

Effect of mixing modes on integrated process of co-pyrolysis of coal and biomass with CO₂ reforming of methane to improve tar yield

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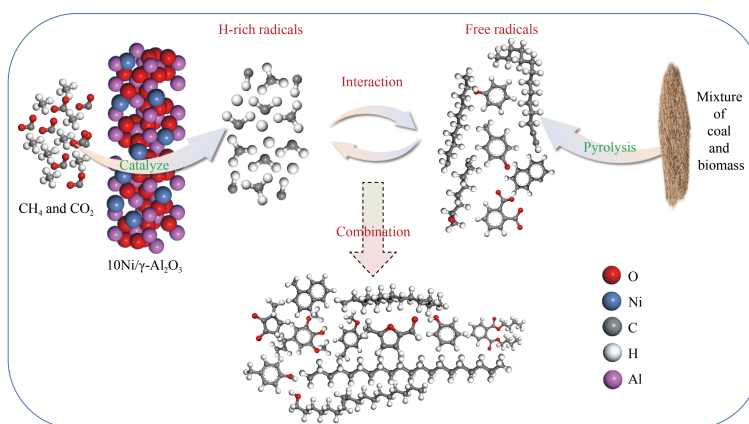
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Abstract: To investigate influence of mixing modes on integrated process of co-pyrolysis of coal and biomass with CO₂ reforming of methane (CP-CRM), Naomaohu coal (NMH) and elm (ELM) were chosen and three mixing modes (NMH/ELM, ELM/NMH and Blends) were examined over Ni-based reforming catalysts prepared by ball milling, and compared with co-pyrolysis under N₂ atmosphere (CP-N₂). The results show that the products distribution was significantly affected by the mixing mode. Tar yield during CP-CRM under

Blends model was higher than those of NMH/ELM and ELM/NMH, increasing by 35.29% compared with CP-N₂. Meanwhile, light oil content in the tar was higher than those of NMH/ELM and ELM/NMH, but the pitch content was opposite. Phenols content in tar from Blends model was 19.52% higher than that of CP-N₂, along with more free radicals in tar than that of CP-N₂, which was mainly ascribed to the enhanced heat and mass transfer between raw material particles by mechanical mixing, making the co-pyrolysis process more complete. At the same time, the mechanical mixing was conducive to more efficient action of hydrogen-rich free radicals (such as ·H, ·CH_x) on pyrolysis products, suppressing the secondary cracking and polymerization. The results provide a good guidance for regulating tar yield and compositions of the co-pyrolysis process.

Key words: co-pyrolysis; mixing mode; coal; biomass; CO₂ reforming of CH₄; tar



The coal resource in Xinjiang region accounts for over 40% of the national total reserves^[1], and is dominant as low-rank coal with high volatile content. Most studies suggest that pyrolysis technology is an effective route as an efficient utilization based on the quality of low-rank coal^[2]. However, low yield of tar and high content of heavy components in tar are presented due to low H/C atomic ratio of coal. Co-pyrolysis of coal and biomass can solve the

problem, which utilizes hydrogen-rich free radicals generated from pyrolysis of biomass with higher H/C atomic ratio to stabilize the macromolecular free radicals generated from coal pyrolysis and suppresses the polymerization reactions among them, contributing to generate more tar^[3-4]. However, high oxygen content of biomass leads to the efficiency reduction of H that can be effectively transferred into coal. Tarves et al.^[5-6] found that

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tar yield can be significantly increased by coupling the H-rich free radicals generated from methane activation with coal pyrolysis process. Meanwhile, co-pyrolysis of biomass and coal also follows the free radical reaction mechanism, therefore, externally introducing the hydrogen or H-rich free radicals into co-pyrolysis is expected to increase tar yield. Additionally, CH_4 and CO_2 , as co-pyrolysis gas products, can be cyclically utilized through coupling of catalytic CH_4/CO_2 activation with co-pyrolysis process, improving the hydrogen utilization efficiency.

Biomass undergoes pyrolysis before coal during their co-pyrolysis, therefore, the mixing modes will directly affect interactions of volatiles-volatiles, volatiles-char and char-char^[7]. Li et al.^[8] investigated effect of mixing methods on co-pyrolysis behavior of Baiyinhua coal and pine wood on an infrared-heated fixed-bed. They found that the experimental tar yield was approximately 8.29% higher than the theoretical value when coal was placed above pine wood, significantly different from the negative synergistic effect when coal was under pine wood. This was mainly attributed to the fact that H-rich gas produced by rapid pyrolysis of pine wood participated in the interaction between volatiles and coal. Wang et al.^[9] examined effect of filling methods on co-pyrolysis at 500 °C, and the results showed that the highest tar yield and the lowest char yield were obtained when biomass was on the top of coal, which was attributed to that the free radicals formed from biomass pyrolysis reacted with coal. Zhu et al.^[10] further compared effects of mechanical and layered mixing methods on tar yield of co-pyrolysis of Naomaohu coal and pine wood, and also discovered that the U-type method (coal on top and biomass on the bottom) had the highest tar yield, and considered that it was related to the particle packing density and spatial void inconsistency of the raw materials.

Our previous research found that, when Naomaohu coal and elm were mixed using mechanical mixing method and integrated with CO_2 reforming of methane at 500 °C, the tar yield was 35.29% higher than co-pyrolysis alone. To study influence of different mixing modes on the integrated process of co-pyrolysis between coal and biomass with CO_2 reforming of methane to further improve tar yield, in this work, influence of mixing modes was explored *via* an infrared-heated fixed-bed. Influences of mixing modes on interaction mechanism between volatiles, char and H-rich free radicals generated by the reforming process during integrated process were clarified by analyzing products distribution, tar quality, tar composition, and concentration of free radicals in the tar.

1 Experimental

1.1 Materials

Naomaohu coal (NMH) and elm (ELM) from Xinjiang were chosen as pyrolysis materials. Prior to co-pyrolysis run, they were first ground and sieved to 80–100 mesh, and then dried at 105 °C for 3 h. The total amount of raw materials used in each test was 2 g. Their proximate and ultimate analyses are listed in Table 1.

1.2 Preparation of catalysts

A self-made catalyst of 10Ni/ $\gamma\text{-Al}_2\text{O}_3$ was used for dry reforming of methane (CRM), which was prepared *via* ball-milling using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (from Xilong Scientific Co., Ltd), $\gamma\text{-Al}_2\text{O}_3$ (from Shanghai Macklin Biochemical Co., Ltd) and $(\text{NH}_4)_2\text{CO}_3$ (from Tianjin Beilian Fine Chemical Development Co., Ltd) as raw materials with a theoretical loading of 10% Ni. The detailed procedures are as follows: a certain amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\gamma\text{-Al}_2\text{O}_3$ and $(\text{NH}_4)_2\text{CO}_3$ were first placed in a ball mill tank (ratio of ball to material being 2/1 and ratio of big ball (8 mm) to small ball (6 mm) of 2/1), and then an appropriate amount of deionized water was added. After the sample in the ball mill tank was milled for 1 h at 400 r/min, it was dried at 105 °C for 6 h and calcinated at 500 °C with 5 °C/min in muffle furnace for 4 h. The resultant sample was pressed and ground to 20–40 mesh. Before test the sample was reduced in 15 mL/min H_2 at 700 °C with 10 °C/min for 2 h to prepare 10Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalyst. 1 g catalyst were used in each experiment.

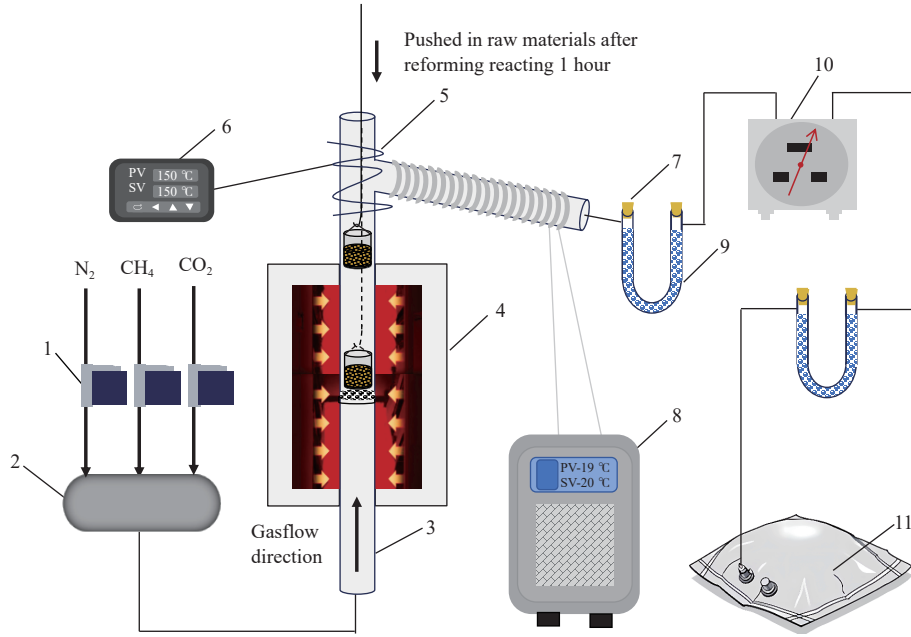
1.3 Co-pyrolysis of coal and biomass

The integrated co-pyrolysis of NMH and ELM with CRM (labelled as CP-CRM) was performed on an infrared-heated fixed-bed as illustrated in Figure 1. The detailed experimental procedures are as follows: 1 g catalyst was placed on a sieve plate of quartz tube with length of 805 mm and inner diameter of 21 mm. 2 g mixture of NMH and ELM with mass ratio of 1/3 was put into a metal mesh cylinder suspended on the top of quartz tube (outside the heating zone). Before experiment, the reactor was purged with high-purity N_2 for protecting the catalyst from deactivation due to prolonged exposure to air.

Table 1 Proximate and ultimate analyses of NMH and ELM

Sample	Proximate analysis w/%				Ultimate analysis $w_{\text{daf}}/\%$					H/C atomic ratio
	M_{ad}	A_{d}	V_{daf}	FC_{daf}^*	C	H	N	S	O^*	
NMH	6.69	5.07	50.55	49.45	73.25	5.70	1.01	0.27	19.77	0.93
ELM	5.32	5.86	78.95	21.05	51.05	6.02	0.96	0.12	41.85	1.42

ad: air dry basis; d: dry basis; daf: dry ash-free basis; *: by difference.



1-mass flow meter; 2-mixing tank; 3-quartz tube; 4-infrared-heated fixed bed; 5-heating belt; 6-temperature controller; 7-rubber plug; 8-cold trap; 9-U type drying pipe; 10-wet gas flow meter; 11-gas bag.

Fig. 1 Schematic diagram of the experimental apparatus

After 20 min, the reaction system was switched to a mixed atmosphere of 50 mL/min N_2 , 125 mL/min CH_4 and 125 mL/min CO_2 for about 30 min to remove air. Thereafter, the reactor was heated from room temperature to the desired temperature of 500 °C at 10 °C/s. After holding for 60 min, the metal mesh cylinder was quickly pushed into the constant temperature zone, and the integrated process of co-pyrolysis of coal and elm with CRM was held for 30 min. The generated volatiles were carried into cold trap (−20 °C) by carrier gases and condensed for subsequent analysis. The non-condensable gas was measured by wet gas flow meter, and then gathered by gas bag for GC-4000A analysis (East-West Analytical Instrument Co., LTD). The solid product was cooled and then weighed. The mass of water in liquid product was obtained according to ASTM D95-2013. The experiments were carried out at least three times to assure the reliability. For co-pyrolysis in N_2 of 300 mL/min (CP- N_2), all processes were the same as the integrated process except for no catalyst, CO_2 and CH_4 .

According to different mixing modes of coal and biomass, it can be divided into mechanical blending and layered placement forms as shown in Figure 2. It was denoted as NMH/ELM (NMH above ELM), ELM/NMH (ELM above NMH) and Blends (mechanical blending).

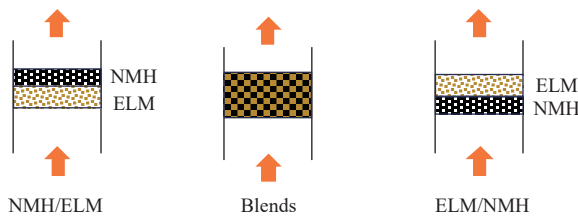


Fig. 2 Schematic diagram of the mixing modes of NMH and ELM

1.4 Yield calculation

The yields of tar (Y_{tar}), char (Y_{char}), water (Y_{water}), gas (Y_{gas}) (on dry ash-free basis), component yield (Y_i , mL/g) of i gas and conversion of CH_4 and CO_2 were calculated by the following equations:

$$Y_{tar} = \frac{W_{tar}}{W_0 \times (1 - A_d)} \times 100\% \quad (1)$$

$$Y_{char} = \frac{W_{char}}{W_0 \times (1 - A_d)} \times 100\% \quad (2)$$

$$Y_{water} = \frac{W_{water}}{W_0 \times (1 - A_d)} \times 100\% \quad (3)$$

$$Y_{gas} = 100\% - Y_{tar} - Y_{char} - Y_{water} \quad (4)$$

$$V_i = V_{total} \times f_i \quad (5)$$

$$Y_i = \frac{V_{i,out} - V_{i,in}}{W_0 \times (1 - A_d)} \times 100\% \quad (6)$$

$$x_{CH_4} = \frac{V_{CH_4,in} - V_{CH_4,out}}{V_{CH_4,in}} \times 100\% \quad (7)$$

$$x_{CO_2} = \frac{V_{CO_2,in} - V_{CO_2,out}}{V_{CO_2,in}} \times 100\% \quad (8)$$

where A_d was ash content of material, %; W_{tar} , W_{char} , W_{water} , and W_0 were weights of tar, char, water and material (the mixture of NMH and ELM), respectively (g); V_i and V_{total} were volumes of i gas and total gas, mL; f_i was relative content of i gas; $V_{i,out}$ and $V_{i,in}$ were outlet and inlet volumes of each gas component, respectively (mL); x_{CH_4} and x_{CO_2} were conversion (%) of CH_4 and CO_2 , respectively.

1.5 Characterization

To understand pyrolysis characteristics of coal and elm, thermogravimetric (TG) analysis was performed on TGA8000 thermogravimetric analyzer (PerkinElmer, America). The heating procedures were as follows: 10 mg sample heated from 40 to 950 °C at 10 °C/min and held for 30 min in 100 mL/min N₂.

The fraction distribution of tar was analyzed on Agilent GC7890B according to the ASTM D2887. Before the measurement, CS₂ was chosen as solvent to obtain oil-water mixture, and then anhydrous sodium sulfate was added to remove water and then filtered. Finally, the liquid volume was fixed to 25 mL by volumetric flask. The fractions were classified into light oil (< 170 °C), phenol oil (170–210 °C), naphthalene oil (210–230 °C), wash oil (230–300 °C), anthracene oil (300–360 °C) and pitch (> 360 °C) according to the boiling points. And the fractions with boiling point below 360 °C were defined as the light tar.

The compositions of tar were determined by GC-MS with chromatographic column of Elite-5MS. The test conditions are as follows: the temperature was first raised to 60 °C, then increased to 120 °C at 3 °C/min and held for 5 min, and then heated to 220 °C at 3 °C/min and held for another 5 min, finally increased to 270 °C at 2 °C/min and held for 5 min. The solvent delay time was 5.2 min. Each compound was matched with the standard spectrum in NIST2017 mass spectrogram library.

The concentration of stable free radicals in tar was tested on a paramagnetic resonance spectrometer (Bruker EMXplus-6/1, Germany) with central field of 3510 G and sweep width of 100 G. The resonance frequency was 9.85 GHz, and sweep time was 30 s. The modulation amplitude was 4 G, and the modulation frequency was 100 kHz.

2 Results and discussion

2.1 TG/DTG analysis

Thermal gravimetric analysis of NMH and ELM is conducted and shown in Figure 3. The total weight loss of

NMH at final temperature of 950 °C is 47.21%, which is significantly lower than that of ELM (78.46%). The DTG curve indicates that NMH has three weight loss stages, corresponding to removal of moisture in coal^[11], release of volatiles^[12], and decomposition of minerals in coal^[13–14]. However, ELM pyrolysis has five weight loss peaks, which are attributed to removal of moisture^[15–16], release of small molecule compounds (such as H₂O, CO, CO₂, etc.)^[17–19], decomposition of cellulose, hemicellulose, high-molecular-weight organic compounds and lignin, release of a large amount of volatile components^[20–21], decomposition of lignin and unheated residual substances^[22–24], and decomposition of minerals in ELM.

ELM pyrolysis occurs before coal, especially, the peak temperature corresponding to the maximum weight loss rate of ELM is significantly lower than that of coal. Therefore, it is necessary to perform rapid heating to reduce the asynchronous reaction time between them in order to achieve a synergistic effect during co-pyrolysis process. Accordingly, the method of first raising temperature of fixed-bed reactor to setpoint, and then rapidly pushing the mixture of coal and biomass into reactor is adopted. This is aimed at minimizing the time of asynchrony as much as possible for facilitating transfer of hydrogen-rich components from ELM pyrolysis to NMH, enhancing synergy of their co-pyrolysis.

2.2 Influence of mixing modes on products distribution and gas compositions of the integrated process

Figure 4 shows products distribution and gas compositions of CP-N₂ and CP-CRM under different mixing modes. The tar yield increases significantly, while char and gas yield decrease during CP-CRM compared with those of CP-N₂ under same mixing method. This is mainly attributed to the fact that free radicals generated during co-pyrolysis can be stabilized by ·H and ·CH_x produced in CRM process, thereby the polymerization is inhibited, contributing to a decrease in char (and gas) and an increase in tar yield^[25]. Additionally, an increase in water yield is mainly attributed to the reverse water-gas shift reaction in the CRM process^[26–27].

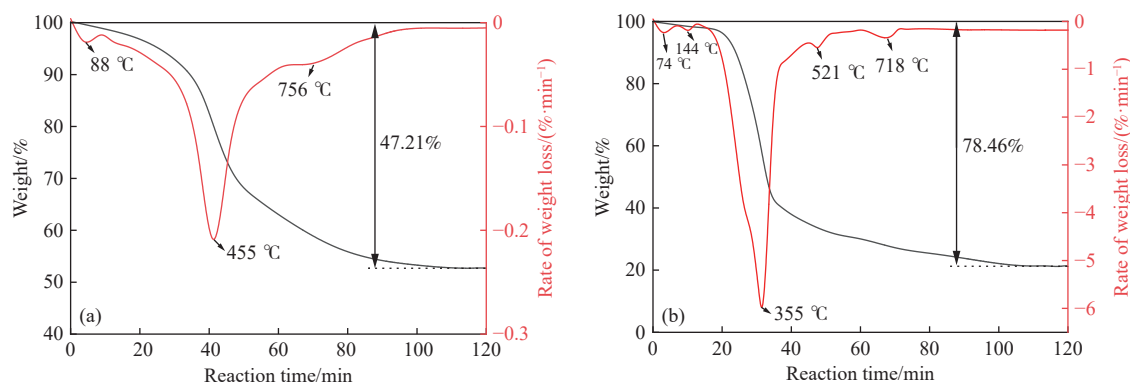


Fig. 3 TG/DTG curves of NMH (a) and ELM (b) samples

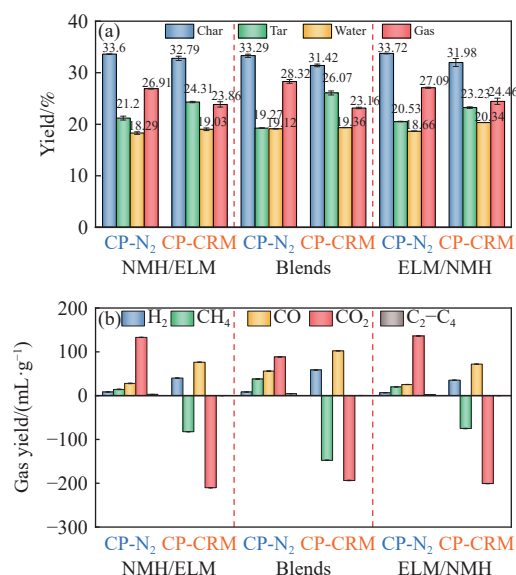


Fig. 4 Products distribution (a) and gas compositions (b) of CP-N₂ and CP-CRM in different modes

When N₂ is used as pyrolysis atmosphere, tar yield follows the order of NMH/ELM > ELM/NMH > Blends, along with the largest tar yield of 21.20% under NMH/ELM mode. It is reported that interaction between free radicals from ELM and NMH pyrolysis promoted the formation of tar^[28]. When biomass is on the upper layer (ELM/NMH), most of free radicals generated from biomass pyrolysis cannot combine with free radicals from coal pyrolysis under action of constantly flowing pyrolysis atmosphere, resulting in lower tar yield. As for mixing mode (Blends), some pyrolysis substances from biomass may cover the surface of coal particles, inhibiting release of volatiles from coal. However, influence of mixing method on tar yield is different during integrated process compared with CP-N₂. Tar yield (35.29%) increases significantly under co-pyrolysis mode of blends compared with stratified mixing methods (NMH/ELM, ELM/NMH). It is analyzed that mechanical mixing is conducive to mass transfer between raw material particles, and H-rich free radicals (such as ·H, ·CH₃) produced by CRM can fully act on the free radicals from pyrolysis of ELM and NMH. This inhibits or weakens influence of some substances from biomass pyrolysis covering surface of coal particles. Thus, the secondary cracking and polymerization reactions are reduced, and thereby, increasing the tar yield, which is consistent with the lowest char yield obtained from pyrolysis mode of Blends.

Figure 4(b) compares effects of mixing modes and co-pyrolysis methods on gas yields. Gas products under different mixing modes are all positive value and dominated by CO₂ in CP-N₂ pyrolysis. However, CO₂ yield is the lowest, and generation of CO and CH₄ is the highest during co-pyrolysis in Blend modes. It is considered that CO₂ produced in this mode reacts with char to form CO, which is consistent with the lowest char yield and the highest gas yield under the co-pyrolysis mode. During CP-CRM both CH₄ and CO₂ yields are negative, indicating that they participate in co-pyrolysis process through catalytic

activation. Especially, reduction of CH₄ is the most significant when co-pyrolysis is carried out under the Blends method, meaning that more free radicals generated from CRM combine with free radicals generated by biomass and coal pyrolysis, resulting in the highest tar yield. For ELM/NMH and NMH/ELM, the probability of free radicals generated from CRM combining with free radicals generated by ELM pyrolysis becomes smaller when ELM is on the upper layer, resulting in higher amounts of CH₄ and CO₂ than that of NMH/ELM method. These results reflect influence of mixing method on interaction between free radicals from CRM and free radicals from co-pyrolysis.

2.3 Influence of mixing modes on tar of from the Integrated process

2.3.1 Fraction distribution of tar

As shown in Figure 5, fraction distribution of co-pyrolysis tar is also affected by mixing method of ELM and NMH. For both CP-N₂ and CP-CRM, light oil content in tar obtained from Blends is higher than that from stratified mixing method, accompanied with lower pitch content. It is analyzed that some substances produced from biomass pyrolysis will cover the surface of coal particles under Blends mode^[29], causing secondary reactions of pyrolysis volatiles under the action of minerals in both biomass and coal, which reduces content of heavy components and increases in content of light oil in tar. Moreover, the secondary reactions of tar are inhibited to a certain extent due to effect of hydrogen-rich free radicals produced by CRM. Thus, light oil content corresponding to CP-CRM in Blends method is reduced by 7.82%, and pitch content increases by 8.24% compared with CP-N₂, but the tar quality is still better than that of stratified placement. Besides, it is found that CP-CRM has a smaller impact on fraction distribution of tar under co-pyrolysis of stratified placement compared with co-pyrolysis in N₂ atmosphere.

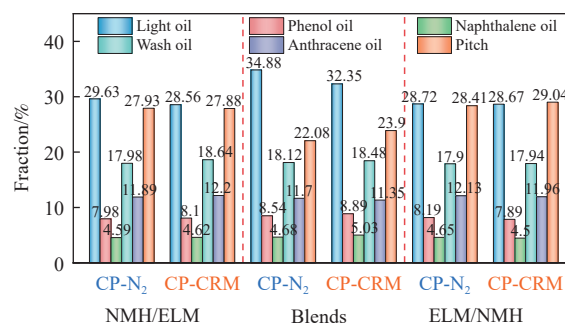


Fig. 5 Fraction distribution of CP-N₂ and CP-CRM in different modes

2.3.2 GC-MS analysis of tar

Figure 6 compares compositions distribution of co-pyrolysis tar under different mixing methods. Obviously,

changes of tar compositions in CP-CRM are significant compared with CP-N₂, especially, the content of phenols increases significantly. Phenols content from NMH/ELM pyrolysis shows the most significant increase by 33.27%, while it is 19.52% under Blends.

It is analyzed that H-rich free radicals generated during CRM process first combine with free radicals generated by ELM pyrolysis when NMH is on the upper layer, stabilizing the phenoxide free radicals produced by ELM, resulting in the increase of phenols content in tar^[8]. When ELM is on the upper layer, part of free radicals from CRM combines with free radicals generated by coal pyrolysis. As a result, free radicals amount from CRM process decreases. They participate in stabilization of the phenoxide free radicals produced by ELM, thus resulting in smaller increase in phenols content. For mechanical mixing, it may lead to further reactions of generated phenolic substances due to occurrence of the secondary reactions forming benzene and naphthalene, which leads to a reduction of increase degree. Additionally, under the Blends mode content of ketone in tar increases, while content of aliphatic hydrocarbons decreases, which is significantly different from the case of layered mixing method. Thus, different mixing methods not only affect the products distribution but also the tar compositions. Layered placement is helpful for increasing content of phenols in tar, providing a possibility for directional generation of products.

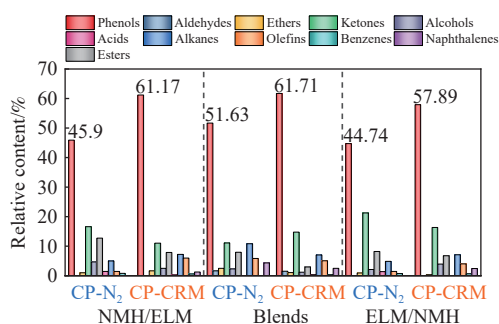


Fig. 6 Tar components during CP-N₂ and CP-CRM in different modes

2.3.3 Free radical concentration analyses of tar

Co-pyrolysis process is a free radical reaction, concentration of stable free radicals in pyrolysis tar can help to further understand the mechanism of increase in tar yield during co-pyrolysis. Table 2 shows that for pyrolysis tar under N₂ different mixing methods significantly affect concentration of free radicals in tar. For NMH/ELM concentration of free radicals is the lowest. It is mainly attributed to that H-rich free radicals from biomass pyrolysis are carried by N₂ and then combine with those from coal pyrolysis, thereby significantly reducing the amounts of free radicals in tar. For ELM/NMH interaction between free radicals is relatively weak, leading to the highest number of free radicals. When CRM is coupled with co-pyrolysis, concentration of free radicals in tar is reduced to a certain extent compared with that in N₂ except for

Blends. This indicates that free radicals produced by CRM combine with the free radicals formed during co-pyrolysis, which reduces the number of stable free radicals in tar. When ELM and NMH are mixed for co-pyrolysis, concentration of free radicals in tar is slightly higher than that of tar obtained under N₂. It is analyzed that although H-rich free radicals produced by integrated process inhibit occurrence of reaction where volatiles of biomass cover surface of coal particles and undergo condensation to form char, generation of relatively large tar molecules under Blends may be the reason for higher concentration of free radicals.

Table 2 Free radicals content in CP-N₂ and CP-CRM tar under different mixing modes

Tar sample	Spin concentration (spin/mm ³ , ×10 ¹¹)
NMH/ELM (CP-N ₂)	4.65
NMH/ELM (CP-CRM)	4.61
Blends (CP-N ₂)	4.81
Blends (CP-CRM)	4.86
ELM/NMH (CP-N ₂)	4.93
ELM/NMH (CP-CRM)	4.85

3 Conclusions

Effect of mixing methods on products distribution, tar quality, tar composition and free radical concentration in tar during co-pyrolysis in CP-N₂ and CP-CRM processes was examined. Compared with CP-N₂ mechanical mixing method in CP-CRM process showed more significant increase in tar yield (35.29%). The Blends method resulted in higher content of light oil in tar compared with the layered placement method, and lower content of pitch in both CP-N₂ and CP-CRM. Meanwhile, introduction of CRM lowered content of phenols in tar. Compared with CP-N₂, the NMH/ELM mode in CP-CRM process improved phenols content by 33.27%, and the Blends mode was 19.52%. The placement method also affected free radical concentration in co-pyrolysis tar. Among them, free radical concentration in tar under NMH/ELM mode was the lowest in CP-N₂. The free radical concentration in tar during CP-CRM process was lower than that in CP-N₂, which was attributed to that free radicals generated during the reforming process stabilized timely free radicals from pyrolysis of ELM and NMH.

Declaration of Competing Interest

The authors declare no conflict of interest.

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淖毛湖煤与榆木混合方式对共热解耦合 CH_4/CO_2 重整产物影响研究

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摘要: 为探究混合方式对煤和生物质共热解耦合甲烷二氧化碳重整(CRM)过程的影响, 本研究以淖毛湖煤(NMH)和榆木(ELM)为研究对象, 采用球磨法制备 Ni 基重整催化剂, 考察了分层放置(NMH/ELM、ELM/NMH)与机械混合(Blends)三种混合方式对耦合共热解(CP-CRM)的影响规律, 并与氮气气氛下共热解(CP-N₂)相对比。结果表明, 混合方式显著影响共热解过程产物分布。机械混合方式下 CP-CRM 焦油产率高于分层放置方式, 与 CP-N₂ 相比提高 35.29%; 同时焦油中轻油含量也高于分层放置方式, 沥青含量低于分层放置方式; 焦油中酚类物质含量较 CP-N₂ 提高 19.52%; 焦油中自由基浓度也高于 CP-N₂。分析认为, 机械混合增强了原料颗粒间的传热与传质, 使得热解反应更加充分, 同时机械混合有利于 CRM 产生的富氢自由基(如 $\cdot\text{H}$ 、 $\cdot\text{CH}_3$)更高效地作用于热解中间产物, 减少二次裂解和缩聚反应, 这为共热解过程调控焦油产率和组成提供指导。

关键词: 共热解; 混合方式; 煤; 生物质; 甲烷二氧化碳重整; 焦油

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