

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Catalytic Fast Pyrolysis of Lignocellulosic Biomass to Benzene, Toluene, and Xylenes

William H. Gong

## Abstract

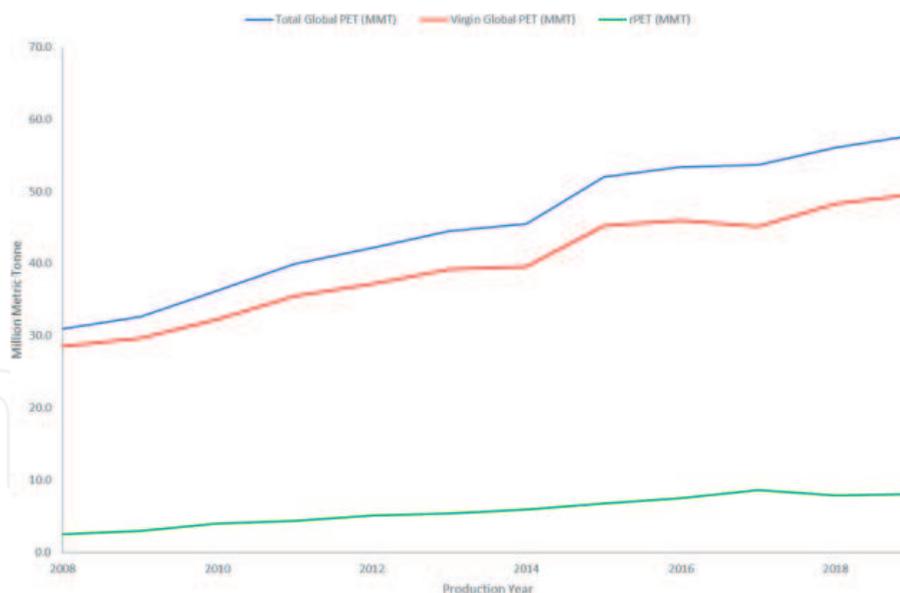
Catalytic Fast Pyrolysis is a rapid method to depolymerize lignocellulose to its constituent components of hemicellulose, cellulose, and lignin. The pyrolysis reaction in absence of oxygen occurs at a very high heating rate to a targeted temperature of 400 to 600 °C for very short residence time. Vapors which are not condensed and are then contacted with a catalyst that is efficient to deoxygenate and aromatize the pyrolyzed biomass. One class of highly valuable material that is produced is a mixture of benzene, toluene, and xylenes. From this mixture, *para*-xylene is extracted for further upgrading to polyethylene terephthalate, a commodity polyester which has a demand in excess of 80 million tonnes/year. Addressed within this review is the catalytic fast pyrolysis, catalysts examined, process chemistry, challenges, and investigation of solutions.

**Keywords:** CFP, Catalytic Fast Pyrolysis, BTX, Benzene, Toluene, Xylene, Lignocellulose, Cellulose, Hemicellulose, Lignin, Minerals

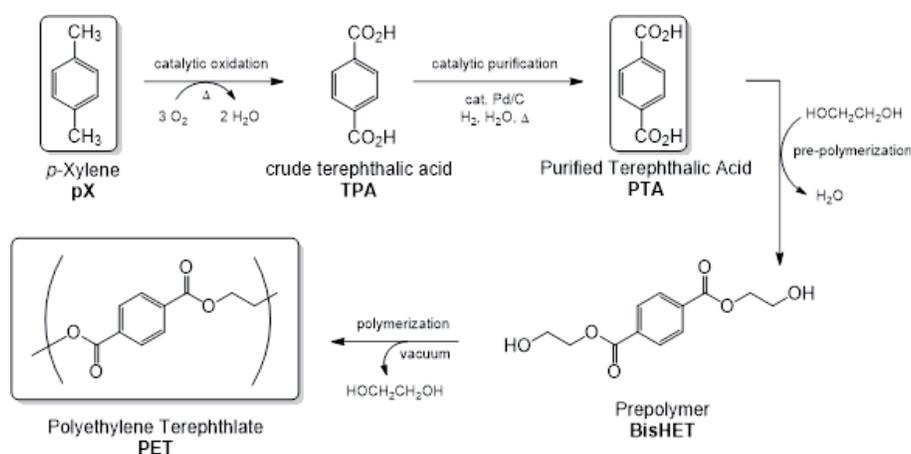
## 1. Introduction

*para*-Xylene (pX) is a key raw material in the production polyethylene terephthalate (PTA) before it is combined with mono ethylene glycol (MEG) to produce polyethylene terephthalate (PET), one of the largest and fastest globally growing polymers. Demand for pX is driven by the global polyester growth. Global polyester consumption is currently around 80 million tonnes/year. Using application of PET in fiber, this polyester is produced in 57.7 million metric tonne in 2019. Since 2008, the average growth in production has an annual increase of 5.9% (see **Figure 1**) [1]. Industry forecasts are that polyester will continue to grow at approximately 4% annually. While there is also increased focus on recycling polyester (a.k.a. rPET), most industry experts also see continued demand growth in virgin material due to limits on the availability of recycled polyester and need for virgin material to meet quality and specifications of many applications. Over the span between 2008 and 2019, rPET produced has ranged from 2 to 9% of total global PET for fiber applications. Currently, PTA is produced from pX where 0.58 tonnes of pX are required to produce one tonne of polyester, resulting in global demand for pX of about 50 million tonnes (**Figure 2**).

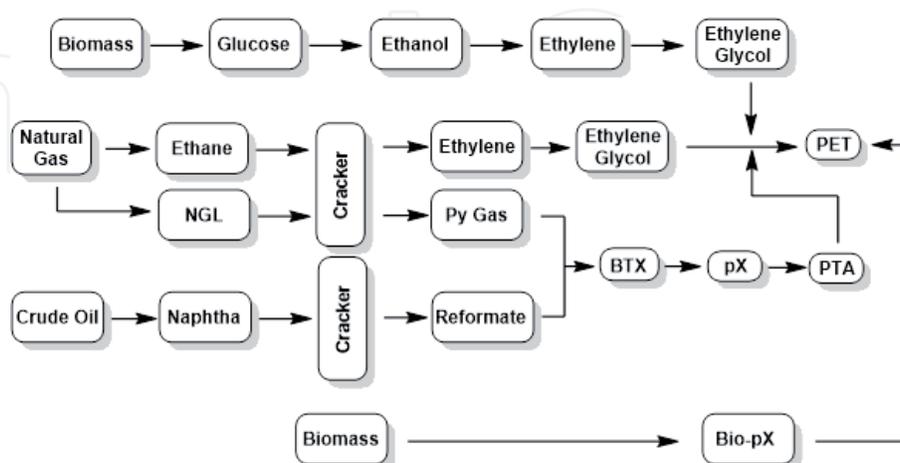
**Figure 3** displays the supply chain to produce PET. Virtually all PET is produced from fossil fuel resources. pX is produced from mixed xylenes that are derived from crude oil, and MEG is produced from ethylene primarily derived from natural gas. There is a commercial bio-based route to MEG that starts from ethanol produced



**Figure 1.**  
Annual PET Fiber produced from 2008 to 2019.



**Figure 2.**  
Pathway from p-xylene to polyethylene terephthalate (PET).



**Figure 3.**  
Supply chain to PET.

from biomass by dehydration to ethylene, oxygenation to ethylene oxide, and hydrolysis to MEG. Bio-based MEG is used to produce a partial bio (~30%) PET. At the current time, there are no commercial routes to bio-pX.

Conventional pX technology is based on the isomerization of mixed xylenes which has been practiced commercially for decades. The mixed xylenes are produced by catalytic reforming of naphtha, which produces a C<sub>8</sub> stream that includes the three xylene isomers and ethylbenzene. Other routes to mixed xylenes are from the pyrolysis gasoline stream produced in a naphtha steam cracker. The main commercial routes used to separate the pX isomer are crystallization, which takes advantage of the different freeze points of the ortho-, meta- and para- isomers, or via selective adsorption separation processes.

As a result of growing concerns about climate change, companies, governments, and consumers are increasing their focus on ways to reduce the carbon footprint of materials and offer more sustainable products. Consequently, companies are looking at new and innovative technologies to produce pX from renewable biomass resources rather than from crude oil, to enable production of a 100% bio polyester product. This report focuses catalytic fast pyrolysis (CFP) of lignocellulose to bio-oils which are refined to bio-pX with the objective to reduce carbon footprint in comparison to petro-pX. There are other processes currently being developed for bio-pX, but a discussion of these processes are beyond the scope of this paper.

As the world is emerging from the global pandemic of 2020–2021, increasingly, big companies have turned their focus on sustainability and establishing aggressive targets to reduce the carbon footprint of their products and over time move toward a net-zero carbon profile. It was earlier in 2009 Coca-Cola announced their rollout of the PlantBottle™ [2]. Coca-Cola's mission is to reduce reliance on non-renewable resources, and reduce CO<sub>2</sub> emission in polyethylene terephthalate (PET). Currently, only 30% of the PET in PlantBottle™ is made from bio-MEG. A commercialized process for bio-PTA process would enable Coca-Cola (and others) to produce 100% bio-PET PlantBottle™. Advantageously, bio-PET production would be a “drop-in” into existing PET assets. By 2012, Coca-Cola, Ford, Heinz, Nike, and Procter & Gamble founded the “Plant PET Technology Collaborative” and announced their mission [3]:

“PTC members are committed to supporting and championing research, expanding knowledge and accelerating technology development to enable commercially viable, more sustainably sourced 100% plant-based PET plastic while reducing the use of fossil fuels”. Similarly, Danone, Nestlé Waters, Origin Materials and PepsiCo formed the NaturALL Bottle Alliance in 2018. Since Coca-Cola's 2009 announcement, many have gravitated to the challenge to develop bio-PTA.

The reduced carbon footprint of bio-pX, and consequently bio-polyester, can contribute to meeting these carbon reduction goals for companies that participate in the polyester value chain, and this is the key business driver behind the increasing interest in routes to bio pX. The bottom line: once bio-pX is available, oxidation of bio-pX to bio-PTA would produce 100% bio-PET.

## **2. Biomass catalytic pyrolysis and upgrading to aromatics**

Anellotech, a Pearl, NY start-up chemical company founded in 2008, has developed a feedstock flexible, in situ catalytic fast pyrolysis process to convert low-cost lignocellulosic biomass solids to a range of hydrocarbons containing valuable benzene, toluene, and xylenes (BTX). These monoaromatics are further refined to produce bio-pX which are valuable feedstocks for bio-PTA [4–13]. In situ CFP technology was originally developed by Dr. George W. Huber, Harvey Spangler Professor of Chemical Engineering at the University of Wisconsin-Madison.

Anellotech has partnered with Suntory, a global consumer beverage company. The technology has been jointly developed by IFPEN, Axen (a subsidiary of

IFPEN), and Johnson Matthey. IFPEN is tasked with scale-up, Axen for technology marketing, and Johnson Matthey for catalyst development. On May 6, 2019, Anellotech announced successful six months of operations of their Bio-TCat™ continuous process in their Silsbee, TX pilot plant. The bio-pX process yield ranged from 22 to 24%, 98% C<sub>6</sub>+ aromatics. Currently, Anellotech is seeking partners and funding to construct their first commercial CFP based bio-pX plant (500 bone-dry tonnes/day of loblolly pine and target production of 40,000 tonnes BTX and C<sub>9</sub>+ aromatics per year).

Pyrolysis is an extraordinarily complex, thermochemical reaction which can be operated in slow or fast mode to yield products ranging from solids to liquids and gas. Pyrolysis is challenged by high feedstock complexity and the multiphase nature of this process. More than 300 compounds are found in an acidic, aqueous, unstable, and viscous heterogeneous mixture (a.k.a. pyrolysis oil) of esters, alcohols, ketones, aldehydes, and carboxylic acids [14–16]. By themselves, these oxygenates have little fuel value. However, they can be catalytically upgraded to aromatic hydrocarbons, particularly bio-pX. The upgrading catalyst must maintain stability and tolerate wide range of oxygenates [17]. CFP can convert the entire plant, not just sugars, which makes this thermochemical process advantageous to fermentation [18].

Zeolites, particularly HZMS-5, have proven to be effective catalysts for pyrolysis oil upgrading to benzene, toluene, and xylenes (BTX). Crystalline zeolites have well-defined microporous structures with pore sizes ranging from 5 to 12 Å. Zeolites are acidic materials with controllable acid site densities. CFP must operate under O<sub>2</sub>-free, optionally ambient pressure, and does not require H<sub>2</sub> (a.k.a. hydroprocessing), but operating under H<sub>2</sub> atmosphere might offer advantage of decreased coking (discussed later in this chapter).

Temperature is an important parameter. In CFP, a moderate temperature of approximately 450 to 550 °C is optimum to produce mainly liquids, but the heating and subsequent cooling rates must be extremely high. The biomass must be ground to a finely divided material with averaged particle sizes of less than 3 mm. The cost of the process is inversely proportional to the averaged particle size. The pyrolysis vapor must condense quickly to avoid unwanted secondary reactions such as cracking. Alkali and alkaline earth metal ions in biomass feed pose substantial challenges to the process (addressed in Pretreatment) [17, 19–33].

### 3. In situ vs. ex situ CFP

There are two process schemes that can be employed in CFP: in situ and ex situ [32, 34]. Pyrolysis and catalytic upgrading that occur in the same zone is in situ. This “one-pot” process is lower in cost than ex situ. However, in situ CFP is sensitive biomass feed content of inorganics, and minimum catalyst/biomass ratio where 10:1 gives highest yield of aromatics [35].

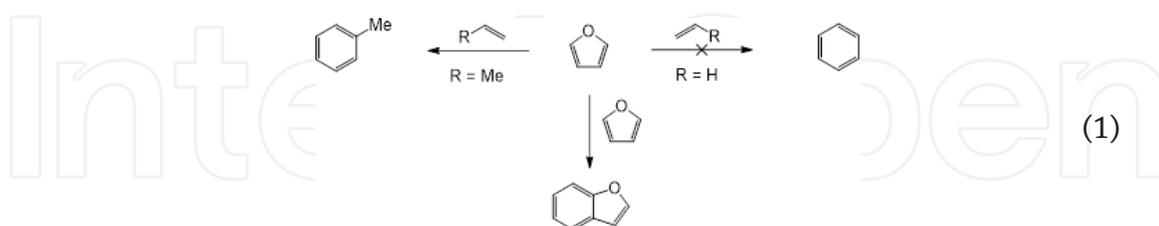
Pyrolysis and catalytic vapor upgrade that occur in separate zones (two-stage) is ex situ CFP. This mode of operation affords the advantage to exclude biochar and metallic ionic impurities from the catalyst which can extend catalyst lifetime. Additionally, the temperature of pyrolysis and vapor upgrade can be independently controlled, an option not available for in situ CFP. BioBTX operates an ex situ pyrolysis process, and has developed an integrated cascading pyrolysis reactor. Their two-stage process excludes non-volatile impurities from entering catalyst pores and this provides the benefit of improved catalyst vapor contact [26].

A comparison of in situ and ex situ CFP of hybrid poplar at 700 °C was conducted in a microreactor. In situ CFP produced 5.4% olefins and 26.1% aromatics.

While operating in an ex situ mode, up to 17.4% olefins and 18.9% aromatics were made. The carbonaceous material yields for in situ and ex situ were 31.3% and 18.6%, respectively. Temperature strongly influenced the product distribution in ex situ. A comparison of both modes of operations in a mini-plant for CFP of pinewood was conducted [36]. An analysis of ex situ economics has also been published [37].

#### 4. Mechanism

Fast pyrolysis rapidly depolymerizes lignocellulose to its constituents: hemicellulose, cellulose, and lignin. Under these conditions, cellulose is depolymerized to glucose, hemicellulose to C<sub>5</sub> sugars, and lignin to phenolic compounds [22, 38, 39]. Once glucose is made, it is quickly dehydrated to anhydrosugars which are then converted to furanics. Furanics are diffused into zeolite pores where it is combined with in situ olefins and undergo Diels Alder cyclization and dehydration to aromatics. Zeolite imparts a “confinement effect” for chemicals undergoing dehydrocyclization within the catalyst interior and once formed, monoaromatics exit the catalyst [40]. At a molecular level, at 450–600 °C, the furanic oxygen coordinates to Al of the zeolite. Deoxygenation of organics result in elimination of CO<sub>2</sub>, CO, and H<sub>2</sub>O. As a test of this hypothesis, furan and olefins were used as models in HZSM-5 catalyzed upgrading. HZSM-5 has a three-dimensional pore structure with intersecting systems of 10-membered ring pores. The dimension of ring pores is nearly ideal for production of pX: 5.1 x 5.5 Å (sinusoidal pores), and 5.3 x 5.6 Å (straight pores) [41]. HZSM-5’s utility in conversion of oxygenates to aromatics was demonstrated by Mobil’s commercial methanol-to-gasoline process. Within HZSM-5, ethylene and furan did not yield benzene, but replacement of ethylene by propylene led to toluene [42]. Likewise, 2-methylfuran and propylene produced xylenes. In the absence of olefins, Diels Alder dimerization and dehydration of furan results in benzofuran (Eq. (1)). Graphitic coke was also deposited onto the catalyst, which contributed to catalyst deactivation in about 30 minutes. When the upgrading temperature was increased to 650 °C, the selectivity was shifted to olefins.



Other investigators have examined conversion of methylated furan over Ga/HZSM-5 [43]. Even though model compounds were used, the reaction network was extremely complex due to numerous secondary reactions at 300–500 °C. Coking became a dominant reaction at temperature above 500 °C.

A “technical catalyst” such as extruded Al<sub>2</sub>O<sub>3</sub>-HZSM-5 was explored in CFP of pine wood and cellulose at 500 °C [44]. The focus of the study was on effect of pyrolysis temperature. The type of coke made was highly dependent on the feedstock. Yet, even by 2020, the mechanism of CFP remained elusive. Gaps still exist between theoretical models and applied pyrolysis. Thus far, there is still insufficient information generated from a single biomass source [45]. High aromatics selectivity and strong resistance to catalyst deactivation are keys to the success of CFP for bio-pX. Therefore, extensive efforts have been directed toward zeolite modifications.

## 5. Zeolites for CFP

Zeolites are microporous crystalline materials of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  that have Brønsted and Lewis acidic sites [17, 46]. HZSM-5 also have ordered structure microporous structures. In the refining process, zeolites are integral to crude oil conversions in the gas phase. The feed for these refining processes are bereft of minerals, oxygenates, and water. Under these conditions, zeolite lifetimes are quite long. However, conversion of biomass occurs in a condensed, aqueous phase, which are highly challenging conditions for zeolites. Oxygenate conversions are difficult to achieve because of their tendency to coke. In addition to BTX, CFP produces a very large volume of wide variety of hydrocarbons, valuable for fuel (fuel gas, gasoline and diesel blendstock). Therefore, the literature on CFP catalyst development is quite voluminous due to interests in bio-fuels.

A comparison of HZSM-5, HY, H-BEA, and H-mordenite for pyrolysis oil upgrading has been made [37, 47]. A method to evaluate catalysts for ex situ vapor upgrading is the pyroprobe analytical pyrolyzer. This important tool provides high heating rates and means to analyze complex mixtures of products [48]. An examination of feeds ranging from glucose, xylitol, cellulose, to cellobiose was explored with catalyst candidates of HZSM-5, silicalite, H-BEA, HY, and  $\text{SiO}_2/\text{Al}_2\text{O}_3$ . Based on this study, HZSM-5 has been found to be the highest performing catalyst. Pore characteristics and shape selectivity for monoaromatics of HZSM-5 are superior to other zeolites. Another comparison study was conducted on HZSM-5, MCM-41, and HY [49]. HZSM-5 was again the most effective zeolite among this group to produce up to 33.1% BTX and 86.4% aromatics selectivity.

The silica-alumina ratio (SAR) of HZSM-5 is also an important parameter for deoxygenation reactions [50]. As the SAR is reduced, the density of Brønsted acids increases. Other zeolites of similar SAR were inferior to HZSM-5 because they were not microporous. Mesoporous zeolites were not selective for aromatics. For example, sulfated  $\text{ZrO}_2$  is a superacid, a property important for aromatics formation, but this metal oxide was ineffective because of the absence of shape-selectivity. Coupling  $\text{ZrO}_2$  to MCM-41 resulted in higher levels of pyrolysis vapor deoxygenation and was found to be stable against coking.

## 6. Zeolite modifications

Because HZSM-5 plays such a vital role in CFP, numerous investigations have been launched to determine whether modifications of the physical structure can improve aromatics selectivity and minimize coking. Modification of zeolite's pore mouth sizes can improve the catalyst for improving of BTX selectivities [51, 52]. Specifically, narrowing the pore mouth openings by chemical deposition techniques was explored [53]. The deposited chemicals also covered external acid sites, which can improve pX selectivity [5]. Phosphorous-modified HZSM-5 promoted greater space confinement and increased pX selectivity. A comparison of various deposited silicon materials was conducted by KH550, TEOS, and methyl silicone oil [54, 55]. KH550 modification of HZSM-5 increased furan conversion to 24.5% aromatics vs. 18.8% unmodified HZSM-5 (see reference [5]). Coking of the modified catalyst was also reduced from 44.1 to 26.7%. A decrease in benzene and increase in toluene and naphthalenes selectivities were observed. Chemical liquid depositions of  $\text{TiO}_2$  to HZSM-5 also resulted in improvements to BTX yields from 17.0 to 23.5%, and reduced levels of coking [56].

The other direction to zeolite modifications is to create mesopores. Unilamellar mesoporous MFI nanosheets (UMN) were tested against another mesoporous material, Al-SBA-15 [57]. UMN has stronger acid sites which result in greater cracking

and deoxygenation activities. Ketones and alcohols were converted to furanics and aromatics. Another method to produce mesopores is NaOH desilication of HZSM-5 [58]. This method was successful to create intraparticle mesoporous materials which then improved diffusion. By coupling ZrO<sub>2</sub> with desilicated zeolites, a more active zeolite was accompanied with longer catalyst lifetimes [19]. The resulting coke was “softer” (i.e. less aromatic) and was easier to remove. A two-stage microporous and mesoporous vapor upgrading system was examined [59]. In this case, HZSM-5 and MCM-41 (3:1) were evaluated. By increasing the MCM-41 loading, more xylenes were made than toluene. A comparison of chemical liquid deposition (CLD) and acid dealumination (AD) of HZSM-5 was conducted [60]. CLD decreased pore size while AD increased pore size. In both cases, decrease of strong acid sites occurred. CLD boosted BTX yield to 37.2% while AD produced 30.4%. In both cases there was a decrease in indene, naphthalenes, and coke precursors.

Most recently, Li et al. reported development of a core-shell catalyst of HZSM-5@MCM-41 made from an external recrystallization method [61]. HZSM-5@MCM-41 required a lower temperature of 500 °C to produce hydrocarbons, versus 550 °C for unmodified HZSM-5. Monoaromatic hydrocarbons produced from rape straw pyrolysis was as high as 11.43 wt%, which is 2.5 times higher than obtained from HZSM-5. Furthermore, HZSM-5@MCM-41 produced less graphitic coke.

## 7. Metal doped HZSM-5

The literature is replete with studies of metals doped HZSM-5 to investigate their effects of CFP catalyst. Zeolites metalated even at low concentrations beneficially resulted in accelerated deoxygenation by decarbonylation, decarboxylation, dehydration, and olefin aromatization of pyrolysis products. In some cases, there were reduced coke formation by decreasing selectivities to polycyclic aromatic hydrocarbons. **Table 1** summarizes the metals dopant and their references. Among these metals, gallium, iron, zinc, molybdenum, nickel, and copper increased for deoxygenations, dehydrocyclization, and aromatization.

Investigators also examined combinations of metals to determine whether there were accumulated benefits in CFP. For example, Ga and Ni are perhaps the most investigated metal additives, and they have been combined for CFP [63]. Ga-Ni reduced acidity, and reduced formation of polyaromatic hydrocarbons which could explain the reduced coking. Another combination is Cu-Ni which was examined in hydroprocessing (CFP under H<sub>2</sub> atmosphere) [108]. Ni-Fe produced an additive effect. Individually, Fe increased yields of monoaromatics, while Ni increased yields of naphthalenes [82]. When combined, this catalyst generated more monoaromatics and naphthalenes. The doping of these metals onto HZSM-5 increased the concentration of strong acid sites, but also resulted in more coke formation.

Molybdenum is already a highly active metal when doped in HZSM-5 in zeolites [111]. When Mg was combined with Mo in HZSM-5, higher selectivities to monoaromatic hydrocarbons and decreased polyaromatics selectivities were achieved. Phosphorous modified HZSM-5 and doped with Zn decreased external acidity of catalyst surface while the internal acid sites were left unchanged. This modification resulted in improvements in this CFP catalyst [107]. HF modification of HZSM-5 and later doped by Ni produced a catalyst that increased yields of BTX [110]. The acid modification created mesopores and reduced Brønsted acidity via dealumination.

Certain combinations of metals and nonmetals behaved as “noble-metal-like” catalysts [106]. Therefore Ni-Mo<sub>2</sub>N was prepared and confirmed that Ni further extended performance of Mo<sub>2</sub>N [112].

Entry	Metals/Additives	References
1	Ga	[24, 26, 62–79]
2	Fe	[26, 63, 66, 75, 80–88]
3	Pt	[72, 89–92]
4	Zn	[26, 63, 77–80, 85, 86, 93–96]
5	Mo	[24, 63, 76, 77, 90, 91, 97–100]
6	Ni	[24, 26, 63, 67, 73, 82, 87, 90, 92, 96, 100–102]
7	Co	[26, 63, 73, 80, 85, 90, 92, 96, 102]
8	Cu	[63, 92, 96, 97, 101, 103]
9	Mn	[63]
10	La	[86, 93, 94]
11	Mg	[93, 94, 96]
12	Ce	[93, 94]
13	Ca	[86, 96, 104]
14	Pd	[73]
15	Sn	[105]
16	WO <sub>3</sub>	[91]
17	Mo <sub>2</sub> N	[106]
18	W <sub>2</sub> P	[106]
19	MoP	[106]
20	WP	[106]
21	Zn/P	[107]
22	Ga-Ni	[63]
23	Ni-Cu	[108, 109]
24	Ni-HF	[110]
25	Fe-Ni	[82]
26	Mo-Mg	[111]
27	Ni-Mo <sub>2</sub> N	[112]
28	Ce-Zr	[113]
29	Ga-Mo	[114]
30	Fe-Ca	[115]

**Table 1.**  
Metals and additives to HZSM-5 for CFP.

## 8. Catalyst deactivation

In almost every publication concerning CFP catalyst or process development, investigators have identified catalyst deactivation to be the single greatest challenge to this process. The catalyst lifetime can be as short as minutes. There are three types of deactivations and of which, two are irreversible deactivations. The most common form of deactivation results from coke buildup on acid sites within the zeolite pores and renders the catalyst inactive [116]. Coking is most rapid when the catalyst/biomass ratio is less than one and particularly at low SAR. The second type of deactivation results from metal oxides deposited in zeolite which can result

in irreversible deactivation if these salts are not removed [117]. Thirdly, zeolite dealumination can occur and result in irreversible deactivation.

Coke deactivation most rapidly occurs among highly acidic zeolites of low silica/alumina ratio (SAR) [118]. Ironically, low zeolite SAR are most active for aromatics [82, 119]. Individual lignocellulosic components caused deactivation differently [120]. Depolymerized lignin mainly deactivates by coking on zeolite surfaces because lignin monomers (mostly phenolics) cannot diffuse into the microchannels of HZSM-5 [121]. Cellulose pyrolysis products are responsible for coking within the interior of the zeolite and this leads to occlusion [121]. A study into deactivation mechanism was conducted from in situ CFP pine wood [121]. Fresh catalyst produced mainly aromatics and olefins with no detectable levels of oxygenates. As the campaign progresses, the catalyst/biomass ratio began to decrease, and oxygenates began to breakthrough, including phenolics. When the catalyst/biomass ratio reached 1:3, complete deactivation will have occurred.

Not all oxygenates deactivate HZSM-5 at the same rate [122]. One team examined the effects of upgrading ethanol-only, ethanol+acetic acid, ethanol+ethyl acetate, and ethanol+acetaldehyde. Acetic acid in the vapor strongly adsorbed onto zeolite surfaces and promoted formation of polyaromatic hydrocarbon precursors to coke. Acetaldehyde deactivated 10X more than ethanol. While ethyl acetate did not directly adsorb onto catalyst surfaces, the reaction conditions rapidly hydrolyzed ethyl acetate to acetic acid which then immediately deactivated the catalyst.

An extruded HZSM-5 (a.k.a. “technical catalyst”) containing an alumina binder was also examined in its deactivation in ex situ CFP of cellulose and pinewood [44]. CFP of cellulose generates smaller oxygenates, which diffused into the zeolite to produce a “catalytic coke”, made via a ring-growth mechanism involving H-transfer at temperatures above 200 °C [123]. Initial formation of monoaromatics led to formation of polyaromatic hydrocarbons, coke precursors. It is not surprising to learn that the coking mechanism of oxygenates is similar in pathways to coke formation in petroleum refining [118]. Lignin forms “thermal coke” from condensation of lignin monomers, and easier to remove because they accumulate on the surfaces of the zeolite [118]. High temperature combustion readily regenerates coke-deactivated HZSM-5.

The presence of water liberated from the pyrolysis can accumulate in the catalyst [118, 124]. Later, at high regeneration temperature, steaming can result in dealumination of the zeolite via leaching. In addition to removal of strong acid-site aluminum, there can be a loss of surface area even after one regeneration cycle [44, 51]. As a further complication, during the regeneration, hot spots can appear and irreversibly damage the catalyst. Successive regeneration increases the risk of further dealumination and reduction in micropore volumes, particularly at high regeneration temperature of 650–670 °C [118]. Therefore, these investigators recommended limiting the O<sub>2</sub> concentration to 15% and include 5% steam to preserve catalyst lifetime [125]. Use of this method was found to preserve catalyst stability for up to 30 regeneration cycles. The formation of aromatics and olefins was stable at about 31.3% [125].

Alkaline and alkaline earth metal ions (AAEMs) are part of the plant’s nutrient to enable the plant to grow [15, 126]. Lignocellulose is comprised of four different types of materials: lignin, cellulose, hemicellulose, and inorganics. AAEMs and other metal salts are represented by the inorganics fraction. A measurement of ash content provides a direct correlation of mineral concentration in the feed. Mechanistically, alkali metal salts also ion-exchanged with the proton of Brønsted acid sites and this reduces zeolite activity [118]. This was demonstrated from an on-purpose potassium ion exchange with HZSM-5 (up to 2.85 wt%) which resulted in drastic reduction of catalyst acidity, leading to lower yields of carbons [127]. Within the pyrolysis process itself, AAEMs can catalyze unwanted secondary reactions,

including cracking, decarboxylation, and dehydration, resulting in a loss of liquid yields [34]. Carbon oxides and water were increased by 10% due to these inorganic components, changing the product distribution [118, 128]. Among the metal ions that are highly detrimental to the process are  $K > Na > Ca$ , and the concentration of potassium in the feed is inversely proportional to aromatics [129]. Furthermore, Xiao et al. studied the effect of potassium salts on CFP of a model feed, 2-methylfuran [130]. The experiments were conducted by deposition of potassium salts into HZSM-5. Neutral KCl was less harmful than basic  $K_2CO_3$  which produced lower yields of aromatic hydrocarbons and gases. The negative effects were due to loss of acidity and erosion of physical structure of HZSM-5, particularly when the  $K_2CO_3$  concentration was as high as 1.0 wt%.

Magnesium is also present, but it is not as harmful as the other metal ions. Other inorganic ions that need to be monitored include Cl, S, P, and N [131]. Particularly, CFP of guayule, a perennial woody shrub, can produce upgraded products containing 80 to 700 ppm sulfur which can be detrimental to any sulfur sensitive downstream processes [132].

Because of the nature of the process, it is in situ CFP that is most sensitive to AAEMs in the feed. Even at levels as low as 0.1 wt% in the feed, AAEMs can greatly impact the pyrolysis process. Aggravating this situation is the variation of feedstock which also varies the inorganic component concentrations. Switchgrass as a feed results in high ash content [118, 131]. Versus pinewood (0.49 wt%), Switchgrass can contain around 2.6 wt% ash comprised of metal oxides. Crop selection is crucial to preserve performance of CFP [15, 133]. Feed pretreatment can be an option to minimize the deleterious effects of AAEMs.

## 9. CFP feed pretreatment

Two main strategies have been published to combat the challenges of pyrolysis: torrefaction and acid-washing of lignocellulose. Torrefaction is low temperature, slow pyrolysis of less than 60 minutes, and installed upstream to CFP. During torrefaction, removal of undesirable acetic acid and guaiacol from the feed improves the downstream CFP. Typical temperature of torrefaction ranges from 250 to 300 °C [112]. When torrefaction was tested on pinewood conversion at 250 °C, the resulting CFP step produced 30% more aromatics. Other feedstocks such as corn cobs produced a lower O/C ratio in the CFP product [134].

Acid-washing of finely divided lignocellulose can extract AAEMs from the feed. The wash step is conducted under very mild conditions, but it is necessary that thorough drying is conducted prior to CFP [51]. For example, rice husks are washed at 30 °C by acetic acid [84, 135]. Use of acids such as acetic acid or mineral acids can add significant variable costs to the process. One investigator recommended using acetic acid recovered from the pyrolysis process for the wash. Extreme aqueous washing must be avoided as the extraction can result in undesirable changes in hemicellulose and cellulose. Formation of sticky materials can coat catalyst bed particles and risk defluidization [136]. Aqueous HCl washing of the spent catalyst to remove deposited minerals is also necessary to maintain catalyst lifetime [118].

A comparison of both processes was studied to determine their effects on aromatics yield. Acid-leaching promoted the formation of levoglucosan. Torrefaction promoted the formation of catechols and guaicol. It was determined that acid leaching + CFP made less aromatics than torrefaction + CFP [137]. Both processes were conducted in series in the CFP of rice husk [135]. Lower levels of volatiles were made in the pyrolysis result in lower yields of oxygenates and higher yields of aromatics. However, severe torrefaction conditions due to longer residence

time can result in cross-linking of lignocellulose, resulting in more charring and reduced formation of aromatics. A combination of both processes did result in higher yields of products [136].

One team of investigators described development of ultrasonic pretreatment [138]. This mechanical method excludes use of toxic chemicals. Ultrasound promotes cleaving of  $\alpha$ -O-4 and  $\beta$ -O-4 linkages and overall decreased crystallinity of lignocellulose and increased yield of pyrolysis oils. CFP can accommodate a wide

Feedstock	References
Beatle killed trees	[139]
Pine wood	[36, 60, 67, 97, 101, 106, 111, 121, 128, 140–146]
Pine bark	[58]
Pinecones	[145]
Pinyon juniper	[58]
Beech wood	[58]
Maple wood	[148]
Hybrid poplar	[58, 147]
Yellow poplar	[76]
Red oak	[147]
Oakwood	[149]
Quercus Mongolia	[74]
Eucalyptus	[63, 68, 87]
Willow wood	[66]
Guayule Bagasse	[150]
Corn cobs	[141, 151]
Corn stover residue	[58]
Corn stalk	[88]
Straw	[141, 152]
Sunflower Stalk	[153]
Switch grass	[58, 127, 131]
Mandarin residue	[72]
Citrus unshiu	[119]
Rice Husk	[84, 109, 135, 154–156]
Bamboo sawdust	[56, 157]
Giant cane	[158]
Sugarcane bagasse	[147]
Wheat straw	[91, 98, 159]
Rape straw	[61]
Xylitol	[160]
Cotton stalk	[80]
Jatropha residues	[73]
Miscanthus	[57, 161]
Peanut shells	[162]

Feedstock	References
Microalgae	[70, 140]
Seaweed	[140]
Fish discards	[140]
Guaiacol	[52]
Acetic Acid	[52]
Furanics	[5, 38, 42, 43, 52, 54, 78, 130, 148, 163–168]
Glucose	[148, 160, 169, 170]
Lignin	[121, 141, 171]
Hemicellulose	[141, 171]
Cellulose	[44, 57, 80, 113, 120, 121, 141, 160, 161, 171–174]
Cellbios	[160]
Glycerol	[175, 176]

**Table 2.**  
*Feedstocks used in CFP.*

variety of feedstocks. **Table 2** summarizes the feedstocks examined, which include woody plants of varying levels of lignin, cellulose, and hemicellulose. The most frequently studied woody biomass for pyrolysis was pinewood. Also included in this table are references to studies of model feeds.

Glucose is one of the intermediate products made in pyrolysis [169]. This monosaccharide is rapidly converted to anhydrosugars before they are dehydrated to furanics and subsequently to aromatics. Sophisticated isotopically labeled glucose experiments permitted an elucidation of the mechanism of glucose conversion [170]. Single ring aromatics contained  $^{13}\text{C}$  labels and later these labels began to appear in naphthalene rings, evidence for a ring growth mechanism from monoaromatics to polyaromatics. Other studies included a study of the conversion of other model feeds to aromatics under identical conditions [80, 121, 140–142, 147, 160, 161, 171]. Glycerol CFP is of interest because of its availability from the production of fatty acid methyl esters for bio-diesel [175, 176].

## 10. Catalytic Co-pyrolysis (CCP)

Investigators recognized that pyrolysis produced improved product quality when a second feed was added to the process [22, 24]. The co-feed can include coal, plastics, tire, and sludge. N.Y. Chen et al. first reported in 1986 that the hydrogen to carbon effective ratio ( $H/C_{eff}$ ) can predict the outcome of pyrolysis [177]. This ratio is calculated according to the following formula (Eq. (2)).

$$\frac{H/C_{eff}}{C} = H - 2(O) \quad (2)$$

When this ratio is less than one, coke is expected to be made in high yields. For example, glucose has a ratio of zero, sorbitol has 0.333, glycerol has 0.667, xylitol has 0.400 and petroleum is greater than two [160]. As a feed, lignocellulose is highly deficient in hydrogen. It might be plausible to increase this ratio by

co-feeding a material rich in hydrogen [19, 27]. By increasing this ratio, not only is coke reduced, but higher yields of aromatics and olefins result. Other means to increase this ratio is to pretreat the feed by hydrogenolysis [178]. An *ex situ* co-pyrolysis strategy to increase BTX yield was cleverly conducted by removing BTX from the product stream to leave behind polyaromatic hydrocarbons. This high molecular weight material was then hydrogenated to produce polycyclic aliphatic hydrocarbons. This hydrogenated fraction was then co-pyrolyzed with glycerol to produce higher yields of BTX [176].

The upgrading of furanics to aromatics was benefitted by the co-addition of olefins [42, 119, 163, 177, 179, 180]. While co-addition of ethylene and propylene was effective to produce more aromatics, investigators recognized that the process must now incorporate flammable gases. An alternative to olefins utilization was to co-add methanol to the pyrolysis. Under the upgrading conditions, methanol to *in situ* olefins can occur to produce the dienophiles required for furanic Diels Alder reactions. Therefore, 2-methylfuran (2-MF) and methanol co-addition resulted in boosting aromatics yield while coke was reduced [168]. When the MeOH/2-MF ratio was increased from zero to 3:1, 2-MF conversion was increased from 39.8% to as high as 96.5% at an optimal ratio of 2:1. Of course, not all furanics were equally converted. A comparison of 2,5-dimethylfuran (DMF), furan, and furfural revealed that electron-rich DMF quickly reacted while the electron-deficient furfural lagged behind: DMF > furan > furfural [94]. In addition to aromatics, CO<sub>2</sub>, CO, and other olefins were also made at 400–600 °C [38]. Unavoidably, formation of graphitic coke on catalyst surfaces resulted in its deactivation within 30 minutes. Methane was examined as a co-feed in the catalytic upgrading [164]. This co-feed was beneficial, an indication that methane could be activated by this catalyst to yield more aromatics, but coke formation also increased.

CCP was applied to a mixture of sawdust and methanol. This combination reduced coke and char and improved aromatics yields [77, 93, 181]. However, the researchers could not exclude the possibility that a background methanol to aromatics process was also occurring. Another team examined CCP of other co-feeds such as methanol, polyethylene terephthalate (PET), and calcium formate with pinewood [182]. Of these three, calcium formate was found to be most effective at calcium formate/pinewood of 3:1. In fact, co-feeding calcium formate did not produce a large increase in aromatics vs. control (10.65% vs. 9.23%), but this co-pyrolysis reduced the polyaromatic hydrocarbons yield (1.94% vs. 2.49%). The authors speculated that the calcium salt helped to maintain catalyst activity within the hydrocarbon pool of the zeolite.

A patent was granted to Anellotech for co-feeding oxygenates such as acetone into pyrolysis to enhanced pX yield [183]. The oxygenates utilized are low value byproducts from other industrial processes. Such oxygenates include acetone from the phenol process, furfural, hexanol, and hexanoic acid from other sources. Furfural was less effective, but the formation of xylenes was enhanced by hexanol and hexanoic acid co-additions. Other oxygenates include fermentation products [184]. Co-pyrolysis of citrus unshiu peel and alcohols, ketones, and furanics has been reported [119]. In this case, two different zeolites were compared: HZSM-5 (23) and HBEA (25). The key difference between both zeolites was that HBEA produced more coke.

Tail Gas Reactive or Recycle Pyrolysis (TGRP) is an interesting process that recycles non-condensable pyrolysis gases to the pyrolysis step [150, 166, 185, 186]. Recycling this gas to pyrolysis provides a reductive, low acidic atmosphere which benefits CFP by increasing the H/C<sub>eff</sub>. The condensable gas fraction was separated, including unwanted carboxylic acids and furfural which are detrimental to vapor upgrading. Up to 10X more BTX was produced when TGRP was incorporated in comparison to CFP-only.

Other non-conventional processes could also improve CFP yields. One example is addition of ball bearings to the catalyst bed to increase residence time which provided higher hot surface areas [187]. This modification increased cracking reaction and produced 3X more BTX. The downside is formation of more polyaromatic hydrocarbons. An alternative to thermal heating, microwave energy can also be used. Microwave assisted pyrolysis (MOP) does not require agitation and fluidization [56, 188].

## **11. Outlook for CFP**

CFP is a rapid process to produce a high volume of hydrocarbons of which BTX is a small fraction. CFP must be co-located with a petroleum refining complex to take in bio-naphtha which could be directed to bio-gasoline production. The refining complex must also include a pX extraction process to separate pX from mX and oX as well as a process to isomerize the pX lean stream. Every means to improve CFP should be taken, including pretreatment, torrefaction, co-pyrolysis with hydrogen-rich feed, and tail gas recycled pyrolysis to increase BTX yields. Investigations into development of an even more active metalated HZSM-5 catalyst to increase monoaromatics selectivity and resistance to coking will remain subjects of intense interests.

### **Author details**

William H. Gong  
Independent Technical Consultant, Lombard, Illinois, USA

\*Address all correspondence to: [whgong@comcast.com](mailto:whgong@comcast.com)

### **IntechOpen**

© 2021 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

## References

- [1] "Preferred Fiber & Materials Market Report 2020", *Textile Exchange*, [https://textileexchange.org/wp-content/uploads/2020/06/Textile-Exchange\\_PREFERRED-FIBER-MATERIAL-MARKET-REPORT\\_2020.pdf](https://textileexchange.org/wp-content/uploads/2020/06/Textile-Exchange_PREFERRED-FIBER-MATERIAL-MARKET-REPORT_2020.pdf);
- [2] Coca-Cola Press Release. Coca-Cola Introduces Plant-Based Plastic Bottles, May 18, 2009.
- [3] P.B. Smith, Bio-Based Sources for Terephthalic Acid. In: Green Polymer Chemistry: Biobased Materials and Biocatalysis, ed. H.N. Cheng, American Chemical Society, Washington, DC, 2015, pp. 453-469.
- [4] Tullo A. Anellotech Advancing Bio-Aromatics. *Chem. Eng. News*. 2016, 94.
- [5] Cheng YT, Wang Z, Gilbert CJ, Fan W, Huber GW. Production of p-Xylene from Biomass by Catalytic Fast Pyrolysis using ZSM-5 Catalysts with Reduced Pore Openings. *Angew Chem Int Ed*. 2012; 51: 11097-11100.
- [6] <https://www.ifpenergiesnouvelles.com/article/bio-paraxylene-production-path-100-bio-based-bottles>
- [7] [https://anellotech.com/sites/default/files/Anellotech\\_Technology%20Update\\_2019.05.06.pdf](https://anellotech.com/sites/default/files/Anellotech_Technology%20Update_2019.05.06.pdf)
- [8] Scott A. Investors Chase Bioaromatics. *C&EN*. February 24, 2020, 18-19.
- [9] Huber GW, Cheng YT, Carlson T, Vispute T, Jae J, Tompsett G. Catalytic Pyrolysis of Solid Biomass and Related Biofuels, Aromatic, and Olefin Compounds. US 8,277,643 B2, October 2, 2012.
- [10] Rahman MM, Liu R, Cai J. Selective Aerobic Oxidation of Furfural to Maleic Anhydride with Heterogeneous Mo-V-O Catalysts. *Fuel Process Technol*. 2018; 180: 32-46.
- [11] Dickerson T, Soria J. Dehydro-Aromatization of Cyclohexene-carboxylic Acids by Sulfuric Acid: Critical Route for Bio-Based Terephthalic Acid Synthesis. *Energies*. 2013; 6: 514-538.
- [12] Balasundram V, Ibrahim N, Kasmani RM, Isha R, Hamid MKA, Hasbullah H. Catalytic Upgrading of Biomass-Derived Pyrolysis Vapour over Metal-Modified HZSM-5 into BTX: A Comprehensive Review. *Biomass Conv. Bioref*. 2020; doi.org/10.1007/s13399-020-00909-5.
- [13] A.V. Bridgwater. Review of Fast Pyrolysis of Biomass and Product Upgrading. *Biomass Bioenergy*. 38 (2012), 68-94.
- [14] Bridgwater AV, Peacocke GVC. Fast Pyrolysis Processes for Biomass. *Renew Sustain Energy Rev*. 2000; 4: 1-73.
- [15] Bridgwater T. Challenges and Opportunities in Fast Pyrolysis of Biomass: Part I. *Johnson Matthey Technol Rev*. 2018; 62: 118-130.
- [16] Bridgwater AV. Production of High Grade Fuels and Chemicals from Catalytic Pyrolysis of Biomass. *Catal Today*. 1996; 28: 285-295.
- [17] Taarnning E, Osmundsen CM, Yang X, Voss B, Andersen SI, Christensen CH. Zeolite-Catalyzed Biomass Conversion to Fuels and Chemicals. *Energy Environ Sci* 2011; 4: 793-804.
- [18] Mettler MS, Vlachos DG, Dauenhauer PJ. Top Ten Fundamental Challenges of Biomass Pyrolysis for Biofuels. *Energy Environ Sci* 2012; 5: 7797-7809.
- [19] Liu J, Hou Q, Ju M, Ji P, Sun Q, Li W. Biomass Pyrolysis Technology by Catalytic Fast Pyrolysis, Catalytic Co-Pyrolysis and Microwave-Assisted

- Pyrolysis: A Review. *Catalysts*. 2020; 10: 742.
- [20] Yan K, Li H. State of the Art and Perspectives in Catalytic Conversion Mechanism of Biomass to Bio-Aromatics. *Energy Fuel*. 2021; 35: 45-62.
- [21] Cai R, Pei X, Pan H, Wan K, Chen H, Zhang Z, et al. Biomass Catalytic Pyrolysis over Zeolite Catalysts with an Emphasis on Porosity and Acidity: A State-of-the-Art Review. *Energy Fuel*. 2020; 34: 11771-11790.
- [22] Wang G, Dai Y, Yang H, Xiong Q, Wang K, Zhou J, et al. A Review of Recent Advances in Biomass Pyrolysis. *Energy Fuel*. 2020; 34: 15557-15578.
- [23] Liu R, Rahman MM, Sarker M, Chai M, Li C, Cai J. A Review on the Catalytic Pyrolysis of Biomass for the Bio-Oil Production with ZSM-5: Focus on Structure. *Fuel Process Technol*. 2020; 199: 106301.
- [24] Rahman MM, Liu R, Cai J. Catalytic Fast Pyrolysis of Biomass over Zeolites for High Quality Bio-Oil - A Review. *Fuel Process Technol*. 2018; 180: 32-46.
- [25] Shi Y, Xing E, Wu K, Wang J, Yang M, Wu Y. Recent Progress on Upgrading of Bio-Oil to Hydrocarbons over Metal/Zeolite Bifunctional Catalysts. *Catal Sci Technol* 2017; 7: 2385-2415.
- [26] Lok CM van Doorne J, Almansa GA. Promoted ZSM-5 Catalysts for the Production of bio-Aromatics, a Review. *Renew Sustain Energy Rev*. 2019 113: 109248.
- [27] Chen X, Che Q, Li S, Liu Z, Yang H, Chen Y, et al. Recent Developments in Lignocellulosic Biomass Catalytic Fast Pyrolysis: Strategies for the Optimization of Bio-Oil Quality and Yield. *Fuel Process Technol*. 2019; 196: 106180.
- [28] Huber GW, Iborra S, Corma A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem Rev*. 2006; 106: 4044-4098.
- [29] Tan S, Zhang Z, Sun J, Wang Q. Recent Progress of Catalytic Pyrolysis of Biomass by HZSM-5. *Chin J Catal*. 2013; 34: 641-650.
- [30] Rezaei PS, Shafaghat H, Daud WMSW. Production of Green Aromatics and Olefins by Catalytic Cracking of Oxygenate Compounds Derived from Biomass Pyrolysis: A Review. *Appl Catal A: General*. 2014; 469: 490-511.
- [31] Grams J, Ruppert AM. Development of Heterogeneous Catalysts for Thermo-Chemical Conversion of Lignocellulosic Biomass. *Energies*. 2017; 10: 545.
- [32] Galadima A, Muraza O. In situ Pyrolysis of Biomass with Zeolite Catalysts for Bioaromatics/Gasoline Production: A Review. *Energy Con. Manage*. 2015; 105: 338-354.
- [33] Mukarakate C, Evans RJ, Deutch S, Evans T, Starace AK, ten Dam J, et al. Reforming Biomass Derived Pyrolysis Bio-Oil Aqueous Phase to Fuels. *Energy Fuels*. 2017; 31: 1600-1607.
- [34] Mullen CA. Upgrading of Biomass via Catalytic Fast Pyrolysis (CFP). In: *Chemical Catalysts for Biomass Upgrading*, ed. M. Crocker and E. Santillan-Jimenez, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2020, pp. 1-33.
- [35] Wang Y, Liu Q. Manganese-Catalyzed Dehydrogenative/Deoxygenative Coupling of Alcohols. *Synlett*. 2020; 31: 1464-1473.
- [36] Yildiz G, Pronk M, Djokic M, van Geem KM, Ronsse F, van Duren R, et al. Validation of a New Set-Up for Continuous Catalytic Fast Pyrolysis of Biomass Coupled with Vapour Phase Upgrading. *J Anal Appl Pyrolysis* 2013; 103: 343-351.

- [37] Jeong J, Lee HW, Jang SH, Ryu S, Kim YM, Park R, et al. In-situ Catalytic Fast Pyrolysis of Pinecone over HY Catalysts. *Catalysts*. 2019; 9: 1034.
- [38] Cheng YT, Huber GW. Chemistry of Furan Conversion into Aromatics and Olefins over HZSM-5: A Model Biomass Conversion Reaction. *ACS Catal*. 2011; 1: 611-628.
- [39] Ding SM, Fan MH, Wang TJ, Li QX. Transformation of Biomass into Aromatics with Zeolite Catalysts. *Chin J Chem Phys*. 2014; 27: 361-367.
- [40] Galadima A, Muraza O. In situ Fast Pyrolysis of Biomass with Zeolite Catalysts for Bioaromatics/Gasoline Production: A Review. *Energy Conv Manage*. 2015; 105: 338-354.
- [41] Ramasamu KK, Wang Y. Ethanol Conversion to Hydrocarbons on HZSM-5: Effect of Reaction Conditions and Si/Al Ratio on the Product Distributions. *Catal Today*. 2014; 237: 89-99.
- [42] Cheng YT, Huber GW. Production of Targeted Aromatics by using Diels-Alders Classes of Reactions with Furans and Olefins over ZSM-5. *Green Chem*. 2012; 14: 3114-3125.
- [43] Uslamin EA, Kosinov NA, Pidko EA, Hensen EJM. Catalytic Conversion of Furanic Compounds over Ga-Modified ZSM-5 Zeolites as a Route to Biomass-Derived Aromatics. *Green Chem*. 2018; 20: 3818-3827.
- [44] Luna-Murillo B, Pala M, Paioni AL, Baldus M, Ronsse F, Prins W, et al. Catalytic Fast Pyrolysis of Biomass: Catalyst Characterization Reveals the Feed-Dependent Deactivation of a Technical ZSM-5-Based Catalyst. *ACS Sustain Chem Eng*. 2021; 9: 291-304.
- [45] Hu B, Zhang B, Xie WL, Jiang XY, Liu J, Lu Q. Biomass Catalytic Pyrolysis over Zeolite Catalysts with an Emphasis on Porosity and Acidity: A State-of-the-Art Review. *Energy Fuel*. 2020; 34: 10384-10440.
- [46] Ennaert T, van Aelst J, Dijkmans J, de Clerq R, Schutyser W, Dusselier M, et al. Potential and Challenges of Zeolite Chemistry in the Catalytic Conversion of Biomass. *Chem Soc Rev*. 2016; 45: 584-611.
- [47] Adjaye JD, Bakhshi NN. Production of Hydrocarbons by Catalytic Upgrading of a Fast Pyrolysis Bio-Oil. Part I: Conversion over Various Catalysts. *Fuel Process Technol*. 1995; 45: 161-183.
- [48] Carlson TR, Tompsett GA, Conner WC, Huber GW. Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks. *Top Catal*. 2009; 52: 241-252.
- [49] Zhu JF, Wang JC, Li QX. Transformation of Bio-Oil into BTX by Bio-Oil Catalytic Cracking. *Chin J Chem Phys*. 2013; 26: 477-483.
- [50] Kelkar S, Saffron CM, Andreassi K, Li Z, Murkute A, Miller DJ, et al. A Survey of Catalysts for Aromatics from Fast Pyrolysis of Biomass. *Appl Catal B: Environ*. 2015; 174-175: 85-95.
- [51] Deischer J, Schute K, Neves DS, Ebert BE, Blank LM, Palkovits R. Aromatisation of Bio-Derivable Isobutyraldehyde over HZSM-5 Zeolite Catalysts. *Green Chem*. 2019; 21: 1710-1717.
- [52] Che Q, Yi W, Liu Y, Wang X, Yang H, Chen H. Effect of Mesopores in ZSM-5 on the Catalytic Conversion of Acetic Acid, Furfural, and Guaiacol. *Energy Fuels*. 2021; 35: 6022-6029.
- [53] Huber GW, Cheng YT, Wang Z, Fan W. Method for Converting a Hydrocarbonaceous Material to a Fluid Hydrocarbon Product Comprising p-Xylene. US 2013/0324772 A1, December 5, 2013.

- [54] Zhang H, Luo M, Xiao R, Shao S, Jin B, Xiao G, et al. Catalytic Conversion of Biomass Pyrolysis-Derived Compounds with Chemical Liquid Deposition (CLD) Modified ZSM-5. *Bioresour Technol* 2014; 155: 57-62.
- [55] Zhang B, Zhong Z, Chen P, Ruan R. Microwave-Assisted Catalytic Fast Pyrolysis of Biomass Bio-Oil Production using Chemical Vapor Deposition Modified HZSM-5 Catalyst. *Bioresour Technol*. 2015; 197: 79-84.
- [56] Du H, Zhong Z, Zhang B, Shi K, Li Z. Ex-situ Catalytic Upgrading of Vapors from Microwave-Assisted Pyrolysis of Bamboo with Chemical Liquid Deposition Modified H-ZSM-5 to Enhance Aromatics Production. *J Anal Appl Pyrolysis*. 2020; 149: 104857.
- [57] Lee LW, Park SH, Jeon JK, Ryoo R, Kim W, Suh DJ, et al. Upgrading of Bio-Oil Derived from Biomass Constituents over Hierarchical Unilamellar Mesoporous MFI Nanosheets. *Catal Today*. 2014; 232: 119-126.
- [58] Li J, Li X, Zhou G, Wang, W, Wang C, Komarneni S, et al. Catalytic Fast Pyrolysis of Biomass with Mesoporous ZSM-5 Zeolites Prepared by Desilication with NaOH Solutions. *Appl Catal A: General*. 2014; 470: 115-122.
- [59] Ratnasari DK, Yang W, Jonsson PG. Kinetic Study of an H-ZSM-5/Al-MCM-41 Catalyst Mixture and its Application in Lignocellulose Biomass Pyrolysis. *Energy Fuels*. 2019; 33: 5630-5637.
- [60] Zhang H, Shao S, Luo M, Xiao R. The Comparison of Chemical Liquid Deposition and Acid Dealumination Modified ZSM-5 for Catalytic Pyrolysis of Pinewood using Pyrolysis-Gas Chromatography/Mass Spectrometry. *Bioresour Technol*. 2017; 244: 726-732.
- [61] Li X, Ge S, Shao S, Lv Z, Xiang X, Cai Y. Promoted Production of Hydrocarbons in the Catalytic Pyrolysis of Rape Straw over Composite HZSM-5@MCM-41 Catalysts. *J Anal Appl Pyrolysis*. 2021; 157: 105067.
- [62] Cheng YT, Jae J, Shi J, Fan W, Huber GW. Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts. *Angew Chem Int Ed*. 2012; 51: 1387-1390.
- [63] Schultz EL, Mullen CA, Boateng AA. Aromatic Hydrocarbon Production from Eucalyptus Urophylla Pyrolysis over Several Metal-Modified ZSM-5 Catalysts. *Energy Technol*. 2017; 5: 196-204.
- [64] Park HJ, Heo HS, Jeon JK, Kim J, Ryoo R, Jeong KE, et al. Highly Valuable Chemicals Production from Catalytic Upgrading of Radiata Pine Sawdust-Derived Pyrolytic Vapors over Mesoporous MFI Zeolites. *Appl Catal B: Environ*. 2010; 95: 365-373.
- [65] Uslamin EA, Luna-Murillo B, Kosinov N, Bruijninx, Pidko EA, Weckhuysen BM, et al. Gallium-Promoted HZSM-5 Zeolites as Efficient Catalysts for the Aromatization of Biomass-Derived Furan. *Chem Eng Sci*. 2019; 198: 305-316.
- [66] Zhang H, Zheng J, Xiao R. Catalytic Pyrolysis of Willow Wood with Me/ZSM-5 (Me = Mg, K, Fe, Ga, Ni) to Produce Aromatics and Olefins. *Bioresour Technol*. 2013; 8: 5612-5621.
- [67] Yung MM, Stanton AR, Iiisa K, French RJ, Orton KA, Magrini KA. Multiscale Evaluation of Catalytic Upgrading of Biomass Pyrolysis Vapors on Ni- and Ga-Modified ZSM-5. *Energy Fuel*. 2016; 30: 9471-9479.
- [68] Mullen CA, Tarves PC, Raymundo LM, Schultz EL, Boateng AA, Trierweiler JO. Fluidized Bed Catalytic Pyrolysis of Eucalyptus over HZSM-5: Effect of Acid Density and Gallium Modification on Catalyst Deactivation. *Energy Fuel*. 2018; 32: 1771-1778.

- [69] Kelkar S, Saffron CM, Li Z, Kim SS, Pinnavaia TJ, Miller DJ, Kriegel R. Aromatics from Biomass Pyrolysis Vapour using a Bifunctional Mesoporous Catalyst. *Green Chem.* 2014; 16: 803-812.
- [70] Du Z, Ma X, Li Y, Chen P, Liu Y, Lin X, et al. Production of Aromatic Hydrocarbons by Catalytic Pyrolysis of Microalgae with Zeolites: Catalyst Screening in a Pyroprobe. *Bioresour Technol.* 2013; 139: 397-401.
- [71] Schutlz EL, Mullen CA, Boateng AA. Aromatic Hydrocarbon Production from *Eucalyptus urophylla* Pyrolysis over Several Metal-Modified ZSM-5 Catalysts. *Energy Technol.* 2017; 5: 196-204.
- [72] Kim JW, Park SH, Jung J, Jeon JK, Ko CH, Jeong KE, et al. Catalytic Pyrolysis of Mandarin Residue from the Mandarin Juice Processing Industry. *Bioresour. Technol.* 2013; 136: 431-436.
- [73] Vichaphund S, Aht-ong D, Sricharoenchaikul V, Atong D. Production of Aromatic Compounds from Catalytic Fast Pyrolysis of *Jatropha* Residues using Metal/HZSM-5 Prepared by Ion-Exchange and Impregnation Methods. *Renew Energy.* 2015; 79: 28-37.
- [74] Farooq A, Moogi S, Kwon EE, Lee J, Kim YM, Jae J, et al. Catalytic Upgrading of *Quercus Mongolica* under Methane Environment to Obtain High Yield of Bioaromatics. *Environ Pollut.* 2021; 272: 116016.
- [75] Dai G, Wang S, Zou Q, Huang S. Improvement of Aromatics Production from Catalytic Pyrolysis of Cellulose over Metal-Modified Hierarchical HZSM-5. *Fuel Process. Technol.* 2018; 179: 319-323.
- [76] Moogi S, Jae J, Kannapu HPR, Ahmed A, Park ED, Park YK. Enhancement of Aromatics from Catalytic Pyrolysis of Yellow Poplar: Role of Hydrogen and Methane Decomposition. *Bioresour Technol.* 2020; 315: 123835.
- [77] Cai Q, Yu T, Meng X, Zhang S. Selective Generation of Aromatic Hydrocarbons from Hydrotreating-Cracking of Bio-Oil Light Fraction with MO<sub>x</sub> Modified HZSM-5 (M = Ga, Mo and Zn). *Fuel Process Technol.* 2020; 204: 106424.
- [78] Espindola JS, Gilbert CJ, Perez-Lopez OW, Trierweiler JO, Huber GW. Conversion of Furan over Gallium and Zinc Promoted ZSM-5: The Effect of Metal and Acid Sites. *Fuel Process Technol.* 2020; 201: 106319.
- [79] He Y, Zhu L, Luo Y, Fan M, Yang M, Zhang Y, et al. Selective Upgrading of Biomass Pyrolysis Oil into Renewable p-Xylene with Multifunctional M/SiO<sub>2</sub>/HZSM-5 Catalyst. *Fuel Process. Technol.* 2021; 213: 106674.
- [80] Li P, Chen X, Wang X, Shao J, Lin G, Yang H, et al. Catalytic Upgrading of Fast Pyrolysis Products with Fe-, Zr-, and Co-Modified Zeolites Based on Pyrolyzer-GC/MS Analysis. *Energy Fuels.* 2017; 31: 3979-3986.
- [81] Mullen CA, Boateng AA. Production of Aromatic Hydrocarbons via Catalytic Pyrolysis of Biomass over Fe-Modified HZSM-5 Zeolites. *ACS Sustain Chem Eng.* 2015; 3: 1623-1631.
- [82] Persson H, Duman I, Wang S, Pettersson LJ, Yang W. Catalytic Pyrolysis over Transition Metal-Modified Zeolites: A Comparative Study between Catalyst Activity and Deactivation. *J Anal Appl Pyrolysis.* 2019; 138: 54-61.
- [83] Sun L, Zhang X, Chen L, Zhao B, Yang S, Xie X. Comparison of Catalytic Fast Pyrolysis of Biomass to Aromatic Hydrocarbons over ZSM-5 and Fe/ZSM-5 Catalysts. *J Anal Appl Pyrolysis.* 2016; 121: 342-346.
- [84] Zhang S, Zhang H, Liu X, Zhu S, Hu L, Zhang Q. Upgrading of Bio-Oil from Catalytic Pyrolysis of Pretreated Rice Husk over Fe-Modified ZSM-5

- Zeolite Catalyst. *Fuel Process Technol.* 2018; 175: 17-25.
- [85] Li P, Li D, Yang H, Wang X, Chen H. Effects of Fe-, Zr-, and Co-Modified Zeolites and Pretreatments on Catalytic Upgrading of Biomass Fast Pyrolysis. *Energy Fuels.* 2016; 30: 3004-3013.
- [86] Che Q, Yang M, Wang X, Yang Q, Williams LR, Yang H. et al. Influence of Physicochemical Properties of Metal Modified ZSM-5 Catalyst on Benzene, Toluene and Xylene Production of Biomass Catalytic Pyrolysis. *Bioresour. Technol.* 2019; 278: 248-254.
- [87] Arteaga-Perez LE, Capiro OG, Romero R, Degado A, Olivera P, Ronsse F, et al. In situ Catalytic Fast Pyrolysis of Crude and Torrefied *Eucalyptus Globulus* using Carbon Aerogel-Supported Catalysts. *Energy.* 2017; 128: 701-712.
- [88] Cai M, Liu R, He Y. Effects of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio and Fe Loading Rate on Selection of Aromatics and Kinetics of Corn Stalk Catalytic Pyrolysis. *Fuel Process Technol.* 2020; 206: 106458.
- [89] Wang JX, Cao JP, Zhao XY, Liu SN, Ren XY, Zhang LY, et al. In Situ Upgrading of Cellulose Pyrolysis Volatiles using Hydrofluorinated and Platinum-Loaded HZSM-5 for High Selectivity Production of Light Aromatics. *Ind Eng Chem Res* 2019; 58: 22193-22201.
- [90] Thangalazhy-Gopakumar S, Adhikari S, Gupta RB. Catalytic Pyrolysis of Biomass over H+ZSM-5 under Hydrogen Pressure. *J. Am. Chem. Soc.* 2012; 26: 5300-5306.
- [91] Eschenbacher A, Saraeian A, Shanks RH, Mentzel UV, Jensen PA, Henriksen UB, et al. Micro-Pyrolyzer Screening of Hydrodeoxygenation Catalysts for Efficient Conversion of Straw-Derived Pyrolysis Vapors. *J Anal Appl Pyrolysis.* 2020; 150: 104868.
- [92] Stanton AR, Iisa K, Yung MM, Magrini KA. Optimizing Catalytic Pyrolysis of Rubber Seed Oil for Light Aromatics and Anti-Deactivation of ZSM-5. *J Anal Appl Pyrolysis.* 2018; 135: 199-208.
- [93] Chang R, Zhu L, Jin F, Fan M, Liu J, Jia Q, et al. Production of Bio-Based *p*-Xylene via Catalytic Pyrolysis of Biomass over Metal Oxide-Modified HZSM-5 Zeolites. *J Chem Technol Biotechnol.* 2018; 93: 3292-3301.
- [94] Zhu L, Fan M, Wang Y, Wang S, He Y, Li Q. Selective Conversion of Furans to *p*-Xylene with Surface-Modified Zeolites. *J Chem Technol Biotechnol.* 2019; 94: 2876-2887.
- [95] Su X, Zan W, Bai X, Wang G, Wu W. Synthesis of Microscale and Nanoscale ZSM-5 Zeolites: Effect of Particle Size and Acidity of Zn Modified ZSM-5 Zeolites on Aromatization. *Catal Sci Technol.* 2017; 7: 1943-1952.
- [96] Zheng Y, Wang F, Yang X, Huang Y, Liu C, Zheng Z, et al. Study on Aromatics Production via the Catalytic Pyrolysis Vapor Upgrading of Biomass using Metal-Loaded Modified H-ZSM-5. *J Anal Appl Pyrolysis.* 2017; 126: 169-179.
- [97] Huang Y, Wei L, Crandall Z, Julson J, Gu Z. Combining Mo-Cu/HZSM-5 with a Two-Stage Catalytic Pyrolysis System for Pine Sawdust Thermal Conversion. *Fuel.* 2015; 150: 656-663.
- [98] Eschenbacher A, Saraeian A, Shanks BH, Mentzel UV, Jensen PA, Henriksen UB, et al. Performance-Screening of Metal-Impregnated Industrial HZSM-5/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Extrudates for Deoxygenation and Hydrodeoxygenation of Fast Pyrolysis Vapors. *J Anal Appl Pyrolysis.* 2020; 150: 104892.
- [99] Sun L, Wang Z, Chen L, Yang S, Xie X, Gao M, et al. Catalytic Fast

- Pyrolysis of Biomass into Aromatic Hydrocarbons over Mo-Modified ZSM-5 Catalysts. *Catalysts*. 2020; 10: 1051.
- [100] Ren YX, Cao JP, Zhao SX, Zhao XY, Liu TL, Feng XB, et al. Encapsulation Ni in HZSM-5 for Catalytic Hydrolysis of Biomass to Light Aromatics. *Fuel Process Technol* 2021; 218: 106854.
- [101] Kumar R, Strezov V, Kan T, Weldekidan H, He J, Jahan S. Investigating the Effect of Mono- and Bimetallic/Zelite Catalysts on Hydrocarbon Production during Bio-Oil Upgrading from Ex Situ Pyrolysis of Biomass. *Energy Fuel*. 2020; 34: 389-400.
- [102] Illiopoulou EF, Stefanidis SD, Kalogiannis KG, Delimitis A, Lappas AA, Triantafyllidis KS. Catalytic Upgrading of Biomass Pyrolysis Vapors using Transition Metal-Modified ZSM-5 Zeolite. *Appl Catal B: Environ*. 2012; 127: 281-290.
- [103] Chaihad N, Anniwaer A, Karnjanakom S, Kasai Y, Kongparakul S, Samart C, et al. In-situ Catalytic Upgrading of Bio-Oil Derived from Fast Pyrolysis of Sunflower Stalk to Aromatic Hydrocarbons over Bifunctional Cu-Loaded HZSM-5. *J Anal Appl Pyrolysis*. 2021; 155: 105079.
- [104] Che Q, Yang M, Wang X, Chen X, Chen W, Yang Q, et al. Aromatics Production with Metal Oxides and ZSM-5 as Catalysts in Catalytic Pyrolysis of Wood Sawdust. *Fuel Process Technol*. 2019; 188: 146-152.
- [105] Shang J, Fu G, Cai Z, Feng X, Tuo Y, Zhou X, et al. Regulating Light Olefins or Aromatics Production in ex-situ Catalytic Pyrolysis of Biomass by Engineering the Structure of Tin Modified ZSM-5 Catalyst. *Bioresour Technol*. 2021; 330: 124975.
- [106] Lu Q, Guo H, Zhou M, Cui M, Dong C, Yang UP. Selective Preparation of Monocyclic Aromatic Hydrocarbons from Catalytic Cracking of Biomass Fast Pyrolysis Vapors over Mo<sub>2</sub>N/HZSM-5 Catalyst. *Fuel Process Technol*. 2018; 173: 134-142.
- [107] Zhang J, Qian W, Kong C, Wei F. Increasing *para*-Xylene Selectivity in Making Aromatics from Methanol with Surface-Modified Zn/P/ZSM-5 Catalyst. *ACS Catal*. 2015; 5: 2982-2988.
- [108] Yin W, Koekhorst A, Venderbosch RH, Bykova MV, Khromova SA, Yakovlev VA, et al. Catalytic Hydrotreatment of Fast Pyrolysis Liquids in Batch and Continuous Set-Ups using a Bimetallic Ni-Cu Catalyst with a High Metal Content. *Catal Sci Technol*. 2016; 6: 5899-5915.
- [109] Chen H, Cheng H, Zhou F, Chen K, Qiao K, Lu X, et al. Catalytic Fast Pyrolysis of Rice Straw to Aromatic Compounds over Hierarchical HZSM-5 Produced by Alkali Treatment and Metal-Modification. *J Anal Appl Pyrolysis*. 2018; 131: 76-84.
- [110] Wang JX, Cao JP, Zhao XY, Liu SN, Ren XY, Zhao M, et al. Enhancement of Light Aromatics from Catalytic Fast Pyrolysis of Cellulose over Bifunctional Hierarchical HZSM-5 Modified by Hydrogen Fluoride and Nickel/Hydrogen Fluoride. *Bioresour Technol*. 2019; 278: 116-123.
- [111] Li K, Zhang G, Wang Z, Hu B, Lu Q. Calcium Formate Assisted Catalytic Pyrolysis of Pine for Enhanced Production of Monocyclic Aromatic Hydrocarbons over Bimetal-Modified HZSM-5. *Bioresour Technol*. 2020; 315: 123805
- [112] Liu Q, Wang J, Zhou J, Yu Z, Kwang K. Promotion of Monocyclic Aromatics by Catalytic Fast Pyrolysis of Biomass with Modified HZSM-5. *J Anal Appl Pyrolysis*. 2021; 153: 104964.
- [113] Li W, Zhu Y, Li S, Lu Y, Wang J, Zhu K, et al. Catalytic Fast Pyrolysis of

- Cellulose over  $\text{Ce}_{0.8}\text{Zr}_{0.2-x}\text{Al}_x\text{O}_2$  Catalysts to Produce Aromatic Hydrocarbons: Analytical Py-GC/MS. *Fuel Process Technol.* 2020; 205: 106438.
- [114] Cai Q, Yu T, Zhang S. Enhanced Aromatic Hydrocarbon Production from Bio-Oil Hydrotreating-Cracking by Mo-Ga Modified HZSM-5. *Fuel.* 2020; 269: 117386.
- [115] Lu Q, Yuan S, Liu C, Zhang T, Xie X, Deng X, et al. A Fe-Ca/SiO<sub>2</sub> Catalyst for Efficient Production of Light Aromatics from Catalytic Pyrolysis of Biomass. *Fuel.* 2020; 279: 118500.
- [116] Illiopoulou EF, Stefanidis S, Kalogiannis K, Psarras AC, Delimitis A, Triantafyllidis KS, et al. Pilot-Scale Validation of Co-ZSM-5 Catalyst Performance in the Catalytic Upgrading of Biomass Pyrolysis Vapours. *Green Chem.* 2014; 16: 662-674.
- [117] Wang D, Zhu Y, Chen J, Li W, Luo F, Li S, et al. Catalytic Upgrading of Lignocellulosic Biomass Pyrolysis Vapors: Insights into Physicochemical Changes in ZSM-5. *J Anal Appl Pyrolysis.* 2021; 156: 105123.
- [118] Lijun PKW, Zhang H, Vitidsant T, Reubroycharoen P, Xiao R. Influence of Inorganic Matter in Biomass on the Catalytic Production of Aromatics and Olefins in a Fluidized-Bed Reactor. *Energy Fuels.* 2017; 31: 6120-6131.
- [119] Kim BS, Kim YM, Jae J, Watanabe C, Kim S, Jung SC, et al. Pyrolysis and Catalytic Upgrading of Citrus unshiu Peel. *Bioresour Technol.* 2015; 194: 312-319.
- [120] Stanton AR, Iisa K, Mukarakate C, Nimlos MR. Role of Biopolymers in the Deactivation of ZSM-5 During Catalytic Fast Pyrolysis of Biomass. *ACS Sustain Chem Eng.* 2018; 6: 10030-10038.
- [121] Kukarakate C, Zhang X, Stanton AR, Robichaud DJ, Ciesielski PN, Malhotra K, et al. Real-Time Monitoring of the Deactivation of HZSM-5 during Upgrading of Pine Pyrolysis Vapors. *Green Chem.* 2014; 16: 1444-14461.
- [122] Ramasamy KK, Gerber MA, Flake M, Zhang H, Wang Y. Conversion of Biomass-Derived Small Oxygenates over HZSM-5 and its Deactivation Mechanism. *Green Chem.* 2014; 16: 748-760.
- [123] Zhang H, Shao S, Xiao R, Shen D, Zeng J. Characterization of Coke Deposition in the Catalytic Fast Pyrolysis of Biomass Derivatives. *Energy Fuels.* 2014; 28; 52-57.
- [124] Liu C, Wang H, Karim AM, Sun J, Wang Y. Catalytic Fast Pyrolysis of Lignocellulosic Biomass. *Chem Soc Rev.* 2014; 43: 7594-7623.
- [125] Shao S, Zhang H, Xiao R, Li X, Cai Y. Controlled Regeneration of ZSM-5 Catalysts in the Combined Oxygen and Steam Atmosphere used for Catalytic Pyrolysis of Biomass-Derivates. *Energy Conv Manage.* 2018; 155: 175-181.
- [126] Guidicianni P, Gariulo v, Grottola CM, Alfe M, Ferreiro AI, Mendus MAA, et al. Inherent Metal Elements in Biomass Pyrolysis: A Review. *Energy Fuels.* 2021; 35: 5407-5478.
- [127] Mullen CA, Botaeng AA, Dadson RB, Hashem FM. Biological Mineral Range Effects on Biomass Conversion to Aromatic Hydrocarbons via Catalytic Fast Pyrolysis over HZSM-5. *Energy Fuel.* 2014; 28: 7014-7024.
- [128] Yildiz G, Ronsse F, Venderbosch R, van Duren R, Kersten SRA, Prins W. Effect of Biomass Ash in Catalytic Fast Pyrolysis of Pine Wood. *Appl Catal B: Environ.* 2015; 168-169: 203-211.
- [129] Mahadevan R, Adhikari S, Shakya R, Wang K, Dayton D, Lehrich M, et al. Effect of Alkali and

- Alkaline Earth Metals on in-situ Catalytic Fast Pyrolysis of Lignocellulosic Biomass: A Microreactor Study. *Energy Fuels*. 2016; 30: 3045-3056.
- [130] Xiao J, Yang M, Che Q, Chen Y, Chen X, Yang H, et al. Effect of Potassium on Catalytic Characteristics of ZSM-5 Zeolite in Fast Pyrolysis of Biomass-Based Furan. *J Anal Appl Pyrolysis*. 2021; 157: 105230.
- [131] Mullen CA, Boateng AA. Accumulation of Inorganic Impurities on HZSM-5 Zeolites during Catalytic Fast Pyrolysis of Switchgrass. *Ind Eng Chem Res*. 2013; 52: 17156-17161
- [132] Ma N, Song Y, Han f, Waterhouse GIN, Li Y, Ai S. Highly Selective Hydrogenation of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran at Low Temperature over a Co-N-C/NiAl-MMO Catalyst. *Catal Sci Technol*. 2020; 10: 4010-4018.
- [133] Wang K, Zhang J, Shanks BH, Brown RC. The Deleterious Effect of Inorganic Salts on Hydrocarbon Yields from Catalytic Pyrolysis of Lignocellulosic Biomass and its Mitigation. *Appl. Energy*. 148 (2015), 115-120.
- [134] Zheng A, Zhao Z, Huang Z, Zhao K, Wei G, Wang X, et al. Catalytic Fast Pyrolysis of Biomass Pretreated by Torrefaction with Varying Severity. *Energy Fuel*. 2014; 28: 5804-5811.
- [135] Zhang S, Zhu S, Zhang H, Chen T, Xiong Y. Catalytic Fast Pyrolysis of Rice Husk: Effect of Coupling Leaching with Torrefaction Pretreatment. *J Anal Appl Pyrolysis*. 2018; 133: 91-96.
- [136] Xin X, Torr KM, Pang S, van de Pas D, Cooke-Willis M, Mercader FDM. Catalytic Fast Pyrolysis of Demineralized Biomass in a Fluidized Bed Reactor: Effects of Acid-Leaching and Torrefaction Pretreatments. *Energy Fuel*. 2020; 34: 568-578.
- [137] Xin X, Pang S, de Miguel Mercader F, Torr KM. The Effect of Biomass Pretreatment on Catalytic Pyrolysis Products of Pine Wood by Py-GC/MS and Principal Component Analysis. *J Anal Appl Pyrolysis*. 2019; 138: 145-153.
- [138] Karnjanakom S, Guan G, Asep B, Hao X, Kongparakul S, Samart C, et al. Catalytic Upgrading of Bio-Oil over Cu/MCM-41 and Cu/KIT-6 Prepared by  $\beta$ -Cyclodextrin-Assisted Coimpregnation Method. *J. Phys. Chem. C*. 2016; 120: 3396-3407.
- [139] Luo G, Resende FLP. In-Situ and Ex-Situ Upgrading of Pyrolysis Vapors from Beetle-Killed Trees. *Fuel*. 2016; 166: 367-375.
- [140] Lorenzetti C, Conti R, Fabbri D, Yanik J. A Comparative Study on the Catalytic Effect of H-ZSM5 on Upgrading of Pyrolysis Vapors Derived from Lignocellulosic and Proteinaceous Biomass. *Fuel*. 2016; 166: 446-452.
- [141] Zheng A, Zhao Z, Chang S, Huang Z, Wu H, Wang X, et al. Effect of Crystal Size of ZSM-5 on the Aromatic Yield and Selectivity from Catalytic Fast Pyrolysis of Biomass. *J Mol Catal A: Chemical*. 2014; 383-384: 23-30.
- [142] Mante OD, Agblevor FA. Catalytic Pyrolysis for the Production of Refinery-Ready Biocrude Oils from Six Different Biomass Sources. *Green Chem*. 2014; 16: 3364-3377.
- [143] Muragappan K, Mukarakate C, Budhi S, Shetty M, Nimlos MR, Roman-Leshkov Y. Supported Molybdenum Oxides as Effective Catalysts for the Catalytic Fast Pyrolysis of Lignocellulosic Biomass. *Green Chem*. 2016; 16: 5548-5557.
- [144] Rahman MdM, Chai M, Sarker M, Liu R. Catalytic Pyrolysis of Pinewood over ZSM-5 and CaO for Aromatic Hydrocarbon: Analytical Py-GC/MS Study. *J Energy Inst*. 2020; 93: 425-435.

- [145] Neupane S, Adhikari S, Wang Z, Ragauskas AJ, Pu Y. Effect of Torrefaction on Biomass Structure and Hydrocarbon Production from Fast Pyrolysis. *Green Chem.* 2015; 17: 2406-2417.
- [146] Srinivasan V, Adhikari S, Chattanathan SA, Park S. Catalytic Pyrolysis of Torrefied Biomass for Hydrocarbons Production. *Energy Fuels.* 2012; 26: 7347-7353.
- [147] Ghorbannezhad P, Firouzabadi MD, Ghasemian A, de Wild PJ, Heeres HJ. Sugarcane Bagasse *ex-situ* Catalytic Fast Pyrolysis for the Production of Benzene, Toluene, and Xylenes (BTX). *J Anal Appl Pyrolysis.* 2018; 131: 1-8.
- [148] Foster AJ, Jae J, Cheng YT, Huber GW, Lobo RF. Optimizing the Aromatic Yield and Distribution from Catalytic Fast Pyrolysis of Biomass over ZSM-5. *Appl Catal A: General.* 2012; 423-424; 154-161.
- [149] Mihalcik DJ, Boateng AA, Mullen CA, Goldberg NM. Packed-Bed Catalytic Cracking of Oak-Derived Pyrolysis Vapors. *Ind Chem Eng Res.* 2011; 50: 13304-13312.
- [150] Elkasabi Y, Mullen CA, Boateng AA. Distillation and Isolation of Commodity Chemicals from Bio-Oil Made by Tail-Gas Reactive Pyrolysis. *ACS Sustain Chem Eng.* 2014; 2: 2042-2052.
- [151] Zhang H, Xiao R, Huang H, Xiao G. Comparison of Non-Catalytic and Catalytic Fast Pyrolysis of Corn cob in a Fluidized Bed Reactor. *Bioresour Technol.* 2009; 100: 1428-1434.
- [152] Zhang H, Xiao R, Jin B, Shen D, Chen r, Xiao G. Catalytic Fast Pyrolysis of Straw Biomass in an Internally Interconnected Fluidized Bed to Produce Aromatics and Olefins: Effect of Different Catalysts. *Bioresour Technol.* 2013; 137: 82-87.
- [153] Karnajankom S, Siriya-Umporn T, Bayu A, Kongparakul S, Samart C, Fushimi C, et al. High Selectivity and Stability of Mg-Doped Al-MCM-41 for in situ Catalytic Upgrading Fast Pyrolysis Bio-Oil. *Energy Conv Manage.* 2017; 142: 272-285.
- [154] Li Z, Zhong Z, Zhang B, Wang W, Seufitelli GVS, Resende FLP. Effect of Alkali-Treated HZSM-5 Zeolite on the Production of Aromatic Hydrocarbons from Microwave Assisted Catalytic Fast Pyrolysis (MACFP) of Rice Husk. *Sci Total Environ.* 2020; 703: 134605.
- [155] Li Z, Zhong Z, Zhang B, Wang W, Wu W. Catalytic Fast Pyrolysis of Rice Husk over Hierarchical Micro-Mesoporous Composite Molecular Sieve: Analytical Py-GC/MS Study. *J Anal Appl Pyrolysis.* 2019; 138: 103-113.
- [156] Zhang Z, Cheng H, Chen H, Chen K, Lu X, Ouyang P, et al. Enhancement in the Aromatic Yield from the Catalytic Fast Pyrolysis of Rice Straw over hexadecyl Trimethyl Ammonium Bromide Modified Hierarchical HZSM-5. *Bioresour Technol.* 2018; 256: 241-246.
- [157] Du H, Zhang Z, Zhang B, Shi K, Li Z. Ex-situ Catalytic Upgrading of Vapors from Microwave-Assisted Pyrolysis of Bamboo with Chemical Liquid Deposition Modified HZSM-5 to Enhance Aromatics Production. *J Anal Appl Pyrolysis.* 2020; 149: 104857.
- [158] Chandler DS, Resende FLP. Comparison between Catalytic Fast Pyrolysis and Catalytic Fast Hydrolysis for the Production of Liquid Fuels in a Fluidized Bed Reactor. *Energy Fuel.* 2019; 33: 3199-3209.
- [159] Hu C, Zhang H, Xiao R. Effects of Nascent Char on ex-situ Catalytic Fast Pyrolysis of Wheat Straw. *Energy Conv. Management.* 2018; 177: 765-772.
- [160] Carlson TR, Vispute TP, Huber GW. Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived

- Compounds. *ChemSusChem*. 2008; 1: 397-400.
- [161] Gamliel DP, Cho HJ, Fan W, Valla JA. On the Effectiveness of Tailored Mesoporous MFI Zeolites for Biomass Catalytic Fast Pyrolysis. *Appl Catal A: General*. 2016; 522: 109-119.
- [162] Fang S, Shi C, Li P, Zhang Y, Chang C. Effects of Metal-Modified ZSM-5 Catalysts on Product Characteristics Based on the Py-GC/MS of Peanut Shells. *Ind Chem Eng Res*. 2020; 59: 17307-17314.
- [163] Zheng A, Zhao Z, Chang S, Huang Z, Zhao K, Wu H, et al. Maximum Synergistic Effect in the Coupling Conversion of Bio-Derived Furans and Methanol over ZSM-5 for Enhancing Aromatic Production. *Green Chem*. 2014; 16: 2580-2586.
- [164] Gunawardena DA, Fernando DS. Screening of Transition Metal/Oxide-Impregnated ZSM-5 Catalysts for Deoxygenation of Biomass Oxygenates via Direct Methane Intervention. *Biofuels*. 2018; 9: 113-120.
- [165] Gou J, Wang Z, Li C, Qi X, Vattipalli V, Cheng YT, et al. The Effects of ZSM-5 Mesoporosity and Morphology on the Catalytic Fast Pyrolysis. *Green Chem*. 2017; 19: 3549-3557.
- [166] Gilbert CJ, Espindola JS, Conner WC, Trierweiler JO, Huber GW. The Effect of Water on Furan Conversion over ZSM-5. *ChemCatChem*. 2014; 6: 2497-2500.
- [167] Zhao Y, Pan T, Zuo Y, Guo QX, Fu Y. Production of Aromatic Hydrocarbons through Catalytic Pyrolysis of 5-Hydroxymethylfurfural from Biomass. *Bioresour Technol*. 2013; 147: 37-42.
- [168] Wang C, Si Z, Wu X, Lv W, Bi K, Zhang X, Chen L, et al. Mechanism Study of Aromatics Production from Furans with Methanol over Zeolite Catalysts. *J Anal Appl Pyrolysis*. 2019; 139: 87-95.
- [169] Jae J, Tomsett GA, Foster AJ, Hammon KD, Auerbach SM, Lobo RF, et al. Investigation into the Shape Selectivity of Zeolite Catalysts for Biomass Conversion. *J Catal*. 2011; 279: 257-268.
- [170] Carlson TR, Jae J, Huber GW. Mechanistic Insights from Isotopic Studies of Glucose Conversion to Aromatics over ZSM-5. *ChemCatChem*. 2009; 1: 107-110.
- [171] Wang K, Kim KH, Brown RC. Catalytic Pyrolysis of Individual Components of Lignocellulosic Biomass. *Green Chem*. 2014; 16: 727-735.
- [172] Hoff TC, Gardner DW, Thilakarathne R, Wang K, Hansen TW, Brown RC, et al. Tailoring ZSM-5 Zeolites for Fast Pyrolysis of Biomass to Aromatic Hydrocarbons. *ChemSusChem*. 2016; 9: 1473-1482.
- [173] Karanjkar PU, Coolman RJ, Huber GW, Blatnik MT, Almalkie S, de Bruyn Kops SM, et al. Production of Aromatics by Catalytic Fast Pyrolysis of Cellulose in a Bubbling Fluidized Bed Reactor. *AIChE J*. 2014; 60: 1320-1335.
- [174] Hassan NS, Jalil AA, Hitam AA, Vo DVN, Nabgan W. Biofuels and Renewable Chemicals Production by Catalytic Pyrolysis of Cellulose: A Review. *Environ Chem Lett*. 2020; 18: 1625-1648.
- [175] He S, Muizebelt I, Heeres A, Schenk NJ, Bles R, Heeres HJ. Catalytic Pyrolysis of Crude Glycerol over Shaped ZSM-5/Bentonite Catalysts for Bio-BTX Synthesis. *Appl Catal B: Environ*. 2018; 235: 45-55.
- [176] Genuino HC, Muizebelt I, Heeres A, Schenk NJ, Winkelman JGM, Heeres HJ. An Improved Catalytic Pyrolysis Concept for Renewable

Aromatics from Biomass Involving a Recycling Strategy for Co-Produced Polycyclic Aromatic Hydrocarbons. *Green Chem.* 2019; 21: 3802-3806.

[177] Chen NY, Degnan TF, Koenig LR. Liquid Fuel from Carbohydrates. *Chemtech.* 1986; 16: 506-511.

[178] Zhang H, Cheng YT, Vispute TP, Xiao R, Huber GW. Catalytic Conversion of Biomass-Derived Feedstocks into Olefins and Aromatics with ZSM-5: The Hydrogen to Carbon Effective Ratio. *Energy Environ Sci.* 2011; 4: 2297-2307.

[179] Carlson TR, Cheng YT, Jae J, Huber GW. Production of Green Aromatics and Olefins by Catalyzing Fast Pyrolysis of Wood Sawdust. *Energy Environ Sci.* 2011; 4: 145-161.

[180] Huber GW, Zhang H, Carlson T. Method for Producing Fluid Hydrocarbons. US 2013/0060070 A1, March 7, 2013.

[181] Zhang H, Carlson TR, Xiao R, Huber GW. Catalytic Fast Pyrolysis of Wood and Alcohol Mixtures in a Fluidized Bed Reactor. *Green Chem.* 2012; 14: 98-110.

[182] Li K, Wang ZX, Zhang G, Cui MS, Lu Q, Yang YP. Selective Production of Monocyclic Aromatic Hydrocarbons from ex situ Catalytic Fast Pyrolysis of Pine over the HZSM-5 Catalyst with Calcium Formate as a Hydrogen Source. *Sustain Energy Fuels.* 2020; 4: 538-548.

[183] Mazanec T, Schmelzer E, Pesa F. Chemical Intermediates by Catalytic Fast Pyrolysis Process. US 9,249,080 B2, February 2, 2016.

[184] Sudarsanam P, Peeters E, Makshina EV, Parvulescu EV, Sels BF. Advances in Porous and Nanoscale Catalysts for Viable Biomass Conversion. *Chem Soc Rev.* 2019; 48: 2366-2421.

[185] Elkasabi Y, Mullen CA, Boateng AA. Aqueous Extractive Upgrading of Bio-Oils Created by Tail-Gas Reactive Pyrolysis to Produce Pure Hydrocarbons and Phenols. *ACS Sustain Chem Eng.* 2015; 3: 2809-2816.

[186] Elkasabi Y, Wyatt V, Jones K, Strahan GD, Mullen CA, Boateng AA. Hydrocarbons Extracted from Advanced Pyrolysis Bio-Oils: Characterization and Refining. *Energy Fuel.* 2020; 34: 483-490.

[187] Horne PA, Williams PT. Upgrading of Biomass-Derived Pyrolytic Vapours over Zeolite ZSM-5 Catalyst: Effect of Catalyst Dilution on Product Yields. *Fuel.* 1996; 75: 1043-1050.

[188] Zhang X, Rajagopalan K, Lei H, Ruan R, Sharma BK. An Overview of Novel Concept in Biomass Pyrolysis: Microwave Irradiation. *Sustain Energy Fuels.* 2017; 1: 1664-1699.