Review

Biomass Pyrolysis Technology by Catalytic Fast Pyrolysis, Catalytic Co-Pyrolysis and Microwave-Assisted Pyrolysis: A Review

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Abstract: With the aggravation of the energy crisis and environmental problems, biomass resource, as a renewable carbon resource, has received great attention. Catalytic fast pyrolysis (CFP) is a promising technology, which can convert solid biomass into high value liquid fuel, bio-char and syngas. Catalyst plays a vital role in the rapid pyrolysis, which can increase the yield and selectivity of aromatics and other products in bio-oil. In this paper, the traditional zeolite catalysts and metal modified zeolite catalysts used in CFP are summarized. The influence of the catalysts on the yield and selectivity of the product obtained from pyrolysis was discussed. The deactivation and regeneration of the catalyst were discussed. Catalytic co-pyrolysis (CCP) and microwave-assisted pyrolysis (MAP) are new technologies developed in traditional pyrolysis technology. CCP improves the problem of hydrogen deficiency in the biomass pyrolysis process and raises the yield and character of pyrolysis products, through the co-feeding of biomass and hydrogen-rich substances. The pyrolysis reactions of biomass and polymers (plastics and waste tires) in CCP were reviewed to obtain the influence of co-pyrolysis on composition and selectivity of pyrolysis products. The catalytic mechanism of the catalyst in CCP and the reaction path of the product are described, which is very important to improve the understanding of co-pyrolysis technology. In addition, the effects of biomass pretreatment, microwave adsorbent, catalyst and other reaction conditions on the pyrolysis products of MAP were reviewed, and the application of MAP in the preparation of high value-added biofuels, activated carbon and syngas was introduced.

Keywords: biomass; catalysts; fast pyrolysis; co-pyrolysis; microwave-assisted

1. Introduction

With the increase of energy demand and population around the world, fossil fuels are used in large quantities and gradually exhausted, which aggravates the energy crisis and increasingly serious environmental problems. Therefore, people begin to pay attention to the exploitation and utilization of renewable resources and explore new green alternatives [1]. As an important renewable energy source, biomass can be derived from energy crops, forest wood and agricultural residues, which have advantages over traditional fossil fuels due to their environmental friendliness and easy access [2]. Through thermochemical conversion processes such as gasification, liquefaction, pyrolysis, and fermentation, biomass can produce more valuable products than biomass raw materials [3–5].

Biomass pyrolysis can decompose lignocellulosic biomass into liquid fuel, non-condensable gas, and bio-char under anaerobic conditions. It includes slow, fast, and flash solutions. Compared with the other two pyrolysis types, fast pyrolysis can convert biomass into more liquid products under

certain controlled conditions. Because of its better economic returns, fast pyrolysis has a certain development prospect in the future [6,7]. Compared with biomass, the bio-oil gained from pyrolysis has the advantage of easy handling and transportation, high energy density, and can be used as liquid fuel and chemical raw materials. However, bio-oil has the disadvantages of high oxygen content, high acidity, high viscosity, low calorific value and instability compared with petroleum, which limits the use of bio-oil. Therefore, it is worthwhile and necessary to improve the character of bio-oil, although it has been found that the use of a zeolite catalyst can also reduce the yield of bio-oil [8].

Some methods have been developed to improve the quality of bio-oil, mainly the introduction of catalysts to selectively change the distribution of pyrolysis products. One method is hydrodeoxygenation (HDO) [9]. Under conditions of noble metal catalyst and hydrogen, the content of oxygen in the product is reduced. Another method is catalytic fast pyrolysis (CFP) [10]. HDO has a high deoxidization efficiency. Some studies have shown that HDO has great advantages in increasing liquid hydrocarbon yield, increasing gaseous olefins and reducing coke yield [11]. However, HDO needs precious metals and hydrogen, and its cost should be considered in application. Zeolite catalyst is the most widely used catalyst in CFP. Many studies have proven that the presence of zeolite catalyst can promote the deoxidation of bio oil and increase the content of hydrocarbons in bio oil [12–14].

In recent years, in order to improve the deactivation of the zeolite catalyst and further improve the quality of bio-oil, many scholars have modified the zeolite catalyst, and some new mesoporous catalysts have emerged, such as catalytic co-pyrolysis (CCP) and microwave-assisted pyrolysis (MAP). CCP uses hydrogen-rich substances and biomass to feed together to obtain an appropriate H/C-eff ratio, so as to alleviate the deactivation of catalyst and obtain high quality products. MAP is a new type of microwave heating, which is more efficient and energy-saving than the traditional electric heating method. It has been extensively used in the preparation of bio-oil, pyrolysis gas and bio-char. There are also some review articles on these two technologies [15,16]. This paper will introduce the latest research progress of catalysts in CFP, including the selectivity of catalyst, the function of modification on the yield and components. This review will focus on the synergistic effect of plastics and tires as the main co pyrolysis products in CCP and the mechanism analysis of related catalysts. In addition, the influence of reaction conditions on the products in MAP and the application of MAP in pyrolysis were discussed.

2. Catalysts in Catalytic Fast Pyrolysis

2.1. Traditional Zeolite Catalysts

Zeolite is derived from aluminate and silicate species (i.e., AlO_4 and SiO_4), which can be called hydroaluminosilicate compounds. In the process of chemical reaction, zeolite can show different open cavities and crystal structures through structural upgrading. Natural zeolites such as mordenite have been found in rocks, and synthetic zeolites such as HZSM-5, H-Beta, H-Y and their modified forms are widely used in research and industry [13]. Zeolite catalysts are highly applied into the catalytic upgrading of petroleum and biofuels due to their acidity, pore structure, ion exchange characteristics and shape selectivity. The zeolite catalyst also has excellent alkylation and aromatization ability. It can transform biomass or pyrolysis steam into more desired products such as aromatics, which provides a low energy way to improve product quality [17]. Recent studies of traditional zeolite catalysts in CFP are shown in Table 1.

Table 1. Application of traditional zeolite catalyst in catalytic fast pyrolysis (CFP).

Biomass	Catalyst	Reaction Conditions				Reactor	Major Product	Ref.
		Feedstock/ Catalyst (Weight)	Temp. (°C)	Acidity	Operating Mode			
Jatropha residues	HZSM-5	1:1	500	40	-	Pyroprobe pyrolyzer	Aliphatics, aromatics, Phenols, Ketones	[18]
Corn cob	ZSM-5	1:2	550	27	In situ	Double-shot pyrolyzer	Aromatic hydrocarbons	[19]
Corn cob	HZSM-5	1:2	550	27	In situ	Double-shot pyrolyzer	Aromatic hydrocarbons	[19]
Kraft lignin	ZSM-5	1:2	600	11.5	Ex situ	Fixed-bed reactor	Alkyl-Phenols, aromatics	[20]
Kraft lignin	ZSM-5	1:2	600	25	Ex situ	Fixed-bed reactor	Alkyl-Phenols, aromatics	[20]
Kraft lignin	ZSM-5	1:2	600	40	Ex situ	Fixed-bed reactor	Alkyl-Phenols, aromatics	[20]
Lignin	ZSM-5	1:1	450	80	In situ	Fixed bed reactor	Monomeric aromatics, Phenolics	[21]
Poultry litter	ZSM-5/MCM-41	10:1	500	-	Ex situ	Microwave oven	Toluene, xylene, PAHs, benzene	[22]
Wood sawdust	ZSM-5	10:1	600	17.3	Ex situ	CDS Pyroprobe 5200HP pyrolyser	Aromatic hydrocarbons, phenols	[23]
Pinewood sawdust	ZSM-5	0.25:1~2:1	500	46	-	CDS Pyroprobe 5200 HP pyrolyzer	Aromatic hydrocarbons, phenolics	[24]
Sawdust	HZSM-5	-	400~600	25	In situ	Drop tube quartz reactor	Aromatics, olefins	[25]
Sawdust	HZSM-5	-	400~600	50	In situ	Drop tube quartz reactor	Aromatics, olefins	[25]
Sawdust	HZSM-5	-	400~600	80	In situ	Drop tube quartz reactor	Aromatics, olefins	[25]
Maize straw	ZSM-5@SBA-15	1:2~2:1	400~700	-	In situ	Fixed-bed	Phenols, hydrocarbons	[26]
Soda lignin	ZSM-5	1:2	500~900	30~40	-	CDS Pyroprobe 5200HPR	Aromatics, phenol, catechol	[27]
Soda lignin	Y-Zeolite	1:2	500~900	8~9	-	CDS Pyroprobe 5200HPR	Aromatics, phenol, catechol	[27]
Corn cob	HZSM-5	1:2	700	25	-	-	Acetonitrile, aromatics, pyridines	[28]
Corn cob	MCM-41	1:2	700	-	-	-	Acetonitrile, aromatics	[28]
Corn cob	HY	1:2	700	-	-	-	Acetonitrile, aromatics	[28]
Corn cob	Hβ	1:2	700	25	-	-	Acetonitrile, pyrroles	[28]
Lignin	MCM-41	1:2	600	-	Ex situ	Fixed bed	Aromatic amines, N-doped carbon	[29]
Lignin	β-Zeolite	1:2	600	50	Ex situ	Fixed bed	Aromatic amines, N-doped carbon	[29]
Lignin	HZSM-5	1:2	600	50	Ex situ	Fixed bed	Aromatic amines, N-doped carbon	[29]
Lignin	HY	1:2	600	7.5	Ex situ	Fixed bed	Aromatic amines, N-doped carbon	[29]
Cellulose	ZSM-5	2:1~1:4	600	25	In situ	Fixed bed	Light olefins (C_2H_4, C_3H_6)	[30]

Microporous zeolites have become a research hotspot as catalysts of biomass catalytic pyrolysis. Heather et al. used granular HZSM-5 zeolite to carry out the pyrolysis of the beetle-killed lodgepole pine in a new type of fast ablation reactor. The experiment produced the lowest yield of coke (9.4 wt%) and the highest yield of aromatic hydrocarbons (3.5 wt%), with very high selectivity (94%) to benzene, toluene and xylene (BTX) [31]. Zhang et al. added a certain amount of hexadecyl trimethyl ammonium bromide (CTAB) into HZSM-5 to form a hierarchical structure, and prepared a modified catalyst for the rapid pyrolysis of rice straw. Compared with HZSM-5, the proper addition of CTAB can decrease the yield of coke and increase the yield of aromatics, but the excessive addition of CTAB will lead to the opposite result. The catalyst HZ-0.01 (CTAB/SiO_2 molar ratio is 0.01) with the best addition ratio is obtained [32].

In addition to HZSM-5 zeolite, Hβ zeolite and a graded molecular sieve have also been developed. The main modification of zeolites for the production of biofuels from lignocellulosic biomass is reductive aromatization. Compared with common HZSM-5 zeolite, the hierarchical molecular sieves can produce a large number of heavy hydrocarbons (oxygen free) and have better selectivity and slower deactivation for heavy bio-oil components [33]. Some scholars have studied MCM-22 molecular sieve catalysts with different Si/Al ratios (20 and 40, respectively) and discover that reducing the Si/Al ratio of zeolites has a negative effect, mainly because the higher acid sites promote the serious cracking of bio-oil vapor, resulting in the increase of gaseous hydrocarbon production and the formation of coke. The MCM-22 catalyst is superior to the ZSM-5 catalyst in the production of high oxygen content aromatics [34].

In another study, HZSM-5 and Hβ zeolites were prepared by alkali post-treatment, both of which produced more mesopores under the original micropores. The analysis shows that under different alkali desilication sources, the specific surface area of mesopores formed in Hβ zeolites is directly related to the alkalinity of alkali solution, while the surface area of mesopores in HZSM-5 zeolite is basically unchanged. The yield of condensable volatiles on the optimized Hβ zeolites is about twice that of the parent Hβ zeolites, which improved its mass transfer ability, due to the increase of the mesoporous specific surface area. The deoxidization ability of HZSM-5 zeolite after optimization was also improved and the coke formation process was restrained to a certain extent [35]. Zhang et al. prepared ZSM-5/MCM-41 catalyst with MCM-41 as shell layer and ZSM-5 as inner core and discussed the effect of NaOH concentration on the pyrolysis of poultry manure [22].

It is a good way to prepare high quality bio oil by the pyrolysis of biomass with zeolite catalyst. The selectivity of aromatics and other products is not the same with different Si/Al ratio and pore size. As mentioned before, many zeolites, such as HZSM-5, ZSM-5 and H-Beta zeolites, have been well used in the study of catalytic pyrolysis. The structure of zeolites changes with the pore size and their connectivity. Zeolite has Bronsted and Lewis acid sites and Bronsted acid site is the main catalytic center. The active sites and different pore sizes of molecular sieves can promote the deoxidation of oxygen-containing compounds and improve the yield of aromatics. In the rapid pyrolysis of zeolite catalyst, the main reaction pathway is hydrocarbon pool mechanism, deoxidation, cracking, aromatization, aldehyde condensation and ketone reaction. Zeolite is more suitable as a selective catalyst. The conversion of oxygen-containing compounds into hydrocarbons in the framework of the molecular sieve depends on the shape selectivity of pore space and pore size of the molecular sieve.

2.2. Metal Modified Zeolite Catalysts

If the hydrocarbon generated in the pyrolysis reaction cannot be desorbed, they will oligomerize into coke in the zeolite pore, blocking the active site and causing the deactivation of the catalyst. Metal modification is another way to improve the catalytic activity of zeolite catalysts. Adding metals to the hierarchical ZSM-5 catalyst can promote deoxidation through decarboxylation and decarbonylation process and can further improve the performance of CFP of biomass to aromatics [36]. Recent studies of metal modified zeolite catalysts in CFP are shown in Table 2.

Table 2. Application of metal modified zeolite catalysts in CFP.

Biomass	Catalyst	Reaction Conditions				Reactor	Target Product	Ref.
		Biomass/ Catalyst (Weight)	Temp. (°C)	Sweeping Gas (N_2) Rate (mL/min)	Si/Al			
Alkali ligniin	Fe/ZSM-5	1:2	400–700	100	25	Quartz reactor	Light olefins, aromatics	[37]
Corn cob	Ni/HZSM-5	1:2	550	1	27	Double-shot pyrolyzer	Aromatic hydrocarbons	[19]
Lignin	Ni/ZSM-5	1:1	450	97	80	Fixed bed reactor	Monomeric aromatics Phenolics	[21]
woodchips	MgO/HZSM-5	5:1	500	100	-	Fixed bed	Bio-oils, char	[38]
woodchips	MgO/H-Beta	5:1	500	100	-	Fixed bed	Bio-oils, char	[38]
woodchips	ZnO/HZSM-5	5:1	500	100	-	Fixed bed	Bio-oils, char	[38]
woodchips	ZnO/H-Beta	5:1	500	100	-	Fixed bed	Bio-oils, char	[38]
Beech sawdust	Fe/ZSM-5	10:1	500	400	80	Fixed bed	Phenolic compounds	[39]
Wood sawdust	Fe/ZSM-5	10:1	500–800	-	16.6	CDS Pyroprobe 5200HP pyrolyser	Aromatic hydrocarbons	[23]
Wood sawdust	CaO/ZSM-5	1:5	600	-	38	CDS Pyroprobe 5250HP pyrolyser	Aromatics (xylene, toluene, benzene)	[40]
Wood sawdust	Al_2O_3/ZSM-5	1:5	600	-	38	CDS Pyroprobe 5250HP pyrolyser	Aromatics (xylene, toluene, benzene)	[40]
Wood sawdust	ZnO/ZSM-5	1:5	600	-	38	CDS Pyroprobe 5250HP pyrolyser	Aromatics (xylene, toluene, benzene)	[40]
Corn cob	Ga/HZSM-5	1:2	550~700	80 [a]	25	-	Acetonitrile, Aromatics	[28]
Wheat straw	ZnO/HZSM-5	-	600	-	50	fixed bed	Aromatic amines N-doped carbon	[29]
Wheat straw	ZnO/HY	-	600	-	7.5	fixed bed	Aromatic amines N-doped carbon	[29]
Cellulose	Fe/ZSM-5	2:1~1:4	600	100	25	Fixed bed	Light olefins (C_2H_4, C_3H_6)	[30]
Sawdust	Zn/ZSM-5	1:4		-	38	CDS Pyroprobe 5250 pyrolyser	Benzene, toluene, xylene	[41]
Sawdust	Fe/ZSM-5	1:4		-	38	CDS Pyroprobe 5250 pyrolyser	Benzene, toluene, xylene	[41]
Sawdust	Ca/ZSM-5	1:4		-	38	CDS Pyroprobe 5250 pyrolyser	Benzene, toluene, xylene	[41]
Sawdust	Ce/ZSM-5	1:4		-	38	CDS Pyroprobe 5250 pyrolyser	Benzene, toluene, xylene	[41]
Sawdust	La/ZSM-5	1:4		-	38	CDS Pyroprobe 5250 pyrolyser	Benzene, toluene, xylene	[41]

[a]—helium (He).

Chen et al. found that treating HZSM-5 with an appropriate amount of nickel and copper can improve the activity of catalyst and obtain more aromatics, but the high metal loading will reduce the aromatics yield [42]. Mesopores can be introduced into the catalyst through alkali treatment to improve the aromatics yield. Dai et al. added Ni to the hierarchical ZSM-5 catalyst to perform the CFP of corn cob. They found that the adjunction of Ni improved the framework structure of ZSM-5 catalyst and reduced the activation energy of reaction kinetics. Although the microporous volume and specific surface area of Ni modified ZSM-5 catalyst decreased in N_2 adsorption desorption (N_2-BET) characterization, it produced a higher aromatics yield, especially the content of monoaromatics [19]. Liang et al. found that ZSM-5 catalyst modified by transition metals (cobalt, nickel and zinc) can significantly heighten the production of bio-oil. The modified catalyst retains the topological structure of the original catalyst and the selectivity of aldehyde/ketone and phenol compounds increases (50% area of GC/MS). Zn/ZSM-5 (Si/Al = 46) is the best catalyst of them [43].

In another research of sludge catalytic pyrolysis, HZSM-5 supported with metal (nickel, cobalt) promoted the production of H radicals. The presence of metal makes the sludge pyrolysis generate more monocyclic aromatic hydrocarbons (MAHs) and increase the total carbon yield of aromatics. In addition, the aromatics yield of Ni-loaded HZSM-5 is higher than that of co-loaded HZSM-5 [44]. Mullen et al. studied the Fe modified HZSM-5. Experimental results revealed that the selectivity of the catalyst for benzene and naphthalene formation was higher than that of HZSM-5 [45]. In addition, the Fe/ZSM-5 catalyst has also been widely used in the study of fast pyrolysis of lignin to produce aromatics and light olefins. In the fixed bed reactor, the total acidity of the catalyst will increase with the increase of Fe loading, and the number of acid centers, pore volume and specific surface area will change. The acid centers affect the formation of low-carbon olefins, while aromatics are mainly affected by the total acidity. The maximum carbon yield, including aromatic compounds and light olefins, is 12.8% at the optimum temperature (600 °C) and Fe loading (3 wt.%) [37].

Polycyclic aromatic hydrocarbons (PAHs) in bio-oil produced by catalytic pyrolysis biomass are toxic substances, which will have a negative impact on the utilization of aromatics. In addition, PAHs are also easy to lead to coke deposition, resulting in catalyst deactivation [46]. Lu et al. supported Mo_2N, W_2N, MoP and WP on zeolite catalyst carrier (Hβ, HY and HZSM-5), to prepare a series of noble metal catalysts. Through the analysis of cracking products, it was found that Mo_2N/HZSM-5 could distinctly reduce the formation of PAHs, increase the amount of MAHs, and improve the anti-deactivation performance of the modified catalyst [47]. Lu et al. also prepared Mo_2N/HZSM-5, $Ti(SO4)_2$/HZSM-5 and $Ti(SO4)_2$-Mo_2N/HZSM-5 catalysts. Experiment results proved that $Ti(SO4)_2$-Mo_2N/HZSM-5 catalyst had the best catalytic selectivity for MAHs, significantly increased the productivity of MAHs and adjusted the distribution of MAHs and PAHs [48]. They believed that Mo_2N on the catalyst facilitated the generation of the hydrogen source, retained the activity of the hydrocarbon pool and prevented the oxidant from further polymerizing into PAHs. The addition of Ti $(SO4)_2$ improved the B-acid ratio of the modified catalyst and boosted the aromatization reaction to generate more MAHs.

ZSM-5 catalyst is insufficient in deoxidization and the pyrolysis products need more deoxidization. The basic metal oxides can dislodge oxygen from the acid in the form of CO_2, reduce the acidity and improve the calorific value of the pyrolysis bio-oil.

Some scholars have studied the influence of the mixed catalysis and sequential catalysis of base catalysts (CaO, MgO and SrO) and HZSM-5 catalyst in the reactor on the aromatics yield. The results show that the mixed catalyst modification has more significant deoxygenation activities and phenol selectivity compared with the sequential reaction. Moreover, base catalyst and HZSM-5 have a synergistic effect on the production of monocyclic aromatics and the mixture of CaO and HZSM-5 can markedly improve the selectivity of toluene and xylene [49].

Qi et al. investigated the CFP reaction of propane on ZSM-5 and $CrOx/Al_2O_3$ mixed catalysts, and the results indicated that the mixed catalysts could significantly increase the yield of aromatic hydrocarbons, and the selectivity of toluene with the optimal mass ratio of $CrOx/Al_2O_3$/ZSM-5 was 2. On the other hand, the addition of CrOx increased the activity of the ZSM-5 catalyst and slowed the

coking and deactivation of the catalyst [50]. Under the catalysis of CoOx/HZSM-5, the fast pyrolysis of biomass to acetonitrile in the atmosphere of ammonia was studied. The results show that the (–Co–O–Si–) sites of CoOx/HZSM-5 catalyst can promote the formation of acetonitrile. As the dominant product of cellulose, acetonitrile is formed either through the dehydration or dehydrogenation of imine and amide. C_2 oxygenated compounds such as acetaldehyde and acetic acid were selectively pyrolyzed by cellulose, which further reacted with ammonia to produce imine and amide [51].

It can be seen that the metal modification can improve the activity of the zeolite catalyst, promote the deoxygenation of oxygenated compounds during pyrolysis, and increase the content of aromatic hydrocarbons and other related target products. Metal loading can change the pore volume, specific surface area and acidity of the catalyst, which in turn affects the selectivity of related products. In fact, metal-doped catalysts make up for the lack of traditional zeolite catalysts in terms of deoxidation and target product selectivity. Catalysts that have been used in rapid pyrolysis include metal oxides, metal salts, precious metal-based catalysts, transition metal nitrides and carbides. In addition, the metal-modified catalyst also plays a role in slowing the coking and deactivation of the catalyst. However, the more metal loading is not the better; the appropriate amount of metal should be loaded according to the biomass and catalyst type.

2.3. Other Metal Catalysts

In recent years, in addition to the traditional zeolite catalysts and metal modified zeolite catalysts which are widely used in CFP, scholars have also studied the influence of metal catalysts on the yield and composition of CFP products.

Tan et al. carried out the ex situ catalytic pyrolysis experiment of SiO_2/Al_2O_3 [52]. The results revealed that although the liquid yield decreased slightly, aromatics and hydrocarbons increased. The catalyst has good deoxidation and regeneration properties. Kar et al. used V_2O_5 as a catalyst in pyrolysis to compare with the non catalytic pyrolysis of biomass. In the sub components of toluene and ethyl acetate prepared by catalytic pyrolysis, the oxygen content decreased, the carbon content increased, and the calorific value increased about 76%. In the future, they have more potential as a liquid fuel [53]. Gautam et al. studied the CFP of microalga and prepared γ-Al_2O_3, Mo/γ-Al_2O_3 and Co-Mo/γ-Al_2O_3 catalysts. The results proved that the Co-Mo/γ-Al_2O_3 catalyst with the ratio of 1:3 of catalyst-to-algae increased the yield of aliphatic olefins and long chain nitriles at 500 °C. The selectivity of Co-Mo/γ-Al_2O_3 to dimethyl ethylene and 1-isocyanobutane was 35%, which was higher than that of Mo/γ-Al_2O_3 (30.6%) and γ-Al_2O_3 (25.7%) [54]. Zhang et al. introduced ZrO_2 and CeO_2 into the γ-Al_2O_3 catalyst to prepare composite mesoporous catalyst. They found that the introduction of ZrO_2 can break the pyrolysis debris into small molecular compounds, inhibit the formation of coke, and improve the productivity of water gas. It can also be observed that the loading of Ce on the catalyst increased the deoxidation effect and the proportion of hydrocarbons in the liquid fuel and reduced the coke yield. Furthermore, the ratio of oxygenated aromatis to aliphatic hydrocarbons is arranged in the order of CeO_2/γ-Al_2O_3/ZrO_2 > γ-Al_2O_3/ZrO_2 > γ-Al_2O_3 > no catalyst [55].

Mg-Al-mixed oxides with diverse Mg/Al ratios were investigated as catalysts for biomass CFP. The catalyst with lower aluminum content is helpful for deoxidation, because the concentration of alkaline center is increased and oxygen is removed in the form of H_2O and CO_2, which further promotes the ketalization and aldol condensation of pyrolysis materials [56]. The catalyst with Mg/Al = 4.0 has the largest pore size and specific surface area, and the productivity of bio-oil is slightly higher than that of ZSM-5 at comparable level. Wang et al. conducted the CFP of glucose, cellobiose and cellulose with the catalyst of NaY. The results showed that NaY molecular sieve can significantly improve the content of furans and aromatics in the pyrolysis products of glucose, cellobiose and cellulose. The reactions of dehydration, decarbonylation or decarboxylation and fragmentation/retro-aldol took place on the surface of NaY, and the formation of aromatics and phenols is affected by the intermediate products, which is produced by cracking at the catalyst active center [57].

2.4. Deactivation and Regeneration of Zeolite Catalyst

The coking and deactivation of the catalyst is an important and challenging problem in CFP, which reduces the selectivity of the reaction products, thereby affecting the upgrade of the pyrolysis products and the life of the catalyst. Coke formation is the main cause of catalyst deactivation during fast pyrolysis [58]. The deposition of carbonaceous substances in the pores of the zeolite causes the blockage of the pores and the diffusion of pyrolysis products becomes difficult. On the other hand, the loss of key active sites in zeolite is the main reason leading to the decrease of catalyst activity [59,60]. Generally, coke or coke precursors of PAHs are generated by dehydrogenation, oligomerization, and other related reactions. As the number of catalytic pyrolysis cycles continue to increase, some reaction products that cause catalyst deactivation will increase. It was also found that the structural properties of the deposited coke catalyst have changed significantly. Stanton et al. found that the reaction mechanism of lignin and cellulose to produce coke is different [61]. The extension of the aromatization reaction in the acid center causes the cellulose to crack the steam to produce coke, which further seals the internal acid center. This blocks the escalation reaction, reduces PAH selectivity, and promotes the formation of oxygenated intermediates. The lignin cracking steam mainly forms coke by coking on the outer surface of ZSM-5, which leads to the inactivation of the surface cracking ability, but does not limit the active acid sites entering the microchannel. The results also confirmed that the coke generated in the catalytic pyrolysis of biomass is the main reason for the reduction of aromatics. Studies have also shown that gases generated during pyrolysis can also poison the Bronsted acid site of the catalyst [62].

In addition to blocking the pores or active sites of the catalyst with carbonaceous materials and causing the deactivation of the zeolite catalyst, the properties of the zeolite itself, such as related acidity and topology, also have an important effect on catalyst deactivation and overall stability. According to research, the degree of coke formation is related to the topology and acidity of the zeolite [63]. In a certain ratio of biomass to catalyst (1:5), the coke deposition of H-BEA (Si/Al = 25) catalyst is larger than that of the H-ZSM-5 (Si/Al = 23) catalyst in the process of lignin upgrading. Increasing the Si/Al ratio of H-BEA and H-ZSM-5 catalysts can reduce the amount of solid residues. Higher acid concentration and strength can easily increase coke formation and accelerate catalyst deactivation, which can be explained by two aspects [64]. On the one hand, higher acid site density leads to a more continuous reaction process, which increases the formation possibility of condensation, and finally accelerates the formation of coke. On the other hand, strong acidity accelerates the consumption rate of coke precursor, which leads to the acceleration of the coking process. The topological structure of zeolite is similar to that of the channel and the corresponding topological structure of different zeolite materials is different. It is reported that H-SAPO-34 has a large cavity and narrow connection, while HZSM-5 has an interconnection channel. The deactivation rate of H-SAPO-34 is faster than HZSM-5 [65]. The influence of topology results in such a result between zeolites. In addition, the reaction temperature also affects the formation of coke deposits and catalyst deactivation. Studies have shown that a large amount of coke material will be deposited, due to the formation of oligomer species and the repolymerization of bio-oil components such as phenol and benzene at temperatures of <450 °C [66]. Other derivatives of cyclic ketone and furans can also be converted into carbonaceous deposits at low temperatures. In the rapid pyrolysis of biomass, it is difficult to directly determine the deposit that can most inactivate the catalyst, due to the complexity of the deposit. A higher reaction temperature can significantly reduce the amount of coke deposited, however, it may cause the polymerization of derived aromatic compounds [67]. Ma et al. found that calcining spent catalyst in air at high temperature (above 550 °C) can remove coke and restore porosity and catalytic activity, but this recovery is not complete, which is due to the irreversible change of catalyst structure in the process of deactivation and regeneration [68].

Zeolite is rapidly inactivated due to the coking of the catalyst, and needs to be regenerated during CFP to restore catalyst activity. Catalyst type and reaction conditions affect the regeneration degree of the catalyst [69]. Therefore, the regeneration procedure should be established according to the raw materials, catalysts, process conditions, etc. The reaction/regeneration cycle of the catalyst in CFP

has been studied and shows good stability [70–73]. Carlson et al. studied ten reaction-regeneration cycles of the ZSM-5 catalyst [74]. It was found that the metal in the biomass was deposited on the catalyst after about 3 h of regeneration in the air. The total acidity of the catalyst decreases after 10 reactions at low temperature. The slight decrease in acidity level is related to the decrease in the intensity of the low-temperature peak from the ammonia temperature programmed desorption (TPD) curve. Yildiz et al. studied eight consecutive reaction/regeneration cycles on the newly-built semi-continuous pyrolysis unit [75]. The catalyst was regenerated through a programmed temperature increase (to 600 °C), and the performance of the regenerated catalyst was observed. The catalyst was more active in the first two cycles, but apparently lost activity in the last few cycles, showing that the regeneration efficiency was greatly reduced and the yield tended to return to the value of non-catalytic cracking. It was also observed that the ZSM-5 catalyst partially lost activity in the product distribution during a series of eight reaction/regeneration cycle experiments, and the regeneration was not complete. However, the activity in the formation of valuable target compounds (aromatics and phenols) is largely maintained. Exposure of the catalyst to pyrolytic carbon during regeneration leads to accumulation of biomass ash in the reactor, which is the main reason for incomplete regeneration.

In order to understand the effective regeneration conditions of zeolite used for CFP, Yung et al. conducted a series of experiments to determine the effect of regeneration temperature on the activity of ZSM-5 (SiO_2/Al_2O_3 = 30) [76]. The catalyst used for pine wood pyrolysis steam upgrading was oxidized in 4% O_2 at 500–700 °C, and reused for upgrading to evaluate the degree of catalyst regeneration. Replace the CFP reactivity with the ethylene model compound aromatization reaction to understand the biomass CFP reaction and regeneration process. Both sets of results show that ZSM-5 for biomass CFP can be completely regenerated at 650 °C and 700 °C within 20 min. If the catalyst is regenerated at 500 °C, the catalyst activity may never be fully recovered, although some coke will be removed. The characterization of the catalyst shows that a higher regeneration temperature is more effective for restoring Bronsted acid sites and catalyst mesoporosity, which is attributed to the rapid removal of aromatic coke deposits. In addition, the regeneration at 650 °C and 700 °C resulted in a slightly higher total porosity, due to the additional mesoporosity formed by the catalyst vapor compared to the original catalyst. Paasikallio et al. conducted a catalytic pyrolysis experiment using ZSM-5 in a biomass feed facility, to study the product quality of deoxidized pyrolysis oil under the condition of continuous catalyst regeneration [77]. They used different regeneration times and temperatures to prove the feasibility of periodic regeneration of the catalyst in the fluidized bed reactor. Under typical fast pyrolysis conditions, the catalyst begins to deactivate within 10–30 min, and the stronger the catalyst is, the faster it deactivates. The time required for catalyst regeneration depends on the air flow rate and the corresponding temperature. Prolonging the time after a certain limit has no significant effect on the regeneration results. The temperature has a significant effect on the combustion effect of the carbon deposits on the catalyst. A temperature of about 600 °C is not sufficient to remove all coke deposits. Increasing the temperature to about 680 °C can increase the efficiency of coke combustion, but it will reduce the specific surface area after catalyst regeneration. The results show that, compared with the bubbling fluidized-bed reactor (BFB), the circulating fluidized-bed reactor (CFB) type has better operation in the catalytic pyrolysis process, in terms of steam residence time, catalyst activity and regeneration characteristics.

The spent catalyst was calcined in air above 550 °C to remove the coke, which restored the porosity and activity to a great extent [68,78]. However, the recovery of catalytic activity is incomplete, due to the irreversible structural changes during the process of deactivation and regeneration. The performance of the reactivated catalyst can be optimized by fine-tuning the reaction conditions and catalyst regeneration. Mild oxidation conditions such as low temperature and slow heating are beneficial for catalyst regeneration. The performance of the catalyst after regeneration is generally lower than that of the original catalyst, but the study of ex situ CFP on silica-alumina catalyst shows that the yield and deoxidization degree of aromatics in the fifth round of catalyst regeneration are higher than those in the first round, which proves that the silica alumina catalyst has satisfactory reusability [52]. Using the

same catalyst to realize the ex situ CFP in the continuous reaction regeneration cycle is an effective way to avoid catalyst poisoning and prolong the life of the catalyst during the biomass pyrolysis process [79].

In general, it is necessary to perform the periodic regeneration of the catalyst in order to maintain the significant activity of the catalyst during continuous pyrolysis. New catalyst formulations, improved catalyst regeneration procedures and the optimization of temperature and space velocity are all potential strategies to further improve the results of CFP. Various catalysts have been studied in the literature using various scales and reactor types, and it remains to be seen whether these results can be well extended to actual pyrolysis processes under specific operating conditions.

3. Catalytic Co-Pyrolysis

The application of zeolite catalysts improves the yield of aromatics and olefins in bio-oil, but still produces a large number of solid residues, including biochar and coke. Although CFP of biomass can promote the generation of aromatics and the removal of oxygen in pyrolysis products, it leads to hydrogen deficiency and limits the content of hydrocarbons [11]. Moreover, the deactivation of the catalyst due to coking in the pyrolysis process has to be considered [61]. In order to make up for this defect, adding a hydrogen-rich material and biomass for CCP is considered as an effective way to alleviate the hydrogen shortage and reduce the amount of coke [80]. Many co-pyrolysis studies have shown that there is a prominent synergistic effect between biomass and co-reactants, which promotes the reduction of oxygenated compounds and improves the productivity of biofuel [81–84]. The co-pyrolysis of biomass and hydrogen-rich raw materials can effectively transform these wastes into useful chemical raw materials, which is of great significance for environmental pollution control and the comprehensive utilization of resources.

3.1. Co-Reactants in CCP

It is pointed out that the CCP of biomass and some hydrogen-rich substances (plastics, tires, etc.) can increase the productivity of aromatics. Recent studies about CCP are listed in Table 3. Among them are most of the research on the co-pyrolysis of plastics, such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS) [85–87]. In addition, waste tires and household garbage are used as additives in co-pyrolysis [88,89].

The CCP of xylan, cellulose, lignin and PE was analyzed in a series micro cracking furnace. It was found that the co-pyrolysis of biomass and PE improved the yields of aromatics and aliphatic hydrocarbons compared with their separate pyrolysis [90]. The co-pyrolysis of xylan and PE enhanced the yield of acetic acid, furan and dianhydride by 45%, and PE improved the yield of phenol monomers by promoting the depolymerization of lignin. On the other hand, the short carbon chain alkanes and olefins produced by biomass further facilitated the depolymerization of polyethylene. Studies have shown that the co-pyrolysis of lignin and LDPE can obviously reduce the coke. On the one hand, as a hydrogen donor, LDPE can eliminate side functional groups including methoxyl, and reduce the carbonization process of lignin. On the other hand, LDPE generates less charcoal during the pyrolysis process [91]. The largest content of the products is methoxyphenols in the separate CFP of lignin. With the increase of LDPE ratio in the mixture, more hydrogen radicals are served, and the content of phenol and alkylphenol increases significantly, while the proportion of methoxyphenols decreases due to the removal of the methoxyl group. Ding et al. conducted the CCP of xylan and LLDPE under the catalysis of HZSM-5, and experimental results revealed that the optimal ratio of xylan and LLDPE pyrolysis to obtain the highest aromatics yield (40%) was 1:1. The addition of LLDPE significantly reduced the content of oxygenates and converted them to hydrocarbons. Furthermore, the dominant mechanisms for the formation of hydrocarbons by furan compounds and non-furan compounds (ketones, aldehydes, acids, etc.) are the Diels–Alder reaction and the hydrocarbon pool mechanism, respectively [92]. Experimental results revealed that, with the increase of the ratio of LLDPE, the yield of MAHs increased, and the generation of PAHs was suppressed. The kinetics and

thermal behavior of co-pyrolysis of biomass and plastic were performed, and the experiment results proved that co-CFP technology can significantly reduce co-pyrolysis energy consumption [93,94].

In addition to LLDPE, HLDPE has also been extensively studied in co-pyrolysis. Xue et al. studied $MgCl_2$ and HZSM-5 catalyzed pine pyrolysis and HDPE co-pyrolysis experiments and obtained higher aromatic selectivity. The increase in aromatics yields is due to the reaction between the furfural obtained from the catalytic cracking of pine sawdust/$MgCl_2$ mixture and the short-chain olefins obtained from HDPE catalytic cracking [95]. In the co-pyrolysis of waste vegetable oil and HDPE, it was found that the yield of hydrocarbon fuels increased as the amount of HDPE added increased. In addition, hydrocarbon fuels have lower viscosity, higher heating value, and better fluidity, and their quality is higher than that of biodiesel [96]. It has been reported that the co-pyrolysis of boxwood with HDPE has a synergistic effect in the preparation of aromatics, especially xylene and toluene. The yield of aromatics obtained in the experiment is significantly higher than the theoretical yield, which is attributed to the enhanced Diels–Alder type reaction between furan produced from biomass pyrolysis and olefins produced from HDPE pyrolysis [97].

As a co-reactant in co-pyrolysis, PP has also been conducted in enhancing the quality and productivity of bio-oil. There is a synergistic effect in the pyrolysis process of green algae and PP. The coal coke yield is reduced, while the gas yield is increased. At the same time, the co-pyrolysis of green algae and PP inhibits the formation of nitrogen-containing compounds and promotes the generation of aromatics. This is mainly because the addition of PP increases H/C-eff and reduces the oxygen content in bio-oil. Additionally, the catalytic deoxygenation of molecular sieve catalysts HZSM-5 also plays a major role during pyrolysis [98]. The pyrolysis products of cellulose and PP on mesoporous catalysts (MCM-41 and Al-MCM-41) were analyzed by Py-GC/MS. The results indicated that CCP of cellulose and PP could significantly reduce the yield of furan, aliphatic and other oxygen-containing compounds, and improve the yield of aromatics and olefins [99]. This provides a way to solve the problems of the high acid content, low calorific value and high oxygen content of biofuel. Kumar et al. performed the in situ CCP of lignocellulosic biomass, PP and PS. When the feed proportion of biomass to plastic was 1:2, the selectivity of aromatics produced by PP and PS as co-reactants were 49% and 82%, respectively. The co-pyrolysis of lignocellulose and PS gained higher value ethylbenzene and styrene monomers at the appropriate ratio. The co-pyrolysis of lignocellulose and PP increased the H/C-eff ratio, and achieved higher overall yields of olefins and monoaromatics [100].

As a kind of polymer, waste tire has similar characteristics with plastic, and it also accounts for a certain proportion in the municipal solid waste. Landfilling is not a good method of disposal, due to the hard-to-degrade nature of used tires. Pyrolysis technology provides a promising approach to the disposal of waste tires. In recent years, there have been many research studies focusing on the co-pyrolysis of biomass and waste tires. Chen et al. studied the co-pyrolysis of kitchen waste and waste tires on the ZSM-5 catalyst. Experimental results revealed that pyrolysis can inhibit non hydrocarbon compounds and increase the content of hydrocarbons, especially olefins. The pyrolysis of kitchen waste and tires can reduce the activation energy of the reaction and show a coupling effect [101]. In another study of grape seed and waste tires, results indicated that adding waste tires (40%) to the feed can improve the yield of the organic phase and decrease the oxygen content, reducing the defects of acidity and the instability of biofuels. The co-pyrolysis of biomass and tires can gain higher value compounds, and the interaction between free radicals in the pyrolysis products is inseparable [102].

Table 3. Summary of studies on the catalytic co-pyrolysis (CCP) of biomass with hydrogen-rich materials.

Types of Materials			Reaction Conditions				Results		Ref.
Biomass	Co-Reactant	Catalyst	Biomass to Co-Reactant Ratio	Temp. (°C)	Reactor		Mainly Compounds		
Lignin	LDPE	MgO/HZSM-5	1:0	550	Microwave oven		Phenolic compounds		[91]
Lignin	LDPE	MgO/HZSM-5	2:1	550	Microwave oven		Phenolic compounds, aromatics		[91]
Lignin	LDPE	MgO/HZSM-5	1:1	550	Microwave oven		Aromatics, phenolic compounds		[91]
Lignin	LDPE	MgO/HZSM-5	1:2	550	Microwave oven		Aromatics		[91]
Corn stover	LDPE	CeO_2/HZSM-5	1:1	600	Tandem catalytic bed		Aliphatics, aromatics		[103]
Lignin	LDPE	Zn/lignin-char	-	500	Microwave oven		hydrocarbons, ketones, phenols		[104]
Cellulose	LLDPE	Non-Catalyst	1:1	600	Semi-batch		Hydrocarbons, sugars		[105]
Cellulose	LLDPE	MgO	1:1	600	Semi-batch		Hydrocarbons		[105]
Cellulose	LLDPE	MgO/C	1:1	600	Semi-batch		Hydrocarbons, MAHs		[105]
Cellulose	LLDPE	MgO/Al_2O_3	1:1	600	Semi-batch		Hydrocarbons		[105]
Cellulose	LLDPE	MgO/ZrO_2	1:1	600	Semi-batch		Hydrocarbons, oxygenate		[105]
Sugarcane bagasse	HDPE	FAU-EAFS	3:2	400	Fixed-bed		Hydrocarbons, aromatic, alcohol		[106]
Sugarcane bagasse	HDPE	FAU-EAFS	3:2	500	Fixed-bed		Hydrocarbons, alcohol		[106]
Sugarcane bagasse	HDPE	FAU-EAFS	3:2	600	Fixed-bed		Hydrocarbons, acid, alcohol		[106]
Switchgrass	PE	HZSM-5	1:1	500	-		Aromatic, hydrocarbons, Alkyl benzenes		[107]
Lignin	PP	HZSM-5	1:1	200	Microwave reactor		Aromatics, alkenes, cycloalkanes		[108]
Lignin	PP	HZSM-5	1:1	250	Microwave reactor		Cycloalkanes, aromatics, alkenes		[108]
Lignin	PP	HZSM-5	1:1	300	Microwave reactor		Aromatics, cycloalkanes, alkenes		[108]
Lignin	PP	HZSM-5	1:1	350	Microwave reactor		Alkenes, aromatics, cycloalkanes		[108]
Bamboo	PP	HZSM-5	1:0	250	Microwave oven		Oxygen-cont. aromatics, Oxygen-cont. aliphatics		[109]
Bamboo	PP	HZSM-5	2:1	250	Microwave oven		Aliphatics hydrocarbons, aromatics		[109]
Bamboo	PP	HZSM-5	1:1	250	Microwave oven		Aliphatics hydrocarbons, aromatics		[109]
Bamboo	PP	HZSM-5	1:2	250	Microwave oven		Aliphatics hydrocarbons		[109]
Bamboo	PP	HZSM-5	0:1	250	Microwave oven		Aliphatics hydrocarbons, aromatics		[109]
Laminaria japonica	PP	HZSM-5	1:1	600	Fixed-bed		MAHs, other hydrocarbons, PAHs		[110]
Laminaria japonica	PP	Pt/Meso MFI	1:1	600	Fixed-bed		MAHs, PAHs, Other hydrocarbons		[110]
Laminaria japonica	PP	Meso MFI	1:1	600	Fixed-bed		MAHs, PAHs, Other hydrocarbons		[110]
Laminaria japonica	PP	Al-SBA-16	1:1	600	Fixed-bed		Other hydrocarbons, MAHs, PAH, oxygenates		[110]
Rice straw	PP	HZSM-5	1:1	500	Microwave oven		Aliphatic HCs, MAHs		[111]
Bagasse	PP	HZSM-5	1:1	500	Microwave oven		Aliphatic HCs		[111]
Rice straw	PS	HZSM-5	1:1	500	Microwave oven		MAHs		[111]
Bagasse	PS	HZSM-5	1:1	500	Microwave oven		MAHs, PAHs		[111]
Cellulose	PP	HZSM-5	1:1	500	Microwave oven		BTEXs, Light olefins		[112]
Lignin	PS	Spent FCC	1:1	600	Continuous fluidized bed		Styrene		[113]
Cellulose	PS	HZSM-5	2:1	550	Pyroprobe pyrolyzer		Benzene, polyaromatics		[114]
Grape seeds	Waste tires	Ca-based-1	5:1	-	Auger reactor		Aromatics, cyclic HC, olefin		[115]
Bamboo sawdust	Waste tires	HZSM-5/MgO	2:3	550	A tandem reactor		Aromatics hydrocarbons, olefins		[116]

3.2. Mechanism of Catalyst in CCP

In the CCP of biomass and co-reactants, the catalyst has a vital effect on chemical reactions and product distribution. The introduction of various catalysts makes the CCP mechanism more complicated, but it is necessary to research the reaction mechanism of the catalyst site. Ryu et al. studied the CCP of cellulose and LLDPE on three MgO impregnated catalysts (MgO/C, MgO/Al$_2$O$_3$ and MgO/ZrO$_2$). The experimental results indicated that MgO/C has higher selectivity for aromatics than other catalysts. This is because the plastic provides a hydrogen donor to efficiently convert the furan compounds produced by cellulose on MgO/C to aromatic hydrocarbons [105]. Ding et al. pyrolyzed xylan and LLDPE in a double catalyst bed (CaO/HZSM-5), to increase the aromatics yield from 27% (HZSM-5) to 40% (CaO/HZSM-5). The results show that CaO can effectively convert acid to ketone, and then ketone is aromatized on HZSM-5. LLDPE derived olefins further improve the hydrocarbon generation by participating in the hydrocarbon pool reaction and Diels–Alder reaction. Furthermore, compared with the single HZSM-5 catalyst bed, the double catalytic section of CaO and HZSM-5 can increase the yield of olefins and aromatics, and has great prospects for increasing the value of pyrolysis products [117].

The catalytic effect of mesoporous Al-MCM-41 and microporous HZSM-5 catalysts on the co-pyrolysis of yellow poplar and HDPE was carried out. It was found that the aromatics and gas yields of the HZSM-5 catalyst were higher, which indicated that the pyrolysis products of long chain hydrocarbons from HDPE pyrolysis were more easily converted into aromatics. On the other hand, HZSM-5 catalyst produces less coke compared with Al-MCM-41. This is because the weak acidity of Al-MCM-41 can not effectively catalyze the deoxidization of biomass pyrolysis products, resulting in the priority of oxygen-containing compounds on the catalyst surface to generate coke [97]. The properties of catalysts, such as acidity and pore size, are important factors affecting catalytic pyrolysis, which are also reflected in CCP. The co-pyrolysis of yellow poplar and HDPE (1:1) on three mesoporous solid acid catalysts (meso-MFI, meso-Y and Al-SBA-15) was discussed. Meso-MFI catalysts with high acidity lead to an increased yield of aromatics and low-carbon olefins produced by pyrolysis, compared to the other two catalysts with lower acidity. experimental yields, indicating that the process of coke formation from pyrolysis was suppressed in the presence of HDPE hydrogen donors [118]. Experimental results revealed that the acidity of ZSM-5 is stronger than that of Al-SBA-15, so it has better aromatics generation characteristics in the CCP of cellulose and LLDPE [119]. Another co-pyrolysis research study found that the number of acid centers in meso-MFI was larger than that in Pt/meso-MFI, which may be due to the loss of some acid centers on the meso-MFI, because of platinum loading. However, Pt/meso-MFI has higher actual deoxidation efficiency and aromatic yield than MFI, which is attributed to the catalytic cracking and deoxidization [110]. Compared with Al-SBA-16, HZSM-5 has a strong acid. Nevertheless, the deoxidization efficiency of HZSM-5 is less than that of the Al-SBA-16 catalyst, mainly because HZSM-5 has a smaller pore structure and Al-SBA-16 does not have excellent mesoporous structure performance. It also shows that the pore size of the catalyst has an important influence on the catalytic performance and the deoxidization efficiency of oxygenated compounds.

Lee et al. investigated the co-pyrolysis of cellulose and PP on HZSM-5 and HBeta catalysts, and the results showed that the yield of aromatics obtained on HZSM-5 catalysts (30, 50, and 80) was higher than that of HBeta (25) catalysts. NH3-TPD analysis shows that HBeta has a higher acid center density than HZSM-5 (30, 50, and 80), which means that HBeta has a higher acidity than HZSM-5, although HBeta (25) has a lower SiO$_2$/Al$_2$O$_3$ ratio than the HZSM-5 catalyst [112]. The co-pyrolysis of cellulose and PP has a synergistic effect in the production of aromatics. The co-pyrolysis of bagasse and PS on mesoporous metal oxides (MgO, CaO) and microporous HZSM-5 was studied. Compared with single HZSM-5, the mixture of HZSM-5 and CaO in a proper proportion can reduce the oxygen-containing compounds and increase the monocyclic aromatics, which may be attributed to the further decomposition of some heavy compounds into aromatics on microporous HZSM-5 after conversion to light compounds on mesoporous calcium oxide. In addition, increasing the proportion

of MgO in the MgO/HZSM-5 catalyst can increase the content of aromatic hydrocarbons, which shows that the basic catalyst promotes the process of deoxidation and aldehyde condensation, as well as the conversion of acid to ketone [120]. Compared with CaO catalyst, basic MgO has better catalytic performance and an excellent performance in improving crude oil quality.

It can be said that the inherent nature of hydrogen deficiency of lignocellulosic biomass is an important reason for the high yield of coke and low aromatics. A suitable hydrogen-carbon effective (H/C eff) ratio can reduce the formation of coke and increase the carbon efficiency of aromatics. CCP is based on the mechanism of synergy to make lignocellulosic biomass co-react with a hydrogen-rich source to obtain a better product. In the above analysis, waste plastics and waste tires are the most common reactants of fast pyrolysis, which are easily available sources of hydrogen. The co-feeding of polymer waste and biomass in catalytic pyrolysis is very beneficial for energy recovery and environmental protection, and CCP technology is better than the pyrolysis of biomass alone. The advantages of CCP in improving the quality and yield of bio-oil products increase the possibility of their commercialization in the future.

4. Microwave-Assisted Pyrolysis Technology

MAP technology is a new technology that has been widely studied and used in the field of pyrolysis in recent years. Microwave technology is used in various disciplines, especially in the production of clean energy. Microwave refers to electromagnetic waves with a wavelength of 1 mm to 1 m (corresponding frequency is 0.3 to 300 GHz), which is between radio waves and infrared radiation. Different from the traditional external heating methods, such as convection, conduction and radiation, the microwave can penetrate deep inside the biomass raw materials and is a dielectric heating method from the inside to the outside. This heating method can cause intense collisions and friction between molecules to generate heat and heat the object. Microwave thermogravimetric analysis showed that MAP reduced the initial decomposition temperature of biomass components and shifted the fastest weightless region to lower temperature intervals compared with conventional pyrolysis [121]. Therefore, MAP has the advantages of faster heating rate, higher energy utilization rate, shorter reaction time, and better selectivity [122,123].

In the MAP of biomass, the pretreatment methods for biomass, the addition of microwave adsorbents and catalysts and the pyrolysis operation parameters all have an impact on the pyrolysis results. Feng et al. discussed the effect of microwave-assisted formic acid pretreatment on the pyrolysis of beech wood. They found that formic acid pretreatment of beech wood before CFP can increase the productivity of valuable aromatics in the pyrolysis products and decrease the amount of solid residues [124]. In addition, Dai et al. found that microwave-assisted formic acid pretreatment reduced the content of volatile and ash in bamboo sawdust, increased its high calorific value and the content of sugar in pyrolysis products, while the amount of acid, ketone and phenol decreased [125]. This provides an effective method for upgrading the quality of pyrolysis products. Studies have shown that the microwave-assisted acid-treated lignin has improved thermal stability, reduced alkoxyphenols, and increased the yield of phenol in pyrolysis steam. During the pretreatment process, C=O groups are formed, while β-O-4 bonds and aliphatic side chains are cleaved and -OH groups are reduced [126]. Three factors affecting the distribution and content of pyrolysis products were studied: microwave irradiation time, radiation temperature and acid concentration. It was found that the pretreatment with hydrochloric acid could improve the content of bio-oil, and reduce oxygenated compounds such as phenol. Compared with the untreated control group, the coal coke yield decreased by 8% after pretreatment at 150 °C [127,128]. However, the acid concentration and reaction time need to be controlled under appropriate conditions, otherwise it is not conducive to the upgrading of bio-oil. The pyrolysis results of bamboo sawdust showed that microwave temperature was the most important factor and acid pretreatment reduced hydrogen bonding and acetyl groups [129]. Besides, microwave-assisted organic solvent (glycerol) hydrolysis pretreatment can increase the yield of levoglucosan in the process of obtaining dehydrated sugar by the fast pyrolysis of biomass, compared

with the direct pyrolysis of biomass. This also provides a solution to the problem of low anhydrosugars for the fast pyrolysis of biomass [130]. There are also studies showing that microwave-assisted glycerol pretreatment can remove minerals and lignin and increase glucose production during enzymatic hydrolysis [131]. Biomass raw materials usually have a high water content, low viscosity, low calorific value and a difficulty in the ignition of bio-oil. Studies have found that biomass can be roasted before pyrolysis to reduce the moisture content of bio-oil and produce high-quality biofuel [132].

Microwave heating has the characteristics of selective heating. Some biomass with a poor absorption of microwave energy cannot reach the optimal pyrolysis range under dielectric heating. A certain amount of microwave absorbent is usually added to microwave pyrolysis in order to further increase the heating rate [133]. Carbon materials (carbon, biochar, silicon carbide, new graphene aerogels etc.) are very good microwave absorbents, which can rapidly increase the microwave pyrolysis temperature and achieve fast and effective pyrolysis [134–137]. The mixing of biomass and absorbency in MAP includes a premixed method and a non-premixed method; the former is mixing the microwave absorbent and the biomass and the latter is pouring the biomass into the microwave absorbent bed [138]. The adsorbent can also play a certain catalytic role while increasing the heating rate. Compared with the free microwave adsorbent pyrolysis in the microwave pyrolysis of soap materials, using SiC as the adsorbent can improve the overall yield of hydrocarbons and the selectivity of alkanes and aromatics [139]. Activated carbon and brown coal can also be used as catalysts in MAP to increase the heating rate. The results indicated that activated carbon promoted the selective production of phenolic compounds [140]. The addition of microwave adjuvants promotes deoxidation and aromatization during pyrolysis. The use of SiC in the pyrolysis of chlorella, wood chips and mixed samples has achieved higher selectivity to olefins, phenols and alkanes, respectively [141]. Mohamed et al. added a mixture of K_3PO_4 and clinoptilolite or bentonite in the MAP of willow branches. These solid additives are used as both microwave absorbers and catalysts, to increase heating rates and improve the quality of bio-oil and bio-char. Compared with SiC as an absorption material, the introduction of mixed solid additives can obtain a biofuel with a lower water content [142]. The addition of bentonite has also been proven to increase product yield, decrease water content and increase the BET surface area of bio-char. The bio-char obtained has a higher Cd^{2+} removal efficiency [143]. It has also been found that the catalyst mixture affects the type of carbon on the catalyst surface area during pyrolysis. Graphite coke deposited on the catalyst surface can increase the microwave heating rate, while oxidized coke reduces the microwave heating rate [144]. The simultaneous use of a hierarchical ZSM-5/MCM-41 catalyst and a SiC microwave absorber can significantly increase the total hydrocarbon carbon yield [145].

The raw material characteristics and reaction conditions in MAP affect the yield and quality of pyrolysis products. Zhang et al. reviewed the effect of raw material characteristics on MAP and compared its relationship with conventional electric heating [146]. In addition to the load of the microwave absorbent in the reaction conditions, microwave power, reaction temperature and reaction time are also commonly studied process parameters. Li et al. studied the conditions for preparing bio-oil by the MAP of cotton stalk. When the best bio-oil yield was obtained (32.47%), the three operating variables were the reaction temperature of 550 °C, the reaction time of 24 min and the microwave power of 1800 w [147]. The study found that microwave power and pyrolysis time did not obviously affect the yield of the product [148,149]. Zhang et al. reviewed the main operating conditions of MAP and concluded that the optimal microwave power, pyrolysis time and pyrolysis temperature were 300–1500 w, 6–25 min and 400–800 °C, respectively [15]. Catalytic temperature and feed ratio have a key effect on the productivity and composition of bio-oil. As the temperature increases, the liquid yield increases and there is an optimum temperature, because it will decrease as the temperature continues to increase [145,150]. In addition, the optimal pyrolysis temperature and catalytic temperature will not be consistent in the two separate stages of pyrolysis and catalysis, which is a problem to be considered [151]. As mentioned earlier, the catalyst plays a catalytic role in pyrolysis and improves the quality of bio-oil. In addition to carbon materials that act as both microwave absorbers and catalysts, metal oxides (CaO, MgO) and zeolite catalysts (ZSM-5, HZSM-5,

MCM-41) have been used in MAP [22,152–155]. MAP has in situ catalytic pyrolysis and ex situ catalytic pyrolysis modes. Comparing the two forms, the in situ catalysis method is a commonly used pyrolysis method, because the experimental device is simpler, but there are problems of high catalyst deactivation rate and difficult catalyst recovery. Ex situ catalytic reactions require complex experimental equipment, but have the advantages of simple catalyst recovery and low deactivation rate [156]. Moreover, Fan et al. studied the in situ and ex situ catalytic conversion of vapors from MAP of lignin, and the results showed that the bio-oil produced by ex situ catalysis has higher yield, better selectivity to aromatics and lower coke yield, compared with in situ catalytic treatment [157]. Zhang et al. independently controlled microwave pyrolysis and catalytic reforming. The pyrolysis gas generated from the pyrolysis of biomass was catalytically upgraded through a packed bed of the catalyst, which confirmed the good reusability of the catalyst [55].

Because MAP technology can obtain liquid fuel, syngas and solid carbon materials with higher economic value, it has been well applied and studied in pyrolysis. Zhang et al. conducted a microwave pyrolysis of low-grade lignite to produce bio-oil, and found that MAP is more suitable for lignite-to-oil technology than electric heating pyrolysis [158]. It was found that microwave heating can cause cyclization and aromatization reactions in the pyrolysis of bituminous coal. The MAP of bituminous coal can not only change the pore structure of bituminous coal to create a seepage space for the fluid, but also release volatiles and moisture [159]. Wang et al. used modified HZSM-5 catalyst for the microwave-assisted pyrolysis of cellulose, to obtain a higher selectivity of phenol-rich bio-oil [160]. On the other hand, MAPs can be used to selectively produce phenolic compounds, which enables the recycling of waste resources [161]. The integrated recovery process in which vacuum distillation and MAP are connected in series has a good application prospect in the recovery and treatment of waste engine oil [162]. The biodiesel-distilled raffinate was rich in higher molecular weight methyl esters and MAP was used to recover the methyl esters, which proved to have a higher recovery rate [163]. There are certain advantages in using microwave heating technology to combustible gas from biomass pyrolysis. An activated carbon-supported iron (III) ion catalyst was used for MAP to prepare high-synthesis gas. Its H_2/CO was 1.04 and the content was 81.14 vol% [164]. MAP and activated carbon reforming can produce high-value hydrogen-rich syngas from biomass [165]. Bio-char prepared from MAP biomass can be used as an adsorbent to remove phenolic compounds from industrial wastewater [166]. Additionally, Lam et al. combined MAP technology with chemical impregnation activation, to produce activated carbon containing a high content of fixed carbon (83 wt%), and a high BET surface area (1350 m^2/g), which improves the durability of activated carbon, and can be used as a fuel adsorbent [167]. The bio-char produced by microwave-catalyzed pyrolysis has higher porosity and stronger cation exchange capacity compared with the bio-char produced by traditional pyrolysis, which can improve soil water retention capacity and fertile sandy soil [168].

5. Conclusions

CFP is a promising technology to convert solid biomass into liquid biofuel, which can reduce our dependence on fossil fuels in the future. There are some disadvantages of pyrolysis bio-oil, such as high oxygen content, high acidity, low calorific value and poor stability. Zeolite catalyst shows excellent aromatization and alkylation ability in CCP, which can improve the yield and selectivity of aromatics and other products, and make a certain contribution to improve the quality of pyrolysis products. The classification structure and the appropriate number of micropores and mesopores have an important influence on improving the performance of the catalyst. The modification of zeolite catalyst by adding metal has proven to be effective in improving the skeleton structure of a catalyst, increasing the activity of a catalyst and obtaining the desired high yield of product. The number of acid centers, pore volume and specific surface area are important characteristic parameters of catalyst. The coking and deactivation of catalyst is a problem worthy of attention. While improving the quality of pyrolysis products, how to inhibit the deactivation of catalyst and improve the life of catalyst need further study. The reaction mechanism of the zeolite catalyst in CFP has been discussed, but there is

a lack of more in-depth study. In order to obtain the desired target products, directional control of pyrolysis process is needed. Therefore, it is necessary to select the appropriate catalyst and catalytic process according to the composition and characteristics of biomass, so as to selectively enhance the specific reaction. From the perspective of biomass raw materials, CCP can feed biomass together with hydrogen-rich substances in pyrolysis, which solves the problem of biomass hydrogen shortage. Therefore, it has a better prospect than the catalytic pyrolysis of biomass alone. The co-pyrolysis of biomass and hydrogen-rich materials has been proved to have a significant synergistic effect, which can reduce the activation energy of the reaction, improve the yield and quality of pyrolysis products, reduce the amount of coke and provide a method for the recycling of plastics, tires and other wastes. In CCP, the proportion of hydrogen-rich materials and biomass has an important influence on the pyrolysis components. The appropriate pyrolysis conditions should be selected according to the desired target products. Most of this technology is still in the laboratory scale and it needs to be enlarged. The mechanism of hydrocarbon pool reaction and Diels–Alder reaction are proposed to explain the behavior in pyrolysis. The synergistic effect between biomass and co-reactant and the reaction mechanism at catalyst site is obtained by analyzing the pyrolysis products. The specific reaction mechanism in the middle is not very clear, so that further research is still needed by means of new analysis methods. MAP is better than traditional heating in energy utilization, heating rate and selectivity, and it is now recognized as a more effective and stable way of biomass conversion. Appropriate pretreatment is of great benefit to increase the valuable products of pyrolysis products. By adding microwave adsorbent, catalysts and suitable pyrolysis conditions, it is beneficial to obtain a higher quality and yield of biofuels, syngas and high value-added carbon materials. MAP technology has made some progress at present, but there is still a certain gap from the large-scale industrial application of MAP technology. In the future, further efforts are needed in the development of high-efficiency microwave adsorbents, the basic theory of microwave pyrolysis processes, and the reduction of economic cost.

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