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A Study on Pyrolysis of Lignin over Mesoporous Materials

*Abdelrahman Mohamed Rabie and
Marwa Mohamed Abouelela*

Abstract

The aromatics have widespread uses across the chemical industries. Where, the monocyclic aromatics (e.g. BTX) and phenolics compounds are important basic raw materials for several industrial petrochemical processes such as synthetic polymers, detergents, biocides, resins, explosives, etc. Traditional production of these valuable chemicals has been dependent on fossil resources for more than half a century. So, it requires strategies for alternative chemical production from renewable sources especially from nonedible biomass. This chapter presents a review of the recent literature on the fast pyrolysis process for the production of aromatic hydrocarbons using mesoporous catalysts. We focus on the factors that can enhance the yield of aromatics and the lifetime of the catalyst used. Background information on catalyst deactivation during the pyrolysis process was described. The role of mesoporous catalyst's acidity and textural and topological properties of lignin to aromatics conversion was also discussed in detail.

Keywords: pyrolysis, fast pyrolysis, lignin, mesoporous materials

1. Fast pyrolysis of lignin for production of aromatic hydrocarbons by mesoporous catalysts

Catalytic fast pyrolysis of lignin with catalysts to produce aromatic hydrocarbons has attracted many research interests in recent years. Aromatic hydrocarbons, especially benzene, toluene, ethyl benzene and xylenes (BTEX), are considered to be important and valuable chemicals in the petroleum industry (**Figure 1**) [1–5].

Pyrolysis of lignin is the thermal depolymerization of organic materials in an oxygen-free environment in a temperature range of 300–900°C [6–8]. During the thermal decomposition process, hemicellulose, cellulose, and lignin undergo different reactions, leading to a three-stage reaction: moisture removal, main depolymerization, and biochar formation [9]. Fast pyrolysis is considered one of the most economical and highly efficient technologies to convert biomass and lignin to bio-oil and high valuable chemical products [10].

Catalytic fast pyrolysis (CFP) is a further modification of fast pyrolysis directed toward the production of hydrocarbon fuels. By pyrolyzing biomass in the presence of a catalyst, it is possible to catalyze the direct production of aromatic hydrocarbons such as benzene, toluene, and xylenes [1, 3, 11–16].

Catalytic fast pyrolysis has several advantages over other biomass conversion approaches. (1) All of the desired chemistry can occur in a single reactor using

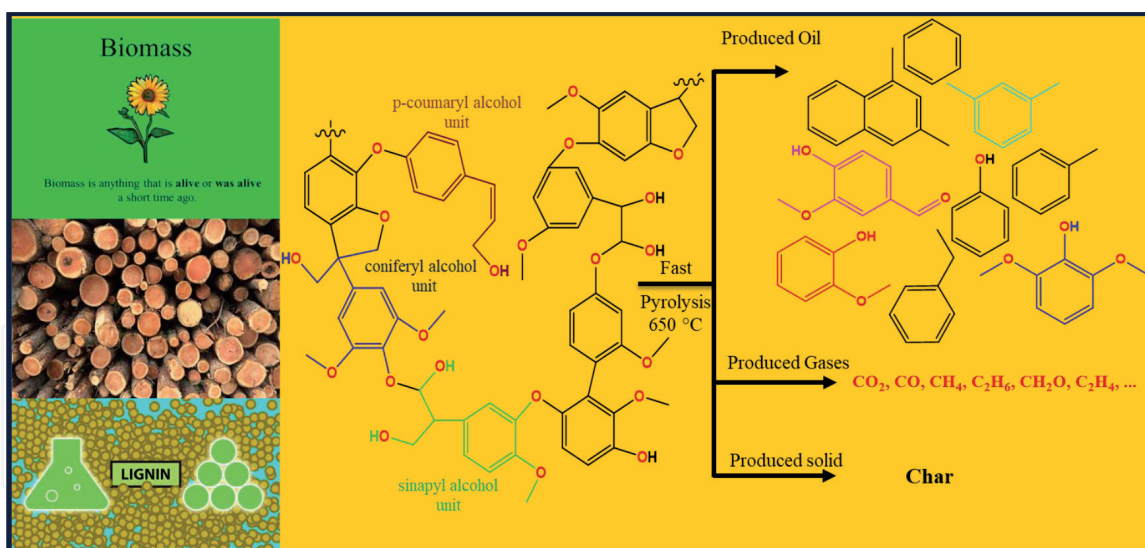


Figure 1.
Various products of fast pyrolysis of lignin.

inexpensive aluminosilicate catalysts. (2) Catalytic fast pyrolysis can be used to process a range of different lignocellulosic feedstocks with only simple pretreatment (drying and grinding, for example) prior to reaction. (3) The aromatics produced through catalytic fast pyrolysis can readily be blended into the existing gasoline infrastructure to reduce the use of crude oil [17].

Lignin is an aromatic and optically inactive amorphous heteropolymer, which is often synthesized by free radical assisted peroxidase mediated dehydrogenation of phenylpropanoid precursors, namely coniferyl alcohol, p-coumaryl alcohol, and sinapyl alcohol, joined altogether via non-hydrolysable linkages. The ratios of these three monolignols vary significantly among different plant species. For example, coniferyl alcohol is abundant in soft wood lignin while hard wood lignin comprises both coniferyl and sinapyl alcohols; however, grass lignin contains all three monolignols [18].

2. Factors that influence the pyrolysis process

The bio-oil yield from catalytic fast pyrolysis of lignin differs according to many parameters including kind of the catalyst, reactor types, temperature and the rate of heating, and reaction time, which can be explained in following subdivisions.

2.1 Kind of the catalyst

The catalyst throughout the pyrolysis process causes cracking reactions and improves the quality of biomass pyrolysis products, relying on the operating conditions. The catalyst kind and reactor design play a vital role in the production of primary products during the pyrolysis process. Gaseous and liquid products can be produced by the catalytic cracking of the primary pyrolysis vapors.

Oxygenated products can be reduced by utilizing zeolite-type catalysts [19]. Zeolite-type catalysts have been studied in the pyrolysis process of lignin. Jackson et al. [20] studied the catalytic pyrolysis of lignin over KZSM-5, HZSM-5, solid phosphoric acid, Al-MCM-41, and Co/Mo/Al₂O₃. Reaction over HZSM-5 generated aromatic compounds (46.7% simple aromatics and 46.2% naphthalenic ring compounds), while reaction over Al-MCM-41 generated 17.3% simple aromatics, 13.5% naphthenic ring compounds, and 66.5% oxygenated aromatics. MCM-41 has

its distinctive advantages. It is suitable for macromolecular catalytic reactions due to its larger pore size; it can make adsorption and separation, and it decreases the resistance of the molecular diffusion in pores.

As well, MCM-41 has a large specific surface area (up to 1000 m²/g), which introduces enough sites on the surface for adsorption and catalytic reactions of reactive components, and it produces comparatively low char products [10] (**Figure 2**).

Mesoporous zeolites catalysts are favorable to inhibit the repolymerization reaction, this because the high surface area and regular pore structures [22, 23], which makes mesoporous supports suitable for the catalytic upgrading of lignocellulose [24]. Mullen and Boateng studied the pyrolysis process of four various lignin sources over CoO/MoO₃ and zeolite H-ZSM5 catalysts. They found that the H-ZSM5 catalyst was more active to produce aromatic hydrocarbons from lignin [25]. Ma et al. reported that H-USY has large enough pore size and the produced molecules during the fast pyrolysis process of alkaline lignin were able to penetrate the pores of the zeolite catalyst. The inside reaction could prevent the formation of char [26]. Thepparat et al. compared the influence of NiMo/Al₂O₃ and mesostructured silica catalysts on the depolymerization reaction of organosolv lignin extracted from woody eucalyptus. They found that MCM-41 and SBA-15 produced the lowest char yield [27].

2.2 Reactor types

Reactors, where the pyrolysis process takes place, play an essential role in the yield and composition of bio-oil produced from lignin pyrolysis; this is because it associates with the rate of the heating of the system, method of heat transfer, residence time of volatiles and conversion capacity of lignin. In the fast pyrolysis of lignin, the outside heating pyrolysis reactors and internal heating pyrolysis reactors are used [28].

2.3 Exterior heating pyrolysis reactors

Fluidized reactor and Fixed-bed reactor are mostly utilized in the outside heating pyrolysis system, in which the heat transmits from the exterior surface to the interior of the material. Fixed-bed reactor consists of a feeding unit, a gas flowing

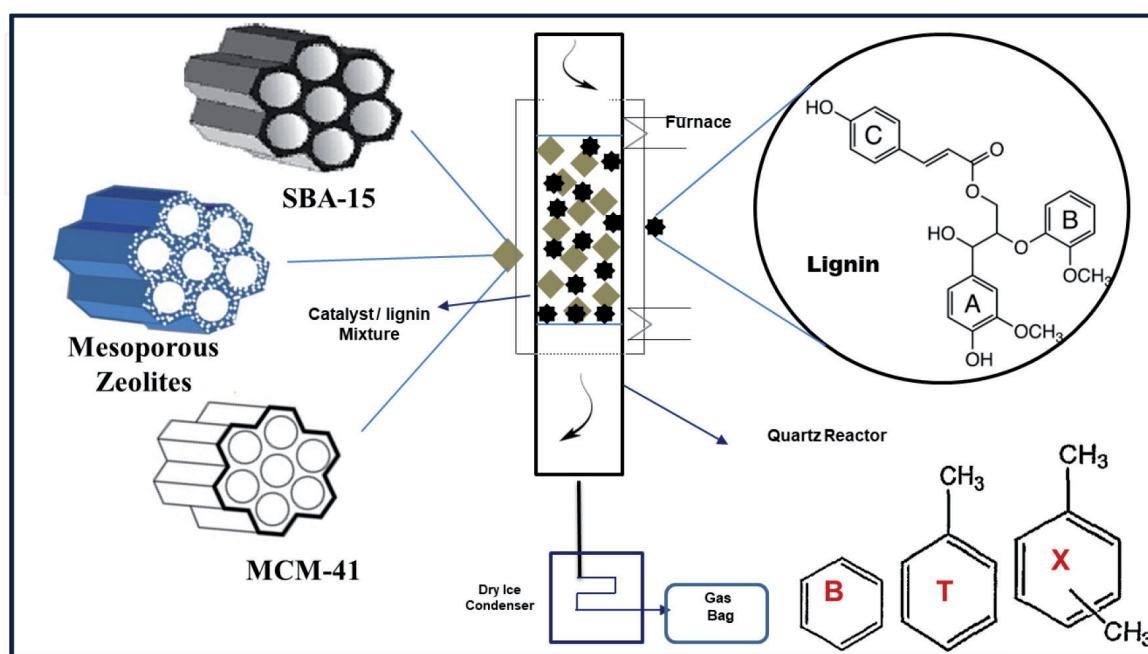


Figure 2.
 Catalytic fast pyrolysis using different mesoporous materials [21].

unit, and a static bed (reaction bed), and a product exit was utilized in reactions that took place between gas phase (gaseous reactants) and solid phase (catalyst bed). Recently, Fixed-bed reactor has been widely used in the pyrolysis process of lignin or biomass. Generally, the heater that supplies the energy for pyrolysis of lignin is the electric furnace [20, 29]. The rate of heating is uneven and the efficiency of heating is low; this is because the furnace is usually attached on the periphery of the fixed bed. So, the yield of bio-oil is low and the end products are less homogenous.

However, fixed bed is appropriate for the catalytic pyrolysis process. Catalytic pyrolysis of lignin can produce High yield of aromatic compounds [30]. This is because the primary products from catalytic pyrolysis of lignin necessarily pass through the long catalytic bed (static bed), introducing more contacting opportunity for pyrolysis vapors and catalyst. Fluidized-bed reactor supplies more enormous heating for the pyrolysis process compared to fixed-bed reactor. Fluidized-bed reactor is a chamber that facilitates the mixing of gas substrates or liquid with solid particles acting as a fluid. The fluidization increases the mixing and interaction among gas and particles, resulting in efficient heat transfer symmetric temperature, and superb reaction rate.

The pyrolysis process of lignin in fluidized-bed reactor produced higher yield of bio-oil. In addition, the pyrolysis process of lignin in fluidized bed reactor produces lower guaiacols compared to the pyrolysis process in fixed-bed reactor. Even though the selectivity relies on diverse factors such as reaction conditions and the source of lignin, the high heat transfer effectiveness of fluidized-bed also secures equal high temperature during the pyrolysis process, which is contributory to demethoxylation reaction of lignin [31]. Anyhow, fluidized-bed reactor has some flaws for the pyrolysis process of lignin. The highest temperature was noticed nearly in the upper border of the bed [32] because of the continuous reaction of pyrolysis vapors in the part, indicating that undesirable side reaction happens out of the fluidized bed and in completed pyrolysis reaction in the cell of the fluidized bed, which could produce more of undesirable by-products. So, it was noticed that the most desired products were commonly gotten at the half length of the reactor [33].

2.4 Interior heating pyrolysis reactors

In fluidized bed and fixed reactors, furnace, catalyst, and hot gases are utilized as heating media, which provide the energy to the substance from the exterior surface to the interior center. These ineffectual traditional pyrolysis processes are usually producing low yield of bio-oil with low quality. Nowadays, microwave technology introduces unprecedented techniques for pyrolysis. Microwave radiation produces energy as a result of the interaction among polar molecules present in the material and electromagnetic field; the heat transmits from the interior to the exterior surface of the substance [34]. Microwave-assisted pyrolysis indicates high energy effectiveness and supplies identical interior heating. Pyrolysis process by microwave produces uniform products due to the distinctive thermal gradients [35].

Unlike traditional heating, microwave heating provides quick quenching of pyrolysis vapors, which avoid the second decomposition reactions of the primary products. Compared to pyrolysis by electric heating, the pyrolysis process by microwave assists the production of phenolic compounds from lignin [36]. In addition, esters and hydrocarbons in bio-oil steeply rose compared to that gained from electric-heating pyrolysis due to the formation of hot points formed by microwave heating, which facilitates the conversion of guaiacols to gases such CO and H₂ [37].

2.5 Temperature and the rate of heating

Temperature has a crucial effect in the catalytic fast pyrolysis of lignin. To decrease the secondary reactions of primary vapors which decline the yield and quality of liquid products, a quick heating and cooling of primary vapors should be used [38]. As well as, the slow heating rate produces high yield of char [39]. Temperature has a vital influence on the yield of char and its properties. High temperatures lead to lower yield of char in all of pyrolysis reactions. The first cause for this is the removing of many volatile substances from the char at high temperatures, resulting in a decline in the char yield. For instance, the char yield declines from 31 to 17% with a rise in the temperature from 638K to 879K [40]. Low temperatures lead to imperfect decomposition of biomass resulting in a high quantity of unpyrolyzed solid materials in char content. Also, temperature has an influence on the composition of the char, chars obtained at high temperatures having high carbon content [41, 42]. At the temperatures higher than 773K, The char contains more than 85wt% carbon [43]. The yield of Liquid products increases by raising the pyrolysis temperatures up to an extreme value, at 673–823 K, but it greatly relies on other operating factors. For a diverse of feedstock sorts, it has been studied that the extreme yield of pyrolysis oil is produced at temperatures of about 673–823 K with a constant decline in char yield and rise in gas yield.

2.6 Effect of the reaction time

The time when the biomass was sustained at a specific pyrolysis temperature is the reaction time. In batch systems, the reaction time must be adequate to achieve the required result in the process. Secondary reactions of primary vapors can occur under long reaction time such as carbonization, thermal cracking, and gasification that lead low bio-oil yield [44, 45]. As well as, the reaction time is essential for the reactor configuration step. Tsai et al. [45] studied the pyrolysis process of rice husk in fixed bed reactor, they observed That, the bio-oil yield rose by rising the reaction time from 1 min to 2 min. However, the yields after that were noticed to decline slightly at long holding time.

2.7 Effect of lignin source

The source of lignin and method of isolation have a great impact on the pyrolysis process and the distribution of pyrolysis products. Wang et al. [46] studied the pyrolysis process of various four sorts of lignin, Klason lignin (KL), alkali lignin (AL), milled wood lignin (MWL), and organosolv lignin (OL), separated from the same pine wood, by TG-FTIR and Py-GC/MS as well as ^{13}C NMR spectroscopy. The ^{13}C NMR indicated chemical structure of these separated lignin's is diverse. Ether bonds such as $\beta\text{-O-4}$ have lower thermal stability and can decompose readily at low temperatures. So, lignin's containing more ether bonds could show weaker thermal stability. Alkali lignin and milled wood lignin, because they contain more $\beta\text{-O-4}$ bonds in their structures, have a lower temperature at maximum weight loss rate (346 and 359°C, respectively) than OL (396°C) or KL (405°C). So, the pyrolysis process of AL and MWL produced more phenolic compounds at lower temperatures. The predominate products in pyrolysis of these softwood lignin's are guaiacyl-type compounds due to shortage of syringyl-type unit in the structure of softwood and the highest yield of phenol was achieved at 600°C.

Mullen and Boateng [25] studied the pyrolysis of lignin from four various sources over an acidic zeolite (HZSM-5) and a mixed metal oxide catalyst (CoO/MoO₃). Even though two catalysts formed to be efficient catalysts for deoxygenation reaction, enhancing the formation of aromatic hydrocarbons from lignin, the acidic HZSM-5 was observed to be more active than CoO/MoO₃.

3. Deactivation of the catalysts

Phenolic compounds produced from Lignin pyrolysis are substantially adsorbed on acidic sites of zeolite catalyst, and could behave as a coke precursor and produce a great amount of coke [47]. A great amount of coke produced from catalytic fast pyrolysis of lignin commonly leads to quick deactivation of zeolite catalysts, which declines the carbon conversion effectiveness [48]. Ivanov et al. studied the deactivation of H-ZSM5 zeolite by the formation of coke and the regeneration in the production of phenol from nitrous oxide oxidation of the benzene [49]. They observed that the main reason for the deactivating effect of coke is the poisoning of active sites. A large content of coke requires to be removed for the regeneration of the catalytic activity of the catalyst.

4. The role of mesoporous catalyst acidity and textural topology

There have been many recent studies on the role of mesoporous catalysts in fast pyrolysis of lignin to aromatic compounds [20, 50–56].

In our previous publication [36] we studied the production of highly selective BTX from catalytic fast pyrolysis of lignin over supported mesoporous silica. We found that the yield of BTX rose from 17.0% in the case of MCM-48 to 32.5% in the case of Al/MCM-48 (8.4%) and 49.4% in the case of Zr/MCM-48 (2.9%) due to enhancing the acidity of the catalysts. Between the studied catalysts, Zr⁴⁺ loaded onto MCM-48 was considered a favorable catalyst for lignin pyrolysis with high activity and selectivity to BTX yield.

A.M. Elfadly et al [57] studied the Production of aromatic hydrocarbons from catalytic pyrolysis of lignin over acid-activated bentonite clay. They found that the catalytic fast pyrolysis of lignin over HCl-activated bentonite (mainly montmorillonite) produced a diverse of aromatics such BTX, naphthalene, indenenes, and alkyl benzene, with extraordinary selectivity toward O&P-xylenes. The production of o&p-xylenes was remarkably improved at a temperature of about 550–650°C. Thus, it would be favorable to carry out the catalytic pyrolysis over HCl-activated bentonite if O&P-xylenes are the required products. They concluded that the enhanced activity of HCl-activated bentonite is due to the improvement in the textural characteristics and strong Bronsted acid sites resulted from acid treatment. H₂SO₄ and H₃PO₄ treatments formed an amorphous material and caused the destruction of the bentonite crystalline structure. Thus, these substances showed inactivity in catalytic fast pyrolysis of lignin.

Victoria B. F. Custodis et al [58] studied the Catalytic Fast Pyrolysis of Lignin over High Surface Area Mesoporous Aluminosilicates, and they focused on the influence of Acidity and Porosity. The results revealed that the acid sites (mild Bronsted and stronger Lewis) are responsible for catalyzing the pyrolysis intermediates to produce lower oxygenated phenolic compounds and aromatic

hydrocarbons. MCM-41 in nano size produced a high yield and selectivity of aromatic hydrocarbons. The two most important factors are diffusion, which is affected by the pore and grain size, and the active site, which may be moderately acidic by Lewis acid sites. Nanosized grains and moderate acidity are important ingredients for a perfect catalyst for catalytic fast pyrolysis of lignin. Nanosized Al-MCM-41(50) formed the highest quantity of aromatic hydrocarbons (containing naphthalenes) (peak area 80%) compared to all mesoporous catalysts.

Lee et al. [59] studied the conversion of lignin over Al-MCM-48. Al-MCM-48 enhanced the production of light phenolic compounds extremely. The yields of aromatics and hydrocarbons were also improved by catalytic upgrading. Al-MCM-48 promoted the cracking, aromatization, and deoxygenation reactions, like decarbonylation. The hydrocarbons yield increased with increasing catalyst quantity to reach C/L = 1:5. This was due to the increased opportunity of catalytic reactions to occur on the acidic sites of the catalyst, such as cracking, decarboxylation, decarbonylation, and aromatization. Most produced hydrocarbons were cyclic and aromatic compounds, such as BTX. This indicates that phenolic compounds were transformed to cyclic and aromatic hydrocarbons by catalytic deoxygenation and cracking over Al-MCM-48 catalyst. However, the total quantity of aromatics and hydrocarbons was low compared to that of phenolic compounds. This is due to the weak acid sites of Al-MCM-48. The production of aromatics and hydrocarbons is enhanced over strong Bronsted acid sites, which are not present on Al-MCM-48. Furthermore, Si-MCM-48, which doesn't contain acid sites, exhibited lower deoxygenation effectiveness than Al-MCM-48.

Yi-Xin Chen et al [60] studied the arene production by W₂C/MCM-41-catalyzed upgrading of vapors from fast pyrolysis of lignin. The experiments were carried out in a micro pyrolyzer-gas chromatography/mass spectrometer (P-GC/MS). A range of W₂C/MCM-41 catalysts with various catalyst loading quantities (Si/W) was prepared, and the activity, selectivity, and the stability degree of the catalysts were studied. They found that the catalyst with Si/W = 50:1 showed the best activity and the highest arene yield. Also, the increase in the loading percent of catalyst can enhance the cracking reaction of pyrolysis vapors. The mechanism of lignin fast pyrolysis included dehydration, demethylation, and rearrangement reactions. They concluded that MCM-41 catalysts have the best activity to catalyze the production of monocyclic arenes from primary pyrolysis vapors. In addition, they showed a high stability in catalytic fast pyrolysis of lignin. So, the modified mesoporous MCM-41 catalysts with tungsten carbide are favorable catalysts in catalytic fast pyrolysis of lignin.

Lee et al. [61] studied the catalytic fast pyrolysis of lignin over mesoporous Y zeolite using Py-GC/MS. The catalytic fast pyrolysis of lignin was taking place at 500°C using pyrolysis gas chromatography/mass spectrometry. Mesoporous Y zeolite and mesoporous material, Al-MCM-41, were tested for the catalytic fast pyrolysis of lignin. The noncatalytic pyrolysis of lignin produced phenolic compounds as a main product; this is because lignin composition mainly includes phenyl propane units. Catalytic upgrading of primary pyrolysis vapors increased the yields of low-molecular-mass phenolic compounds, monocyclic aromatics, and poly aromatic hydrocarbons (PAHs). The production of monocyclic aromatics and PAHs was increased significantly when the more acidic mesoporous Y zeolite was utilized. In contrast, the yield of alkoxy phenolic compounds was greater when the low acidic Al-MCM-41 was tested. Increasing mesoporous Y/lignin ratio showed

a sharp increase in the yield of monocyclic aromatic compounds and PAHs; also, the yield of light phenolics increased, but the yield of total phenolic compounds declined.

Ming-hui Fan et al [62] studied the Catalytic Depolymerization of lignin for the production of BTX. The conversion of lignin to benzene, toluene, and xylenes (BTX) was tested over the HZSM-5 and MCM-22 catalysts; the HZSM-5 catalyst indicated the largest yield of BTX. They studied various reaction conditions, involving temperature, the catalyst/lignin ratio, and the gas flow rate. The carbon yield of BTX was nearly 25.3 C-mol% in the presence of HZSM-5 catalyst at a temperature of 550°C, a flow of N₂ 300 cm³/min, and a catalyst/lignin ratio of 2:1. HZSM-5 showed the best activity due to the mild acidity; in addition, the small pore size are useful for cracking and the deoxygenation reactions of lignin. Temperature has a high impact on the product distribution. The BTX selectivity increased by raising the temperature, but high temperature may lead to the production of olefins and alkanes due to a second cracking reaction. The BTX selectivity is strongly associated with the catalyst/lignin ratio, and the optimum ratio of catalyst to lignin was nearly 2:1. More increase of the catalyst/lignin ratio will decline the BTX yield, which leads to an increase in the yield of gas products. They observed that the reaction time should be carefully controlled to obtain high-yield BTX. The production of BTX was performed through depolymerization of lignin followed by the deoxygenation reaction.

The influence of various catalysts on the yield of aromatics during the fast pyrolysis process of biomass is summarized in **Table 1**.

Based on these studies, high quality aromatic compounds will be produced by a suitable choice of catalyst and reaction conditions.

Tang S et al. [64] studied the catalytic pyrolysis of lignin over hierarchical HZSM-5 zeolites prepared by posttreatment with alkaline solutions. They observed that the alkali treatment of HZSM-5 enhanced the catalytic activity of HZSM-5 zeolite for cracking of bulky oxygenates produced from lignin pyrolysis to form aromatic hydrocarbons. The HZSM-5 zeolite treated with 0.3 mol/L NaOH was the best choice for the catalytic fast pyrolysis of lignin for the production of aromatic hydrocarbons.

Compared to the parent HZSM-5, alkali-treated HZSM-5 zeolite showed greater selectivity to aromatic hydrocarbons by the catalytic fast pyrolysis of lignin. Some of the silicon species from the zeolite structures are removed during alkali treatment, forming new intracrystalline mesopores in the HZSM-5 grains, destroying a portion of the crystalline structure, and reducing the density of strong acid sites, which are the catalytic sites responsible for the conversion of oxygenated compounds to aromatic hydrocarbons. Even though the density of strong acid sites in zeolites is declined by alkali treatment, the effectiveness of transforming of bulky oxygenates to aromatic hydrocarbons is improved.

Catalytic pyrolysis of lignin with red mud derived hierarchical porous catalyst for the production of alkyl-phenols and hydrocarbons was studied by Wang et al. [65]. They investigated the catalytic behavior of the synthetic ACRM catalyst in the thermal decomposition of lignin. The prepared ACRM catalyst had a well-structured hierarchical porosity, which could enhance the specific surface area and the dispersion of acidic sites and active metal oxides. These enhanced properties of the ACRM showed high catalytic activity during the catalytic pyrolysis of lignin vapors. The catalyst increased the production of alkyl phenols and aromatic hydrocarbons in bio-oil by about 74% at 550°C, due to promoting the dehydroxylation, demethoxylation, demethylation, and alkylation reactions [66].

Catalyst	Type of feed	Used reactor	Pyrolysis condition	Yield of aromatics (BTX) (%)	Yield of phenols (%)	Ref
Al-MCM-41(50)	Alkaline lignin	Quartz reactor with G'C/MS	C/L ratio = 4:1, temperature at 650°C in a helium atmosphere at a heating rate of 20 cm s ⁻¹ , and reaction time = 20 s.	80	15	[58]
Al-MSU-J (50)2	Alkaline lignin	Quartz reactor with GC/MS	C/L ratio = 4:1, temperature at 650°C in a helium atmosphere at a heating rate of 20 cm s ⁻¹ , and reaction time = 20 s.	53	25	[58]
Al-SBA-15(50)-2	Alkaline lignin	Quartz reactor with GC/MS	C/L ratio = 4:1, temperature at 650°C in a helium atmosphere at a heating rate of 20 cm s ⁻¹ , and reaction time = 20 s.	57	22	[58]
AB(HCl)	Alkaline lignin	In a down-flow fixed-bed quartz reactor	At temperature 650°C, flow of N ₂ = 75 ml/min and C/L ratio 3:1.	18	2	[57]
Al-MCM-48	Lignin powder (kraft, alkali)	Py-GC/MS	Pyrolysis performed at 500°C, lignin/Al-MCM-48 = 1/5.	3.82	11.17	[59]
W ₂ C/ MCM-41	Alkaline lignin	Micro pyrolyzer-gas chromatography/ mass spectrometer (P-GC/MS)	Reaction conditions: 750°C, 20 s, C/L = 10:1.	14.22	0.67	[60]
	Sulfur-free lignin from wheat straw	Flow system	Pyrolysis performed at T = 550°C, f(N ₂) = 300 cm ³ /min, and a catalyst/lignin ratio of 2.	25.3	3	[62]
MCM-22	Sulfur-free lignin from wheat straw	Flow system	Pyrolysis performed at T = 550°C, f(N ₂) = 300 cm ³ /min, and a catalyst/lignin ratio of 2:1.	19	3.5	[63]
MCM-48	Alkaline lignin	Fixed-bed quartz reactor system	Pyrolysis performed at T = 600°C, f (N ₂) = 25 ml/min, and a catalyst/lignin ratio of 3:1.	17	1.12	[21]
Al/MCM-48	Alkaline lignin	Fixed-bed quartz reactor system	Pyrolysis performed at T = 550°C, f (N ₂) = 25 ml/min, and a catalyst/lignin ratio of 3:1.	32.5	5.6	[21]
Zr/MCM-48	Alkaline lignin	Fixed-bed quartz reactor system	Pyrolysis performed at T = 550°C, f (N ₂) = 25 ml/min, and a catalyst/lignin ratio of 2:1.	49.4	1.09	[21]

Table 1.
Influence of various catalysts on the yield of aromatics during the fast pyrolysis process of biomass.

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Author details

Abdelrahman Mohamed Rabie* and Marwa Mohamed Abouelela
Petrochemical Department, Egyptian Petroleum Research Institute, Cairo, Egypt

*Address all correspondence to: abdo3040@yahoo.com

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