Na/CO ₂ Synergism)	7.15% decrease	CO, CH ₄	Fixed-bed reactor, GC-MS	Na/CO ₂ synergism increased light oil yield and gas release.
Zhao et al. [31] (2025)	~10% decrease	CO, CH ₄	Fixed-bed reactor, NaNO ₃ with CO ₂	NaNO ₃ with CO ₂ improved light oil yield and promoted tar cracking.
Luo et al. [19] (2016)	Increased with pressure	CO ₂ , CH ₄	Fixed-bed reactor, CO ₂ atmosphere	CO ₂ increased the gas yield, and Na/CO ₂ decreased the tar yield.
Dong et al. [29] (2020)	Significant decrease	CO, CH ₄	Fixed-bed reactor, Na-loaded coal	Ion-exchange Na reduced tar and soot yield.

As shown in Figure S3, total CO₂ release decreased with increasing Na content, indicating Na promoted the CO₂ gasification reaction. After 3 min of reaction, Na catalysis intensified the reaction between CO₂ and the carbon matrix, leading to a significant decrease in CO₂ concentration and a gradual increase in CO concentration. Total CO gas volume increased with Na loading. Compared to 0%NaC, H₂O yield for 1%NaC and 3%NaC increased by 3.9% and 8.1%, respectively, while CH₄ yield decreased by 1.5% and 2.4%. This suggests the possible occurrence of the reaction: $2CO_2 + CH_4 \rightarrow 3CO + H_2O$, reducing CH₄ yield.

Analysis of total gas volume during gasification (Figure S4) showed that compared to 0%NaC-CO₂-1, total gas volume for 1%NaC-CO₂-1 and 3%NaC-CO₂-1 increased by 101 vol.% and 141 vol.%, respectively, while decreasing by 105 vol.% for 5%NaC-CO₂-1. The maximum gas increment occurred at 3%NaC, with CO constituting the highest proportion. CO formation is primarily linked to the decomposition of carboxyl groups, ether structures, oxygen heterocycles, quinones, and carbonates at high temperatures, indicating that Na promoted the decomposition of these functional groups. The decrease in total gas at 5% Na may result from partial catalyst deactivation and the formation of Na-carbon compounds that inhibit the decomposition of oxygen heterocycles and reactive groups, such as carboxyl, hydroxyl, and ether linkages.

3.2.3. Effect of Na/CO₂ Synergism on Homogeneous Transformation of Coal Tar

Section 3.1.2 demonstrated the influence of Na content on tar molecular weight (MW) distribution. To further investigate the homogeneous transformation law of coal tar under Na/CO₂ synergism, the average MW distribution of tar products was analyzed (Figures S5 and S6). Tar product MW was mainly distributed between 150 and 250. Compared to tar under an N₂ atmosphere, the content within this MW range decreased significantly by approximately 1%. Furthermore, under Na catalysis, the relative MW of tar components gradually shifted towards lower values, as large molecules decomposed into smaller ones, leading to a significant decrease in their proportion. In summary, during the homogeneous transformation of tar by CO₂, Na promoted the cracking of large molecular weight compounds to some extent, shifting the average MW distribution of homogeneous transformation products towards lower values.

Quantitative analysis of the relative content changes in different MW substances in tar (combined with Table 4) revealed that the products mainly included phenolic compounds, PAHs, and oxygen-containing compounds. High-content components included phenol (9.25 min), m-cresol (10.9 min), 2,5-dimethylphenol (12.4 min), 2-methylnaphthalene (14.3 min), biphenyl (15.4 min), acenaphthene (19.8 min), fluorene (18 min), dibenzofuran (17.2 min), 9-hydroxyfluorene (21.8 min), phenanthrene (20.3 min), 1-methylphenanthrene (21.5 min), pyrene (23.6 min), tetramethylindene (24.9 min), cyclohexasiloxane (14.19 min), and dodecamethylpentasiloxane (16.38 min), constituting over 50% of the total tar. After Na/CO₂ synergism, the content of light compounds like phenol and m-cresol exceeded 10% in some cases, indicating an increase in light components after CO₂ homogeneous transformation. Compared to 0%NaT-CO₂, the content of phenol, m-cresol, and 2,5-dimethylphenol in 5%NaT-CO₂ increased by 12.26%, 0.72%, and 0.56%, respectively, while acenaphthene, tetramethylindene, and 1,2-diphenylbenzene decreased by 2.19%, 2.12%, and 0.99%. This indicates that under Na/CO₂ synergism, the content of certain light phenolic compounds increased significantly during homogeneous transformation, while the content of some PAHs decreased. Expanded Table 4 data: Light phenolics (phenol + m-cresol + 2,5-dimethylphenol) rose by 58.7% (5%NaT-CO₂ vs. 0%NaT-CO₂); total PAHs fell by 28.4%. Na/CO₂ caused 2.1–3.5 time higher phenolic increments than Na alone, and 1.8–2.4 time greater PAH reductions than CO₂ alone. Cyclosiloxanes were 1.5–2.3 times higher than Na alone.

Table 4. GC/MS tar analysis results of different coal samples reacting in a CO₂ atmosphere (>5%).

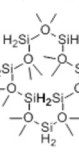
No.	RT (min)	M.W.	Composition Structure	0%NaT-CO ₂	1%NaT-CO ₂	3%NaT-CO ₂	5%NaT-CO ₂
1	9.25	94		12.19	16.04	18.61	24.45
2	10.87	108		12.76	11.23	11.57	13.48
3	19.80	152		6.43	2.39	1.74	2.18
4	18.04	166		6.42	6.75	7.58	8.10
5	17.23	168		6.54	7.22	7.05	6.68
6	20.29	178		5.74	6.90	7.88	6.95
7	23.99	266		6.43	0.00	0.00	3.41
8	16.38	384		0.00	9.67	8.30	11.54
9	14.19	444		3.77	5.80	4.72	7.82
10	16.38	518		0.00	9.67	8.30	0.00

Figure 9 shows the significant influence of Na/CO₂ homogeneous transformation on the light/heavy oil distribution of coal tar. Light oil yield was 20.75% for 0%NaT-CO₂, increasing by 1.48%, 4.56%, and 12.42% for 1%NaT-CO₂, 3%NaT-CO₂, and 5%NaT-CO₂,

respectively. The light oil proportion increased by up to approximately 0.44 times with Na loading, indicating Na/CO₂ synergism promoted the cracking of heavy components, increasing light oil content.

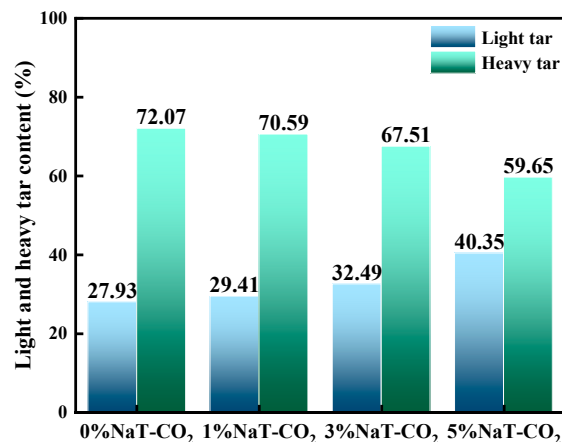


Figure 9. Distribution of light and heavy oil of coal tar products under a CO₂ atmosphere.

Compared to 0%NaT-N₂, light oil yield for 0%NaT-CO₂ increased only by 1.21%, suggesting CO₂ has a minor effect on light/heavy tar composition during homogeneous transformation. However, under Na/CO₂ synergism, light oil yield increased by 10.27%, 21.15%, and 13.16% for 1%NaT-CO₂, 3%NaT-CO₂, and 5%NaT-CO₂, respectively, compared to 0%NaT-N₂. Similarly, for used tire pyrolysis liquids, formaldehyde polycondensation (HCl-catalyzed) + NMP extraction reduced harmful components in its ≤200 °C fraction, enabling use as high-quality gasoline components or mastic plasticizers [32]. This further validates targeted pyrolysis liquid regulation as a reliable way to improve industrial value. This indicates that the synergistic action of Na and CO₂ intensified the cracking of heavy oil in tar, increasing small-molecule compound content and thereby enhancing light oil yield. Potential reasons are: (1) Na and CO₂ provide more active sites for tar cracking, breaking C-C and carbon-heteroatom bonds in large molecules like complex PAHs to generate small molecules; (2) As a catalyst, Na may alter the chemical equilibrium and reaction direction within the tar system, suppressing polymerization; (3) Na significantly changes tar surface tension and solubility, facilitating the separation of dissolved/associated light oil components. Therefore, the relative light oil content followed the order: Na/CO₂ > CO₂ > Na. The change in relative light/heavy oil content demonstrates the strong synergistic effect of Na/CO₂ during coal tar homogeneous transformation.

Notably, the 40.35% light oil yield under Na/CO₂ synergism provides a viable technical route for large-scale coal-to-liquid (CTL) processes, as light oil can be directly upgraded to high-value transportation fuels or aromatic chemical feedstocks. Meanwhile, enhanced CO production (especially at 3% Na loading) enables precise regulation of syngas H₂/CO ratios—a critical parameter for optimizing Fischer–Tropsch synthesis efficiency. Furthermore, CO₂ incorporation in this system aligns with carbon circular economy goals for coal conversion, realizing CO₂ valorization while reducing emissions.

3.2.4. Homogeneous Transformation Mechanism of Coal Tar Under Na/CO₂ Synergism

Quantitative analysis of coal tar composition under a CO₂ atmosphere (Figure 10) revealed high contents of PAHs and phenolic compounds, exceeding 60%. For 0%NaT-CO₂, PAHs, phenolics, cyclosiloxanes, oxygen-containing compounds (OOS), and nitrogen-containing compounds (ONS), the contents were 43.65%, 41.66%, 4.65%, 9.23%, and 0.8%, respectively. With increasing Na loading (1%, 3%, and 5%), PAHs decreased by 7.34%, 7.25%, and 11.26%, respectively, indicating that Na/CO₂ synergism promoted PAH de-

composition. This is attributed to the following points: (1) under CO₂, Na may facilitate C-C bond cleavage and ring-opening reactions in coal tar, generating free radicals that attack PAH structures; (2) as a catalyst, Na promotes the reaction between CO₂ and H₂, generating more H₂, which catalyzes the hydrogenation of PAHs, converting them stepwise into mono-aromatics or aliphatics.

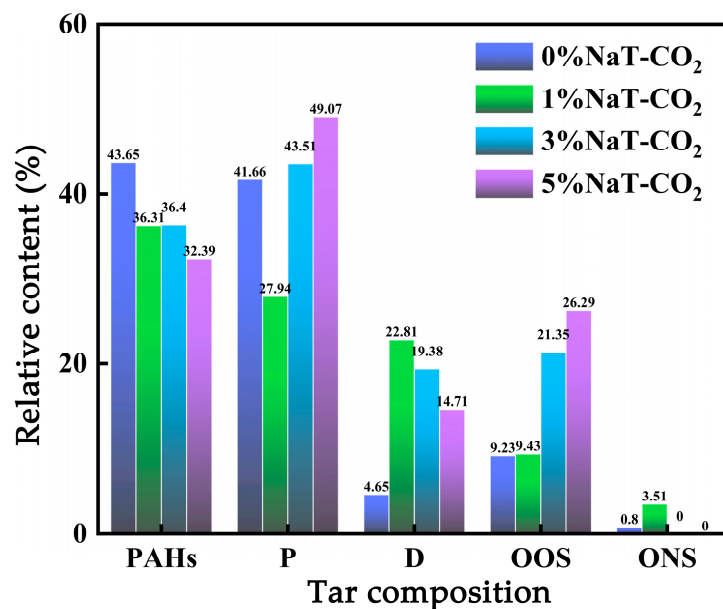


Figure 10. Distribution of coal tar components under a CO₂ atmosphere.

Compared to 0%NaT, phenolics decreased by 13.72% for 1%NaT but increased by 1.85% and 7.41% for 3%NaT and 5%NaT, respectively. At low Na, phenolics likely undergo addition or condensation reactions with other small molecules formed during gasification, converting into more complex non-phenolic compounds. At higher Na, abundant active sites facilitate reactions between CO₂ and C/H/O elements in coal, forming intermediates that convert to phenolics. Na may also enhance the activation capability of aromatic rings, making them more susceptible to oxidative hydroxylation by CO₂, increasing phenolic content [33]. GC-MS MW data: Low-MW (<200 Da) components rose from 38.2% (0%NaT-CO₂) to 61.8% (5%NaT-CO₂); high-MW (>250 Da) fell to 11.2%. The low/high-MW ratio (L/H) increased by 48.9% (Na/CO₂) vs. 29.5% (Na alone), proving synergistic tar “lightening”.

Cyclosiloxane content increased by 18.16%, 14.73%, and 10.06% for 1%NaT, 3%NaT, and 5%NaT, respectively, suggesting Na catalysis promotes the formation of siloxane intermediates from Si and CO₂, which polymerize into cyclosiloxane structures. OOS content increased by 0.2%, 12.12%, and 17.06%, indicating Na activates C-C and C-H bonds in coal tar, enabling CO₂ to react and introduce oxygen atoms, forming various OOS.

In summary, during homogeneous transformation, Na/CO₂ synergism increases phenolic compounds, cyclosiloxanes, and OOS content while decreasing PAHs.

Figure 11 present the effect mechanism of Na/CO₂ synergism on the homogeneous transformation characteristics of coal tar. Under Na/CO₂ synergism, tar composition and content changed markedly, demonstrating that Na promotes homogeneous transformation. Na’s influence primarily manifests in promoting aromatic ring cracking reactions and the release of free radicals [34]. Based on free radical theory, Na catalyzes the generation of abundant active radicals (O·/OH·/H·) at high temperatures, which react with other substances to form different tar products. CO₂ acts as a mild oxidant (CO₂ + e → CO + O· + e), reacting with Na-activated aromatic rings to introduce hydroxyl groups, forming phenolics [35]. Furthermore, increasing Na content severely disrupts aromatic ring structures. Active

oxygen repeatedly attacks aromatic rings, while active molecules react with hydrocarbons, promoting volatile gas release and inhibiting aromatic polymerization [36].

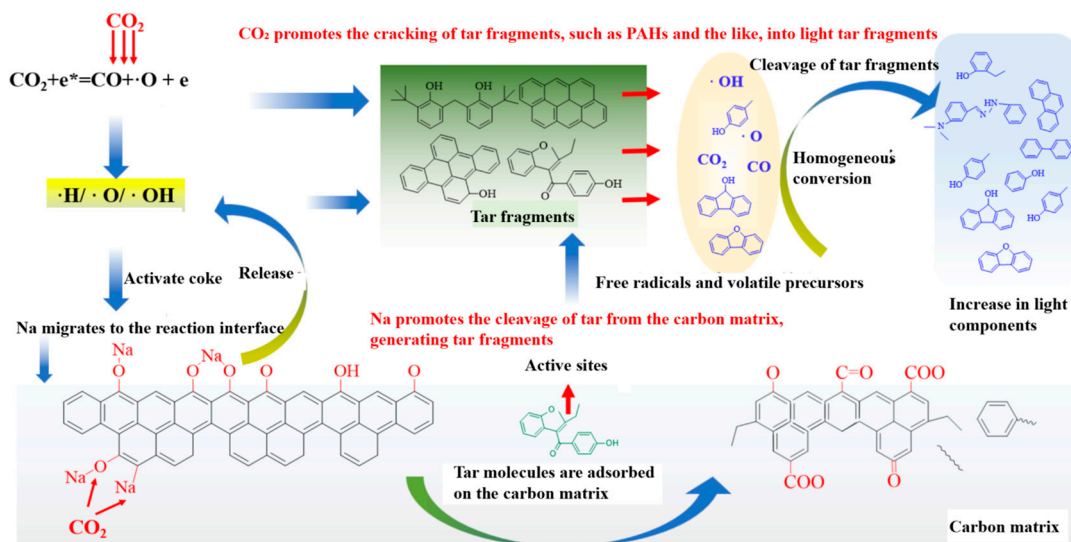


Figure 11. The effect mechanism of Na/CO₂ synergism on the homogeneous transformation characteristics of coal tar.

In conclusion, under Na/CO₂ synergism, the oxidative cracking process of tar is promoted, while aromatic polymerization is inhibited. Na increases the quantity of tar fragments during coal tar pyrolysis, while CO₂, as an activator, enhances the reaction probability between tar fragments and active radicals. This promotes the gradual conversion of light tar components into stable small-molecule compounds, achieving homogeneous transformation of tar.

4. Conclusions

This work employed GC-MS coupled with flue gas analysis to investigate the influence of Na alone and Na/CO₂ synergism on the generation and transformation characteristics of tar and gaseous products during coal pyrolysis at high temperatures. The homogeneous transformation mechanism of coal tar under Na/CO₂ synergism was revealed. The main conclusions are as follows:

- (1) Na prolonged the gas release duration and increased the yields of H_2O , CO , CO_2 , and CH_4 . At 5% Na loading, gas production increased sharply: CO_2 , CO , and CH_4 yields increased by approximately 49 vol.%, 382 vol.%, and 251 vol.%, respectively. The increments for CO and CH_4 were about 8 times and 3 times greater than those for CO_2 and H_2O .
- (2) The effect of Na on coal tar was closely dependent on its concentration. At low concentrations (1%, 3%), Na acted as a catalyst and interacted with cross-linking points during pyrolysis, promoting condensation reactions among light components. Conversely, at high concentration (5%), Na provided abundant active sites for tar cracking reactions. This facilitated the cleavage of large molecules in heavy oil (e.g., complex polycyclic aromatic hydrocarbons), decomposing them into more radical fragments and increasing light oil content. Furthermore, increasing Na content elevated the proportion of polycyclic aromatic hydrocarbons (PAHs) and phenolic compounds while reducing the proportions of cyclosiloxanes, oxygen-containing compounds, and nitrogen-containing compounds.
- (3) Light oil yields under the action of Na alone, CO_2 alone, and Na/ CO_2 synergism were 27.18%, 27.93%, and 40.35%, respectively. This demonstrates the pronounced

synergistic effect of Na/CO₂ during tar homogeneous transformation. Na/CO₂ synergism promoted tar cracking into radical fragments. Active radicals reacted with C-C bonds in aromatic rings, converting them into light tar molecules, thereby achieving homogeneous transformation of coal pyrolysis tar by CO₂. It increased the content of phenolic compounds, cyclosiloxanes, and oxygen-containing compounds, while decreasing the content of PAHs.

- (4) The Na/CO₂ synergism provides a scalable technical route for clean coal valorization—40.35% light oil yield supports coal-to-liquid process upgrading, and enhanced CO production enables precise syngas H₂/CO ratio tuning for Fischer–Tropsch synthesis, aligning with carbon neutrality via CO₂ reuse. In the future, focus on molecular simulations and quantum chemical calculations, which are still required to investigate the formation mechanism of multi-active-site coke and the influence mechanism of the Na/CO₂ coupling on the homogeneous conversion of coal tar at the molecular structural level.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app152111331/s1>.

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Conflicts of Interest: Author Feng Wang was employed by the Xinjiang Xinye State-Owned Property Management (Group) Co., Ltd. The remaining authors declare that the re-search was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Wu, X.; Liu, Z.; Fan, W.; Zhou, C.; Liu, S.; Chen, J.; Guo, H. Effect of metal elements in coal ash on NO release characteristics during oxy-fuel combustion at high temperature. *J. Energy Inst.* **2021**, *94*, 107–119. [\[CrossRef\]](#)
2. Zhang, Z.; Zhou, H.; Wang, X.; Zhang, L.; Rao, P.; Zhu, H. Influence Mechanism of Water-Soluble Sodium on Zhundong Coal Pyrolysis. *ACS Omega* **2022**, *7*, 11862–11870. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Liang, D.; Xie, Q.; Wei, Z.; Wan, C.; Li, G.; Cao, J. Transformation of alkali and alkaline earth metals in Zhundong coal during pyrolysis in an entrained flow bed reactor. *J. Anal. Appl. Pyrolysis* **2019**, *142*, 104661. [\[CrossRef\]](#)
4. Yuan, Y.; Li, S.; Yao, Q. Dynamic behavior of sodium release from pulverized coal combustion by phase-selective laser-induced breakdown spectroscopy. *Proc. Combust. Inst.* **2015**, *35*, 2339–2346. [\[CrossRef\]](#)
5. Liu, N.; Huang, H.; Feng, J.; Li, R.; Huang, X.; Wu, Y. Effects of alkali and alkaline earth metals in biomass on co-pyrolysis characteristics and product distribution of coal and biomass. *Fuel* **2025**, *389*, 134551. [\[CrossRef\]](#)
6. Yan, L.-J.; Bai, Y.-H.; Kong, X.-J.; Li, F. Effects of alkali and alkaline earth metals on the formation of light aromatic hydrocarbons during coal pyrolysis. *J. Anal. Appl. Pyrolysis* **2016**, *122*, 169–174. [\[CrossRef\]](#)

7. He, Y.; Wang, J.F.; Zhang, Y.J.; Song, X.D.; Su, W.G.; Bai, Y.H.; Lü, P.; Yu, G.S. Influence of Structural Properties of Al₂O₃ on Alkali Metal Adsorption and Catalytic Tar Cracking Performance during High-Temperature Co-Pyrolysis of Coal and Biomass. *Coal Convers.* **2025**, *48*, 70–79. [\[CrossRef\]](#)
8. Kong, L.; Bai, J.; Li, W. Viscosity-temperature property of coal ash slag at the condition of entrained flow gasification: A review. *Fuel Process. Technol.* **2021**, *215*, 106751. [\[CrossRef\]](#)
9. He, Q.; Xu, J.; Jiang, X.; Wang, C.; Jiang, M.; Wei, Y.; Jiang, L.; Xu, K.; Wang, Y.; Su, S.; et al. Effects of AAEMs on the char heterogeneous structure evolution during Zhundong coal pyrolysis: Insights from micro-Raman spectroscopy. *Fuel* **2023**, *347*, 128378. [\[CrossRef\]](#)
10. Yang, Y.; Lin, X.; Chen, X.; Guo, W.; Wang, Y.; Zhang, J.; Kawa, O. Investigation on the effects of different forms of sodium, chlorine and sulphur and various pretreatment methods on the deposition characteristics of Na species during pyrolysis of a Na-rich coal. *Fuel* **2018**, *234*, 872–885. [\[CrossRef\]](#)
11. Lu, R.; Wang, J.; Liu, Q.; Wang, Y.; Te, G.; Ban, Y.; Li, N.; Zhang, X.; He, R.; Zhou, H.; et al. Catalytic effect of sodium components on the microstructure and steam gasification of demineralized Shengli lignite char. *Int. J. Hydrogen Energy* **2017**, *42*, 9679–9687. [\[CrossRef\]](#)
12. Zhao, Y.; Xing, C.; Shao, C.; Chen, G.; Sun, S.; Chen, G.; Zhang, L.; Pei, J.; Qiu, P.; Guo, S. Impacts of intrinsic alkali and alkaline earth metals on chemical structure of low-rank coal char: Semi-quantitative results based on FT-IR structure parameters. *Fuel* **2020**, *278*, 118229. [\[CrossRef\]](#)
13. Qiu, P.; Du, C.; Liu, L.; Chen, L. Hydrogen and syngas production from catalytic steam gasification of char derived from ion-exchangeable Na- and Ca-loaded coal. *Int. J. Hydrogen Energy* **2018**, *43*, 12034–12048. [\[CrossRef\]](#)
14. Liu, S.; Tuo, K.; Wang, L.; Chen, G.; Ma, W.; Fang, M. Microwave-assisted metal-catalyzed pyrolysis of low-rank coal: Promising option towards obtaining high-quality products. *J. Energy Inst.* **2020**, *93*, 1602–1614. [\[CrossRef\]](#)
15. Li, Y.N. Study on Na/Ca-Catalyzed Coal Pyrolysis Characteristics and Tar Product Regulation. Master's Thesis, Shenyang Aerospace University, Shenyang, China, 2022. [\[CrossRef\]](#)
16. Wang, P.; Jin, L.; Liu, J.; Zhu, S.; Hu, H. Analysis of coal tar derived from pyrolysis at different atmospheres. *Fuel* **2013**, *104*, 14–21. [\[CrossRef\]](#)
17. Lee, S.-R.; Lee, J.; Lee, T.; Tsang, Y.F.; Jeong, K.-H.; Oh, J.-I.; Kwon, E.E. Strategic use of CO₂ for co-pyrolysis of swine manure and coal for energy recovery and waste disposal. *J. CO₂ Util.* **2017**, *22*, 110–116. [\[CrossRef\]](#)
18. Oh, J.-I.; Lee, J.; Lee, T.; Ok, Y.S.; Lee, S.-R.; Kwon, E.E. Strategic CO₂ utilization for shifting carbon distribution from pyrolytic oil to syngas in pyrolysis of food waste. *J. CO₂ Util.* **2017**, *20*, 150–155. [\[CrossRef\]](#)
19. Luo, K.; Zhang, C.; Zhu, S.; Bai, Y.; Li, F. Tar formation during coal pyrolysis under N₂ and CO₂ atmospheres at elevated pressures. *J. Anal. Appl. Pyrolysis* **2016**, *118*, 130–135. [\[CrossRef\]](#)
20. Bai, Y.; Wang, P.; Yan, L.; Liu, C.; Li, F.; Xie, K. Effects of CO₂ on gas evolution and char structure formation during lump coal pyrolysis at elevated pressures. *J. Anal. Appl. Pyrolysis* **2013**, *104*, 202–209. [\[CrossRef\]](#)
21. Sun, M.; Zhang, D.; Yao, Q.; Liu, Y.; Su, X.; Jia, C.Q.; Hao, Q.; Ma, X. Separation and Composition Analysis of GC/MS Analyzable and Unanalyzable Parts from Coal Tar. *Energy Fuels* **2018**, *32*, 7404–7411. [\[CrossRef\]](#)
22. GB/T212-2008; Proximate Analysis of Coal. China Standards Press: Beijing, China, 2008.
23. Xiao, N.; Luo, H.; Wei, W.; Tang, Z.; Hu, B.; Kong, L.; Sun, Y. Microwave-assisted gasification of rice straw pyrolytic biochar promoted by alkali and alkaline earth metals. *J. Anal. Appl. Pyrolysis* **2015**, *112*, 173–179. [\[CrossRef\]](#)
24. Liu, M.; Li, X.; Wang, X.; Bai, J.; Kong, L.; Bai, Z.; Li, J.; Li, H.; Xing, L.; Li, W. Insights into the effect of particle size on coal char particle gasification by thermogravimetric analyzer and high temperature stage microscope. *Fuel* **2022**, *313*, 123010. [\[CrossRef\]](#)
25. Dong, L.; Han, S.; Yu, W.; Lei, Z.; Kang, S.; Zhang, K.; Yan, J.; Li, Z.; Shui, H.; Wang, Z.; et al. Effect of volatile reactions on the yield and quality of tar from pyrolysis of Shenhua bituminous coal. *J. Anal. Appl. Pyrolysis* **2019**, *140*, 321–330. [\[CrossRef\]](#)
26. Xu, K.; Hu, S.; Wang, Y.; Zhang, L.; Su, S.; Jiang, L.; Xu, J.; Ouyang, Z.; Xiang, J. Relation between char structures and formation of volatiles during the pyrolysis of Shenhua coal: Further understanding on the effects of mobile phase and fixed phase. *Fuel Process. Technol.* **2018**, *178*, 379–385. [\[CrossRef\]](#)
27. Wu, D.; Dong, H.; Luan, J.; Du, Q.; Gao, J.; Feng, D.; Zhang, Y.; Zhao, Z.; Li, D. Reaction Molecular Dynamics Study on the Mechanism of Alkali Metal Sodium at the Initial Stage of Naphthalene Pyrolysis Evolution. *Energies* **2023**, *16*, 6186. [\[CrossRef\]](#)
28. Li, R.; Chen, Q.; Zhang, H. Detailed Investigation on Sodium (Na) Species Release and Transformation Mechanism during Pyrolysis and Char Gasification of High-Na Zhundong Coal. *Energy Fuels* **2017**, *31*, 5902–5912. [\[CrossRef\]](#)
29. Dong, H.; Zhang, Y.; Du, Q.; Li, D.; Feng, D.; Gao, J.; Wu, S.; Luan, J. Roles of Ion-Exchangeable Sodium in the Conversion Process of Tar to Soot during Rapid Pyrolysis of Two Brown Coals in a Drop-Tube Reactor. *ACS Omega* **2020**, *5*, 9078–9092. [\[CrossRef\]](#)
30. Lu, Q.; Guo, R.; Zhang, H.; Wang, J.-P.; Lu, T.; Li, G.-Y.; Liang, Y.-H. To stimulate, and to inhibit: A theoretical understanding of the sodium-catalytic mechanism of coke gasification. *Chem. Eng. J.* **2022**, *435*, 135091. [\[CrossRef\]](#)
31. Zhao, Z.; Jin, J.; Du, Q.; Li, D.; Gao, J.; Dong, H.; Zhang, Y.; Wu, D.; Yang, X. The synergistic influence mechanism of the alkali metal sodium and CO₂ on coal rapid pyrolysis soot: Experiments and DFT calculations. *Fuel* **2025**, *382*, 133294. [\[CrossRef\]](#)

32. Pyshyev, S.; Korchak, B.; Miroshnichenko, D.; Lebedev, V.; Yasinska, A.; Lypko, Y. Obtaining New Materials from Liquid Pyrolysis Products of Used Tires for Waste Valorization. *Sustainability* **2025**, *17*, 3919. [[CrossRef](#)]
33. Seiji, S.; Katsutoshi, I. Effect of Coal Interaction on Coke Strength. *Tetsu Hagane-J. Iron Steel Inst. Jpn.* **2001**, *87*, 238–244.
34. Zhao, Z.; Gao, J.; Du, Q.; Li, D.; Dong, H.; Zhang, Y.; Li, H. Effect of Na on the condensation reaction of naphthalene molecules during coal pyrolysis. *J. Energy Inst.* **2021**, *98*, 313–321. [[CrossRef](#)]
35. Xu, M.; Wang, R.; Fu, H.; Shi, Y.; Ling, L. Harmonizing the cyano-group and Na to enhance selective photocatalytic O₂ activation on carbon nitride for refractory pollutant degradation. *Proc. Natl. Acad. Sci. USA* **2024**, *121*, e2318787121.
36. Yao, R.; Wei, J.; Ge, Q.; Xu, J.; Han, Y.; Ma, Q.; Xu, H.; Sun, J. Monometallic iron catalysts with synergistic Na and S for higher alcohols synthesis via CO₂ hydrogenation. *Appl. Catal. B* **2021**, *298*, 120556. [[CrossRef](#)]

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