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

William H. Gong

## Abstract

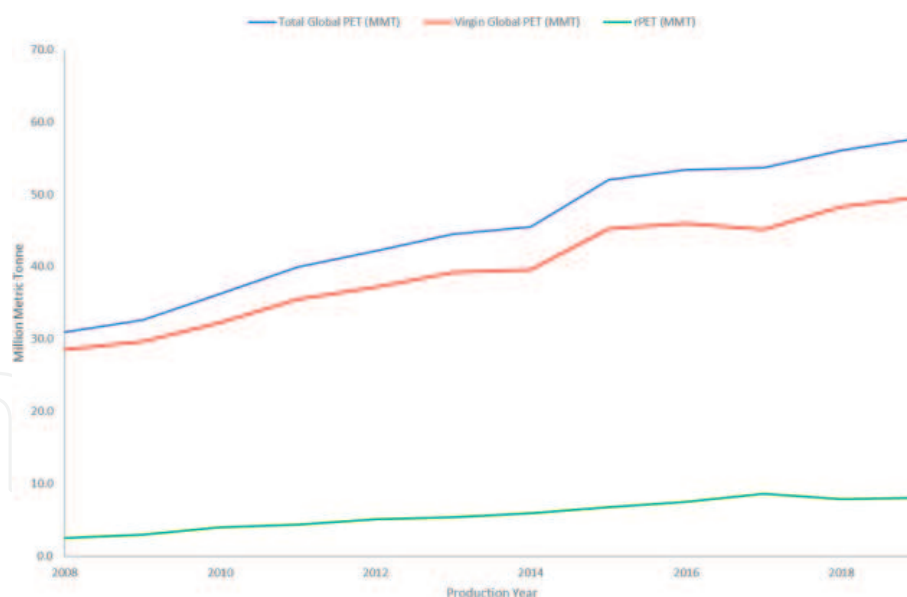
Catalytic Fast Pyrolysis is a rapid method to depolymerize lignocellulose to its constituent components of hemicellulose, cellulose, and lignin. The pyrolysis reaction in absence of oxygen occurs at a very high heating rate to a targeted temperature of 400 to 600 °C for very short residence time. Vapors 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

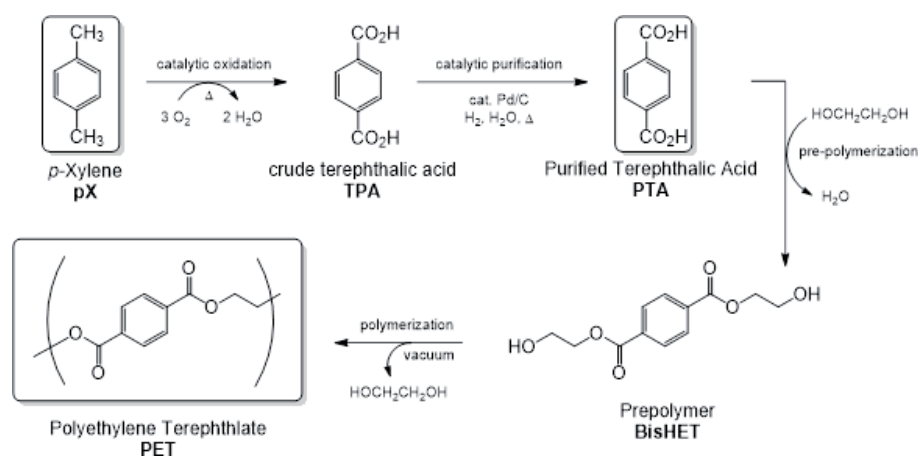
## 1. Introduction

*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 mm tonnes (**Figure 2**).

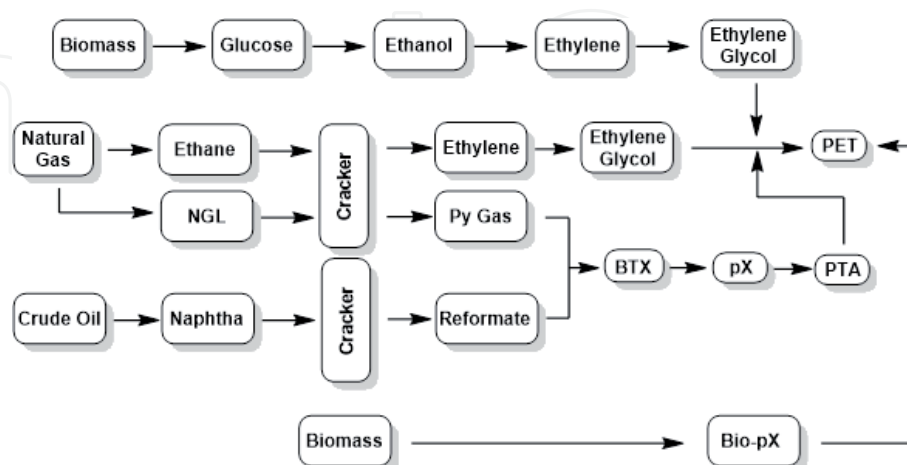
**Figure 3** displays the supply chain to produce PET. Virtually all PET is produced from fossil fuel resources. pX is produced from mixed xylenes that are derived from crude oil, and MEG is produced from ethylene primarily derived from natural gas. There is a commercial bio-based route to MEG that starts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

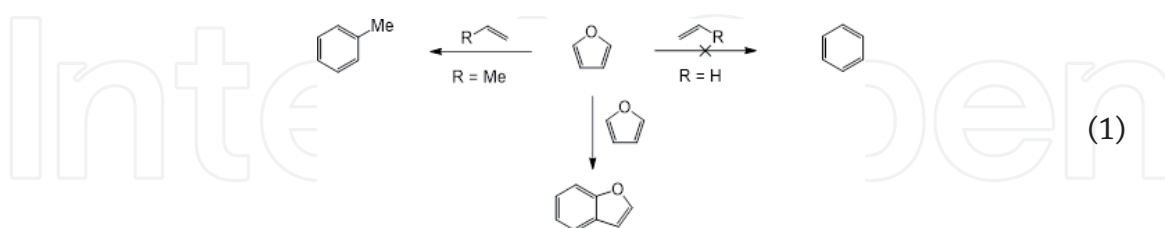
A comparison of in situ and ex situ CFP of hybrid poplar at 700 °C was conducted in a microreactor. In situ CFP produced 5.4% olefins and 26.1% aromatics.



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 feed-stock. 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]   |
| Jatroha 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 mono-saccharide 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 <sup>13</sup>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<sub>eff</sub>) can predict the outcome of pyrolysis [177]. This ratio is calculated according to the following formula (Eq. (2)).

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

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, lignocel-lulose 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.

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