



Review article

Brief review on petroleum coke and biomass/coal co-gasification: Syngas production, reactivity characteristics, and synergy behavior



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ABSTRACT

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Petroleum coke and biomass/coal co-gasification is a promising approach for efficiently integrating the individual advantages of different gasification feedstocks with syngas production. Therefore, research on syngas production, reactivity characteristics, and synergy behavior of co-gasification is critical. In this review, the main reaction processes during co-gasification were described and the influencing factors for syngas production and reactivity characteristics of co-gasification were summarized. Moreover, the non-catalytic/catalytic synergy mechanisms in co-gasification were also discussed in detail. H₂-rich syngas derived from co-gasification could be acquired in case of (i) feedstock with high H/C ratio or alkali and alkaline earth metals (AAEMs) concentrations, (ii) high coal/biomass proportion in blends, (iii) relatively low gasification temperature, and (iv) low O₂ concentration or high steam concentration in gasification agent. Higher co-gasification reactivity could be acquired in case of (i) coal/biomass with more disordered carbon structures, more developed pore structures and higher AAEMs concentrations, (ii) higher coal/biomass proportion in blends, (iii) higher gasification temperature, and (iv) higher O₂ or steam concentration in gasification agent. The synergy behavior on co-gasification reactivity varied as reaction proceeded. The synergy mechanism of co-gasification showed great relationships with the migration and transfer of free radical and inherent AAEMs. The limitations and challenges within this research field were also addressed. For instance, the transfer and migration mechanisms of free radicals and AAEMs during co-gasification, and kinetics models involving parameters related to synergy behavior.

1. Introduction

Petroleum coke (PC) is a critical by-product derived from delayed coking of residual oil [1]. PC is characterized by high carbon content, high calorific value, low ash content and low cost [2]. Therefore, it is generally used as (i) an electrode material (low-sulfur PC) for aluminum smelting and steel making, or (ii) industrial fuel (mid/high-sulfur PC) for power generation. As the deterioration of crude oil, the mid/high-sulfur PC has been dominant in global PC market. On the one hand, the direct utilization of mid/high-sulfur PC as fuel or electrode material inevitably leads to the environmental pollution issues [3,4]. On the other hand, the overall cost for desulphurization of mid/high-sulfur PC (i.e., low-sulfur PC production from mid/high-sulfur PC) is high. Therefore, researchers

and industry have put increasing attentions on developing a technology to realize the direct, clean and high-efficiency conversion of mid/high-sulfur PC [4].

Gasification is an attractive approach for solving the above-mentioned problems regarding to mid/high-sulfur PC by converting the combustible matter in PC into syngas for hydrogen and chemical production, and other process industries (Fig. 1). Moreover, sulfur in PC is converted into elemental sulfur using gasification and Claus process [5,6]. However, the industrial application of PC gasification was seriously limited due to the low gasification reactivity of PC. Hence, higher gasification temperature and longer residence time are required, which directly lead to the high device investment and energy consumption [7–9]. Therefore, numerous studies have focused on the co-gasification of PC with other

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gasification feedstocks, such as coal and biomass.

Coal is the dominant gasification feedstock globally, and coal water slurry and pulverized coal gasification technologies have been widely and successfully applied [10,11]. PC shows similar structural properties to those high rank coal, such as high order degree of carbon structure and undeveloped pore structure [12]. Therefore, PC-coal co-gasification is technically feasible, and has achieved industrial validation [13]. Moreover, co-gasification is favorable for enhancing PC gasification reactivity and partially replacing coal used in gasification [14].

Biomass is a potential gasification feedstock due to the advantages like near-zero carbon emission, large reserves, low pollutant emissions, and high reactivity [15,16]. Co-gasification of PC and biomass may overcome the disadvantages of biomass, such as low energy density, high transportation cost and high tar yield [17]. Moreover, alkali and alkaline earth metals (AAEMs) enriched in biomass improves the activity and syngas production of PC gasification [18,19].

The gasification reactivity is a key parameter for the overall conversion efficiency of carbonaceous feedstocks and the design of industrial gasifiers. Additionally, the gaseous product distribution of gasification has a profound impact on the calorific value and downstream process of syngas [20]. However, the review papers regarding to PC-coal/biomass co-gasification are almost a gap. In this paper, the influencing factors for the reactivity characteristics and syngas production of PC-coal/biomass co-gasification are systematically reviewed. The corresponding synergy mechanism of co-gasification is also reviewed. Moreover, the deficiencies in the current research are summarized and future research directions in this field are discussed. This review provides a meaningful reference for future research and application of PC and coal/biomass co-gasification.

2. Chemical reaction process of PC and biomass/coal co-gasification

The reaction process of binary blend co-gasification is commonly divided into two processes: co-pyrolysis and char co-gasification [4]. Co-pyrolysis is an essential pre-step in co-gasification processes with producing of solid char, liquid tar and light gas (H_2 , CO_2 , CO , CH_4 , etc.). The main chemical reactions occurring during co-pyrolysis include distillation, decarboxylation, decarbonylation, and dehydroxylation (Table 1) [21,22]. Char co-gasification is the rate-controlling step in co-gasification process because of its lower reaction rate than that of co-

Table 1
The main chemical reactions during co-pyrolysis process of binary blends.

Product	Main source	Reaction
Tar	Ring with weak bonds	Distillation, Pyrolysis
CO_2	Carboxyl	Decarboxylation
CO	Carbonyl, ether	Decarbonylation
CO	Oxygen-containing heterocycle	Ring cleavage
H_2O	Hydroxyl	Dehydroxylation
Hydrocarbons	Alkyl	Dealkylation
H_2	Aromatic C-H bond	Ring cleavage

pyrolysis. The main chemical reactions during co-gasification include steam gasification, Boudouard, methanation, and water-gas-shift (WGS) reactions (Table 2) [21,23–26].

3. Influencing factors for syngas production of PC and biomass/coal co-gasification

Syngas derived from co-gasification is mainly composed of H_2 , CO, CO_2 , and CH_4 . The product distribution of syngas directly determines

Table 2
The main chemical reactions in the co-gasification process of binary blends.

Reaction	Chemical formula	Heat of reaction (kJ/mol)
<i>Main reactions under O_2, O_2 enriched air, or air atmosphere</i>		
Partial oxidation	$C + 1/2 O_2 \rightarrow CO$	-123.1
Complete oxidation	$C + O_2 \rightarrow CO_2$	-405.9
<i>Main reaction under CO_2</i>		
Second overall reaction	$C_mH_n + CO_2 \rightarrow 2mCO + n/2H_2O$	+980~+3112
Boudouard reaction (gas-solid)	$C + CO_2 \rightarrow 2CO$	+159.7
<i>Main reaction in H_2O</i>		
Steam gasification	$C + H_2O \rightarrow H_2 + CO$	+118.9
WGS reaction	$CO + H_2O \rightarrow CO_2 + H_2$	-45.2
<i>Other reactions may occur in gasification process</i>		
Methanation reaction	$C + 2H_2 \rightarrow CH_4$	-75
Steam reforming reaction	$CH_4 + H_2O \rightarrow CO + 3H_2$	+206.0
CO_2 reforming reaction	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	+222.5

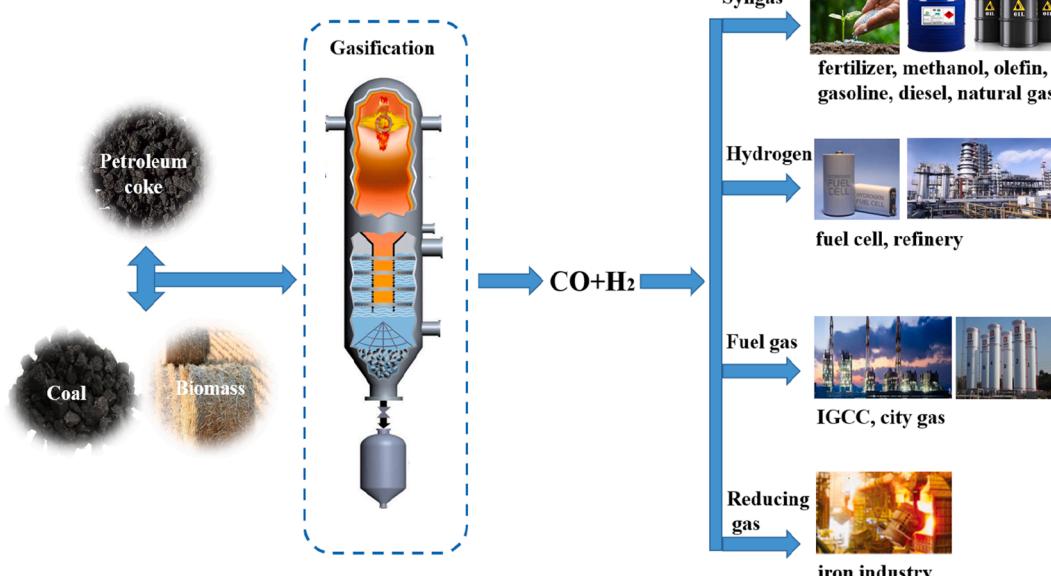


Fig. 1. Industry chain of solid carbonaceous material gasification technology.

the utilization of downstream industry [27]. Therefore, a clear understanding of the influences of various factors (such as gasification temperature, and feedstock type, feedstock blend ratio) on syngas production is necessary. The experimental conditions and conclusions in the related fields are summarized in [Appendix A of Supplementary material](#).

3.1. Feedstock type

Puig-Gamero et al. [19] discovered that the co-gasification of PC and biomass produced more H₂ and less CO than that of PC and coal. Huang et al. [12] and Shen et al. [35] indicated that the effect of coal type on H₂ production in PC-coal co-gasification followed the order of lignite > bituminous coal > anthracite. The main factors affecting H₂ production in steam gasification were the steam gasification and WGS reactions of the raw material [35]. Steam gasification was more obvious for the feedstock with more disordered carbon structure and more developed pore structure [30]. Moreover, the WGS reaction is favored for carbonaceous materials containing more AAEMs due to their catalysis [36,37]. Generally, the AAEMs content and H/C ratio of biomass and coal follow the order of biomass > low rank coal > high rank coal [12,15,19,38,39], which correlates the findings of the above-mentioned studies.

In general, the H₂ content in syngas produced from steam co-gasification is higher for raw materials with higher H/C ratios or AAEMs concentrations.

3.2. Feedstock blended ratio

Several studies [12,32,35] showed that the higher the coal/biomass proportion in blends, the higher the H₂ yields and H₂/CO ratio in co-gasification-derived syngas ([Fig. 2](#)). This mainly attributed to the higher H/C ratio and AAEMs content in biomass/coal than those in PC [32,36,37]. However, there is no consensus for the effect of the feedstock blended ratio on the CO₂ yield in co-gasification. Puig-Gamero

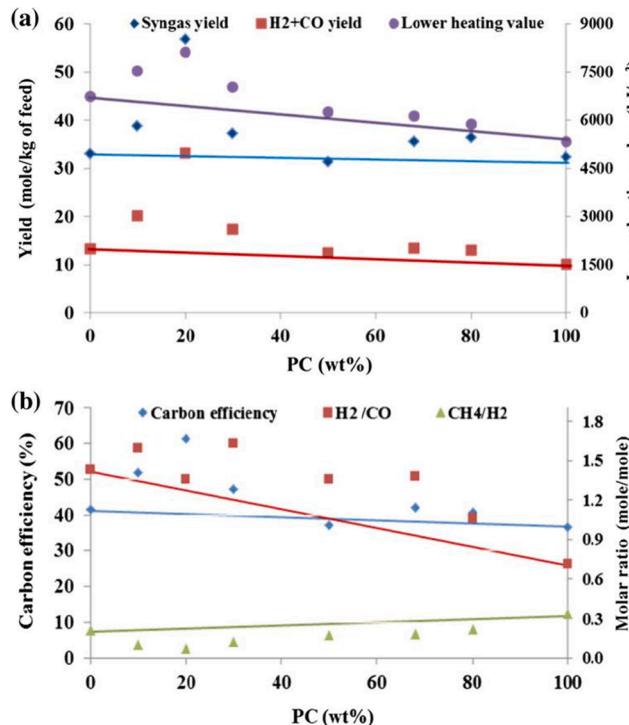


Fig. 2. Effect of feedstock (PC and lignite) blended ratio on (a) syngas product yield, H₂ + CO yield and lower heating value of syngas product, and (b) carbon efficiency, H₂/CO and CH₄/H₂ molar ratios [32].

et al. [29] showed that the CO₂ yield during steam co-gasification initially decreased and then increased as the biomass (almond shell) proportion increased. Shen et al. [35] discovered that the CO₂ yield during steam/O₂ co-gasification increased as coal (subbituminous/bituminous coal) proportion in blends increased. This was mainly attributed to three factors: (i) the O/C ratio of the feedstock, (ii) the carbon conversion/reactivity related to the physicochemical structure of the feedstock, and (iii) the extent of the WGS and Boudouard reactions related to the AAEMs concentration in feedstock [30,36].

3.3. Gasification temperature

During co-gasification, each chemical reaction is interdependent and competitive. However, the order of magnitude of each chemical reaction varies with temperature according to the Gibbs free energy ([Fig. 3](#)). Therefore, the product distribution is strongly influenced by the gasification temperatures. [Fig. 3](#) showed that the WGS reaction weakens but Boudouard reaction strengthens as the gasification temperature increases. Consequently, the CO concentration in syngas increases and those of CO₂ and H₂ decreases, which explains the conclusion of Nemanova et al. [28]. Moreover, high temperature was unfavorable for methane reforming and methanation reactions, leading to low methane yield.

Therefore, the higher the gasification temperature, the lower the (H₂ + CO₂) content in the syngas and the higher the CO production.

3.4. Gasification agent

Researchers have conducted co-gasification experiments using various gasification agents (O₂ or air, steam, and steam + O₂). Compared with O₂, steam leads to a clear increase in the H₂ yield in syngas, which is mainly due to the steam gasification reaction (C + H₂O → H₂ + CO) [12,18,27,29]. Liu et al. [31] showed that a decrease in O₂ concentration in the gasification agent led to an increase in the CO yield in the syngas. Azargohar et al. [32] and Zhang et al. [34] concluded that as the O₂ concentration increased, the syngas yield increased, while the heating value and H₂/CO ratio decreased. This was mainly attributed to the more obvious combustion and oxidation reactions as oxygen content increased [40]. Additionally, Al-Zareer et al. [33] showed that with increasing steam concentration, the H₂ yield increased but the CO yield decreased. This phenomenon was mainly due to the enhancement of steam gasification and WGS reactions at higher steam concentrations

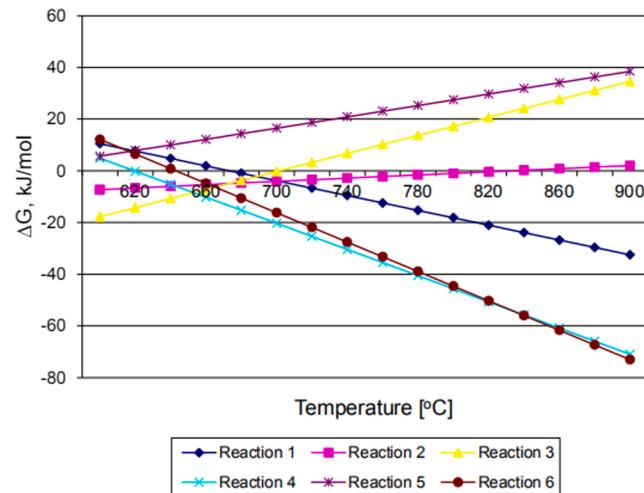


Fig. 3. The Gibbs free energies of gasification reactions at 600–900 °C for reactions: (1) Steam reforming of solid reaction, (2) Water-Gas-Shift reaction, (3) Boudouard reaction (reverse), (4) Steam reforming of methane, (5) Methanation reaction and (6) Dry reforming of methane [40].

[41].

Therefore, an increase in the O₂ content in gasification agent leads to an increase in the syngas yield, but the H₂/CO ratio and calorific value of the syngas decreases. With an increase in the steam flow rate, the H₂/CO ratio in syngas increases.

4. Influencing factors for reactivity characteristics of PC and biomass/coal co-gasification

Numerous factors influence the reactivity characteristics of PC-coal/biomass co-gasification, such as gasification temperature, feedstock type/blended ratio, etc. The experimental conditions and main conclusions of relevant previous studies are summarized in Appendix B of Supplementary material.

4.1. Feedstock type

Compared with high rank coal, biomass or low rank coal generally exhibit more disordered carbon structures, more developed pore structures, and higher AAEMs concentrations. Therefore, the co-gasification reactivity of PC-biomass blends is higher than those of PC-coal blends [50,56], and that of PC-low rank coal is higher than that of PC-high rank coal [35,57]. Edreis et al. [42] conducted studies on co-gasification experiments of PC and five types of biomass (rice husk, and stalk, sawdust, cotton straw, and sugar cane bagasse). The results demonstrate that blends containing sawdust has exhibited co-gasification reactivity, which was mainly due to the highest Na content. Additionally, Liu et al. [9] showed that the co-gasification reactivity of coal and PC was lower than that of coal char and PC.

Thus, the influence of feedstock type on co-gasification reactivity mainly depends on the physicochemical properties of coal or biomass.

4.2. Feedstock blended ratio

Coal/biomass has more developed pore structure, more disordered carbon structure, and higher AAEMs content than PC [26,58]. Therefore, the co-gasification reactivity generally increases with increasing biomass [1,26,28,43,46] or coal proportions in blends [35,57,59] (Fig. 4).

4.3. Torrefaction and hydrothermal carbonization

The disadvantages of biomass, such as low energy density, high tar yield, and high moisture, seriously limit the application of biomass gasification. Therefore, the adoption of pre-treatment methods, such as

torrefaction and hydrothermal carbonization, is crucial in overcoming these problems [60,61].

Wei et al. [1] and Zhang et al. [45] studied the co-gasification characteristics of hydrochar and PC using thermogravimetric analysis (TGA). The results showed that higher co-gasification temperature and hydrochar proportion in blends led to higher co-gasification reactivity. However, researchers have put few efforts on the PC-torrefied biomass co-gasification and the reactivity comparison between PC-raw biomass blends and PC-pretreated biomass blends. Therefore, further studies are required.

4.4. Gasification temperature

Generally, higher temperatures may improve the co-gasification reactivity [1,43,44,48,55], mainly because steam gasification and Boudouard reactions are endothermic [54]. However, Wang et al. [43] showed that increasing temperature at high temperatures had a negligible effect on the co-gasification activity. This may be explained in two ways. (i) Too high temperature caused the melting and volatilization of some metal compounds (Na₂CO₃, K₂CO₃, etc.), weakening the catalytic effect of the inherent mineral matter [62-64]. (ii) As the temperature increased, co-gasification changed from chemical reaction to diffusion-controlled regime [43,65].

4.5. Gasification agent

Edreis et al. [51] showed that the co-gasification reactivity of PC and biomass was higher under steam atmosphere than that under CO₂ atmosphere. This was mainly because the bond energy of O-H was weaker than that of C-O [66]. Moreover, the co-gasification reactivity under steam atmosphere was lower than that under O₂ atmosphere. This was mainly attributed to two factors: (i) the activation energy required for the reaction between fuel and O₂ was lower, and (ii) the reaction was exothermic [26,53,54]. Edreis et al. [26] and Azargohar et al. [32] also revealed that the co-gasification reactivities of PC and biomass/coal blends increased as the steam concentration increased (Fig. 5). This is because the diffusion of gasification agent was enhanced, resulting in the acceleration of the gas-solid reaction [43,67].

5. Synergy behavior and mechanism of PC and biomass/coal co-gasification

5.1. Synergy behavior on syngas production

Few studies have focused on the synergy behavior on syngas

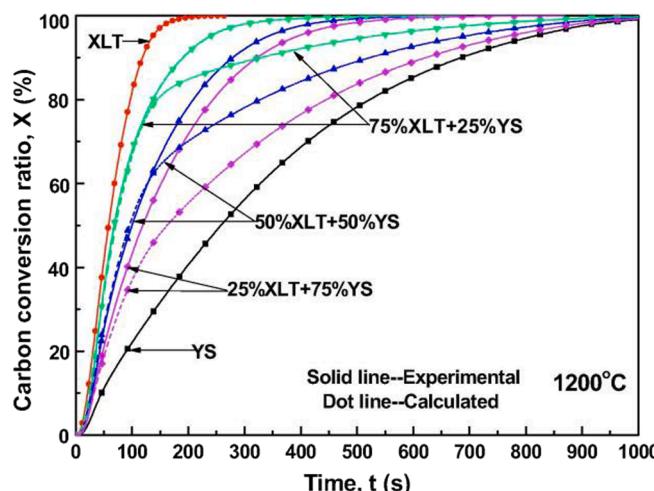
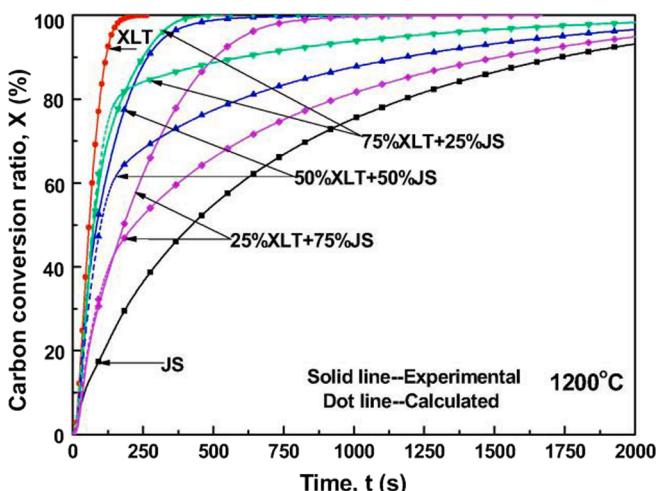


Fig. 4. Effect of blending ratio on co-gasification reactivity of low sulfur/high sulfur PC (YS, JS) with lignite (XLT) [57].



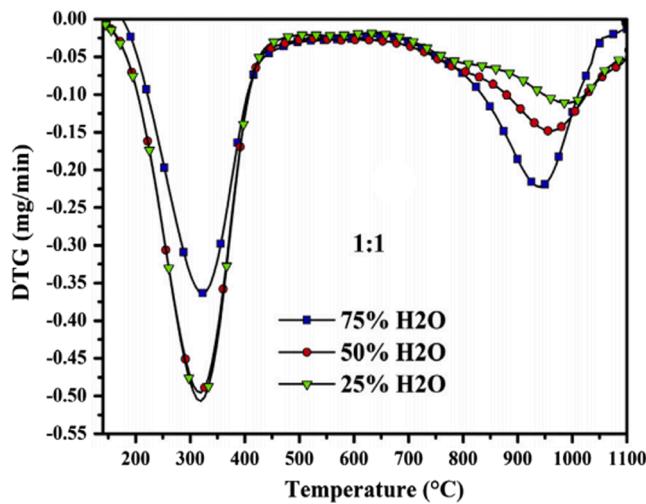


Fig. 5. Effect of steam co-gasification on the thermal behaviour of PC with sugar cane bagasse (1:1) (DTG vs. Temperature) [26].

production in PC-coal/biomass co-gasification. Huang et al. [12] confirmed that there is a synergistic effect on H₂ production during PC-coal co-gasification (Fig. 6). The main reason for it is the catalytic effect of the AAEMs (K, Ca, etc.) in coal on the WGS reaction during PC gasification [36,37].

5.2. Synergy behavior on reactivity characteristics

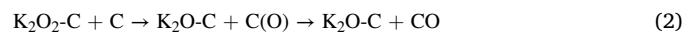
There was a slight inhibition effect or no synergy behavior on reactivity at the initial stage of biomass char and PC co-gasification [44,46,49,50]. Similar conclusions were also reported by Liu et al. [68], who conducted co-gasification studies on raw coal and PC blends. The lack of synergy behavior was mainly attributed to the incomplete formation of the biomass/coal ash [48]. Therefore, there were few chances for the intimate contact between the biomass/coal-derived AAEMs and PC at this stage. The inhibition effect in the early stage of co-gasification was due to the inactivation of AAEMs [69]. Additionally, Wang et al. [43] showed that the synergistic effect on co-gasification reactivity was initially reduced and then enhanced as the conversion increased. This showed close relationships with the AAEMs deactivation at initial stage of co-gasification and then the gradual deposition of biomass ash [1]. Generally, the synergistic effect was enhanced as biomass proportion increased due to the enhanced catalytic effect of biomass-derived AAEMs [1,28,52]. However, an excessively high biomass proportion in the blends hindered the synergistic effect due to the reduction of the carbon active sites [46]. Wei et al. [1,55] verified

that the synergistic effect weakened as the gasification temperature increased due to the enhanced volatilization and deactivation of the AAEMs.

The synergy behavior on the co-gasification reactivity of PC-coal blends was unknown. Therefore, more research is required.

5.3. Synergy mechanism on syngas production of co-gasification

The research on synergy behavior on syngas production from PC and coal/biomass co-gasification is scarce till now, besides that of Huang et al. [12]. Therefore, the synergy mechanism on syngas production in co-gasification is only speculated based on the catalytic mechanism of AAEMs on PC gasification. The key to improving the syngas production in co-gasification is the catalysis of AAEMs (K, Na, Ca, etc.) derived from coal/biomass on the chemical reaction of PC [64,70]. The carbon conversion and syngas yield of non-catalytic gasification are only determined by the amount of C(O) intermediate. However, those of catalytic gasification are also determined by M₂O-C and M₂O₂-C, in addition to C(O). (The corresponding reactions, using a K₂O catalyst as an example, are shown in Eqs. (1)–(3) [64,71]). Thus, AAEMs directly led to an increase in the number of active sites for co-gasification and a decrease in the activation energy of co-gasification [72].



Additionally, the AAEMs had catalytic effects on the WGS reaction [73,74] and inhibition effects on methanation reaction [64,75]. Consequently, syngas quality was improved with high H₂/CO ratio and low CH₄ content in syngas.

5.4. Synergy mechanism on reactivity characteristics of co-gasification

5.4.1. Non-catalytic synergy mechanism

The volatile matter contents of several typical PC, coal, and biomass are listed in Table 3. The volatile contents of biomass is generally higher than those of coal and PC and that of PC is similar to that of anthracite. There are numerous hydroxyl and carboxyl groups in the hemicellulose and cellulose of biomass, which leads to the release of numerous H and OH radicals during pyrolysis/gasification [75,76]. Some biomass/coal-derived free radicals are transferred to the PC surface with C(O) intermediate formation [71,77], and thus improve the PC gasification reactivity (Fig. 7). Li et al. [78] showed that the coal-derived free radicals led to the reduction in the order degree of the carbon structure in PC with forming more small ring structures. However, due to the lack of direct detection methods for free radicals and intermediates, the non-catalytic

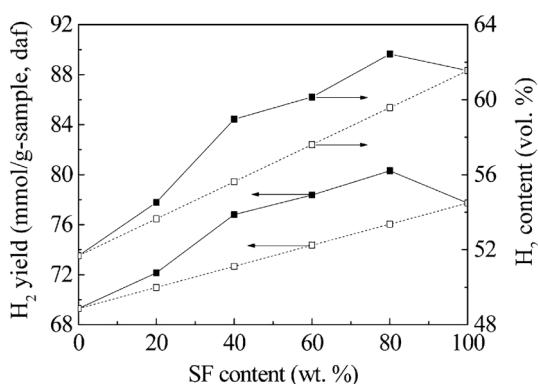


Fig. 6. Experimental and calculated H₂ yields and contents from co-gasification of PC and bituminous coal (SF) blends at the gasification temperature of 1173 K. ■ Experimental values; □ Calculated values [12].

Table 3

Volatile matter content of typical PC, coal and biomass samples (dry basis).

Source	Samples	Volatiles (%)
Huang et al. [12]	PC	9.07
<i>Coal</i>		
Huang et al. [12]	lignite	45.29
Huang et al. [12]	bituminous coal	35.21
Huang et al. [12]	anthracite	8.67
<i>Biomass</i>		
Puig-Gamero et al. [29]	almond shell	76.02
Puig-Gamero et al. [29]	olive pomace	82.48
Wang et al. [43]	millet husk	68.30
Habibi et al. [44]	switchgrass	76.90
Zhang et al. [45]	paper sludge hydrochar	63.84
Wang et al. [46]	corn cob	77.62
Masnadi et al. [49]	sawdust	87.60
Edreis et al. [54]	rice husk	67.78
Edreis et al. [54]	sugar cane bagasse	83.31

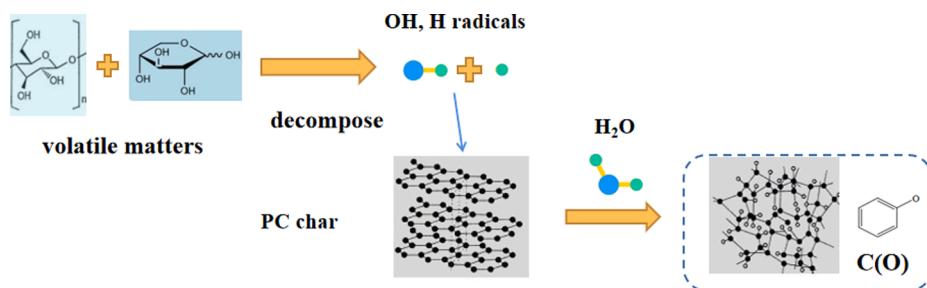


Fig. 7. Schematic diagram for the improvement of PC gasification reactivity by H/OH free radicals derived from biomass/coal.

mechanism of co-gasification based on free radicals has not been determined.

5.4.2. Catalytic synergy mechanism

The AAEMs component containing in biomass/coal is the main reason for the synergistic effect on co-gasification reactivity [26,29,42–44]. The ash contents of common feedstocks are shown in Table 4. Numerous in-depth studies on the mechanism-of-action of AAEMs components on PC gasification have been conducted. Yang et al. [79] proposed catalytic mechanism for different metal compounds, as shown in Fig. 8.

(1) Active intermediate mechanism: First, CO₂ reacts with the PC particle surface to form CO and C(O), and then C(O) is desorbed to form CO [64]. Second, metal cations capture the oxygen ions of CO and react with particle surface to form intermediate M-O-C. Consequently, there is a change in the electronic arrangement of the C atoms with the weakening of C-C bond energy [80,81].

(2) Cyclic redox mechanism: Some metal compounds, such as Na₂CO₃, react directly with carbon [82]. The corresponding reactions are as follows:



First, Na₂CO₃ directly reacts with carbon atoms to form Na vapor (as intermediate product) and CO. Afterwards, Na further reacts with CO₂ to form Na₂O and CO. The intensity of this reaction is related to the adsorption properties of the metal compounds [83].

(3) Intercalation compound mechanism: The transfer of alkali metals to PC during co-gasification leads to the formation of intercalation compounds, which break the dense carbon structure of PC into a more amorphous carbon structure. Thus, PC gasification reactivity is enhanced [82,84].

6. Kinetic models of PC and coal/biomass co-gasification

6.1. Three common kinetic models for co-gasification

Several studies have adopted kinetic models to simulate co-gasification characteristics, as shown in Table 5.

The homogeneous model assumes that the reaction occurs uniformly in the solid, along with changes in particle density and size. The formula for the gasification reaction rate with a reaction order of one is as follows [85,86]:

$$x = 1 - \exp(-kt) \quad (7)$$

$$\frac{dx}{dt} = k(1-x) \quad (8)$$

where x is the carbon conversion, k is the reaction rate constant, t is the reaction time, $\frac{dx}{dt}$ is the reaction rate.

The shrinking core model assumes that the reaction only occurs on the particle surface, and the particles gradually shrink as the reaction proceed. The gasification reaction rate is expressed as follows:

$$\frac{dx}{dt} = k(1-x)^{\frac{2}{3}} \quad (9)$$

The random pore model assumes that the particles contain randomly distributed cylindrical pores of various sizes, and the pores overlap, leading to competition for the reaction area [87,88]. The formulae for the gasification reaction rate are as follows:

$$x = 1 - \exp[-k\tau(1 + \psi k\tau/4)] \quad (10)$$

$$\frac{dx}{dt} = k(1-x)\sqrt{1 - \psi \ln(1-x)} \quad (11)$$

Table 4
Ash content and AAEMs content of typical PC, coal and biomass samples (dry basis).

Source	Samples	Ash content (%)	Ash chemical composition (%)			
			K ₂ O	Na ₂ O	CaO	MgO
Huang et al. [12]	PC	0.15	–	–	–	–
<i>Coal</i>						
Huang et al. [12]	lignite	13.13	0.34	0.13	44.29	3.93
Huang et al. [12]	bituminous coal	6.50	0.71	1.60	34.62	3.91
Huang et al. [12]	anthracite	22.08	1.15	0.61	6.52	0.80
<i>Biomass</i>						
Nemanova et al. [28]	pine pellets	0.52	23.2	1.7	33.0	5.4
Wang et al. [43]	millet husk	8.10	24.6	1.9	5.9	2.3
Habibi et al. [44]	switchgrass	6.30	20.3	1.6	6.4	6.5
Zhang et al. [45]	paper sludge hydrochar	23.74	0.74	0.48	42.76	3.04
Wang et al. [46]	corn cob char	27.22	48.36	1.49	4.15	1.73
Edreis et al. [54]	sawdust	0.40	7.76	12.84	24.89	5.56
Edreis et al. [54]	rice husk	14.91	4.6	1.78	1.15	0.47
Edreis et al. [54]	sugar cane bagasse	4.75	4.41	0.70	7.54	4.41
Edreis et al. [54]	rice stalk	17.09	17.81	0.96	7.68	2.33
Edreis et al. [54]	cotton straw	6.77	25.14	0.68	6.48	3.55

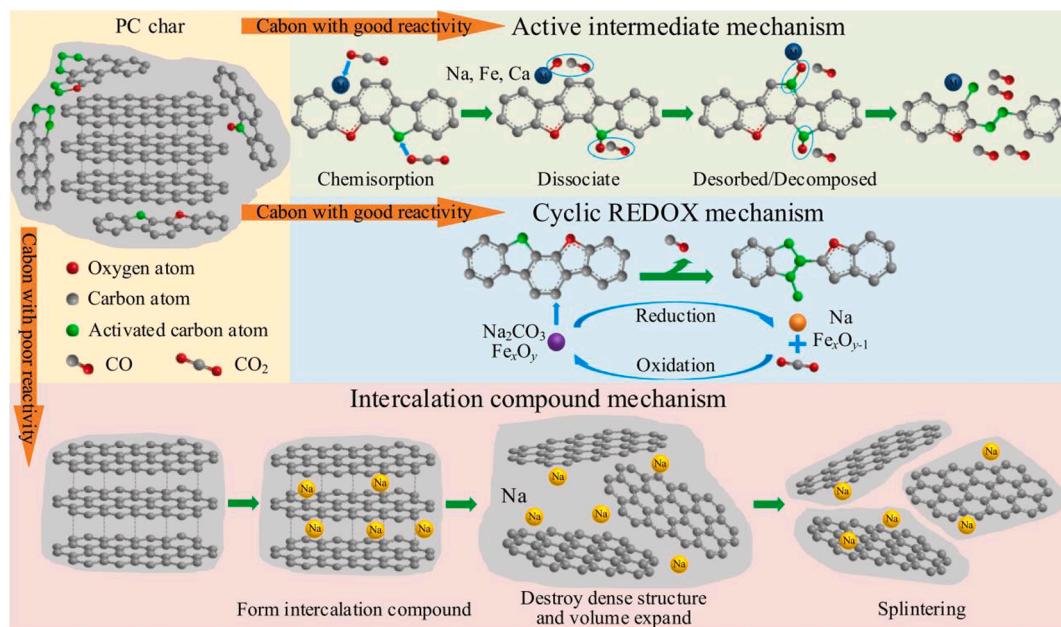


Fig. 8. Mechanism of PC catalytic gasification by metal ions and metal compounds [80].

Table 5
Summary on kinetic models used for co-gasification of PC-coal/biomass blends.

Source	Kinetic models
Edreis et al. [26]	Homogeneous model, shrinking core models
Edreis et al. [42]	Homogeneous model, shrinking core model
Wang et al. [43]	Homogeneous model, random pore model, shrinking core model
Edreis et al. [47]	Homogeneous model, shrinking core model
Fernandes et al. [48]	Random pore model
Edreis et al. [51]	Homogeneous model, shrinking core models
Edreis et al. [54]	Homogeneous model, shrinking core model

$$\tau = \frac{K_s c^n S_0 t}{1 - \varepsilon_0} \quad (12)$$

where c is the concentration of the reaction gas, n is the reaction order, τ is dimensionless time, S_0 is the initial specific surface area of the char, and ε is the structural parameter.

6.2. Analysis of kinetic results

Biomass addition reduces the apparent activation energy of co-gasification, owing to its low gasification activation energy [42,45,53,54]. Thus, the apparent activation energy of co-gasification is reduced as the biomass proportion in blends increases (Fig. 9) [42,45]. Additionally, the shrinking core model is more suitable for PC and biomass/coal co-gasification [26,42,43,51,54], which is well correlated to the structural properties of PC.

7. Conclusions

- (1) H₂-rich syngas derived from PC-coal/biomass co-gasification could be acquired in several cases. (i) feedstock with high H/C ratio or AAEMs concentrations, (ii) high coal/biomass proportion in blends, (iii) relatively low gasification temperature, and (iv) low O₂ concentration or high steam concentration in gasification agent.
- (2) Higher reactivity of PC-coal/biomass co-gasification could be acquired in several cases. (i) coal/biomass with more disordered

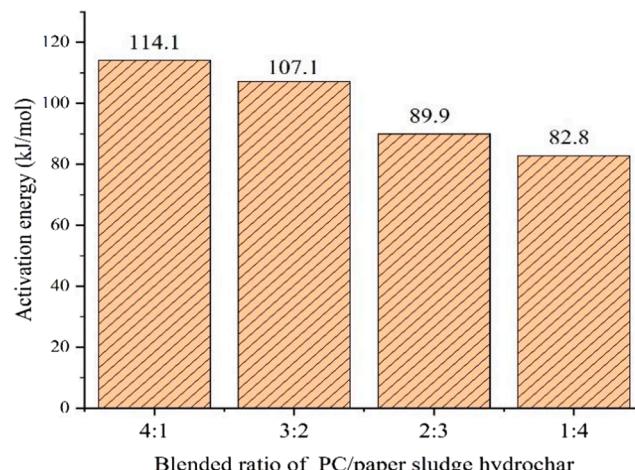


Fig. 9. Activation energy of PC and paper sludge hydrochar co-gasification with different blended ratios [45].

carbon structures, more developed pore structures and higher AAEMs concentrations, (ii) higher coal/biomass proportion in blends, (iii) higher gasification temperature, and (iv) higher O₂ or steam concentration in gasification agent.

- (3) The synergy behavior on co-gasification reactivity of PC-biomass blends varied as reaction proceeded, i.e., no synergy behavior or slight inhibition effect/synergistic effect at the initial reaction stage, and relatively obvious synergistic effect at the mid-late reaction stage. Additionally, the overall synergistic effect was enhanced as biomass proportion in blends increased and gasification temperature decreased.
- (4) The synergy mechanism of PC-coal/biomass co-gasification showed great relationships with the migration and transfer of free radical and inherent AAEMs.
- (5) The activation energy of co-gasification reduced as PC proportion in blends reduced. Moreover, shrinking core model was verified as the most suitable kinetics model for predicting PC-coal/biomass co-gasification reaction.

8. Future perspectives

- (1) Gasification temperature is the crucial operation parameter for industrial gasifiers. Higher temperature is favorable for enhancing co-gasification reactivity, but would hinder WGS reaction meanwhile. Therefore, the optimal co-gasification temperature should be determined in future studies by considering the above two aspects.
- (2) The study on synergy behavior on syngas production of PC-coal/biomass co-gasification and reactivity characteristics of PC-coal co-gasification are especially insufficient. Thus, further research should be carried out.
- (3) Free radical (OH, H, etc.) is one of the main factors influencing co-gasification characteristics. However, the mechanism of free radical transfer during co-gasification is still unknown due to the lack of detection methods of free radical. Therefore, it is meaningful to design a bench-scale gasification reactor coupled with an in-situ free radical detector.
- (4) TGA is the most common method for exploring the reactivity and kinetics of PC-coal/biomass co-gasification at present. However, the disadvantages of TGA such as micro-scale and slow heating rate seriously limit its applicability to practical application. Therefore, researchers should adopt fixed bed, fluidized bed or drop tube reactors to investigate the co-gasification characteristics on a larger scale.
- (5) AAEMs are the key factors affecting co-gasification activity and synergy behavior. However, the complicated mineral matter composition in coal/biomass leads to the unknown catalytic mechanism of AAEMs in co-gasification. Additionally, the transfer pathway of AAEMs during co-gasification remains unclear.
- (6) The current kinetic study ignored the binary particle interaction during co-gasification. Thus, it is critical to involve parameters related to the synergy behavior in the kinetics model of co-gasification to provide a direct, accurate prediction of co-gasification reaction behavior.

Declaration of Competing Interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2021.121517>.

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