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Review Article

Bio-Oil Upgrading over ZSM-5 Catalyst: A Review of Catalyst Performance and Deactivation

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Due to population explosion and industrialization, waste biomass and polymer conversion into biofuel has attracted the interest of researchers. The application of the ZSM-5 catalyst for bio-oil upgrading into renewable biofuels has attracted researchers' efforts as an excellent catalyst. The need for improved biofuel quality with reduced oxygenates has further necessitated the application of catalyzed upgrading techniques. The catalytic performance of the ZSM-5 catalyst was attributed to its exceptional pore structure and window architecture and when it is incorporated with some selected transition metals to improve aromatic hydrocarbon formation. The review revealed that the development of coke deposit on the microspores of the ZSM-5 catalyst hindered the effective transport of large molecular compounds into the active sites for an easy deoxygenation process. Hence, the introduction of mesoporosity, hybrid catalyst development, and tailored crystal growth on the ZSM-5 catalyst could address several hindrances associated to conventional ZSM-5. Therefore, the need for catalyst modification is paramount for ZSM-5 performance during bio-oil upgrading.

1. Introduction

The increase in the dependency on energy-derived fossil fuels has been on the rise around the globe due to an increase in population which has resulted in serious environmental challenges and an energy crisis [1–3]. In addition, the reserves of fossil fuels as global energy sources are depleted at a faster rate considering the dependency on global consumption, most especially, the transportation sector [4]. Presently, hydrocarbon fuels derived from conventional sources have been the major energy source used in internal combustion engines for transportation purposes, and adversely, they produce exhausts with harmful effects on humans and the general ecosystem ranging from environmental pollution to death due to a higher rate of exposure [5].

In recent years, the application of biomass-derived liquid fuels has presented itself as an alternative to fossil-based hydrocarbon fuels for both domestic and industrial uses. The application of biomass-derived fuels is aimed towards improving the energy efficiency and sustainability of the world economy [6]. Ease of accessibility, abundance, and environmental friendliness of biomass have made it an interesting area of research as an energy source for carbon-neutrality towards limiting the emission of greenhouse gases (GHGs) in the surrounding ecosystem [4, 7, 8]. Therefore, the need for conversion of biomass solid wastes into economic liquid fuel has gained tremendous attention; this action promotes waste-to-wealth, reduces indiscriminate burning, and enhances the production of sustainable and renewable alternatives to conventional fuels. The liquid

biofuel produced via this route using the most widely employed method such as pyrolysis is characterized by defects such as high oxygen content as well as low heating value [9, 10]. Hence, the introduction of high heating feedstock with improved hydrogen density into the conversion route would be of immense advantages [11–13]. Such feedstocks with high heating values include the application of the copyrolysis process involving the introduction of polymers to improve the general biofuel performance [14–17].

The low carbon yield of aromatic hydrocarbons (10–30%; low energy-dense hydrocarbons) is associated with bio-oil produced via the catalytic pyrolysis of lignocellulose materials; the introduction of energy-dense hydrocarbons is of importance [18]. Therefore, the copyrolysis of the lignocellulose biomass with polymeric materials will enhance the production of improved biofuels with high carbon yield, heating/calorific value, and aromatic hydrocarbons [19–21]. In order to improve the biofuels obtained from the catalytic fast pyrolysis (CFP) of biomass, the blending of a high H/C_{eff} ratio material to the lignocellulose biomass has been reported by several researchers. Incorporation of polymers would not only enhance the H/C_{eff} ratio but also modify the reaction mechanisms by introducing hydrogen molecules which lead to dehydration via decarboxylation and decarbonylation substitution [22]. The formation of olefins and alkanes from the polymer feedstock has been reported as a hydrogen donor for oxygenate-derived cellulose which retards the formation of coke during the catalytic conversion approach [23]. The incorporation of catalysts such as ZSM-5 has been reported to further enhance the formation of monoaromatic hydrocarbons over polyaromatic hydrocarbons due to their shape selectivity properties. One of the most eminent properties of bio-oil produced via thermochemical approaches is the presence of a high content of oxygenated compounds in the form of acids, ketones, aldehydes, ethers, esters, and phenolics which requires attention [24–26].

In an attempt to produce biofuels having improved fuel properties such as high octane number, low acid value, high heating value, and low viscosity, researchers have worked extensively on the application of several catalyst materials for deoxygenation purposes [27–33]. To achieve an efficient deoxygenation process, catalysts such as ZSM-5 [23, 34–36], SBA-15 [36–38], MCM-41 [37, 39], Y zeolite [37, 40, 41], beta zeolite [40, 42, 43], activated carbon [44, 45], and other novel support materials including metallic oxides [32, 37, 46, 47] have been widely employed. The shape selectivity of a zeolite-based catalyst and its regeneration potential has positioned it as an excellent candidate for biomass conversion and bio-oil upgrading into transportation fuel over other catalysts [48–50]. As regards the low yield of bio-oil in a catalytic pyrolysis system, the formation of secondary cracking of volatile bio-oil into vapour, incomplete heating of feedstocks, and formation of a large amount of incondensable gases have been linked to the drop in the bio-oil yield [51, 52]. Therefore, understanding the characteristics of the ZSM-5 catalyst during biomass pyrolysis is paramount to designing an effective process route. The advantages and the shape selectivity potential of ZSM-5 catalysts have been discussed in detail in this review paper.

The external acid site of the zeolite catalyst has been observed to enhance the conversion of pyrolytic vapour into coke [53]. The application of the ZSM-5 catalyst has been proven to be excellent for the high selectivity of aromatics and shape/product selectivity. The excellent and improved performance of the ZSM-5 catalyst was linked to the presence of moderate pore sizes for oxygenated compounds' diffusion. The application of the ZSM-5 catalyst for bulky molecules present in the biomass in the form of lignin's building blocks has been reported to be ineffective for efficient conversion due to the presence of larger molecular sizes that are more than the micropores present in typical conventional ZSM-5 catalysts. Another challenge associated with the ZSM-5 catalyst during pyrolytic vapour conversion is the dehydration of biomass, which led to a reduction in hydrogen index effectiveness and resulted in the production of a larger amount of carbon material that causes coke deposit. The hindrance of diffusion of volatile vapour by the coke formed through the pores of the catalyst causes swift catalyst deactivation. Therefore, deactivation of ZSM-5 catalysts due to coke formation is one of the major concerns of various researchers. Hence, improving the structural make-up of the ZSM-5-based catalyst is paramount to producing high-yield aromatics and increasing the reusability potential during a thermochemical process.

In this study, a review on the investigation of the ZSM-5 catalyst performance in the upgrading of bio-oil derived from biomass and polymers for improved biofuel production was explored. The techniques for zeolite synthesis, coke formation, and factors affecting catalyst performance were also discussed. We further proposed the possible pathway for improving ZSM-5 performance during the deoxygenation process through pore enhancement and metallic particle incorporation. Furthermore, we proposed reaction pathway for model lignin compounds and a future research direction to enable high aromatic selectivity and reduction in coke (polyaromatic) formations.

2. Renewable Energy Resources and Conversion Methods

Energies that are continuously replenished from the sun, indirectly from the sun, or through the natural mechanisms of other environmental factors are termed renewable energies, which do not include waste materials derived from conventional fuels, energy obtained from fossil resources, and waste obtained from inorganically based feedstock [54, 55]. Through renewable energy technologies, renewable energy feedstocks are converted into useful and or advanced energy materials for power generation or as fuels for both domestic and industrial activities [55]. Several techniques as shown in Figure 1 are mostly used in the conversion of biomass into energy use, but the application of pyrolysis has attracted enormous attention. Following the civilization explosion, the application of renewable sources of energy has been widely employed due to its vast advantages, and as such, they are tagged as the world's fastest growing energy consumption [56]. The adverse consequences of exhaust from conventional energy such as fossil fuels causing global

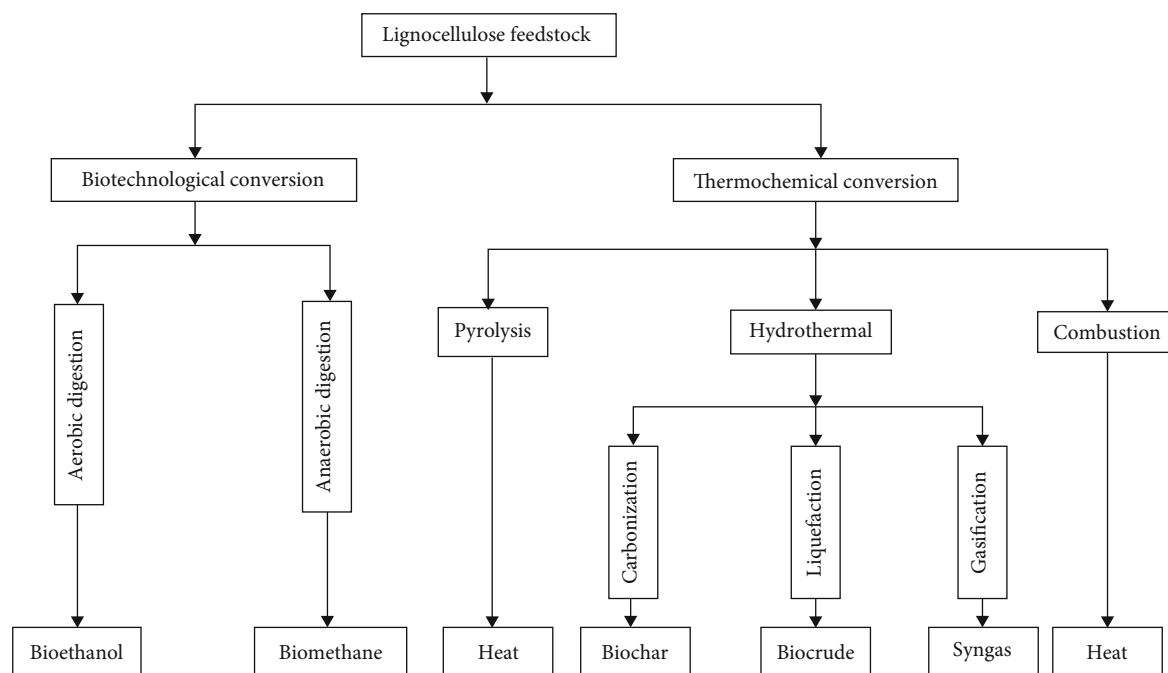


FIGURE 1: Techniques for biomass conversion into energy [62, 63].

warming, volatility in global oil prices, and overdependency on conventional energy resources have depicted renewable energy as a perfect option to balance the world energy crisis [57, 58]. Due to the high rate of energy consumption by the transportation industry, efforts are channeled by researchers to produce highly efficient biofuels with reduced oxygenate from renewable energy sources such as biomass and polymeric waste [40, 59–61].

2.1. Pyrolysis Process. Pyrolysis is a smart thermochemical technique of waste conversion in economic and value-added products such as liquid-oil, solid-fuel, and syngas (H_2 , CO , and CO_2) [64]. It is generally termed a tertiary technique for organic material recycling into useful products at elevated temperatures [65]. Several researchers have investigated the possibilities of biofuel production using the process of pyrolysis [14, 16, 66–68]. Pyrolysis occurs in the absence of air and in the presence of an inert environment for producing fuels of improved properties such as heating value and physiochemical characteristics. The process condition of the pyrolysis system and the procedures of operation define the products' yield as well as the quality [64].

In Table 1, the product distributions of several pyrolysis modes as parameters are depicted. For high-yield bio-oil production, the application of fast pyrolysis techniques is of importance [35, 40, 69]. The process of fast pyrolysis resulted in the production of bio-oil which consists of a high percentage of water (15–35 wt.%), nitrogenous compounds, oxygenates, and organic compounds [66, 70, 71]. The observed high heating value of bio-oil produced via this technique has created wide areas of application including fuels in burners, boilers, furnaces, and internal combustion engines of automobiles when upgraded [38, 67].

Adversely, the occurrence of high oxygen content in bio-oil produced via a fast pyrolysis process lowers its effective application and storage potential due to instability and the observed chemical reactions which lower the quality of bio-oil produced [18, 72–74]. Therefore, to present bio-oil as an economic product for use as a fossil fuel substitute in the transportation sector, researchers have carried out several works on improvement through catalytic hydrodeoxygenation (HDO) techniques [74–78]. The application of HDO techniques has been reported to increase the cost of biofuel production through the application of catalyst and peripheral equipment with possible accompanying hazards via hydrogen injection. To reduce these itemized additional costs incurred via the HDO process, the application of catalytic copyrolysis of lignocellulose materials with polymers has attracted attention via either in situ or ex situ techniques [79–83]. During the conventional pyrolysis process, heat is lost through convection and conduction media. The heat lost during this process reduces the power efficiency of the technique; therefore, there is a need to compare the conventional pyrolysis with the microwave-induced pyrolysis process of biomass conversion into biofuel [84]. It involves the deoxygenation of large organic compounds such as acids, esters, alcohols, and ketones through catalytic cracking over the ZSM-5 catalyst into light hydrocarbons, C_2 – C_6 olefins which are further aromatized into benzene and other AHs (Figure 2). The mechanisms of biomass pyrolysis into bio-oil fractions have been reported to be a difficult task due to the numerous and complex natures of the organic compounds present [2, 85]. The ease of understanding the mechanisms of model organic compounds such as phenol through the hydrodeoxygenation approach has been reiterated by Shafaghat et al. [86] in an attempt to better design the required process conditions, including catalyst development suitable for advanced

TABLE 1: Mode of pyrolysis with respective process conditions and product's distribution [72].

S/N	Pyrolysis mode	Temperature (°C)	Heating rate (°C/s)	Process time (min)	Vap. residence time (s)	Biochar yield (wt.%)	Bio-oil yield (wt.%)	Syn gas (wt.%)
1	Slow pyrolysis	400-900	0.1-10	>5	≤550	25-50	20-40	10-25
2	Fast pyrolysis	450-850	100-200	10-25	0.5-10	15-25	60-75	10-20
3	Flash pyrolysis	600-1200	>1000	<1	<0.5	5-15	25-40	50-60

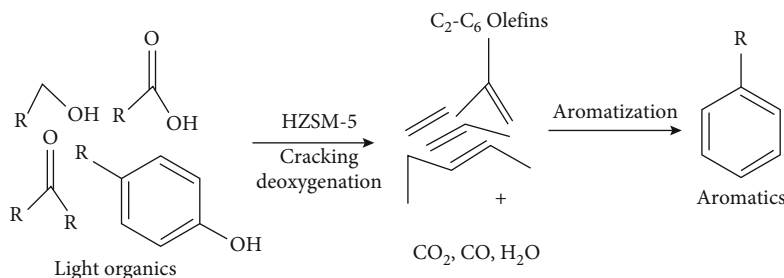


FIGURE 2: Mechanisms of lignin conversion over ZSM-5 catalyst [87, 88].

biofuel production. Typically, the main reaction pathways are largely on the breakage of the C_{aromatic}-OH bond via the deoxygenation process. Figure 3(b) depicts a proposed catalyzed process route for the conversion of phenols/cresol and bio-oil model compounds into aromatic hydrocarbons.

The mechanisms of conversion of cellulose to an aromatic hydrocarbon over the ZSM-5 catalyst are depicted in Figure 2. Through the acid-catalyzed dehydration process in a ZSM-5-catalyzed fast pyrolysis technique, cellulose is converted into an anhydro sugar at the active catalyst site (Figure 3(a)). Through the rearrangement of anhydro sugar, furan compounds are found which are converted into olefins via deoxygenation, oligomerization, cracking, and decarbonylation over the ZSM-5 catalyst [89]. Furthermore, the possibilities of producing the aromatic hydrocarbon through catalytic conversion of cellulose have been presented by Yamazaki et al. [90] over a solid-based catalyst. Figure 3(b) depicts the proposed reaction mechanisms for the conversion of phenols and cresol into the cyclic aromatic hydrocarbon.

2.2. Heat Transfer in Microwave and Conventional Pyrolysis Set-Up. In a conventional pyrolysis system, researchers have established that the concept and accompanied heating mechanism in the process involve convection and conduction from heating coils located in the reactors. Examples of such commonly used reactors in the conversion for recycling of organic wastes include melting vessels, fixed bed, and tubular reactors. The heat transferred during the heating process of valorization of biomass and polymer feedstock was characterized with inefficiency and slow energy transfer that are time consuming and, hence, depict the conventional pyrolysis process as cost ineffective. There is a large loss of energy due to convection and conduction heat transfer mechanisms in an attempt to achieve the set temperature as shown in Figure 4 [72].

The mechanism of heat transfer in a microwave technology positions it as the best alternative over the conventional heating system. In a conventional system, heat energy is transferred from the surface to the core of lignocellulose feedstock through convection, radiation, and conduction approaches. In the microwave heating system, electromagnetic energy is being converted to thermal energy and penetrates directly into the bulk of the feedstocks being pyrolyzed (volumetric heating) without external energy sources [72, 91]. Hence, microwave technology is best described as an energy converter rather than a heat transfer system. The microwave absorber/receptor could be recognized as the main factors that alter the efficiency of the microwave pyrolysis process [91]. The influence of embedding the receptor can directly affect the pyrolysis conditions such as the heating rate as well as the temperature profiles in the microwave system; hence, it is an exceptional factor to be considered in a microwave system [92]. Domínguez et al. [93] reported the effects of graphite and char as a microwave absorber (MA) on the properties of oil products and yield. It was reported that the formation of lighter species of bio-oil products was favoured by the application of graphite as a receptor during the MW pyrolysis (this shows an effective cracking of long-chain aliphatic hydrocarbons) while the yield was favoured by the use of char as a receptor. The application of a zeolite catalyst doped with Mo has been observed to improve the loss tangent factor towards microwave radiation absorbance of heat energy with the aid of cation mobility [94].

2.2.1. Feedstocks and Catalysts for Microwave-Induced Pyrolysis. Zhang et al. [13] reported the production biofuel alkanes and aromatics via microwave-induced pyrolysis of Douglas fir via the application of the ZSM-5 catalyst. Microwave-assisted pyrolysis (MAP) was conducted by feeding the reactor with 40 g of Douglas fir sawdust pellet

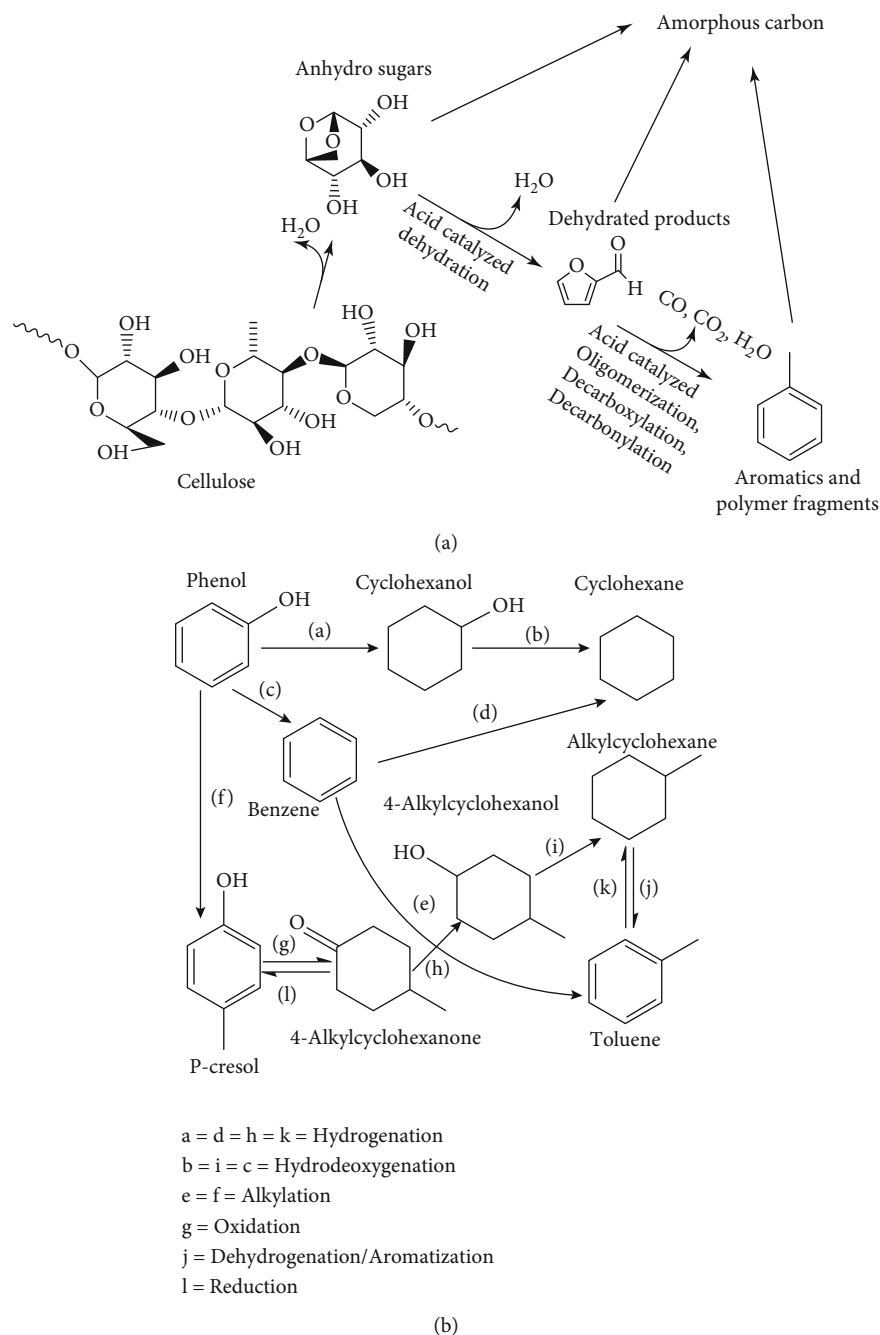


FIGURE 3: Mechanisms of (a) cellulose conversion [89] and (b) proposed mechanisms for phenols/cresol into aromatic hydrocarbon over ZSM-5 catalyst.

and loading with 0.05 g of activated carbon (AC) as a receptor while purging the system with the flow of nitrogen at 1000 mL/min flow rate for a period of 5 min. The obtained bio-oil (5 g) from the microwave pyrolysis process was hydrotreated over 5 and 10 wt.% of a nickel-based catalyst in a hydrogen environment. C₈–C₁₅ paraffin selectivity of 12.63% and 9.48% selectivity of hydroaromatic hydrocarbons was obtained over depolymerization of the biomass feedstock at 375°C for a period of 2 h. In an attempt to improve the energy density through the enhancement of the H/C_{eff} ratio, the application of polymeric materials as

cofeed with biomass has been investigated to improve the overall bio-oil quality [14, 95, 96].

He et al. [97] have demonstrated that the use of the ex situ catalytic pyrolysis of lignocellulose and polymeric materials enhances hydrocarbon content in the liquid product and promotes the aromatic selectivity due to the introduced synergistic effect by the polymeric feedstock. During the ex situ copyrolysis techniques presented by He et al. [97], corn stalks were mixed with HDPE in the presence of the HZSM-5 catalyst. The effects of temperature and biomass to the HDPE ratio were studied to determine the hydrocarbon contents

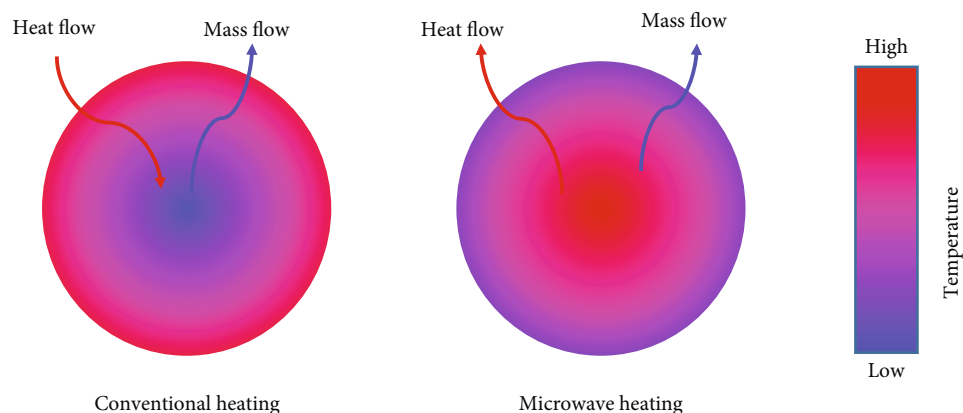


FIGURE 4: Heat transfer in a typical conventional and microwave-induced pyrolysis medium [91].

and liquid yield. The selectivity of high-grade biofuel of C_5 – C_{11} was linked to the structural modification of the HZSM-5 catalyst with 1 : 1 feedstock ratio. The formation of a jet fuel range hydrocarbon was associated with the enhanced carbon yield of 38.51% of hydrogenated organics due the incorporation of plastics into the feed stream.

3. Zeolite Catalysts and Their Synthesis

ZSM-5 (aluminosilicates which are cross-linked with a tetrahedral of aluminate and silicate species), the most widely employed catalyst, has shown high deoxygenation of bio-oil and selectivity to hydrocarbon production to form a high aromatic yield. According to Saleh et al. [98], the application of zeolite catalysts in the pyrolysis process is characterized by its exceptional properties such as excellent active sites and acidity which have been reported to improve both the gaseous and liquid products from biomass and polymeric feedstock pyrolysis. The efficiency of the ZSM-5 catalyst has been reported to improve through doping with several active parts such as Fe, Co, Ni, and Zn [81]. In a typical catalytic microwave-induced pyrolysis process anchored by the ZSM-5-based catalyst, zeolite helps to stabilize acid site formation which aids in C-O and C-C bond splitting which is contained in lignin materials [99]. Hence, to improve the zeolite catalyst efficiency, the ratio of Si/Al is expected to be appreciably moderate to enhance the pore size, acidity, and acid sites which in turn favours the aromatization reaction towards producing high-quality bio-oil [100, 101]. The presence of large cavities in zeolite and the three-dimensional ring enhance the diffusivity into the pores of the catalyst for catalytic cracking of large molecular-sized hydrocarbons [61].


















The application of the ZSM-5 catalyst in several petrochemical industries and valuable chemical development has been widely studied due to its excellent catalytic activity. The formation of coke deposits on micropores of zeolites has limited their applications in deoxygenation of large molecular lignin-based compounds during conversion of pyrolytic vapour [102, 103]. Structural modifications of the external pores of ZSM-5 have been identified to retard coke formation on the external surfaces and further improve the catalytic performance for aromatic selectivity. The applica-

tion of HZSM-5 was identified to be efficient towards hemi-cellulose conversion into aromatics and other value-added chemicals [38, 82, 104]. The limitation of the HZSM-5-based catalyst was associated with the presence of micropores which limit the conversion of large molecular oxygenates derived from lignin into aromatic fuels due to pore blockages [40]. Although, researchers suggest that larger micropores are required for effective cracking of phenols into an economic product through the application of hierarchical zeolite catalysts [61, 105].

The synthesis of hierarchical zeolites has been classified into two main techniques: the bottom-up and top-down synthesis approaches [106–108]. In the bottom-up hierarchical zeolite development, mesopores are introduced into the zeolite matrix during the hydrothermal synthesis stage, while the top-down approach introduces mesopores via postsynthesis methods which include desilication and dealumination which requires the removal of Si and Al atoms from the zeolite structure [105]. The presence of high external acidity with high mesopores having low internal acidity is associated with the top-down synthesis approach unlike the bottom-up approach which is characterized with low external and high internal acidity. High cracking reaction and enhanced product diffusion via the deoxygenation process to form aromatic hydrocarbons require a sufficiently high external acid site rather than an internal site, which is only obtainable in the top-down approach. The bottom-up approach has been linked to zeolite having high affinity to coke formation and therefore a high tendency for catalyst deactivation and high polymerization leading to low aromatic formation. Therefore, for an improved catalytic performance, the top-down approach of the hierarchical zeolite catalyst is highly recommended for biomass pyrolysis to produce high aromatic content HCs.

It is necessary to characterize zeolite following its synthesis before being subjected to a certain area of application. The characterization would help to determine if the produced zeolites possess the required characteristics for the intended application; if not, the need for surface modification to meet certain specifications arises. Table 2 shows the different characterization methods and the relationship of individual properties of the zeolite type on their respective areas of application.

TABLE 2: Characterization and area of application of the three main zeolite catalysts [109].

Important property	Zeolite types		
	Zeolite A	Zeolite Y	ZSM-5
Pore size			
Acidity			
Stability			
Chemical composition			
Si/Al framework			
Structural defect (structure)			
Morphology (particle size)			

From Table 2, the Si/Al ratio in the ZSM-5 catalyst is expected to be monitored to enhance the shape selectivity of the catalyst during the conversion process. It could be concluded that ZSM-5 is highly suitable for bio-oil conversion owing to its ability to selectively permit the diffusion of oxygenated compounds through the external micropores into the internal pores for aromatic hydrocarbon formation [36, 110]. As regards the selectivity behaviour of ZSM-5 catalysts, three well-known possibilities exist: reactant selectivity which occurs when a molecule of the reactant is large enough to diffuse through the external pores of the zeolite material causing diffusion limitation and product selectivity when a molecule of the product is large and diffusion through the internal pores of the zeolite becomes difficult [48, 49]. These conditions necessitate the transition state selectivity which occurs when a specific reaction is too large to be housed within the pores [109]. Therefore, the interest of various researchers has been channeled towards proffering solutions to the diffusion limitation during the conversion process. To solve this challenge, two brilliant methods could be adopted: either through the doping of ZSM-5 with microporous materials or by introducing mesopores on the external sites of the ZSM-5 material. Therefore, the development of hierarchical zeolites has become an interesting area of research for enhancing shape selectivity leading to high zeolite performance, improved bio-oil conversion, and also selectivity to aromatic hydrocarbon [43, 49, 111–114].

3.1. Behaviour of ZSM-5 Catalyst during Bio-Oil Production.

The presence of oxygenate compounds affects several properties in bio-oil. Such properties that are capable of being affected due to the presence of oxygenated compounds include low heating, high H₂O content, high acidity, and lower fraction of hydrocarbons. The itemized adverse effects of oxygenated compounds have hindered the use of bio-oil as a direct fuel in internal combustion engines [48]. The

need to reduce the presence of oxygenates becomes necessary in order to improve bio-oil quality [36]. The application of the ZSM-5 catalyst for bio-oil upgrading into aromatic and aliphatic hydrocarbon products has been widely investigated [115]. The ZSM-5 catalyst has been applied successfully to improve the quality of bio-oil to a more economical product of high aromatics for transportation fuel. The deoxygenation and bifunctional shape selectivity of ZSM-5 have been reported to be responsible for the high yield of light phenols and aromatic hydrocarbons obtained over the catalytic pyrolysis of rice husk using ZSM-5 [31, 116]. Similar observations have been reported where improved physicochemical characteristics of bio-oil such as viscosity and heating value were observed during the pyrolysis of rice straw over dolomites [117]. Although other zeolite types have been used by various authors, undesired products such as polyaromatic hydrocarbons were observed [39, 118].

The micropore nature of the ZSM-5 catalyst favours aromatic yield although with accompanying coke deposit on the micropores' surfaces which therefore deactivates the catalyst and reduces its performance for enhance bio-oil yield and quality [48]. The application of structural modifications in the form of the top-down approach has been recommended to improve ZSM-5 catalyst performance for the deoxygenation process leading to high selectivity to aromatic hydrocarbons [40, 108].

In addition to structural modification of catalyst pores, the introduction of dopants such as metals like Ni, Mo, Ga, Pb, or other metallic oxides has been reported to enhance the performance of ZSM-5 through improved Brønsted acid formation that aids aromatic formation [103]. It is noteworthy to mention that the strong Brønsted acid site and the surface physical properties of the ZSM-5 catalyst become reduced due to excessive loading of the metal catalyst on the ZSM-5 catalysts [119, 120]. These reductions in the itemized properties restrict the reactants' diffusion behaviour via the Brønsted acid sites and thereby hinder the production of a high yield of hydrocarbons. According to the findings of Shi et al. [121], an improved catalytic behaviour of the hierarchical Ni catalyst modification was noticeably improved by monoaromatic hydrocarbons when compared to unmodified ZSM-5. Moreover, the modification of the ZSM-5 catalyst using MgO and CaO oxides has been reported to improve aromatic selectivity [122].

3.2. Factors Influencing ZSM-5 Catalyst Performance. Several influencing factors such as catalyst size, shape selectivity (product shape and reactant selectivity), surface chemistry, and acidity affect the performance of ZSM-5 towards the selective product's formation and feedstock conversion in a pyrolysis and upgrading of oxygenates into a monoaromatic hydrocarbon fuel. The effects of crystal size, mesoporosity, and acidity of the ZSM-5 zeolite (Si/Al ranges from 9 to 42) on the catalytic efficiency during the ex situ catalytic fast pyrolysis (CFP) of lignocellulose feedstock have been reported by Hernández-Giménez et al. [123]. The mesoporosity, crystal size, and acidity play a vital role on the overall activities of the catalyst as regards the yield and selectivity to high aromatic content and low oxygenate formation. Incorporation of zirconium dioxide retards catalyst deactivation

due to its enhanced Lewis acid sites. Using a fluidized bed reactor, the catalyst performance was evaluated where oak biomass was converted into pyrolytic vapour before being contacted with a second reactor of the catalytic bed. The desilication process was observed to enhance the deoxygenation of bio-oil over a long reaction time through mesoporous introduction, which hindered pore occlusion [123].

Che et al. [124] reported the development of mesoporous ZSM-5 catalysts via the green synthesis approach, and its performance in the pyrolysis process was studied. The application of green templates (cellulose, sucrose, and starch) was employed as a structurally directed species towards the enhancement of mesopores on the parent ZSM-5 materials. The application of starch templating promotes the introduction of mesopores of $0.359 \text{ cm}^3 \text{ g}^{-1}$ as compared with the cellulose and sucrose, which only promotes a slight increase in the ZSM-5 zeolite micropore volume. The mesoporous structure which was introduced via the introduction of starch enhanced the ZSM-5 performance by improving the conversion of bulky oxygenates into aromatic hydrocarbons and further suppressed the polymerization reaction. A positive correlation was observed between the amount of starch introduced as a structural directing agent and the amount of benzene, toluene, and xylene obtained.

The effects of crystal size of ZSM-5 on the aromatic yield and selectivity of CFP of the biomass were reported by Zheng et al. [125]. Feedstocks used in this study include corncob, cellulose, pine, hemicellulose, straw, and lignin over the ZSM-5-based catalyst having a Si/Al ratio of 25. ZSM-5 with a crystal size of 200 nm resulted in minimum BTX selectivity and maximum aromatic yield. The impressive performance of this catalyst was linked to its high Brønsted acid site, the low Lewis site, and high micropore surface area, while an aromatic yield of 38.4% was obtained via the pyrolysis of cellulose with 18.4% yield of noncondensable gases. To enhance the performance characteristics of a typical ZSM-5 in order to improve the deoxygenation of bulky compounds, the applications of hierarchical modification have been proposed and applied by several researchers [61, 112, 126–129].

The ability of a catalyst to effectively convert a reactant selectively through shape selectivity is one of the important parameters that have made the research on ZSM-5 an interesting study. Zeolites possess a definite pore size which prevents the diffusion of larger compounds into the inert pores where conversion occurs. Moreover, the products formed within pores of zeolite materials are expected not to be larger than the internal pores of the zeolite to enhance material transport.

3.3. Catalyst Position in a Typical Pyrolysis Process. The position of catalysts in a pyrolysis system is imperative to catalyst activity and conversion of oxygenates into deoxygenated biofuels. The need to effectively crack highly oxygenated compositions of compounds in biomass into fuel and value-added products requires an effective catalyst performance [103]. Catalyst performance in a typical pyrolysis process could be dependent on the position of the catalyst during the pyrolytic vapour-cracking process [82, 130–132]. These positions could be in situ (catalyst and feedstock are

mixed directly in the pyrolysis reactor) or ex situ (catalysts are placed outside the feedstock in a separate chamber where pyrolytic vapour is cracked) pyrolysis. Hence, the unique characteristics of the ex situ approach such as the ability to optimize the pyrolytic vapour conditions and the performance of catalysts have attracted the attentions of numerous researchers [25, 133]. Where catalysts and feedstocks are separately positioned, i.e., ex situ pyrolysis process, the tendency to independently run the cracking of pyrolytic vapour under stand-alone conditions (residence time and reaction temperature) is flexible which enhances the catalyst performance and product yield and quality [133]. The ex situ process further enhances the easy separation of the formed char from the used catalyst and therefore promotes catalyst regeneration and reusability potential. In addition, researchers have reported higher deoxygenation of bio-oils in the ex situ process than in situ due to the nonhomogeneous temperature that the in situ catalytic process was susceptible to [134].

4. Zeolite-Supported Catalyst

The application of a nickel-based catalyst has attracted attention due to its excellent catalytic activity in converting large molecular-based lignocellulose intermediates into smaller compounds and the potential for the HDO process [49, 114, 135, 136]. Nickel, a nonnoble metal in its reduced form, possesses exceptional catalytic properties which promote hydrogenation and the subsequent deoxygenation process during phenol upgrading into transportation fuel through the O-H heterolytic dissociation approach [136]. The possible interaction of Ni with the aromatic rings of phenol has been identified as a possible reason for its effective performance for the HDO process [136]. The improvement in bio-oil yield and selectivity has been reported by Liang et al. [132] during the catalytic pyrolysis of rice straw using the Ni/ZSM-5 catalyst. According to Iliopoulou et al. [137], the application of Ni/ZSM-5 catalysts enhances the formation of an ideal drop-in fuel product (aliphatic hydrocarbons, aromatic hydrocarbons, and alcohols) through the selective hollow cavity.

The aromatic hydrocarbons produced via the catalytic cracking of the lignocellulose biomass are classified into two main categories: monocyclic aromatic hydrocarbons, effectively enhanced due to the presence of dopants (such as Ni) incorporated with the ZSM-5 catalyst (toluene, xylene, benzene, substituted benzene, and indene) over polycyclic aromatic hydrocarbons and oxygenates (anthracene, naphthalene, fluorene, and phenanthrene). It was reported that the production of polycyclic aromatic hydrocarbons (PAHs), an unwanted product of catalytic reaction, is linked to polymerization reactions with possibilities of lowering catalyst performance (the detailed mechanisms are as presented in Figure 5(d), while the two possible catalyst deactivations by sintering are shown in Figure 5(e)). Therefore, the incorporation of metallic dopants on the ZSM-5 catalyst is expected to improve the conversion efficiency of bio-oil's oxygenates and selectivity into products (deoxygenates) with economic potential for possible use as a fuel for transportation industries. Moreover, phenols and furans are considered

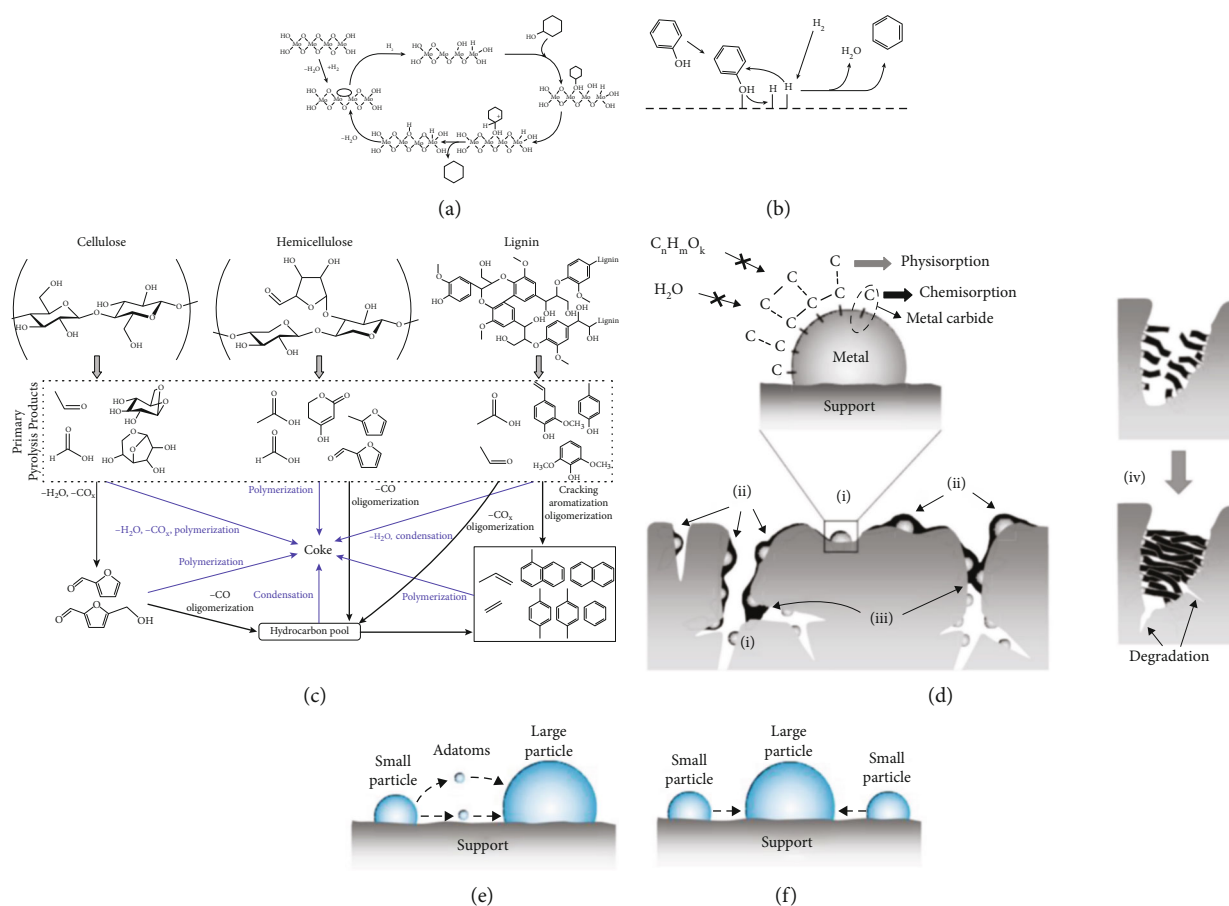


FIGURE 5: Reaction pathways for (a) oxide catalysts and (b) reduced metal catalysts and (c) biomass conversion over ZSM-5 catalyst and (d) catalyst deactivation due to several factors. i: carbon chemisorption or physisorption hindering the access to reactants; ii: metal particle encapsulation; iii: pore plugging; iv: degradation of catalyst structure, for instance, by massive CNT growth. (e) Ostwald ripening and (f) particle migration and coalescence [136, 138, 139].

as excellent value-added chemicals while other undesired products such as polyaromatic hydrocarbons are regarded to possess negative impacts on biofuel properties such as coke formation including the environmental effects of nitrogen-containing compounds.

The introduction of transition metals such as nickel on the surface of a typical ZSM-5 has been observed to not only improve the conversion of oxygenates to aromatic hydrocarbons but also enhance hydrothermal stability of ZSM-5 [135]. The hydrothermal stability of the catalyst is necessary to maintain catalyst performance at an elevated temperature. The stability will further protect the surface structural properties of the catalyst against catalyst sintering and poisoning, which reduces the catalyst's performance towards the deoxygenation process. Additionally, the introduction of the Ni dopant to the ZSM-5 catalyst causes three fundamental changes in the structural composition of the zeolite catalyst. The first is the reduction in the Si/Al ratio which could be the result of overlapping/capping of the Si and Al present in the catalyst. The second observation was the reduction of overall Brønsted acid sites and an increase in the Lewis acidity. The above observations were reported in the findings of Huynh et al. [140]. Furthermore, the introduction of the Ni dopant into the bulk of the ZSM-5 catalyst resulted in

the migration of the dopant into the pore volume of the base catalyst via a sintering approach; this suggests the need for the incorporation of promoters during catalyst development. The occurrence of Brønsted and Lewis acidity sites is responsible for C-O cleavage (at the acid center) via protonation and hydrogen activation which reduces the aromatic ring (at the metal center) of the ZSM-5 catalyst [49]. Although the introduction of Ni on ZSM-5 improves the catalytic performance, the formation of carbon deposits (coke) including the loss of acid sites has been identified as one of the prevailing challenges [49, 141]. A typical mechanism for bio-oil conversion (phenol's component) over the reduced and oxide-based catalyst and the deoxygenation route for the lignocellulose biomass over the ZSM-5 catalyst are presented in in Figures 5(a)–5(c) while the possible catalyst deactivation phenomena are depicted in Figures 5(d)–5(f).

The multifunctionalities of ZSM-5 as a support material as well as a pivotal region for the cracking process which are functions of its pore structures and acidity sites have been observed to enhance the molecular sieve properties during oxygenate conversion [142, 143]. During oxygenate conversions, ZSM-5 among other zeolites has demonstrated an outstanding performance which resulted in improved bio-crude quality and reduced oxygenated compound formation

through a series of accompanied reactions including decarbonylation, cracking, aromatization, decarboxylation, and isomerization which depend on the strong Brønsted acid sites [142, 144, 145]. The molecular sieve characteristic properties of the ZSM-5 catalyst for the high selectivity of aromatic hydrocarbons are favoured due to the presence of strong acidity sites and pore aperture [49, 146]. The pore structure aids in product selectivity, reactant selectivity, and restricted transition state selectivity during the conversion process [146–148]. The acidity sites enable the cleavage of C–C and C–O bonds which enhances the activation of cracking, dehydration, dealkylation, and decarboxylation processes [122, 149, 150], although the microporosity has been identified to hinder the molecular transport of bulky oxygenates into the active sites, thus resulting in coke deposition [23]. Alternatively, the high acidity sites of the ZSM-5 catalyst are not so desirable because of the high cracking reaction which adversely leads to high gaseous hydrocarbon formation and therefore lower biocrude yield.

The selective formation of aromatics through biomass valorization using the Ni/HZSM-5 catalyst has been reported by [135] to exhibit an excellent catalytic property towards the production of aromatics. Thermal catalytic process which comprises two treatment steps (thermal and catalytic reactor) was employed for lignin conversion into added biofuels. Ni-ZSM-5 (Si/Al ratio of 30) was prepared by doping 1 wt.% of nickel on the support materials, and it was reported that the obtained catalyst possessed improved thermal and catalytic activity during the bio-oil conversion into deoxygenated products. The obtained catalyst's properties were found to possess a BET surface area of 170 m²/g and pore volume of 0.57 cm³/g while the coke deposited on the surface of the catalyst was monitored via a GC-MS hyphenated technique. In an attempt to reduce the deposition of coke on the catalyst pores during the conversion process, methanol was blended with the catalyst material. The blending process resulted to about 1.55 wt.% reduction in coke deposition when a 20:80 wt/wt ratio of methanol to bio-oil was studied. The formation of CO and CO₂ during the catalytic cracking process has been associated with the decarboxylation and decarbonylation of oxygenated compounds. The introduction of methanol in the catalyst was reported by Valle et al. [135] to lower coke production, thereby enhancing the biofuel qualities for effective stability during the storage process. The incorporation of nickel dopant on the ZSM-5 catalyst improved the hydrogenation capability, which further increases with an increase in treatment temperature and subsequently increases the yield of aromatic over nonaromatic hydrocarbons. Table 3 shows the review of the existing literature using the zeolite catalyst for the pyrolysis process.

The effect of bifunctional Ni-supported ZSM-5 for the hydrolysis and pyrolysis of lignocellulose biomass was performed by Gamliel et al. [174] while the effects of bimetallic loading on ZSM-5 catalysts are contained in Table 3. The wet impregnation method was employed as the method of the doping process. The effect of zeolite modification on Ni was itemized to improve the products' selectivity during the catalytic conversion process. The excellent characteristics of zeolite doping with nickel metal, which include its

ability to decrease coke and improve aromatic formation, have been linked to the synergetic effects of Ni with zeolite's acid sites.

Of all transition metal-based catalysts used in biomass conversion into aromatic hydrocarbons, the excellent performance has been attributed to Ni-based catalysts over others. Several hindrances have posed a challenge to achieve the optimum performance and deoxygenation potential of Ni-based catalysts in a pyrolysis process. Such challenges include carbon deposition, deactivation, and leaching of active parts of the catalyst materials [49]. The carbon deposition, deactivation, and catalyst leaching are complex phenomena which depend majorly on some factors including the pore structure, temperature of reaction, acidic properties, and feedstocks' properties [18, 49, 175]. The above phenomena have presented tuning the zeolite structure through the doping technique as an attractive field in recent years.

Vichaphund et al. [169] reported the synthesis of aromatic compounds from CFP using *Jatropha* residues over metals/HZSM-5. Two separate techniques of catalyst preparation were adopted: impregnation and ion-exchange approaches to establish the best technique that favours aromatic hydrocarbon formation. Dried *Jatropha* residue with 59.2% cellulose, 22.8% lignin, and 18.0% hemicellulose contents was employed for the study. The HZSM-5 catalyst developed was crystallized at 160°C for a period of 72 h in Teflon-lined autoclave, filtered, washed, dried, and calcined for 5 h at 540°C. The morphology of the Mo/HZSM-5 catalyst exhibited an agglomeration nature. The agglomeration formed on the HZSM-5 catalyst was attributed to the interconnection of particles whose sizes were <5 μm. Comparing the properties of the obtained catalysts via the two employed approaches, ion-exchanged catalysts were found to possess excellent surface area, pore size, and pore volume over those obtained via the impregnation method. The observation on these surface properties could be responsible for the Mo/HZSM-5 catalyst performance for improved selectivity to aromatic hydrocarbons. The findings further revealed that the biomass-to-catalyst ratio of 1:10 of the Mo-supported HZSM-5 catalyst yielded the highest aromatic hydrocarbon selectivity of 97% for ion exchange-derived catalysts. The observable high selectivity of the Mo-HZSM-5 catalyst to aromatic hydrocarbons could be as a result of the high resistance to poisoning during the pyrolysis conversion of hydrogen and CO from *Jatropha* feedstock and the high rate of dispersion of Mo on the HZSM-5 support [46].

Sun et al. [162] reported the effect of the Mo-ZSM-5 catalyst on the CFP of wood sawdust into aromatic hydrocarbons. The wet impregnation method was adopted for the development of the doped catalyst at varied doping percentages and calcined at 550°C for 4 h. During the process, the effects of process parameters (temperature, Mo content, and catalyst-to-biomass ratio) were studied. The highest formation and selectivity to monoaromatic hydrocarbons were observed at a catalyst ratio of 10, reaction temperature of 600°C, and Mo loading of 10 wt.%. The researchers proposed three main mechanisms to have enabled selectivity to monoaromatic hydrocarbons; the first mechanism is the cracking and oxygen removal by Mo oxides (active part of the

TABLE 3: Effects of ZSM-5 catalysts on the pyrolytic conversion of sawdust, kraft lignin, and cellulosic biomass into aromatic hydrocarbons over ZSM-5 and modified ZSM-5 catalysts.

S/N	Biomass feedstock	Operating conditions		Description	Surface area (m ² /g)	Catalyst properties			Observation	Ref
		Temp (°C)	Reactor			Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)	Si/Al		
1	Poplar sawdust	600	Fixed bed	Effects of copyrolysis of poplar sawdust and HDPE over ZSM-5 at two different reaction zones	411.7	0.22	0.55	25	The influence of high acidity in ZSM-5 catalyst aids its catalytic performance. MAH selectivity was favoured at biomass/HDPE ratios of 1:1 About 3.11% reductions in AH yield were observed in Fe-Ni-supported ZSM-5 as compared to the ZSM-5. Fe-Ni/ZSM-5 depicts an enhanced resistance to coke formation	[151]
2	Poplar sawdust	600	Fixed bed	Deactivation and regeneration mechanisms of poplar sawdust pyrolysis over Fe-Ni/ZSM-5 catalysts	316.02	0.27	—	25	Copyrolysis process with the introduction of PE into the pine feedstocks increases the HHV significantly and further decreases the formation of oxygenated compounds in the presence of HZSM-5 catalyst	[153]
3	Pine sawdust	500-700	Fixed bed	Experimental study of the effects of process parameters such as temperature and polymer (polyethylene (PE) and polyethylene terephthalate (PET)) loading on the selectivity of aromatic products	—	—	—	—	At biomass-to-ZSM-5 ratio of 1/10, sawdust feedstock gives the highest formation of AH formation	[154]
4	Sawdust	800	Py-GCM/MS (fixed bed)	Identification of catalytic level of pyrolysis of biomass over ZSM-5 catalyst and AH evaluation	254	0.12	1.79 < Pd < 40	25 < Si/Al < 140	The potency of ZSM-5 towards reducing the production of polyaromatic hydrocarbons was observed while phenols and MAHs were favoured	[155]
5	Sawdust	600	Py-GC/MS (fixed bed)	Effects of NiO and MoO ₃ on the pyrolysis products of sawdust/sewage residue in a Pg/GC-MS reactor	>380	—	0.5	30		

TABLE 3: Continued.

S/N	Biomass feedstock	Catalyst	Operating conditions		Description	Surface area (m ² /g)	Catalyst properties			Ref
			Temp (°C)	Reactor			Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)	Si/Al	
6	Poplar sawdust	Acid-modified ZSM-5	550	Py-GC/MS (fixed bed)	Influence of acid treatment on the catalytic performance of ZSM-5 catalyst over poplar sawdust and HDPE	350	—	—	46	High contents of alkanes and olefins were observed over the acid-modified ZSM-5 catalysts as compared to the parent ZSM-5. Also, 0.5 M acid-modified ZSM-5 depicted the highest selectivity to aromatic hydrocarbon Lower mesoporous ZSM-5 promotes the formation of oxygenated compounds. Bio-oil production was favoured by the acidity, hollowness, and formation of mesopores at the secondary wall in the hollow zeolite. Also, hollowness was observed to retard the formation of coke through stabilization of the poplar sawdust intermediates
7	Poplar sawdust	ZSM-5	500	Fixed bed	Evaluation of hollow zeolite on the selectivity of aromatic hydrocarbon on poplar sawdust pyrolysis	—	—	0.56	50–∞	[157]

TABLE 3: Continued.

S/N	Biomass feedstock	Catalyst	Operating conditions		Description	Surface area (m ² /g)	Catalyst properties		Si/Al	Observation	Ref
			Temp (°C)	Reactor			Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)			
8	Pinewood sawdust	ZSM-5	500	Py-GC/MS and fixed bed	Effects of CaO on the selectivity of ZSM-5 for aromatic formation	360	0.161	—	46	Highest phenolic compounds' yield of 31 wt.% was observed in the pinewood sawdust-to-catalyst (4ZSM-5 : 1CaO) ratio. An improved bio-oil quality of grade G was recorded. This suggests possible conversion of the bio-oil into transportation fuel through an upgrading approach	[158]
9	Sawdust	ZSM-5	550	Py-GC/MS/ fixed bed	Influence of Fe and Zn doping on the catalytic performance of ZSM-5 towards aromatic formation	201.26	0.24	4.79	46	High phenolic yield was enhanced over Fe-ZSM-5 catalyst. The formation of CO and CO ₂ at the gaseous stream indicated an improved decarboxylation and decarbonylation processes during the conversion of the sawdust into bio-oil	[159]
10	Sawdust	HZSM-5	500	Fixed bed	Investigation of HZSM-5 with regard to enhancing the formation of light aromatic hydrocarbon	—	—	—	25	Highest aromatic hydrocarbon formation of 21.8% was obtained over ZSM-5 with Si/Al ratio of 25. The ZSM-5 catalyst was reported to favour aromatization reaction	[160]

TABLE 3: Continued.

S/N	Biomass feedstock	Catalyst	Operating conditions		Description	Surface area (m ² /g)	Catalyst properties			Si/Al	Observation	Ref
			Temp (°C)	Reactor			Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)				
11	Wood sawdust	ZSM-5 (doped with CaO, Al ₂ O ₃ , & ZnO)	500-800	Fixed bed	Effects of metal oxides loading on the aromatic formation of wood sawdust pyrolysis	—	—	—	—	—	The incorporation of CaO and Al ₂ O ₃ promotes the formation of aromatics. On the contrary, ZnO inhibits aromatic hydrocarbon selectivity	[148]
12	Pinewood sawdust	ZSM-5	400-700	Py-GC/MS	Effects of pinewood sawdust to catalyst loading on the aromatic production during the Py-GC/MS pyrolysis	350	—	—	46	—	ZSM-5 catalyst enhances aromatization reaction leading to high formation of aromatic compounds (42.19 wt %) as compared to CaO catalyst	[161]
13	Wood sawdust	Mo/ZSM-5	400-700	Fixed bed	The effects of Mo-ZSM-5 catalysts were investigated using CFP of biomass into aromatic hydrocarbons	—	—	—	—	—	The blockage of the surfaces of ZSM-5 support was observed due to the overlayer of Mo oxides. This resulted in a decrease in B/L ratio of about 72.82%. This phenomenon was reported to favour the production of monoaromatic hydrocarbons (MAHs) at 10 wt.% Mo loading over polyaromatic hydrocarbons (PAHs)	[162]

TABLE 3: Continued.

S/N	Biomass feedstock	Operating conditions		Description	Catalyst properties			Si/Al	Observation	Ref
		Temp (°C)	Reactor		Surface area (m ² /g)	Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)			
14	Poplar sawdust	550	Fixed bed	Pyrolysis of biomass using Fe-supported hierarchical ZSM-5	372.4	0.341	—	25	Desilication process and modification of ZSM-5 catalyst with Fe favour the mesoporosity and acidity, respectively. Also, 4 wt.% Fe loading on ZSM-5 enhances the performance with percentage selectivity towards MAHs of about 15.30%	[163]
15	Poplar sawdust	550	Fixed bed	Catalytic pyrolysis of poplar sawdust over Fe-Ni-supported ZSM-5	316	0.147	—	25	Fe-Ni bimetallic-supported ZSM-5 catalyst promotes additive effect on monocyclic aromatic hydrocarbon production. An increase in toluene yield was observed on Fe-Ni-supported ZSM-5 catalyst	[164]
16	Poplar sawdust	550	Fixed bed	Study on the effect of bimetallic Fe-Ni supported on ZSM-5, deactivation mechanism, and regeneration catalyst during pyrolysis experiment	316.02	0.267	—	25	The activity of the Fe-Ni-loaded ZSM-5 reduces as biomass/catalyst ratio increases with complete catalyst deactivation at biomass/catalyst ratio of 4. Partial irremediable loss of acidic sites and pore geometry was observed on Fe-Ni-supported ZSM-5-regenerated catalyst with 3.11% reduction. Also, the resistance capacity in coke formation in Fe-Ni-supported ZSM-5 was reported to increase	[152]

TABLE 3: Continued.

S/N	Biomass feedstock	Catalyst	Operating conditions		Description	Surface area (m ² /g)	Catalyst properties			Si/Al	Observation	Ref
			Temp (°C)	Reactor			Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)				
17	Wood sawdust	ZSM-5 and Fe-supported ZSM-5	550	Fixed bed	Comparison of CFP of lignocellulose materials to aromatic hydrocarbons using ZSM-5 and Fe-supported ZSM-5 catalysts	313/2.75	0.18/0.18	2.33/2.64	17.3/16.6	Fe/ZSM-5 catalyst was reported to improve oxygenates' conversion and monocyclic aromatic hydrocarbon (MAH) formation compared to the ZSM-5 catalyst. Between 500°C and 600°C reaction temperature, MAH formations were enhanced as compared to 600°C-800°C	[165]	
18	Softwood sawdust	FeNi/ZSM-5	500	fixed bed	Study of the relationship between catalyst deactivation and activity over transition metal-modified zeolites	348	—	—	30	The introduction of metal doping increases the production of aromatic hydrocarbons from 59.0 to 82.8%. MAHs were promoted with Fe doping while Ni additionally enhanced the naphthalene production. The synergetic influence of FeNi/ZSM-5 enhances the production of both MAHs and naphthalene including the reduction in the total acid number (TAN)	[166]	
19	Wheat straw	Ni/ZSM-5	550	Fixed bed	Effects of Ni loading including the Si/Al ratio of ZSM-5 catalyst were studied on product yield distribution	251.2	0.19	9.24	5.18	An increase in Ni loading on the constant Si/Al ratio of 5.18 resulted in a reduction in the formation of phenolic compounds and further improved the selectivity to MAHs	[167]	

TABLE 3: Continued.

S/N	Biomass feedstock	Catalyst	Operating conditions		Description	Surface area (m ² /g)	Catalyst properties			Observation	Ref
			Temp (°C)	Reactor			Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)	Si/Al		
20	Poplar sawdust	Hollow zeolites			Hydrocarbon selectivity and activity of hollow zeolites via catalytic pyrolysis of poplar sawdust		5.6		50	The produced hollow zeolite was efficient for improving hydrocarbon fraction present in the bio-oil through an improved acidity, hollowness, and mesopores of the secondary wall. The hollow fraction in the zeolite stabilized the intermediates and subdued coke repolymerization. The intermediates were converted to aromatic hydrocarbons via the interior acid sites	[157]
21	Oak	Microporous and hierarchical zeolites	500	Fluidized bed	Characterization of heavy products obtained from CFP of oak feedstock	—	—	—	—	Hierarchical zeolites improve the formation of deoxygenated compounds over ZSM-5 due to an enhanced diffusion of oxygenates through the mesopores	[128]
Feedstock: kraft lignin and cellulose											
22	Kraft lignin	Meso-ZSM-5	400-600	Fixed bed	Production of alkyl-phenols and aromatic compounds via CFP of kraft lignin	560	—	9	11.5, 25, and 40	Zeolites with high Si/Al in the pyrolysis process increase alkoxy-phenols and selectivity toward monoaromatic compounds. Temperature within 500-600°C retards char and coke formation on catalyst surface though higher selectivity to MAHs was favoured	[126]

TABLE 3: Continued.

S/N	Biomass feedstock	Catalyst	Operating conditions		Description	Surface area (m ² /g)	Catalyst properties			Observation	Ref
			Temp (°C)	Reactor			Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)	Si/Al		
24	Cellulose, hemicellulose, and lignin	Mo ₂ C-supported HZSM-5	700	Fixed bed	Integration of biomass catalytic pyrolysis and CH ₄ aromatization using Mo-supported HZSM-5 catalysts	467	0.468	4.03	15.5	The application of CH ₄ during the thermal pyrolysis to improve the aromatic yield of lignin from 12.80 to 15.13% while the incorporation of molybdenum-impregnated catalyst promotes deoxygenation process. The yield of aromatic hydrocarbon increased on Na ₂ CO ₃ -modified ZSM-5 catalyst though with an increment in the formation of coke. 0.6 M Na ₂ CO ₃ -treated ZSM-5 resulted in a higher aromatic product of 38.2% and retarded the coke formation	[168]
24	Cellulose	Hierarchical ZSM-5	900	Fixed bed	CFP of cellulose in a microreactor system	336	0.204	—	—	Co, Ni, and Zn metal-supported ZSM-5 catalyst enhanced aromatic selectivity while the Ni-Co/ZSM-5 catalyst improved the thermal degradation of the biomass under TGA observation	[129]
25	Rice straw	M ^{***} -modified ZSM-5	500	Fixed bed	Study on the bio-oil upgrading, kinetic study, and selectivity	—	—	—	46-81		[132]

TABLE 3: Continued.

S/N	Biomass feedstock	Catalyst	Operating conditions		Description	Catalyst properties			Observation	Ref	
			Temp (°C)	Reactor		Surface area (m ² /g)	Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)			Si/Al
26	Jatropha residues	M****-supported ZSM-5	500	Py-GC/MS	Aromatic compound production using CFP of Jatropha residues	530-677	0.19-0.27	22.9-26.0	13.05-20.91	Catalyst produced via metal-ion exchange depicted excellent properties towards selectivity of aromatic hydrocarbons over the impregnated ones. Ion-exchanged catalysts from Mo-supported HZSM-5 depicted highest aromatic selectivity of 97% Acid number increases in Fe loading promote acidity sites in the ZSM-5 framework and, therefore, improved benzene, toluene, and xylene (BTX) formation The production of high olefins was favoured. High carbon yield of 12.8% was obtained at 3 wt.% of Fe-doped ZSM-5 at 600°C High aromatic formation was obtained at ZSM-5 (Si/Al = 30), and the yield reduces from 25 to 7.99 wt.% at Si/Al = 280 in the ZSM-5 catalyst	[169]
27	Hemicellulose	Fe-loaded ZSM-5	600	Fixed bed	Catalytic pyrolysis of hemicellulose for aromatics and light olefin production	—	—	5.5-5.6	25		[170]
28	Lignin	Fe-supported ZSM-5	400-700	Fixed bed	Catalytic pyrolysis of lignin for aromatics and light olefin production	—	—	5.5-5.6	25		[144]
29	Cellulose	ZSM-5	500-600	Fixed bed		400-425	—	—	30-280		[171]

TABLE 3: Continued.

S/N	Biomass feedstock	Catalyst	Operating conditions		Description	Catalyst properties			Si/Al	Observation	Ref
			Temp (°C)	Reactor		Surface area (m ² /g)	Pore volume (cm ³ g ⁻¹)	Pore diameter (Pd) (nm)			
30	Rice husk	Fe/ZSM-5	550	Fixed bed	Catalytic upgrading of bio-oil using Fe-mediated ZSM-5 catalyst	346	0.174	2.014	30	About 4 wt.% Fe doped with ZSM-5 was reported as the optimum catalyst loading for high yield of upgraded bio-oil. Torrefaction process within 210 and 240°C promotes bio-oil upgrading over iron-supported ZSM-5	[172]
31	Rape straw	M ^{**} loaded HZSM-5	500	Fixed bed	Vacuum pyrolysis of feedstock to produce upgraded bio-oil	233.22	0.188	–	–	Fe- and Co-impregnated ZSM-5 catalyst improves MAH yield by about 2.5 times compared to the pristine ZSM-5. Brønsted acid and Lewis acid sites were reduced and increased, respectively, due to the doping with Co and Cu	[173]

M^{**}: Fe, Cu, and Co; M^{***}: Co, Zn, and Ni; M^{****}: Co, Ni, Mo, Ga, and Pd.

catalyst) during the biomass conversion. The intermediates produced from the catalytic activity of Mo oxide-supported ZSM-5 were aromatized via the surfaces and internal pores of the ZSM-5 zeolite into aromatic hydrocarbons. Then, synergistically, the effect between the Mo and ZSM-5 promoted the selectivity and overall conversion process of biomass into aromatic hydrocarbons [162]. Table 3 shows the review of ZSM-5's and metal oxide-modified ZSM-5 catalyst's properties, conditions of pyrolysis, and the observations on the product yield and selectivity to aromatic formation over sawdust, kraft lignin, and cellulosic biomass.

5. The Effective Hydrogen Index (EHI)

The EHI of biomass feedstocks and biomass-derived products are relatively low, ranging from 0 to 0.3, which affect the bio-oil product. According to the findings of Du et al. [176] who worked on the conversion of low hydrogen dense microalgae with an EHI value of 0.23 over zeolite observed that the higher the effective hydrogen index in feedstocks, the higher the effective hydrogen index in the biofuel products. Biomass copyrolysis with feedstocks such as grease, polyethylene, and monohydric alcohols with an effective hydrogen index of 1.5, 2, and 2, respectively, has been reported to aid the hydrogen density in the obtained product. Asadieraghi and Wan Daud [102] reported the catalytic copyrolysis of lignocellulose biomass/methanol as feedstock, and a product with high content of EHI over the HZSM-5 catalyst was obtained. Therefore, the performance of the ZSM-5 catalyst has made the study of its synthesis an important course among other zeolite materials for aromatic hydrocarbon selectivity.

Polymers have been widely applied as a feedstock for the production of biofuel by several researchers [31, 177, 178]. The presence of high hydrogen and heating value in polymeric materials has positioned it as an excellent feedstock for the production of improved biofuel [41, 96, 179]. The application of the pyrolysis process for polymers' conversion has been identified as highly efficient due to its ability to obtain liquid products of about 80 wt.% at considerable operating conditions. The wide range of applications of bio-oil obtained from the pyrolysis of polymers includes applications in furnaces, turbines, boilers, and diesel engines as drop-in fuel.

Three main products have been reportedly formed during polymer pyrolysis. These products include oil, gas, and char which are of economic value. The absence of water as a byproduct aided in the high catalyst efficiency of the pyrolysis of polymeric materials because the presence of water deactivates catalyst materials through the sintering of active parts or via catalytic poisoning of active sites. The quality of biofuels obtained during the pyrolysis of polymers is mainly dependent on process parameters such as temperature, nature of fluidizing medium, catalyst materials, residence time, and reactor design [180]. Several polymeric materials have been widely reported for biofuel production via the pyrolysis technique [69, 82, 118, 179, 181, 182].

Miandad et al. [183] reported the pyrolysis of polymeric feedstocks for the production of biorefinery-based products.

The pyrolysis was performed on single and mixed feedstocks in the presence of a modified zeolite. Higher bio-oil was observed in the PS feedstocks with about 70 wt.%. The bio-oil produced via the catalyzed pyrolysis process produces oil with a high heating value (HHV) ranging from 41.7 to 44.2 MJ/kg which was reported to be closer to the standard value of a conventional diesel. The presence of aromatic hydrocarbons with aliphatic and other accompanied hydrocarbon-containing compounds was also reported from the GC-MS results. Although the authors recommended further refining/upgrade and blending with conventional fuel before being used as alternative energy sources in automobiles. The study further observed that the catalyst developed using thermal-activated natural zeolite (TA-NZ) depicts the highest bio-oil yield during the catalytic conversion of PS feedstock with 70% yield. The high yield observed was attributed to the presence of a cyclic structure, lower degradation temperature, random chain, and end-chain scission degradation in the PS feedstock. The above phenomena led to the formation of a stable benzene ring arrangement which promotes bio-oil production [184, 185].

Zhou et al. [186] reported the pyrolysis of varied plastic materials in a continuous microwave-induced pyrolysis setup for biofuel production. The study reported the effects of operating conditions such as catalyst, temperature, and composition of plastics on product yield and the corresponding composition in the presence of the ZSM-5 catalyst. The effects of a higher temperature of operation were found to enhance wax cracking of useful and stable light hydrocarbons. The introduction of a catalyst into the feedstock improves the conversion and selectivity to gasoline-range hydrocarbon (HC) compounds. At 10 hourly velocity and 893 K, about 73.5% gasoline range HC, 45% aromatics, and 24.6% isomerized aliphatic content were obtained with the corresponding bio-oil yield of 48.9%. Furthermore, the ZSM-5 catalyst was found to have been deactivated due to the observable rapid loss in activity at the feedstock-to-catalyst ratio of 5. The author further depicts that the continuous microwave-induced pyrolysis process has an energy-efficient approach due to the ability to recover large energy from the incondensable gases.

The introduction of the ZSM-5 catalyst according to Zhou et al. [186] includes the ability of the ZSM-5 catalyst to produce bio-oil with moderate hydrocarbon distribution with the highest percentage of gasoline-range aromatics. The composition of plastic feedstock was reported to affect the yield of liquid biofuel and its composition. Polypropylene at a temperature of 893 K was reported to favour high-yield liquid biofuels compared to high density polyethylene subjected to the same conditions of cracking. As regards the liquid biofuel quality, it was reported that less wax was obtained in PP than HDPE feedstock; this was attributed to higher thermal degradation and improved secondary reaction which could be obtained in PP over HDPE. In addition, HDPE molecules were reported to possess a high regular molecular structure, crystallinity, density, and melting point, and this could result in the observable wax formation as a result of incomplete degradation. Therefore, to obtain a wax-free product as in the case of HDPE, a high temperature of operation is required to dislocate the orderly arranged crystals to gain enough kinetic energy for the change of state.

In an attempt to improve bio-oil quality through the pyrolysis of LDPE, Duan et al. [187] have explored the effects of pyrolysis parameters and activation via activated carbon as a catalyst. Several catalyst mixes were developed by varying the volume of the activating agent, H_3PO_4 , on the activated carbon developed from chestnut shells (CNS). The effects of H_3PO_4 /catalyst, carbonization temperature, catalyst/LDPE, and catalytic temperature were studied in the presence of N_2 flow. High molecular hydrocarbons, which are solids at room temperature, were observed at the H_3PO_4 /CNS of 0 and 0.2. The formation of high molecular solids could be attributed to the formation of wax due to the incomplete scission process to give rise to the formation of primary hydrocarbons with light molecular weight. Interestingly, a jet fuel hydrocarbon with C_6 - C_{16} aromatics and aliphatic was obtained at the H_3PO_4 /CNS range from 0.4 to 1.0. The increment in H_3PO_4 /CNS up to 0.8 resulted in an observable increase in polyaromatic hydrocarbons to 32.36% from 10.41% at the H_3PO_4 /CNS ratio of 0.4. The improvement in selectivity at the H_3PO_4 /CNS ratio of 0.8 could suggest the formation of an improved $-\text{PO}$ and $-\text{C}=\text{O}$ which enhanced the presence of more active sites for cracking of larger molecular weight hydrocarbons into lower compounds. To obtain bio-oil of high quantity, a low carbonation temperature of 750°C favours a higher yield, while a high temperature improved the formation of biogas over bio-oil at a temperature of 950°C .

In the catalytic conversion of polymers into biofuels, the formation of wax and polyolefins is regarded as the primary products which occur on the external surfaces of catalyst materials [188]. The wax and polyolefin have the tendency of being converted into compounds with a lower molecular weight with high fuel characteristics for possible usage in internal combustion engines. The formations of secondary products such as aliphatic hydrocarbons are promoted in the internal pores of catalyst materials; hence, the degree of reactant diffusivity during the conversion process is of high demand. The rate of the conversion process is dependent on the molecular weight of the reactants, the pore sizes, and the acidity of the catalyst materials.

The significance of temperature during the pyrolysis of polymeric materials could be said to be the fundamental factor for the cracking process. An increase in reaction temperature in a pyrolysis reactor promotes the disintegration of molecules in polymeric materials which are bonded by a weak Van der Waals force of attraction, and then, the molecules gain higher kinetic energies to enable a change of state from the solid state to gaseous state. At this point, the energy due to Van der Waals forces in the polymeric materials is higher than the heat content which exists in the C-C bond which aids carbon scission [183]. Furthermore, the mechanism of aviation fuel production via the ex situ pyrolysis process has been reported by Duan et al. [187] to entail aromatization, thermal cracking, dehydrogenation, β -scission reaction, and hydrogen transfer reaction as shown in Figure 6.

Dyer et al. [189] reported the catalytic copyrolysis of lignocellulose biomass and waste plastics as an effective path to renewable biofuel production. Feedstocks such as com-

pressed wood, sawdust, and waste plastics such as PP, HDPE, PET, LDPE, and PS were used in the studies under the catalytic activity of the ZSM-5 zeolite in a 2-stage fixed-bed reactor system (Figure 7). During the experiment, a feedstock:catalyst ratio and biomass:plastic ratio were respectively kept at 1:2 and 1:1 throughout under the influence of a nitrogen environment as an inert gas. The catalyst used in the study, ZSM-5, was obtained having the $\text{Si}/\text{Al} = 38$, surface area of $282\text{ m}^2/\text{g}$, and micropore volume of $0.26\text{ cm}^3/\text{g}$. The degradation of the feedstocks was carried out at 500°C . The extent of carbon deposition was investigated via the application of TGA equipment from room temperature to 800°C , heating rate of $15^\circ\text{C}/\text{min}$, and reaction time of 10 min. The introduction of ZSM-5 into biomass pyrolysis resulted in the reduction of the liquid products by 25 wt.% as compared to the noncatalytic process. The reduction in bio-oil yield was linked to the influence of ZSM-5 to improve the formation of CO and CO_2 through oxygen removal. The presence of plastic resulted in a decrease in oxygenated compounds in the bio-oil compared to the pyrolysis of pure biomass. Over 65% reduction of oxygenated compounds was observed in the pyrolysis of biomass with polypropylene and polyethylene with improved content ranges from C_5 to C_{12} fuel hydrocarbon.

The catalytic copyrolysis of PP and *Laminaria japonica* using the zeolite catalyst was investigated by Kim et al. [28]. Catalysts such as HZSM-5, Pt/mesoporous MFI, mesoporous MFI, and mesoporous Al-SBA-16 were investigated for their efficiency for drop-in fuel production. The pyrolysis experiments were executed in a fixed bed reactor with reaction temperature of 500°C and N_2 flow rate of $50\text{ mL}/\text{min}$ for a reaction time of an hour using biomass/polymer and catalyst/feedstock ratios of 1:1 and 1:10, respectively. The catalytic activity of the zeolite materials resulted in the reduction of acid, wax, oxygenates, and H_2O content in the obtained bio-oil. The reduction was associated with the potential of the catalyst materials to improve the formation of CO and CO_2 during the aromatization and deoxygenation of the pyrolysis vapour. The Pt-supported mesoporous MFI catalyst depicted the highest catalytic-upgrading potential. This performance characteristic was attributed to the presence of large pore size, catalytic effect of Pt, and presence of strong acid sites although the cost of platinum for use in industrial scale is a huge drawback.

Kim et al. [190] reported the catalytic copyrolysis of biomass carbohydrates (avicel, xylan, and torrefied avicel) with LLDPE using Al-SBA-15 and mesoporous ZSM-5 ($\text{Si}/\text{Al} = 40$). NH_3 -TPD was employed in the determination of the structural and acid properties of the MZSM-5 and Al-SBA-15 catalysts. The presence of strong acid sites on the mesoporous ZSM-5 catalyst ($1.4\text{ mmol}/\text{g}$) over the Al-SBA-15 ($0.15\text{ mmol}/\text{g}$) was responsible for the effective selectivity of aromatic formation during the catalytic conversion process. Although the Al-SBA-15 possesses a large surface area compared to the MZSM-5 catalyst, the presence of a stronger acid site and micropore volume played an important role in aromatic selectivity. Via the application of a Py-GC/MS/FID tandem μ -reactor, the pyrolysis of the feedstocks was conducted at a temperature of 500°C using a mixture of biomass/polymer-to-catalyst of ratio of 1:1 in an

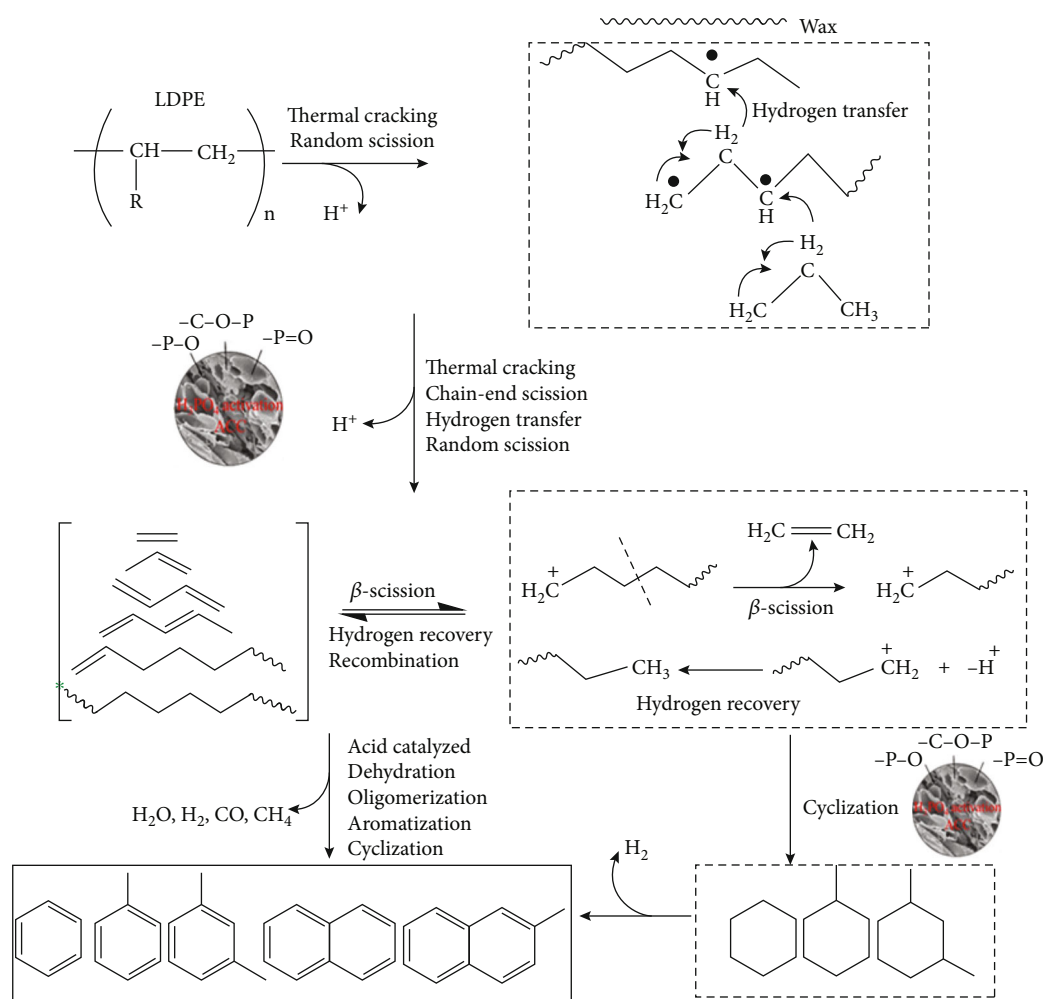


FIGURE 6: Reaction mechanism for the production of aviation fuel from LDPE feedstock [187].

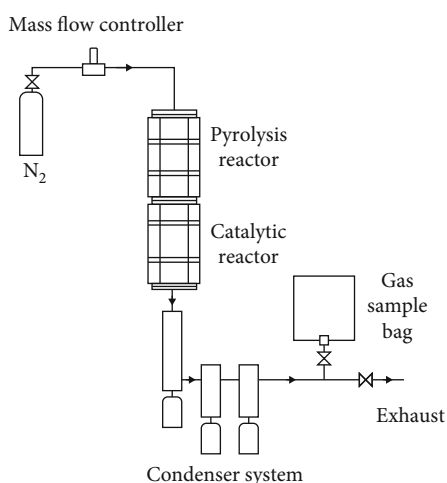


FIGURE 7: Two-stage catalytic pyrolysis of biomass and polymers into transportation fuel [189].

inert environment. The pore size, surface area, and micropore volume were observed to be 4.1 (nm), 371 (m^2/g), and 0.07 (cm^3/g), respectively. The MZSM-5 catalytic conversion of

carbohydrates resulted in the production of bio-oil with a larger quantity of aromatic hydrocarbons over Al-SBA-15. The copolyolysis of biomass with LLDPE results of the bio-oil indicated that the MZSM-5 catalyst produced bio-oil of higher monoaromatic hydrocarbons due to the presence of higher acidic sites which aid the selective cracking of oxygenates into deoxygenated compounds. The Diels-Alder reaction, which exists between the furans obtained from cellulose and the olefins produced from LLDPE, improved the high synergistic formation of MAHs by the catalytic copolyolysis of the feedstocks.

6. ZSM-5 Catalyst Deactivation due to Diffusion Limitation

The catalysts employed in the cracking of biomass and polymers are susceptible to a swift deactivation process which could be via physicochemical occurrence. These phenomena include oxidation of the metallic phase, metal sintering, coke deposit, and thermal degradation of the supported catalyst materials [139]. The coke formation on the surface of catalyst materials is identified as the most serious hindrance to catalyst performance [85].

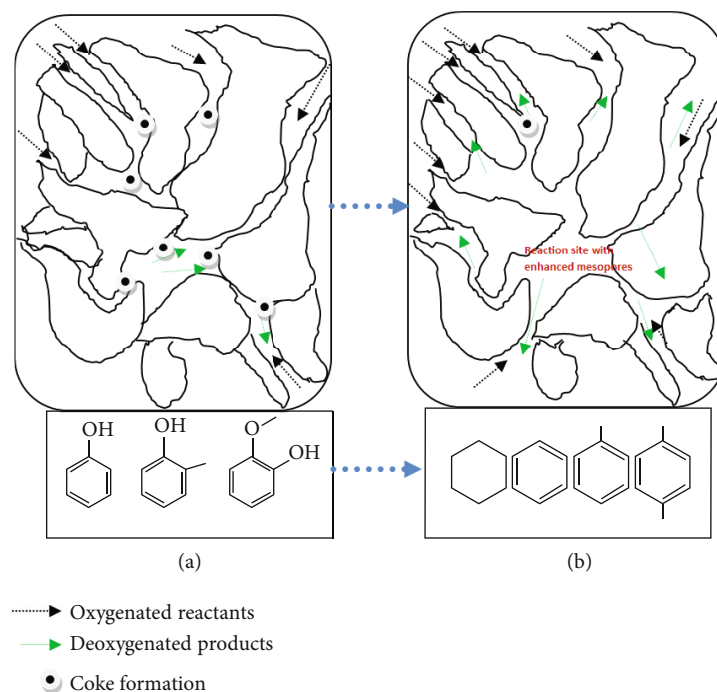


FIGURE 8: (a) Schematic illustration of coke formation mechanism during the pyrolysis process over zeolite catalyst, (b) pore enhancement through the introduction of pore enhancement agents (SDA).

Previous studies have highlighted the formation of coke, a carbonaceous material, which is a mixture of coke and biochar on the surface of acid and/or noble metal acid catalysts during organic compound transformation, which hinders catalysts' performance [39, 191, 192]. Rearrangement and condensation processes have been linked to the formation of coke at a temperature below 200°C during the thermochemical conversion process, and their compositions are related to reactant constituents [193, 194]. Low volatility, low solubility, and high adsorption of coke on two catalyst materials resulted in high retention of coke molecules on the surface of the catalyst which increase the tendency for catalyst deactivation [23, 79, 82]. Figure 8 depicts a conceptualized mechanism for the formation of coke due to the poor pore networks in a typical zeolite framework.

The external acid site of the zeolite catalyst has been reported to be responsible for the conversion of pyrolytic vapour into coke [84]. The hindrance of diffusion of the coke formed through the pores of the catalyst leads to the deposition of coke on the catalyst surfaces and, therefore, causes swift catalyst deactivation [195]. The deactivation of the ZSM-5 catalyst due to coke formation is a concern to researchers towards achieving high catalyst performance. The excellent and improved performance of the ZSM-5 catalyst was associated to the presence of a moderate pore size of about 6 angstroms. The application of the ZSM-5 catalyst for bulky molecules found in biomass materials in the form of lignin has been reported to be ineffective for efficient conversion due to the presence of molecular sizes that are larger than the pore sizes of the ZSM-5 catalyst.

The introduction of alkali Na_2CO_3 into the ZSM-5 catalyst, the dealumination process, and the modification of ZSM-5 active surfaces with metals (transition metals) have

been reported to improve the Brønsted acid sites, stimulate the formation of hierarchical structure, and reduce the formation of coke during the catalytic activities [196]. These itemized processes further aid in the effective deoxygenation of large molecular lignin compounds to form smaller molecules with biofuel properties.

The formation of coke deposits in a typical zeolite catalyst has been studied, and the natures of coke formations were grouped into three main categories: at the micropores, at the external part of the ZSM-5 catalyst, and at the mesopores. The most toxic coke formation that is capable of immediate catalyst deactivation is the coke formed at the micropore sites (as conceptualized in Figure 8), which is highly not desirable as it affects the selectivity and yield of aromatics [105]. As regards the formation of coke at the ZSM-5 external surface, several factors are responsible, and such coke formation has no effect on the catalyst micropores; the pores are still active for reaction. The rate of pyrolytic vapour formation, mass transfer of biomass vapour to the surface of the catalyst, reaction at the surface, and diffusion into the internal parts of the crystals are the major factors that determine the formation of coke on the external surfaces of the ZSM-5 catalyst [197]. Hence, the most toxic of all three points of coke formation is that of coke formation at the micropores of the ZSM-5 catalyst [105]. Therefore, there is a need to improve the formation of external pores and mesoporosity on the surfaces of the zeolite catalyst through the introduction of a hierarchical structure.

6.1. Catalytic Coke Formation during Pyrolysis Process. The deactivation of catalyst materials has been widely believed by researchers to be attributed to the formation of coke. The formation of polyaromatic hydrocarbon (PAH) deposits

on the zeolite paths resulted in the deactivation of zeolite catalysts during the pyrolysis process. The formation of PAHs has a high tendency towards external pore blockage; the acid site, hence, retards the selectivity to aromatic formation. Through surface modification of the zeolite catalyst by improving the porosity (mesopores), the mass transfer limitation is reduced, and the accessibility of oxygenates to acid sites is improved [139]. Furthermore, the application of feedstock modification via copyrolysis of biomass materials with polymer (hydrogen-dense) feedstock improves the catalyst performance and selectivity to aromatic hydrocarbon [23, 166]. Hence, improving the external pores of the zeolite catalyst could aid in reducing catalyst deactivation by diffusion time shortening during pyrolysis of the biomass.

7. Factors Affecting ZSM-5 Performance

The performance of ZSM-5 as a catalyst during the CFP process is favoured by the effective pore distribution, shape selectivity, and acidity [36]. The presence of smaller pores on the ZSM-5 catalyst inhibits the mass transfer of products and reactants. The presence of smaller pores on the surface of the ZSM-5 catalyst reduced the transport efficiency of larger molecular reactants and products and, therefore, resulted in pore blockage and catalyst deactivation [1]. The formation of improved aromatic hydrocarbons has been reportedly improved at a medium pore size between 3 and 7 angstroms while coke formation was linked to larger ZSM-5 pores, and no aromatics were produced in zeolites with small pores [198]. The formation of intermediates of larger molecular sizes during oxygenate conversion has limited the application of the ZSM-5 catalyst to favour aromatic production. Therefore, the development of a hierarchical mesoporous structure of the ZSM-5 catalyst is required for improved aromatic formation and lowers coke deposition.

The formation of the mesoporous structure following the structural modification of the ZSM-5 catalyst creates an effective and efficient diffusion pathway where larger molecular compounds could diffuse to an accessible inlet pore (micropores). At these micropores, it was reported that Brønsted acids exist (Brønsted acid sites) where smaller molecules are formed through the catalytic breakdown of larger molecules from biomass vapour that formed aromatics through diffusion into the micropores [36]. Furthermore, the formations of mesopores promote the transportation of catalytic products and influence the monoaromatics selectivity as shown in Figure 7. Figure 7 depicts the mechanism of molecular transport through the formation of an interconnected mesoporous structure to micropores for enhanced monoaromatic production in a typical zeolite catalyst.

The catalytic activity of Fe- and gallium- (Ga-) modified ZSM-5 zeolite has been studied by Furumoto et al. [199]. The researchers reported that the modification process suppresses the formation of coke and improves the selectivity for propylene production. Lower acidic strength was observed on the Fe-modified ZSM-5 catalyst which causes ineffective cracking due to the presence of insufficient activation energy [199].

8. Shape Selectivity, Advantages, and Disadvantages of ZSM-5 Catalysts

The world of catalytic cracking of biomass is similar to those of conventional fossil fuels where large molecular chain compounds are cracked into smaller monomers of improved quality with the exception of acids, nitrogen sulphur, and mineral which are contained in biomass feedstock [200, 201]. Several advantages of the ZSM-5 catalyst which have made them more attractive on the industrial scale include shape selectivity, solvothermal resistance, deoxygenation potentials, tunable acidity, high resistance to polar and water, and also its versatility to varieties of biomass feedstock. The selectivity of ZSM-5 catalysts favours the production of high-yield aromatic hydrocarbons while the formation of coke is one of the major competing reactions during the catalytic conversion process [36, 50].

The window architecture of ZSM-5 has been found to selectively crack oxygenated compounds into aromatics and cycloalkanes which are important recipes for high-quality bio-oil [3]. This condition at which zeolite selectively permits the transport of reactants and products through the well-defined window is responsible for the term “molecular sieve” [110, 202]. Also, the ZSM-5 pore size and structural characteristic are important parameters which regulate the reactants and products’ diffusivity; hence, the aromatic and olefin selectivity is promoted (shape selectivity). The ZSM-5 pore size and the structural framework are the underlying properties which enhance the product selectivity and the extent of the reactants’ conversion during the catalytic activities of bio-oil conversion into transportation fuels and chemicals [24, 36]. The nature of metal loading adopted during ZSM-5 modifications also affects the overall performance of the catalyst due to surface chemistry modification and the possibilities of influencing the acidic strength of the catalyst; one of the factors that determine the efficiency of the catalyst during the bio-oil upgrading [203]. The performances of ZSM-5 catalysts are related to the presence of micropore sizes present in the framework, and the need to enhance the pores through mesoporous inducement into the external catalyst surface is required for both reactants and products’ transport [79].

As regards the shape selectivity of the conventional ZSM-5 catalysts during the upgrading process, the presence of a 10×10 -ring framework and the smaller pore diameter of 5.0 \AA promote the selectivity of smaller-sized hydrocarbon compounds [203]. In an attempt to improve the performance of the ZSM-5 catalyst, the introduction of Ni was carried out, and there were no changes on the morphology and the structure observed via the SEM images, although the overall crystallinity was observed to be reduced [203]. The catalytic performance of the Ni-supported ZSM-5 catalyst developed for the HDO of anisole and guaiacol shows high selectivity of liquid cyclohexane where the coupling reactions which always resulted in the formation of larger molecules were not observed due to the 10×10 -ring pore architecture of ZSM-5. The undesirable properties which favour isomerization coupling reactions are the presence of a large internal pore and the presence of a high concentration of acid sites. Furthermore, a large pore architecture

(12 × 12-ring) and large acid site concentration enhance ring-opening phenomenon during the HDO process over Ni/beta and Ni/Y catalysts [203]. The role of catalyst acidity and shape selectivity on products from the catalytic fast pyrolysis of beech wood was presented by [36]. The presence of Al framework aids high acidity in the ZSM-5 catalyst and, therefore, promotes deoxygenation, cracking, and aromatization reactions of bulky oxygenated reactants [36]. The shape selectivity of the ZSM-5 catalyst is responsible for its wide range of applications. The shape selectivity of the ZSM-5 zeolite is responsible for coke formation which promotes pore blockage and subsequent catalyst deactivation as a result of mass transfer limitation. These phenomena lower product selectivity and inferably hamper the transition state. Hence, the need to understand the mechanisms of product formation during the catalyst activities of ZSM-5 is important.

9. Future Perspectives

In the biomass feedstock, large molecular structured materials (polycyclic aromatic hydrocarbons) have been observed to hinder the effective performance of microporous ZSM-5 catalysts. This challenge has brought a series of setbacks to the conversion efficiency of zeolite catalysts, and this further leads to high oxygenate in biofuels which affects the direct use of bio-oil as transportation fuel. Furthermore, the low hydrogen-to-carbon ratio reduces the H/C_{eff} and, hence, lowers the fuel performance.

In order to improve the ZSM-5 catalyst performance for high conversion of large molecular biomass compounds or monomers into useful fuel and improved selectivity:

- (1) The structural modification of the ZSM-5 catalyst is of importance. The structural modification could involve the introduction of mesopores on the external surface of the catalysts via hierarchical surface enhancement. The presence of hierarchical pores would help in improving the selectivity of monoaromatic hydrocarbons and the conversion of feedstocks to highly dense deoxygenated compounds
- (2) Surface modifications via doping with active catalyst elements such as transition metals (Fe, Co, Ni, and Mo) are capable of improving catalyst performance owing to their tendency in forming a reactive oxide and reduced metallic particles and complexes when combined in bimetallic or trimetallic catalyst's mixtures. Meanwhile, attention has to be channeled to controlling catalyst sintering through the introduction of promoters and monitored operating conditions
- (3) As regards the catalyst poisoning which results from the in situ approach and the low H/C_{eff} ratio, the introduction of high hydrogen dense feedstock such as bio-oil derived from high-density polyethylene could improve the energy density of the biofuel and, hence, improve the economic value of the obtained product
- (4) Supplementing the overall properties of ZSM-5 through the formation of a hybrid catalyst mix could

improve the overall performance during the deoxygenation process. In this case, the application of nanomaterials is required for shortened kinetics of reaction

- (5) By shortening the crystal sizes for reduced diffusion length together with the hierarchical structure, a secondary pore system formation is maintained to improve the overall stability and product selectivity which could enhance the ZSM-5 catalyst performance
- (6) To reduce the formation of polycyclic aromatic hydrocarbon formations which are linked to pore blockage during product diffusion in the micropore of ZSM-5, the use of the hydrogen spilt-over (HSO) approach should be adopted to generate B-acid sites which act as an active region for catalytic reactions through reaction with intermediates at the surface of their catalyst during the deoxygenation process

10. Conclusion

The production of advanced drop-in fuel via a catalytic deoxygenation process requires the application of an effective and efficient catalyst (ZSM-5) which is capable of improving feedstock cracking, increasing hydrocarbon selectivity, and reducing oxygenated compounds' formation. Hence, ZSM-5 pore structure, surface chemistry, and acidity play important roles during the catalytic deoxygenation of large molecular compounds in bio-oil. The introduction of ZSM-5 surface modification using metallic particles enhances the deoxygenation process while the polycyclic hydrocarbon retards the conversion efficiency. The formation of coke retards the performance of the ZSM-5 catalyst due to the micropore nature of the structure, and the introduction of mesoporosity could be required on the external catalyst surface to promote diffusion. The presence of moderate acidity is required to obtain a high yield of biocrude during the deoxygenation process; hence, understanding the overall behaviour of zeolite properties is required for an efficient modification process.

Data Availability

The data used to support the findings of this review are provided in the manuscript.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors' Contributions

Ishaq Kariim was responsible for the conceptualization, methodology, data curation, formal analysis, funding acquisition, investigation, writing of the original draft, and review and editing of the draft. Hulda Swai provided supervision. Thomas Kivevele was responsible for review and editing of the draft, supervision, and funding acquisition.

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