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# Progress on the Co-Pyrolysis of Coal and Biomass

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## Abstract

In this chapter, the synergistic mechanism and the resulting influence during co-pyrolysis of coal and biomass, are summarized. The properties of coal and biomass, the release and migration of alkali and alkaline earth metals (AAEMs), the interaction between volatile and char, the characteristics of the resulting volatiles, and the physicochemical structure and reactivity of co-pyrolysis char, are also analyzed. In addition, the influence of AAEMs on the properties of the co-pyrolysis products is reviewed. Moreover, the analysis of the co-pyrolysis industry demonstration is also mentioned. Finally, this chapter also proposes some additional possibilities, based on further literature research.

**Keywords:** Co-pyrolysis, Coal/Biomass, Characteristics of co-pyrolysis products, Volatiles-char interaction, Alkali and alkaline earth metals

## 1. Introduction

Energy supply is the fundamental basis for rapid economic growth and sustainable social development. Due to abundant reserves of coal worldwide, it has been become one of the most important fossil fuels of the past two centuries, and may continue to be used, somewhat, for up to an additional 200 years in the future [1]. However, the use of coal can cause serious environmental problems. For example, sulfur dioxide and nitrogen oxides produced while burning coal can pollute the air and water, and are extremely harmful to humans, animals, and other organisms. In addition, coal burning is one of the main sources of greenhouse gas (GHG) emissions, accounting for at least 20–30% of total CO<sub>2</sub> emissions [2].

Biomass energy, resulting from natural photosynthesis, represents a renewable form of energy, and is the fourth largest energy source after coal, oil, and nature gas [3]. It can supply about 14% of the world's energy consumption, and about 38% of the energy consumption in developing countries [4, 5]. Because of its green, low-carbon, clean and renewable characteristics, it has become one of the most important sustainable energy sources [6, 7]. In order to actively respond to climate change, China has announced that it intends to reach its national CO<sub>2</sub> emission peak before 2030, and thereafter achieve carbon neutrality before 2060 [8]. Under this background, biomass energy, as a zero-carbon energy source, will play an important role, and the biomass energy industry will usher in a period of major development opportunities. At present, China produces about 6.3 billion tons of various organic wastes (including: agricultural and forestry residues, domestic waste, domestic

sludge, livestock and poultry manure, fruit and vegetable residues, and industrial organic waste liquids) every year; this organic waste is equivalent to about 800 million tons of standard coal. Of this total amount of organic waste, it is estimated that the amount of biomass resources that can be utilized as an energy source in China each year, is approximately equal to 460 million standard tons of coal [9]. Among these, the amount of agricultural waste is about 400 million tons, which is equivalent to about 200 million tons of standard coal. The amount of forestry waste is about 350 million tons, which is also equivalent to about 200 million tons of standard coal. The remaining organic wastes are equivalent to about 60 million tons of standard coal. The development of biomass energy can result in the utilization of eco-friendly, sustainable energy, and also reduce pollution due to the inappropriate discarding of organic wastes; it can also realize the utilization of an otherwise ignored energy resource. More importantly, the utilization of biomass energy cannot only assist in achieving carbon neutrality, but can also result in “negative” carbon emissions when biomass energy is utilized via carbon capture and storage (BECCS). However, biomass has its drawbacks, such as seasonal harvest rather than year-round availability, wide distribution, low energy density, and high transportation costs [10]. These shortcomings, especially the limited supply of biomass raw materials, currently restrict its large-scale industrial application in China. Unfortunately, China’s current utilization of organic waste energy is less than 5%. But if China can expand its use of available biomass, it can begin to reduce its use of coal.

The co-utilization of coal and biomass can not only reduce the pressure of coal supply and environmental problems, but also save the cost of building direct biomass utilization equipment. In terms of fuel characteristics, coal and biomass also have a great possibility to complement one another. In order to utilize them on a large, efficient scale, the co-utilization of coal and biomass may offer a potential benefit, as a promising technical method. As the initial stage of thermal chemical conversion, the co-pyrolysis process of coal and biomass is very important, since it determines the formation characteristics, structures, and properties of volatiles (gas products), tar (liquid products) and char (solid products). The main components of biomass pyrolysis are volatiles and tar; in comparison, the main component of coal pyrolysis is char, which can reach 40–60%. When biomass is combined with coal, the yield of char is affected by the ratio during the co-pyrolysis of biomass and coal. The reaction of the solid phase product (co-pyrolysis char) is the slowest step in the whole thermochemical conversion process, and its reaction rate determines the rate of the whole thermochemical reaction. On the one hand, during co-pyrolysis, the volatiles produced from the biomass and coal, can interact with the co-pyrolysis char, which leads to changes in the properties of the resulting char and volatiles. On the other hand, the changes in the properties of the char and volatiles, can also affect the interactions between volatiles and co-pyrolysis char. The two are interrelated and influence each other. Therefore, during co-pyrolysis, it is very important to study the interactions between the resulting volatiles and char.

Compared to coal, biomass contains more CaO, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, MgO, Na<sub>2</sub>O and Mn, and less SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> and TiO<sub>2</sub>. Among these, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> belong to alkali and alkaline earth metals (AAEMs) [11]. The content of the alkali and alkaline earth metal oxides in biomass ash exceeds 27%, while the content in coal ash is only 6–10%. The content of silicon and aluminum oxides in biomass ash is 22–57%, while the content in coal ash exceeds 80% [12, 13]. AAEMs play an important role in the process of coupling utilization of coal and biomass, and are good catalysts for combustion and gasification reactions, which can significantly affect the reactivity of the resulting co-pyrolysis char [14]. The presence of AAEMs can affect the dynamic pyrolysis process, and has a direct catalytic effect on the cracking of volatiles and their precursors. However, due to the diversity and

superimposition of the reactions, the nature of the interactions between coal and biomass during co-pyrolysis has not been fully understood, especially the catalytic influence of AAEMs, including the influence mechanism of AAEMs on the volatiles generation, the influence of AAEMs on the interaction between volatiles and char, and the influence of AAEMs on the co-pyrolysis char reaction. Therefore, the chemical mechanism of AAEMs during co-pyrolysis is one of the key issues that needs to be investigated further, regarding the basic research of coal and biomass co-utilization.

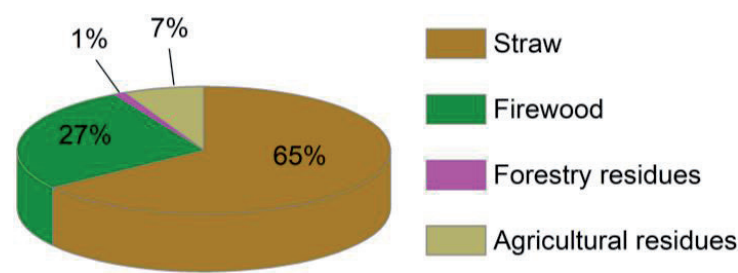
In this chapter, a comprehensive overview of the co-pyrolysis of coal and biomass is presented. The focus of interest is mainly on the chemical mechanisms, during co-pyrolysis. The properties of coal and biomass, the synergistic mechanism, the release and migration of AAEMs, the interactions between volatiles and char, the volatiles production characteristics, the physicochemical structures and reactivity of co-pyrolysis char, are analyzed in this chapter. Moreover, the influence of AAEMs on the properties of the co-pyrolysis products, is also presented.

## **2. Properties of coal and biomass**

Coal is an extremely complex and heterogeneous mixture composed of organic macromolecules and inorganic minerals [11]. It was formed by ancient plants, buried in the ground and experienced complex chemical changes at high temperatures and pressures. The transformation process involved the loss of hydrogen and oxygen and the condensation of carbon. “Coal” can be divided into peat, lignite, bituminous, and anthracite coals, according to the stage of formation and degree of coalification. Although peat is fuel, it is not actually coal, but a “pre-coal”. The main components of the organic macromolecular networks of coal are carbon, hydrogen, oxygen, nitrogen, and sulfur. Calculated by weight, carbon is the main component, accounting for 60% - 95% of the total weight. The carbon content of most coals is below 90%, and the hydrogen content is generally around 5%, while the hydrogen content of coals containing 95% carbon drops to about 2% [15]. The nitrogen content of coals is generally between 1% - 2%. Sulfur is also a very important component of most coals, accounting for 1–4%. The oxygen content is inversely proportional to the carbon content, that is, the higher the carbon content in coal, the lower the oxygen content. The oxygen content in coal is important because coal with more oxygen is more likely to catch fire. Carbon in coal mainly exists in two forms, namely fixed carbon or volatile matter. The ratio of fixed carbon to volatile matter determines the rank of coal [16]. Inorganic minerals account for a small proportion in the overall composition of coal. However, AAEMs in the minerals have obvious catalytic effects on the thermochemical conversion reaction of coal [14, 17].

A wide range of biomass fuels are available in the environment, ranging from wood to materials derived from herbaceous plants and straw. Usually, biomass fuels are classified according to their source and properties. Biomass can be divided into primary residues, secondary residues, tertiary residues, and energy crops according to their sources [18]. Primary residues include biomass such as wood, straw, grain, and corn, which are usually obtained as by-products from forest products and food crops [19]. Secondary residues are derived from biomass materials used in industrial products and food production, such as sawmills, paper mills, food and beverage industries, apricot and other fruit seeds. Tertiary residues include waste materials and dismantled timber, from other previously used biomass materials [20]. Energy crops may include willow, poplar, switchgrass, and miscanthus grass. In addition, biomass can be divided into four types based on properties: woody biomass, herbaceous biomass, organic waste, and aquatic biomass (such as kelp) [21]. Among all these types





**Figure 1.**  
*The proportions of four types biomass with the largest reserves.*

of biomass, the four types of biomass with the largest reserves are straw, firewood, forestry residues, and agricultural residues; their proportions are shown in **Figure 1**.

Biomass is mainly composed of cellulose, hemicellulose, and lignin. Generally, lignocellulosic biomass contains about 35–55% cellulose, 20–35% hemicellulose, and 10–30% lignin [15]. Cellulose is a linear polymer formed by the connection of glucose molecules through ether bonds, which is the most abundant carbohydrate in nature and the main component of plant plasm cells. It decomposes in the temperature range of 240–350°C. Hemicellulose is a mixture of different polysaccharides with a low degree of polymerization and no crystal structure, so it is easily hydrolyzed. The thermal degradation of hemicellulose occurs at temperatures between 130°C and 260°C, mainly above 180°C. Lignin is composed of hydroxyphenyl propane, guaiacyl propane and syringyl propane. These monomers are formed by disordered combination of C-C bonds and C-O bonds through dehydrogenation polymerization. Lignin decomposes over a wide temperature range of 280–500°C.

There are significant differences between biomass and coal in proximate analysis, ultimate analysis, calorific value, ash composition, physical structure, chemical structure, and reactivity. The key differences in the properties of biomass in comparison with coal (see **Tables 1** and **2**) are [6, 11, 24–26]: (1) more moisture and volatiles, less fixed carbon and ash content; (2) more O, H and Cl, less C, N and S; (3)

Fuel	Ultimate analysis (db.% w/w)					Proximate analysis (% w/w)			LHV (MJ/kg)	
	C	H	O	N	S	Ash	VM	FC	M	
Rice husk	35.20	4.79	59.00	1.01	—	9.40	66.12	13.80	10.65	13.12
Bamboo dust	43.45	5.49	50.74	0.33	—	2.68	70.83	15.62	10.87	14.85
Wood Sawdust	42.30	5.17	51.73	0.80	—	1.40	69.29	17.84	11.37	12.86
Cedar wood	51.10	5.90	42.50	0.12	0.02	0.30	80–82	18–20	—	19.26
Olive–oil residue	50.70	5.89	36.97	1.36	0.30	4.60	76.00	19.40	9.50	21.20
Rice straw	38.61	4.28	37.16	1.08	0.65	12.64	65.26	16.55	5.58	14.40
Pine sawdust	50.54	7.08	41.11	0.15	0.57	0.55	82.29	17.16	—	20.54
Spruce wood pellet	49.30	5.90	44.40	0.10	—	0.30	74.20	17.10	8.40	18.50
Marc of grape	49.66	5.56	34.42	2.23	0.14	7.83	65,77	26.40	—	19.51
Coffee husk	46.80	4.90	47.10	0.60	0.60	1.00	74.30	14.30	10.40	16.54
Coffee ground	52.97	6.51	36.62	2.80	0.05	1.00	71.80	16.70	10.50	22.00
Larch wood	44.18	6.38	49.32	0.12	—	0.12	76.86	14.86	8.16	19.45
Grapevine Pruning waste	46.97	5.80	44.49	0.67	0.01	2.06	78.16	19.78	—	17.91

Fuel	Ultimate analysis (db.% w/w)					Proximate analysis (% w/w)			LHV (MJ/kg)	
	C	H	O	N	S	Ash	VM	FC	M	
Jute stick	49.79	6.02	41.37	0.19	0.05	0.62	76–78	21–23	—	19.66
Sugar–cane bagasse	48.58	5.97	38.94	0.20	0.05	1.26	67–70	29–31	—	19.05
Corn cob	40.22	4.11	42.56	0.39	0.04	2.97	71.21	16.11	9.71	16.65
Peach stone	51.97	5.76	40.70	0.79	0.01	0.65	81.30	18.10	8.53	21.60
Wheat straw	46.10	5.60	41.70	0.50	0.08	6.01	75.80	18.10	—	17.20
Cotton stem	42.80	5.30	38.50	1.00	0.20	4.30	72.30	15.50	7.90	15.20
Straw	36.55	4.91	40.70	0.55	0.14	8.61	64.98	17.91	8.50	14.60
Camphor wood	43.43	4.84	38.53	0.32	0.10	0.49	72.47	14.75	12.29	17.48
Beech wood	48.27	6.36	45.20	0.14	—	0.80	81.00	18.00	—	19.20
Switchgrass	47.00	5.30	41.40	0.50	0.10	4.60	58.40	17.10	20.00	18.70
Petroleum coke	92.30	3.40	0.70	0.95	1.17	1.40	6.00	92.10	0.50	36.20
Lignite coal	44.66	3.66	13.90	1.0	0.21	18.42	35.17	28.27	18.4	18.05
Bituminous coal	74.73	4.43	13.68	1.02	0.19	4.08	36.95	56.90	2.07	28.05
Lean coal	66.05	3.25	2.53	1.17	0.19	25.30	20.65	53.15	0.92	24.14
Quinsam mine coal	80.30	5.50	12.60	0.9	0.70	12.90	38.80	49.10	4.20	26.99
Sub-bituminous coal	73.10	4.30	21.10	1.0	0.40	30.50	31.30	38.30	17.5	20.10
Indonesian coal	72.13	6.67	19.58	1.40	0.22	8.39	36.84	42.36	12.42	20.79
Anthracite coal	86.56	4.90	6.20	1.70	0.61	13.71	31.71	54.58	0.34	26.00
Shenmu coal	70.35	4.56	10.53	1.04	0.55	9.19	28.51	58.52	3.78	27.08
Assam coal	61.37	5.27	28.18	0.94	4.24	10.0	40.50	47.50	2.00	22.55

*db: dried basis.*

**Table 1.**  
*Ultimate and proximate analysis of different coal and biomass [22].*

Fuel	Ash composition (wt. %)									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	TiO <sub>2</sub>
Switchgrass (Manitoba, Canada)	52.50	2.10	6.40	0.30	20.30	6.50	1.60	5.00	0.02	2.60
Rice straw (Hubei Province, China)	51.99	0.91	7.68	0.84	17.61	2.33	0.96	2.49	0.04	6.50
Sawdust (Hubei Province, China)	16.47	6.50	24.89	4.57	7.76	5.56	12.84	2.42	0.58	7.64
Pine biomass (Statoil, Norway)	12.80	1.00	33.00	1.70	23.20	5.40	1.70	5.30	—	—
Corn stalks (Heilongjiang Province, China)	29.03	0.83	14.34	1.26	29.41	18.38	0.60	3.00	1.60	0.02
Sub-bituminous coal (Genesee, Alberta, Canada)	57.60	23.60	5.60	2.80	0.80	1.30	2.60	0.10	0.50	2.30

Fuel	Ash composition (wt. %)									
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	TiO <sub>2</sub>
Lignite coal (Inner Mongolia, China)	65.79	14.73	4.33	2.67	1.71	1.44	1.04	0.97	0.50	6.67
Bituminous coal (NSW, Australia)	47.90	26.50	7.90	7.50	0.20	0.60	0.10	1.30	1.90	6.10
Lean coal (Inner Mongolia, China)	53.99	28.44	4.07	3.22	1.56	0.88	2.97	0.97	1.82	4.00
Sub-bituminous coal (Shaanxi province, China)	53.85	11.55	13.94	10.96	0.79	1.38	0.13	0.47	2.65	0.74

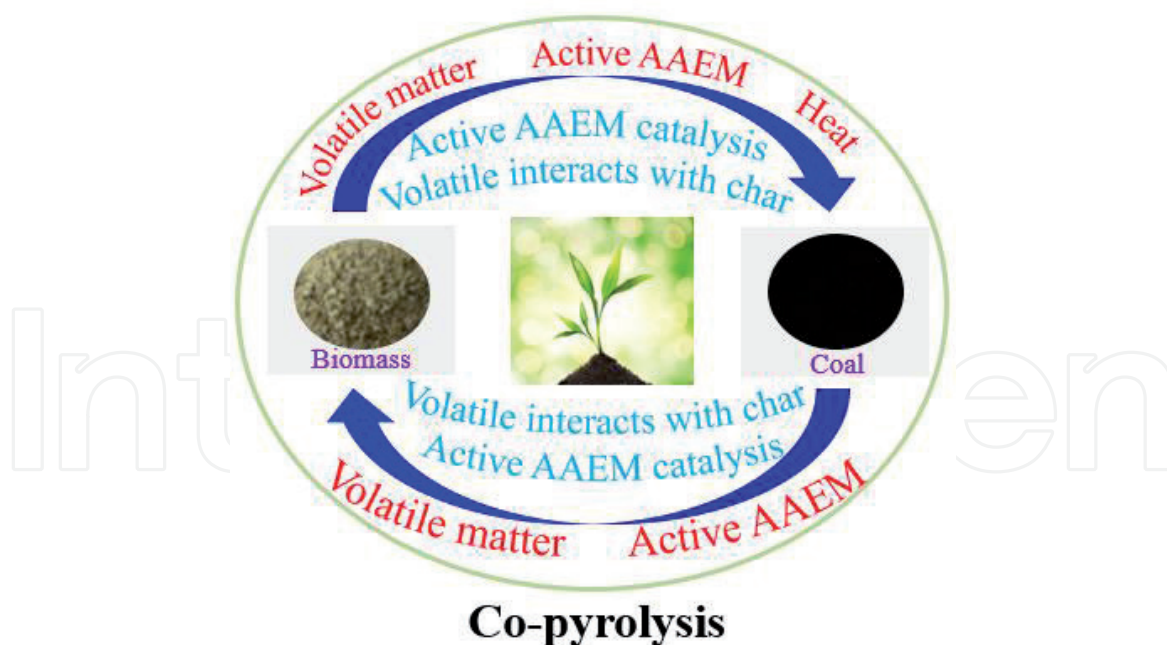
**Table 2.**  
*Ash composition analysis of different coal and biomass (wt%) [22, 23].*

lower calorific value; (4) higher alkali content (especially the herbaceous biomass); (5) lower bulk density, larger specific surface area, more abundant pore structure; (6) more oxygen-containing functional groups (hydroxyl, carboxyl, ether and ketone) with highly reactive groups (–COOH, –OCH<sub>3</sub> and –OH), complexes, light hydrocarbons, carbohydrates, hydroxyl oxides, carbonates, chloride and phosphate, and lower aromatics, functionality, silicate and sulfide; (7) higher reactivity.

**3. Analysis of the synergistic mechanism of the co-pyrolysis of coal and biomass**

The differences in the characteristics of coal and biomass determines their different pyrolysis characteristics. During the pyrolysis process, volatiles and char can interact with each other, and AAEMs can also be released and migrated. Coal and biomass are mixed during pyrolysis, so the volatiles, char and released AAEMs from the pyrolysis of both are also mixed. As a result, there may be synergies between coal and biomass during co-pyrolysis. The synergies may be caused by several factors. First, the H/C ratio of biomass is higher than that of coal, so H<sub>2</sub>, OH and H radicals generated by biomass pyrolysis can migrate to the surface of coal during co-pyrolysis. Additional hydrogen donors may prevent the recombination and cross-linking reaction of free radicals, thus promoting coal decomposition to produce more volatiles [27]. Second, the content of AAEMs in biomass is higher than that in coal, especially the alkali metals [28]. AAEMs in biomass can migrate to the coal matrix during co-pyrolysis, and AAEMs can catalyze the pyrolysis and gas phase reaction of the coal [29]. Third, the heat transfer between coal and biomass may also cause synergistic effects during co-pyrolysis [30]. **Figure 2** shows the factors leading to synergies during co-pyrolysis of coal and biomass.

Typical pyrolysis temperatures for coal are between 350 °C and 650°C, while that of biomass are between 200°C and 400°C. During batch co-pyrolysis, the combination of the free radicals, especially stable and volatile radicals, lead to a reduction in both radical concentration and mass loss. In addition, the main temperature range of free radical interaction was 380°C ~ 600°C [32]. When the heating rate is slow enough, the pyrolysis of coal and biomass may occur independently from each other, and can be clearly distinguished. The synergistic effects could be limited, so it is easier to observe the additive effect. However, Wu et al. [33] observed that the thermogravimetric curve is not equal to the accumulation of the thermogravimetric



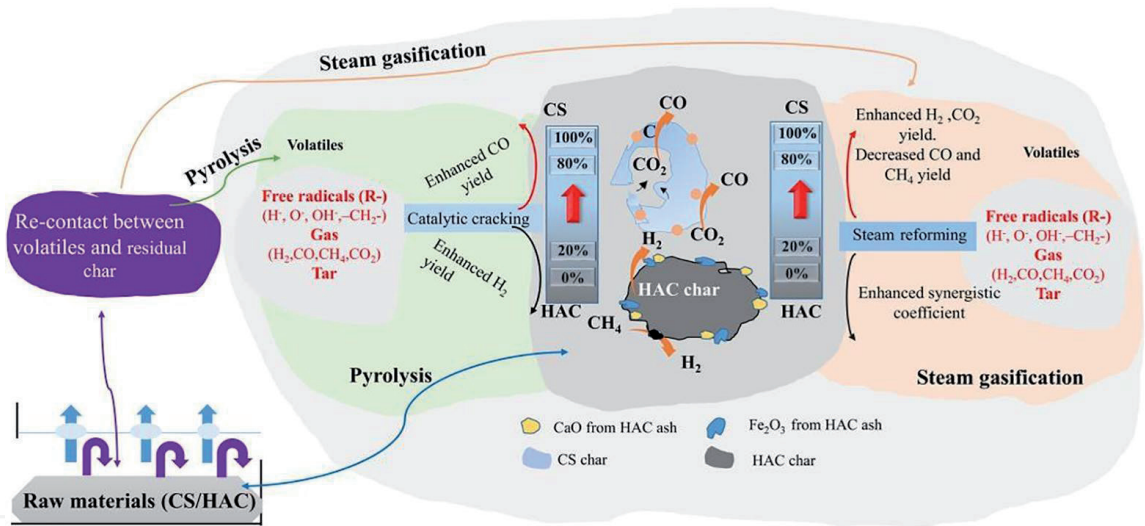
**Figure 2.**  
*Factors leading to synergies during co-pyrolysis of coal and biomass [31].*

curve of the parent fuels, which indicated that there may be synergistic effects during co-pyrolysis. Even in the slow pyrolysis process, the migration of AAEMs can also occur. If the biomass is in close contact with the coal, the migration process is more obvious, and the catalytic effects of AAEMs on volatiles are more prominent. During slow co-pyrolysis of coal and biomass, when the biomass is in the main pyrolysis stage, coal is in the initial pyrolysis stage, and the volatiles generated by the biomass pyrolysis can interact with coal char. When coal is in the main pyrolysis stage, and biomass is in its secondary degassing stage, the volatiles produced by coal pyrolysis can also interact with biomass char [34]. Therefore, during the slow pyrolysis process, even if the main pyrolysis stages of coal and biomass are independent of each other, there are still synergistic or inhibitory effects.

During co-pyrolysis, when the heating rate is fast enough, the pyrolysis processes of coal and biomass can occur simultaneously, and the release of volatiles also overlap. The interaction between volatiles and co-pyrolysis char generated from coal and biomass can occur more easily through the following processes. The volatiles produced by biomass pyrolysis are rich in OH free radicals, H free radicals, and a small amount of other free radicals, which can move to the surface of the coal char, and enter into the char matrix [35]. A large number of fragment structures produced by depolymerization and decomposition of the coal matrix are combined with the above-mentioned small free radicals derived from biomass volatiles, which can inhibit the secondary cracking reaction [34]. In addition, AAEMs contained in biomass volatiles can be moved to the coal char, and AAEMs can significantly promote secondary cracking of volatiles generated from coal pyrolysis [36]. The volatiles produced by coal pyrolysis pass through the surface of the biomass char during the release process, and are catalyzed by AAEMs attached to the surface of biomass char to generate small molecular gases and macromolecular structures. The small molecular gases directly escape, due to their small steric hindrance, but the macromolecular structures remain in the biomass char matrix, and merge with it to form solid products [34]. From literature references since 2010, on the rapid co-pyrolysis of coal and biomass, it can be found that 83% of the studies reported that there are synergistic effects [11]. Yang et al. [37] researched the synergistic effect of cotton stalk (CS) and high-ash coal (HAC) on gas production during co-pyrolysis/gasification, and summarized the main reasons for the synergistic effect.



1. Higher pyrolysis temperature and narrow space were conducive to the diffusion of biomass-derived AAEMs during co-conversion. At high temperatures, the intermediate products from pyrolysis/gasification may participate in the reforming reaction, and produce non-condensable gases ( $H_2$ ,  $CO$ ,  $CO_2$  and  $CH_4$ ). As shown in **Figure 3**, changing the flow mode can prolong the contact time between volatiles and residual char (heterogeneous volatilization-char reaction), thereby increasing the yield of  $H_2$  and  $CO$ , and reducing the yield of  $CO_2$ .
2. During the co-pyrolysis of coal and biomass, the biomass would be rapidly decomposed, and the biomass tar would be adsorbed onto the active sites of the residual char. As the proportion of cotton stalk in the mixture increases, the  $CO$  yield increased. This may be because AAEMs in the char promoted the decomposition of residual tar on the char (tar  $\rightarrow H_2$ ,  $CO$ ; R(1) and R(2), see **Table 3**) [38]. In addition, the  $CO_2$  generated inside the carbon matrix reacted with the char to expand the pores, while the light volatiles reacted with the char on the surface of the char, and consumed the carbon matrix (R(4)) [39]. Moreover, methane reforming (R(7)) and methane decomposition (R(8)) were performed simultaneously at high temperatures.



**Figure 3.** Synergistic mechanisms and reactions in the co-pyrolysis/gasification of CS and HCS [37].

	Reactions	Number
First step	$CS/HCS \rightarrow Gas (H_2, CO, CO_2, CH_4, \text{ and others}) + Tar (C_nH_m) + char$	R(1)
Second step	$Tar (C_nH_m) \rightarrow Gas (H_2, CO, CO_2, CH_4, \text{ and others})$	R(2)
	$Char + H_2O \rightarrow H_2 + CO; Char + 2H_2O \rightarrow 2H_2 + CO_2$	R(3)
	$Char + CO_2 \rightarrow 2CO$	R(4)
	$CO + H_2O \rightarrow H_2 + CO_2$	R(5)
	$CH_4 + H_2O \rightarrow 3H_2 + CO; CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$	R(6)
	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	R(7)
	$CH_4 \rightarrow C + 2H_2$	R(8)

**Table 3.** Important reactions in the co-pyrolysis/gasification of CS and HCS [37].

3. The catalysis of AAEMs in cotton stalk can be enhanced by the addition of H<sub>2</sub>O vapor to promote the reaction of active OH, H and –CH– free radicals with high-ash coal, thereby accelerating the C=C cleavage [28, 40]. During co-gasification, with the increase of cotton stalk ratio, the contents of H<sub>2</sub> and CO<sub>2</sub> increased, while the contents of CO and CH<sub>4</sub> decreased. This was due to the promoted heterogeneous carbon-vapor reactions (R(3) and R(4)) [41], water-gas shift reaction (R(5)), and homogeneous hydrocarbon reforming reactions (R(6) and R(7)) by inherent AAEMs [42].

#### 4. Release and migration of AAEMs from biomass to coal during co-pyrolysis/co-gasification

AAEMs are easy to volatilize when participating in thermal conversion reactions of fuels [43]. In particular, alkali metals have been recognized for a long time to play a key role in the formation of deposits on the heat exchange surfaces of boilers in power stations [44–46]. In addition, the residual AAEMs in char could be effective catalysts for char reactions [43]. Therefore, understanding the release and migration behavior of AAEMs during gasification may assist in the development of AAEMs control technology, to effectively improve char reactivity.

AAEMs in coal and biomass can be divided into three forms: water-soluble state, ion-exchangeable state, and insoluble state. Water-soluble AAEMs and ion-exchangeable AAEMs are collectively called active AAEMs, while insoluble AAEMs are called inert AAEMs [31]. During the process of thermochemical conversion of fuel, active AAEMs can play a prominent catalytic role [14].

During the gasification process, the release of active AAEMs is not only due to evaporation to the gas phase, in the form of inorganic salts such as KCl and NaCl, but also due to release through substitution reactions. During high temperature pyrolysis, a large number of free radicals are generated, which can replace AAEMs bonded to the organic carboxyl group or other functional groups in the form of chemical bonds. It causes the chemical bonds between the char matrix and AAEMs to break, and AAEMs to be released. It is usually approximated by the following reaction [35]:

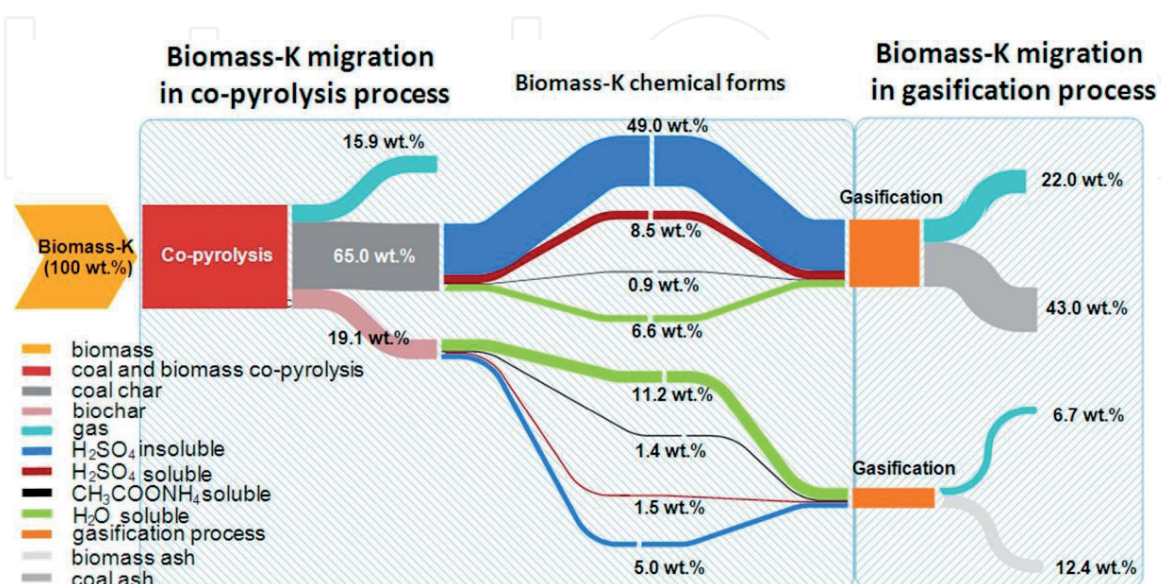


where CM stands for the char matrix, X stands for AAEMs, and R stands for free radical. The valence of the element is another factor affecting the release of AAEMs. Generally, the alkali metals (Na and K) bonded with the functional groups by single bonds are more likely to be released than the alkaline earth metals (Ca and Mg) bonded by double bonds [28, 47]. In addition, the higher the pyrolysis temperature and heating rate, the more AAEMs are released from the coal and biomass [48–50].

However, the migration of AAEMs during co-gasification of coal and biomass is very different from that of coal or biomass gasification alone, and coal could be a key factor for AAEMs migration. Wei et al. [51] pointed out that the co-pyrolysis process mainly promoted the transfer of active K in the co-pyrolysis char, which weakened with the increase of biomass content in the mixture, but the transfer of active Ca was affected by the type of fuel. Ellis et al. [52] pointed out that the catalytically active calcium in biomass minerals and aluminosilicate minerals in coal can react to produce catalytically inert chabazite crystals during co-pyrolysis. Meng et al. [53] found that the content of AAEM in co-pyrolysis char increased with the increase of biomass ratio in the mixture, which was consistent with the conclusions obtained by Weiland et al. [54, 55]. Zhang et al. [10] indicated that K in biomass could be transferred to the surface of coal char during co-pyrolysis and

co-gasification. Chen et al. [56] reported that the presence of coal during co-pyrolysis was not conducive to the volatilization of K and Mg in biomass, but the mixing of coal and corn stalks was conducive to the volatilization of Ca. Guanghui Hu [57] found that during co-pyrolysis of coal and biomass, the amount of K/Na in the biomass released into the gas phase was reduced, and the higher the pyrolysis temperature, the higher the content of K/Na in the char. Tao Ding [58] also found that the volatile amount of K/Na during the co-gasification process of coal and biomass was far less than that during the separate gasification process. Changchun Hu [59] believed that when the co-pyrolysis temperature of coal and biomass exceeded 460°C, the migration of K and Na would occur. In addition, during the subsequent gasification process, the K and Na migrated from the biomass to the coal char could combine with the minerals in coal and be fixed in the ash. It can be concluded that the coupled utilization of coal and biomass can alleviate the high temperature corrosion caused by the release of alkali metals when biomass is used alone. Lin et al. [60] concluded that co-pyrolysis under moderate temperature strongly favored inhibiting potassium from releasing, probably by interfering with free radical reactions. Song et al. [61] researched the migration path of K in biomass during thermal co-processing of coal and biomass (see **Figure 4**), and found that the mixed raw materials released 84.1 wt% (coal char 65.0 wt%, biochar 19.1 wt%) of biomass-K into the co-pyrolysis char, while only 15.9 wt% of biomass-K was released into the gas phase. The biomass-K migrated from the biomass to the coal char, and biochar was in the water-soluble (6.6 and 11.2 wt %, respectively), acetic acid-soluble (0.9 and 1.4 wt%, respectively),  $\text{H}_2\text{SO}_4$ -soluble (8.5 and 1.5 wt%, respectively), and  $\text{H}_2\text{SO}_4$ -insoluble (49.0 and 5.0 wt%, respectively) forms. After gasification, biomass-K accounted for 28.7% wt% in gas phase and 55.4 wt% in ash. Masnadi et al. [62] proposed four possible ways to lose active K during co-gasification: (1) volatilization; (2) forming inert alkali silicate; (3) forming new inert minerals (such as  $\text{KAlSiO}_4$ ,  $\text{KAlSi}_3\text{O}_8$ ) through irreversible reaction with minerals or ash in coal; (4) diffusion or implantation from the reaction surface into the carbon matrix.

During the co-utilization of coal and biomass, in addition to the migration of K from the biomass, the remaining AAEMs in coal and biomass also migrate, but their chemical forms and their migration pathways are not clear. In addition, the migration of AAEMs in coal and biomass to the surface of char and their distribution in



**Figure 4.** Material flow of the biomass-K migration during thermal co-processing of coal and biomass. (pyrolysis:  $\text{N}_2$  atmosphere, 1173 K; gasification: 1173 K, flow rate of  $\text{H}_2\text{O}/\text{O}_2 = 70/30$  mL/min, gasification time = 20 min) [61].

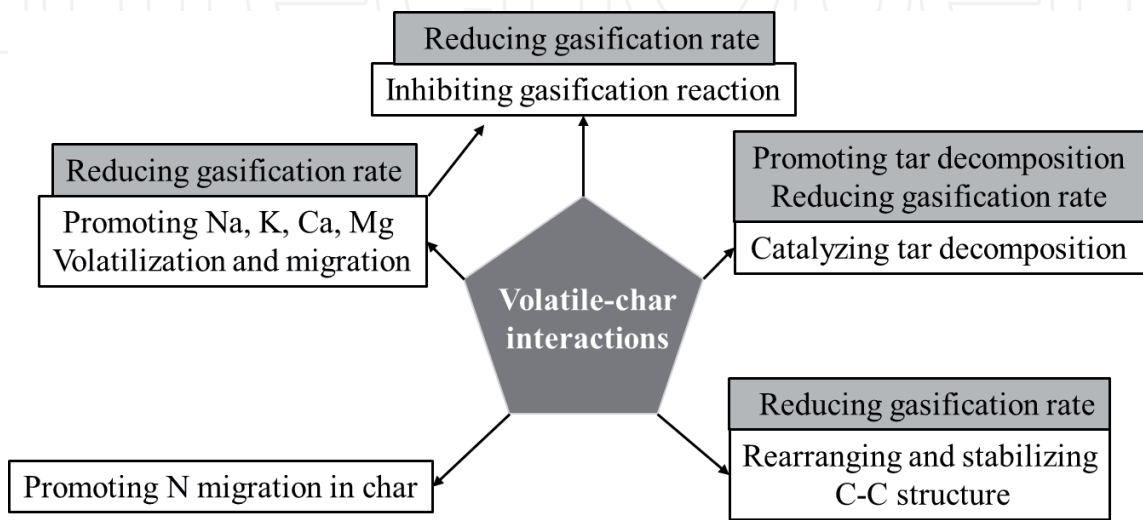


solid phase and gas phase are not well understood. These problems could affect the efficiency of the co-utilization of coal and biomass. Therefore, it is necessary to conduct additional research on the chemical form, migration path, redistribution mechanism and evolution of AAEMs during co-gasification of coal and biomass.

### 5. Volatile-char interactions during co-pyrolysis of coal and biomass

The volatile-char interactions are common phenomena in the thermochemical conversion of low order fuels, and their interaction mechanisms are complex. The essence of volatile-char interactions is the reaction between char and H radicals produced by the cracking and reforming of volatiles. The interactions include not only the catalytic reforming effect of volatiles by char, but also the influence of volatiles on the structure and properties of char [63]. The volatile-char interactions can significantly affect many aspects of the gasification process, such as the volatilization of AAEMs, the evolution of char structure, the dispersion of inherent catalysts and thus the reactivity of char [64]. Therefore, the volatile-char interactions should be fully considered in the utilization of low-order fuels, the beneficial aspects of the volatile-char interactions should be strengthened while the adverse aspects should be weakened or eliminated (see **Figure 5**).

The volatile-char interactions during co-pyrolysis of coal and biomass are more complicated than that of each. Krerkkaiwan et al. [65, 66] found that coal char had catalytic effects on the decomposition of biomass volatiles and heavy aromatic hydrocarbons, and the interactions between biomass volatiles and coal char seriously reduced the gasification reactivity of coal char. Xia Wang [67] reported that lignin volatiles were more difficult than cellulose volatiles to undergo cracking and reforming reactions on the surface of coal char. When the gasification temperature was less than 800°C, biomass volatiles could form carbon deposits on the surface of coal char, which reduced the gasification reactivity of the coal char. Yan et al. [68] indicated that the interactions between biomass volatiles and coal char could reduce the yield of tar, increase the yield of gas volatiles, and change the chemical structure of the coal char. Hu et al. [69] found that the volatile-char interactions can promote the further cracking of tar into non-condensable gas, and can promote the aromatization of char, leading to the reduction of its gasification reaction. It can be found that the volatile-char interactions during co-pyrolysis of coal and biomass have important effects on the characteristics of both volatiles and co-pyrolysis char.



**Figure 5.**  
*The effect of volatile-char interactions on low rank gasification [63].*



During thermochemical conversion of low-order fuel, the volatile-char interactions and AAEMs are interrelated and mutually influenced. On the one hand, the volatile-char interactions can promote the volatilization and migration of AAEMs. On the other hand, active AAEMs can affect the dynamic pyrolysis process of fuel, and have direct catalytic effects on the cracking of pyrolysis volatiles and their precursors, thus affecting the volatile-char interactions during thermochemical conversion. During co-thermochemical conversion of coal and biomass, the relationship between volatile-char interactions and AAEMs is more complex, and it is also a consideration for equipment design and operation. However, there are few reports on this aspect. Therefore, it is recommended that further research be conducted to understand the chemical mechanism of active AAEMs on volatile-char interactions and the influence of these interactions on the volatilization and migration of AAEMs for the efficient utilization of coal and biomass.

## 6. Co-pyrolysis products properties of coal and biomass

The pyrolysis products of coal and biomass include gas, tar, and char, which can be affected by synergistic effects. During co-pyrolysis of coal and biomass, the synergy can be affected by many factors such as: fuel type, blending ratio, heating rate, reactor design, and pyrolysis temperature. **Table 4** showed the effects of temperature and blending ratio on yields of char, tar and gas compared with calculated values. It can be found that the synergy shown by the pyrolysis product yield is not uniform, and can be affected by fuel type, pyrolysis temperature and blending ratio. In addition, the maceral group from low-rank coal can also affect the co-pyrolysis products. Wu et al. [74] researched the main maceral group from low-rank coal and cellulose in lignocellulosic biomass, and found that during co-pyrolysis, the influence of vitrinite on the generation of volatiles was related to the mixing ratio, while inertinite inhibited the generation of volatiles.

### 6.1 Co-pyrolysis volatiles composition of coal and biomass

Volatiles content is one of the important indicators of fuel characteristics, and it has important influences on furnace volume and shape, burner type and air distribution mode. At present, the research on volatiles during co-pyrolysis of coal and biomass mainly focuses on the influence of co-pyrolysis process on the composition and content of volatiles. Wu et al. [75, 76] found that when coal was co-pyrolyzed with wheat straw/biomass model compounds, co-pyrolysis promoted the generation of  $H_2$  and  $CO$ , and inhibited the production of  $CO_2$ . However, the co-pyrolysis of coal and green algae inhibited the generation of  $H_2$  and  $CO$ . Zhang et al. [77] reported that during co-pyrolysis of coal and biomass, the contents of volatile components ( $H_2$ ,  $CO$ ,  $CH_4$  and  $CO_2$ ) were inconsistent with the calculated values, suggesting that there were synergistic effects during co-pyrolysis. Sonobe et al. [30] indicated that the co-pyrolysis of coal and biomass had little effect on the production of  $CO$  and  $CO_2$ , but significantly promoted the production of  $CH_4$ . Soncini et al. [78] pointed out that the increase of biomass during the co-pyrolysis inhibited the production of  $CH_4$ ,  $C_2H_4$ ,  $CO$  and  $H_2$ . Yang et al. [37] researched the gas yield and the gas concentration of the co-pyrolysis of cotton stalk and high-ash coal at different mixing ratios under  $950^\circ C$ , and found that the co-pyrolysis was beneficial to the generation of gas, and can promote the formation of  $H_2$ ,  $CO$  and  $CH_4$  (except 20% cotton stalk), but inhibit the generation of  $CO_2$ . Wu et al. [79] reported that during co-pyrolysis of coal and biomass, the addition of low-rank coal inhibited the formation of  $CH_4$  and  $H_2$ , and the negative synergistic effect was most

Pyrolysis condition				Co-pyrolysis products			#
Samples	Reactor	R <sub>C</sub> (w/w)	T (°C)	Gas	Tar	Char	
				Y <sub>E</sub> /Y <sub>C</sub> (%)	Y <sub>E</sub> /Y <sub>C</sub> (%)	Y <sub>E</sub> /Y <sub>C</sub> (%)	
lignite, safflower seed	fixed-bed reactor	3%	550	24.1/24.7	36.7/33.4	22.0/23.3	[70]
		5%		23.5/24.4	39.6/32.9	21.6/24.0	
		7%		23.7/24.1	37.4/32.4	22.6/24.8	
		10%		23.6/23.6	35.6/31.7	24.4/26.0	
		20%		21.9/22.0	31.4/29.2	28.3/29.9	
		30%		19.8/20.3	25.4/26.6	34.5/33.8	
		50%		17.3/17.1	20.8/21.6	41.2/41.6	
		65%		14.4/19.5	16.8/25.4	46.9/35.7	
		90%		10.7/10.6	11.0/11.5	56.6/57.1	
sub-bituminous, sawdust	fixed-bed reactor	40%	400	21.2/15.2	41.0/45.5	37.8/39.2	[71]
			500	21.4/16.3	43.3/47.4	35.2/36.3	
			600	28.5/23.3	40.7/43.1	30.8/33.6	
			700	32.8/28.0	36.7/39.8	30.6/32.2	
			800	35.7/33.6	33.2/34.6	31.0/31.8	
		20%	600	27.4/26.3	50.1/50.1	22.1/23.6	
		40%		28.5/23.3	40.7/43.1	30.8/33.6	
		60%		26.3/20.2	33.2/36.2	40.5/43.6	
		80%		19.3/14.2	28.0/29.3	52.7/53.5	
low-rank coal, cedar	fixed-bed reactor	25%	450	18.0/18.2	33.6/35.4	34.8/34.2	[72]
			500	22.0/22.2	33.2/35.0	32.2/31.2	
			550	26.3/26.8	31.3/32.0	31.0/29.6	
			600	30.3/33.0	29.7/31.1	28.5/24.9	
			650	33.2/35.6	29.0/29.9	26.9/23.5	
		50%	450	16.5/15.2	28.0/30.1	46.4/45.2	
			500	20.5/18.7	26.9/30.1	43.5/41.7	
			550	25.1/23.0	25.8/27.2	40.1/39.6	
			600	28.7/28.2	25.6/26.9	38.0/35.6	
			650	31.5/30.6	25.2/26.0	36.8/34.1	
		75%	450	14.0/12.1	20.3/24.9	57.3/56.2	
			500	17.2/15.2	21.0/25.1	53.3/52.2	
			550	21.0/19.1	19.0/22.5	50.2/49.5	
			600	24.3/23.4	19.6/22.7	47.9/46.3	
			650	26.4/25.5	20.1/22.2	46.3/44.6	
Lignite, Pine sawdust	fixed-bed reactor	20%	400	41.9/31.6	27.5/30.1	30.6/38.1	[73]
			600	43.1/46.8	13.1/19.9	26.6/29.4	
			900	51.7/49.7	25.7/27.4	22.6/22.9	
		50%	400	35.0/27.2	15.5/20.3	49.6/52.5	
			600	43.5/37.5	15.4/18.9	41.2/43.5	
			900	52.8/44.0	13.1/19.9	34.1/36.1	
		80%	400	31.0/22.8	8.5/10.4	60.5/66.9	
			600	34.5/28.2	11.1/14.0	54.4/57.7	
			900	41.8/38.3	8.5/12.4	49.7/49.3	
R <sub>C</sub> : mixing ratio of coal/mix (w/w); T: temperature; Y <sub>E</sub> , Y <sub>C</sub> : the experimental value and calculated value of yield, respectively.							

**Table 4.**  
Effects of temperature and blending ratio on yields of char, tar and gas compared with calculated values.

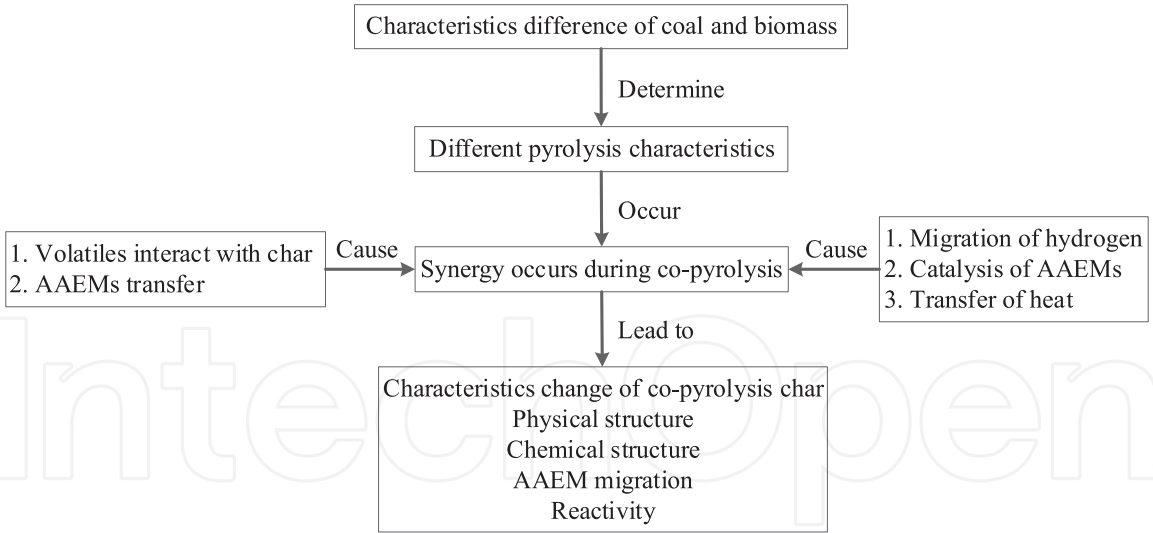
significant at a 50% mass ratio. Ma et al. [80] found that under the condition of cow manure: coal = 1: 3, CO emissions were significantly increased, CO<sub>2</sub> and CH<sub>4</sub> were also increased, and co-pyrolysis were beneficial to syngas production. In addition, for sulfur-containing gases, with the increase of cow manure ratio, the emissions of H<sub>2</sub>S, COS and C<sub>4</sub>H<sub>4</sub>S increase, while the emission of SO<sub>2</sub> decrease. Zhu et al. [72] pointed out that the synergistic effect of gas yield and composition during co-pyrolysis of coal and biomass was affected by pyrolysis temperature and mix ratio. However, to our best knowledge, there are no reports about the influence of AAEMs on the volatiles production characteristics of the co-pyrolysis of coal and biomass.

## 6.2 Co-pyrolysis tar properties of coal and biomass

The composition of tar is extremely complex, and can be used after separation and purification. The tar fractions are further processed to separate a variety of products. The main products extracted are: naphthalene, phenol, phenanthrene, carbazole, and asphalt. The different properties of biomass and coal lead to great differences in the components of their pyrolysis tar. Coal pyrolysis mainly produces heavy tar, while biomass pyrolysis mainly produces light tar. The interaction between coal and biomass during co-pyrolysis could cause changes in the properties of tar. Onay et al. [70] reported that the co-pyrolysis oil obtained with 5% lignite mixed with biomass contains more aliphatic and aromatic fractions, more relatively heavy hydrocarbons, less polar fractions than biomass pyrolysis oil. Jones et al. [81] found that co-pyrolysis of coal and biomass was conducive to the formation of phenols, but not conducive to the formation of aromatics. Tang et al. [82] indicated that co-pyrolysis improved the formation of phenols and naphthalene, while cotton stalk as an additive inhibited phenanthrene formation during co-pyrolysis of cotton stalk and Shenmu coal. Zhu et al. [72] concluded that the increase of cedar sawdust contributed to the positive synergistic effect of light tar, revealing the role of cedar as a hydrogen donor during co-pyrolysis. In addition, reactive H<sub>2</sub> from water-gas shift reaction and hydrogen-rich free radicals such as •CH<sub>3</sub>, •OCH<sub>3</sub> from cedar can inhibit the secondary polymerization to form methyl-contained phenols and naphthalenes instead of 3-ring phenanthrenes and 4-ring pyrenes. Song et al. [73] reported that co-pyrolysis was unfavorable to the formation of benzene, naphthalene, and hydrocarbons in tar, but favorable to the formation of phenols and guaiacol. Zhao et al. [83] found that the co-pyrolysis of cellulose and lignite was conducive to the generation of –OH components, and cellulose could promote the thermal conversion of lignite to a certain extent, resulting in more ketones or esters in the co-pyrolysis tar, which was conducive to improving the quality of liquid products. Zhu et al. [84] reported that the reactive H<sub>2</sub> from water-gas shift reaction and hydrogen-rich radicals such as •CH<sub>3</sub>, •OCH<sub>3</sub> from cedar can inhibit the secondary polymerization to form methylphenol and naphthalene instead of 3-ring phenanthrenes and 4-ring pyrenes during co-pyrolysis of a massive coal and cedar mixture.

## 6.3 Co-pyrolysis char properties of coal and biomass

The interaction between coal and biomass during co-pyrolysis can affect the characteristics of the resulting char, which influences the subsequent reactions. **Figure 6** shows the relationship between characteristics difference of coal and biomass and their co-pyrolysis char properties. Therefore, it is useful to study the characteristics of the resulting char, to understand the conversion mechanism during the co-pyrolysis of coal and biomass. Generally, the characteristics of char are studied from four aspects: physical structure, chemical structure, AAEM migration and reactivity.



**Figure 6.**  
*The relationship between characteristics difference of coal and biomass and their co-pyrolysis char characteristics.*

The change of the surface morphology of the co-pyrolysis char is the most direct manifestation of the interaction between coal and biomass. Wu et al. [76] found that with the increase of co-pyrolysis temperature, the surface of co-pyrolysis char became rougher and the pores became more developed. Wu et al. [85] reported that cellulose can promote the uniformity of co-pyrolysis char, while hemicellulose, lignin and sodium carboxymethyl cellulose were conducive to the three-dimensional development of co-pyrolysis char. Chen et al. [31] pointed out that during co-pyrolysis of coal and biomass, the presence of corn stalks was beneficial to the production of spherical particles from coal char. But the promotion of the corn stalks in removing active AAEMs through acid pickling was greater than that of the original corn stalks. However, Lin et al. [60] concluded that co-pyrolysis hardly influenced the macro-morphology, and structure of the mineral matter. According to current research results, more than 80% of the researches believed that the surface morphology of co-pyrolysis char was changed during co-pyrolysis [11].

During the reaction process of co-pyrolysis char, the pore structure can provide reaction and diffusion channels for some products, and the pore surface is the main location of chemical reaction of adsorption. Therefore, the structure and surface of pores in the char, play an important role in the reaction of chars. Most studies indicate that the growth of pore structure of co-pyrolysis char is affected by the operating temperature, mixing ratio and fuel type. Wei et al. [86] reported that with the increase of the biomass ratio in the mixture, the development of pore structure was first inhibited and then promoted. Wu et al. [87] found that biomass had an inhibitory effect on the development of the surface area and pore volume of co-pyrolysis char, but the average pore size of co-pyrolysis char was affected by the type of raw materials used. Vyas et al. [88] pointed out that the growth of co-pyrolysis char pore structure was affected by operating temperature and mixing ratio. At low co-pyrolysis temperature, the mixing ratio had little effect on the surface area and micropores. However, with the increase of co-pyrolysis temperature, the presence of biomass in the mixture significantly increased the number of micropores in the co-pyrolysis char. Lin et al. [60] found that specific surface area and pore structures of large micropores and mesopores were more impacted than those of ultramicropores, indicating that the influence was mainly from the formation of secondary char.

The chemical structure of organic compounds in co-pyrolysis char is also one of the important factors affecting the reactivity of the char. However, there is little research on the chemical structure of co-pyrolysis char, especially the functional



group structure. Only a few researchers have studied the carbon structure of co-pyrolysis char by Raman spectroscopy. It was found that the more biomass in the mixture, the more favorable the formation of smaller (3–5 rings) aromatic ring structures, and the reduction of larger (no less than 6 rings) aromatic ring structures in the co-pyrolysis char [86]. Wu et al. [85] found that the addition of cellulose inhibited the formation of smaller aromatic ring structures in co-pyrolysis char, while the addition of hemicellulose and lignin contributed to the formation of smaller aromatic ring structures. Chen et al. [56] researched the effects of pyrolysis temperature on the structure and functional groups changes of co-pyrolysis char by Raman and Fourier transform Infrared spectroscopy (FTIR), respectively. They found that with the increase of pyrolysis temperature, the structure of co-pyrolysis char changed from a small aromatic ring system to a large aromatic ring system containing six or more condensed benzene rings through the condensation reaction of the rings, and the aromatic –CH functional groups first increased and then decreased. In addition, the C=O and aliphatic –CH functional groups in the co-pyrolysis char disappeared in the pyrolysis temperature from 600 to 700°C. Chen et al. [31] pointed out that active AAEMs can inhibit the decomposition of aliphatic –CH, C=O and –CH<sub>3</sub> in coal, and can also inhibit the decomposition of O – H, aliphatic –CH, and C – O in biomass. But as the pyrolysis temperature increased, the inhibitory effect gradually weakened or even disappeared.

The co-gasification process of coal and biomass includes two primary steps: the co-pyrolysis of the raw fuel and the co-gasification of the remaining co-pyrolysis char. The gasification reaction rate of co-pyrolysis char is much slower than the release of volatiles during co-pyrolysis. Therefore, the reactivity of co-pyrolysis char becomes one of the important parameters, when evaluating the suitability of industrial gasification materials. It is still uncertain whether the co-pyrolysis process affects the reactivity of the co-pyrolysis char. Most studies found that no matter whether the gasification medium was CO<sub>2</sub>, steam, or air, the co-pyrolysis process could affect the reactivity of the coal/biomass char. Some researchers believe that co-pyrolysis can inhibit the reactivity of the resulting char [52, 86, 89, 90], while others believe that it can promote the reactivity of char [10, 87, 91–95]. In addition, some researchers have found that the influence of co-pyrolysis on char reactivity was affected by gasification temperature [51, 96], mixing ratio [54, 97, 98], raw materials [54, 99] and other co-pyrolysis parameters [23]. Wei et al. [51] researched the co-gasification reactivity of rice straw and bituminous coal/anthracite mixed char; they found that the synergistic effect of co-gasification reactivity of rice straw and bituminous coal mixed char, gradually changed from inhibition to promotion. The co-gasification reactivity of rice straw-anthracite mixed char, gradually strengthened with the increase of the conversion rate, reached the strongest point in the middle stage of co-gasification process, and then began to slowly weaken. Chen et al. [23] also pointed out that with the progress of the co-gasification process, the synergistic effect of the gasification reactivity of the char gradually changed from inhibition to promotion. In addition, the gasification reactivity of co-pyrolysis char was affected by mixing ratio and co-pyrolysis temperature, which was consistent with the research conclusion of Yuan et al. [97], Gao et al. [94], and Mafu et al. [98]. Overall, according to current research results, more than 80% of the researches believed that there were synergistic effects of co-pyrolysis char during co-gasification [11].

The synergistic effect of co-gasification reactivity of co-pyrolysis char is mainly caused by two aspects: the interaction between coal and biomass during co-pyrolysis and the interaction between coal char and biomass char during co-gasification. However, existing research on the influence of these two aspects on the gasification reactivity of co-pyrolysis char is obviously insufficient. Only Chen et al. [23] compared the effects of these two aspects on the co-gasification reactivity; they

found that the interaction between coal and biomass during co-pyrolysis had a more obvious impact on the co-gasification reactivity.

The gasification reactivity of co-pyrolysis char is most likely controlled by mass transfer, pore diffusion and internal chemical reaction. Therefore, for co-pyrolysis char of coal and biomass, its physicochemical structure and catalysis are the most important factors affecting its reactivity. A large number of studies have shown that the co-pyrolysis process can have a synergistic effect on the gasification reactivity of the resulting char, which was mainly due to the catalysis of AAEMs (mainly K and Ca) during the pyrolysis and gasification process [10, 51, 52, 92, 93, 99]. However, the catalytically active Ca and K in the biomass can interact with the aluminosilicate in coal minerals to form catalytically inert  $\text{Ca}_2\text{Al}_2\text{SiO}_7$  and  $\text{KAlSiO}_4$  crystals, thereby reducing the reactivity of co-pyrolysis char [22, 52, 99]. In addition, the rich silica components in biomass ash can also reduce the reactivity of chars by converting the catalytically active K and Ca substances into non-catalytically active substances [10]. Krerkkaiwan et al. [91] found that the reactivity of co-pyrolysis char was higher than that of coal char or biomass char, alone, which was related to the increased surface area and pore volume of co-pyrolysis char, as well as the catalytic effect of the K released by the biomass. Wei et al. [86] and Wang et al. [89] reported that the chemical structure of co-pyrolysis char and the migration of catalytically active AAEMs were the main factors affecting the reactivity of co-pyrolysis char, while the physical structure was a secondary factor. Wu et al. [87, 90] pointed out that the increase of the distance between microcrystalline structures and the number of interlayer defects between adjacent aromatic layers can promote the formation of active sites, thus increasing the reactivity of the co-pyrolysis char. Zhang et al. [100] found that the active AAEMs in coal can increase the reactivity of char during co-gasification, promote the production of  $\text{H}_2$  and  $\text{CO}_2$ , and inhibit the production of CO. Chen et al. [23] found that the active AAEMs in biomass can obviously promote the reactivity of co-pyrolysis char, while the active AAEMs in coal had little effect on the reactivity of the co-pyrolysis char.

Current research on the co-pyrolysis products of coal and biomass seems to be limited to the macroscopic characteristics, such as the yield, properties, and compositions. There are few studies and analyses on the essential causes that affect the co-pyrolysis products. Therefore, it is impossible to clearly understand the production mechanism of products during co-pyrolysis of coal and biomass. In addition, the effect of active AAEMs on the volatiles production during co-pyrolysis of coal and biomass is still unclear, thus further research is recommended. A better understanding of the influence of the physicochemical structure and the active AAEMs on the reactivity of co-pyrolysis char, will be helpful to promote the development of industrial applications for biomass-coal co-pyrolysis. Although some researchers have begun to pay attention to this work, there are still plenty of opportunities for further research and development.

## 7. Industrial demonstration

Yao et al. [101] researched the industrial-scale co-pyrolysis of biomass, waste agriculture film, and bituminous coal, and analyzed it from multi-perspective (energy flow, economic, and socioenvironmental benefits analysis). The composition of different feedstock used in the pyrolysis experiment is shown in **Table 5**. The energy flow analysis showed that the co-pyrolysis processing of fruit tree branch (FTB), bituminous coal (BC), and recycled agriculture film pellets (AFP) resulted in a decrease in energy yield due to the energy loss that occurred during the conversion process. **Table 6** shows the results of the economic analysis of the industrial-scale

Feedstock type	Biomass	Fossil fuel	Plastic waste
Feedstock name	Fruit tree branch	Bituminous coal	Recycled agriculture film pellets
Feedstock code	FTB	BC	AFP
Experiment code	Relative contents added in each experiment (wt%)		
E1	100	0	0
E2	50	50	0
E3	40	40	20
Total mass processed (kg) <sup>a</sup>	450	800	1222

<sup>a</sup>The total mass of material processed in each experiment was to keep the rotation speed constant based on their densities, and the total volume was fixed.

**Table 5.**  
The composition of different feedstock used in the pyrolysis experiment [101].

Category	Term	Unit	E1	E2	E3
Financial data	Total investment	10,000 CNY	213.79	223.37	223.37
	Fixed asset investment		204	204	204
	Average income during operation period		87.6	152.58	166
	Total cost (average during operation period)		72	129.5	129.5
	Total profit (average during operation period)		15.6	23.08	36.5
Financial evaluation indices	Financial internal rate of return (Before tax)	%	10.51%	14.20%	21.26%
	Financial net present value (Before tax)	10,000 CNY	31.09	82.99	185.44
	Payback period (Before tax)	year	8.47	7.19	5.51
Sensitivity analysis	Product critical point	%	4.73	7.05	14.66
	Feedstock critical point	%	10.14	11.07	25.66
	Initial investment critical point	%	16.29	37.69	64.65
BEP analysis	BEP (% , capacity utilization rate)	%	62.63%	53.11%	41.73%

**Table 6.**  
Input data and results of the project economic analysis [101].

co-pyrolysis of FTB, BC, and AFP. From the economic analysis, it can be concluded that the three pyrolysis methods can bring economic benefits. Among them, the economic performance of FTB-BC-AFP co-pyrolysis was the highest, while that of FTB single pyrolysis was the lowest. The annual profit and the internal financial return rate of FTB-BC-AFP co-pyrolysis were three times and 2.1 times higher than that of single pyrolysis, respectively. In addition, the payback period can be shortened by about 3 years. The biochar produced by the three pyrolysis methods conformed to the national standard (GB/T 31862–2015 and GB/T 34170–2017).

The pyrolysis gas meted the calorific value requirements of the national standard (GB/T 13612–2006), and can meet the needs of residents for heating and cooking. Moreover, the implementation of the project has created employment opportunities, and each person can increase their income by 30,000 CNY per year. In addition, The FTB-BC-AFP co-pyrolysis used in this project can replace ~1100 tons of standard coal every year, and reduce CO<sub>2</sub> emission, SO<sub>2</sub> emission, smoke and other pollutants by 1720 tons, 5 ~ 6 tons, and 320 kg per annum, respectively. At the same time, the project recycled 750 tons of plastic waste, which can reduce 50–66.7 km<sup>2</sup> of farmland white pollution and avoid the accumulation of plastic waste.

## 8. Vision and development

In response to China's dual-carbon target, the use of coal should be reduced and eliminated, as burning 1 kg of coal produces 2.62 kg of CO<sub>2</sub>. As a solid fuel with zero carbon emission, the utilization rate of biomass should be increased. China produces more than 1 billion tons of agriculture and forestry waste each year. Due to its low energy density and high transportation cost, on-site treatment of biomass can effectively reduce the cost of recycling. Although co-pyrolysis may lead to energy loss in the conversion process, the addition of coal increases the bulk density of the raw material mixture and improves the processing capacity of the equipment. In addition, co-pyrolysis can improve the combustion characteristics of char and reduce the emission of pollutants. Co-pyrolysis process can not only effectively meet the needs of clean energy in rural areas, but also realize the on-site treatment and utilization of these major solid wastes. Therefore, the co-pyrolysis of biomass and coal is still a valuable method for engineering applications that require the use of coal. Furthermore, the addition of plastics in co-pyrolysis can improve the yield and quality of gas products, and also has certain environmental benefits.

In summary, there are still many deficiencies in the current research on the co-pyrolysis of coal and biomass, and many opportunities to expand the knowledge of the resulting chemistry, e.g., the influence of the interaction between coal and biomass on the respective pyrolysis process and the entire co-pyrolysis process during co-pyrolysis, the influence of co-pyrolysis conditions on the physicochemical structure and AAEMs content of co-pyrolysis char, especially the influence of co-pyrolysis process on subsequent gasification reaction characteristics. Important system parameters to be studied further, include: (a) the ratio, and limits, of biomass to coal; (b) pyrolysis and gasification operating temperatures; (c) the rate of temperature rise in the reaction vessel; (d) the inter-catalytic effects of AAEMs on product yields and compositions; (e) the yields of volatiles (gases), tars (liquids), and chars (solids); (f) the compositions of these products. The goal of all of this current and future biomass-coal co-pyrolysis work should be to reach industrial scale applications for this as soon as possible. With regard to the current global climate change crisis, it is urgent to continue to minimize the use of all fossil fuels, worldwide, especially coal, and to mitigate the emissions of CO<sub>2</sub> into Earth's atmosphere. With that goal in mind, the growing use of biomass, to replace the use of coal, is of paramount importance.

## 9. Conclusion

This chapter has reviewed some of the information regarding the co-pyrolysis of coal and biomass, with a focus on the synergistic mechanism and the resulting influence. The different characteristics of coal and biomass lead to great differences



in their pyrolysis characteristics, resulting in a synergistic effect during co-pyrolysis. The synergistic effect can be caused by the migration of active H radicals from biomass to coal, the catalysis of active AAEMs, and heat transfer during co-pyrolysis [102]. During the co-pyrolysis of coal and biomass, changes in product yields and composition of volatiles, as well as the changes in the physicochemical structure and reactivity of co-pyrolysis char are briefly reviewed. In addition, the release and migration of AAEMs and their catalytic effects, and volatile-char interactions are mentioned. Moreover, the analysis of the co-pyrolysis industry demonstration is also mentioned.

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