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## Chapter

# Catalytic Conversion of Glycerol to Bio-Based Aromatics

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## Abstract

Green application of biodiesel-derived glycerol will boost biodiesel production in terms of sustainability and economics. The glycerol to liquid fuels is a promising route that provides an additional energy source, which contributes significantly to energy transition besides biodiesel. This pathway could generate alkyl-aromatic hydrocarbons with a yield of ~60%, oxygenates, and gases. MFI Zeolites (H-ZSM-5) catalysts are mainly used to propagate the aromatization pathway. This chapter presents the pathways, challenges, catalytic design, influences of catalyst acidity, metal addition, reaction condition, and catalysts deactivation on glycerol conversion to hydrocarbon fuels and aromatics. Studies revealed that time on stream, temperature, and weight hourly space velocity (range of 0.1–1 h<sup>-1</sup>) influences the benzene, toluene, and xylene BTX and benzene, toluene, ethylbenzene, and xylene BTEX yield. Acidity of the H-ZSM-5 could be tailored by metals, additives, and binders. Bronsted acidity promotes coke formation which results in reversible deactivation of the H-ZSM-5 catalyst. It is hoped that this study will promote intensified research on the use of glycerol for purposes of fuel generating and valuable products.

**Keywords:** BTX, BTEX, hydrodeoxygenation, hydrocarbon fuels, glycerol, biodiesel

## 1. Introduction

To achieve complete decarbonization, there is a need to transition from fossil fuels to renewable and sustainable alternative fuels. This is because fossil fuels are major sources of greenhouse gas emissions, which have contributed to rising earth temperatures and adverse climate change. Transportation sectors still rely heavily on fossil fuels and this trend must be discouraged to minimize the emission of noxious CO<sub>2</sub> emissions [1, 2]. Liquid fuels generated from renewable energy sources, for use in heavy-duty vehicles are a promising option to reduce the impact of fossil fuels. Amongst the commercialized fuels from renewable energy, biodiesel has enjoyed wide acceptability because of lower CO<sub>2</sub> and other greenhouse emissions, can directly be used in the current internal combustion engine without modifying the engine design, and requires facile production processes [3, 4]. More importantly, biodiesel can be obtained from natural sources including waste oil, second-generation non-edible seed oil, third-generation, microalgae and fungus, animal fats, etc. [5, 6].

The transesterification reaction of oils (triglycerides) and alcohol is a widely established route for the synthesis of biodiesel [7]. This route involves the reaction of a triglyceride and 3 mols of alcohol (preferably methanol) to produce 1 mol of fatty acid methyl ester (biodiesel) and glycerol as a byproduct. The glycerol produced in this process is about 10 g for every 100 g of biodiesel produced, which renders it abundant [8, 9]. The produced glycerol is cheap because of impurities of methanol, soap, and catalysts that require energy-intensive steps for purification [10, 11]. However, glycerol is a platform molecule with three hydroxyl groups which can be transformed into fuels and fine chemicals. Many reaction pathways such as acetylation [12], carboxylation [13], etherification [14], oxidation, dehydration, gasification, aromatization [15, 16], etc. have been adopted to valorize glycerol.

Conversion of glycerol to liquid hydrocarbon fuel is a very recent and notable research idea, which will boost the biodiesel process. This is because the hydrodeoxygenation and hydroisomerization of vegetable oils to green diesel is capital intensive. Hydrocarbon fuel is vital in energy transition because of its characteristics which include high density and ease of transportation. This liquid hydrocarbon contains mainly alkyl-aromatic hydrocarbons of cumene, xylene isomers, benzene, toluene, and traces of C<sub>9</sub>+ compounds [16–18].

The feed has a significant influence on the aromatic product distribution, coke formation, and the type of aromatic products obtained. When the compounds with a H/C ratio is less than 2, for instance, glycerol with 0.67, are used as feed, increasing coke formation on the catalyst is generally observed. Hence, dilution with water or alcohol is employed. The dilution of glycerol with a solvent that has a H/C ratio of 2 increases the H/C ratio and presents improved catalyst stability. This preferred solvent for dilution is methanol with an effective H/C ratio of 2 [19, 20]. The conversion of glycerol and methanol to gasoline has emerged as a promising route to valorize glycerol [21, 22]. Increasing the methanol/glycerol ratio from 10 to 40% favored the production of oxygenated compounds instead of aromatics. Also, when methanol/glycerol are used as feeds, the formation of trimethylbenzenes and xylenes is obvious. These compounds can be transformed into heavy C<sub>9</sub> aromatics by dealkylation reaction to xylene and toluene (BTX). The use of higher alcohol like isopropanol and isobutanol for dilution results in the preferential generation of ethylmethylbenzenes, and ethylbenzene with xylenes and trimethylbenzenes (BTEX) from the alkylation of ethylene generated from the cracking of the alcohol or dehydration of ethanol [18].

Notably, benzene, toluene, and xylene (BTX) and/or benzene, toluene, ethylbenzene, and xylene (BTEX) have been the main focus of many researchers in this area of study because of the vast industrial applications of these aromatic compounds including their antiknocking characteristics [23]. In addition to the aromatic compounds, oxygenates such as propanal, hydroxyacetone, and propenal (acrolein) are the product of this process [24, 25]. Also, ethylene, methylene, and propylene gases could be derived from this process. The reaction is usually carried out in a fixed bed reactor at ~400°C under excess hydrogen, alcohols, and/or nitrogen gas flowrate at atmospheric pressure [18, 26, 27].

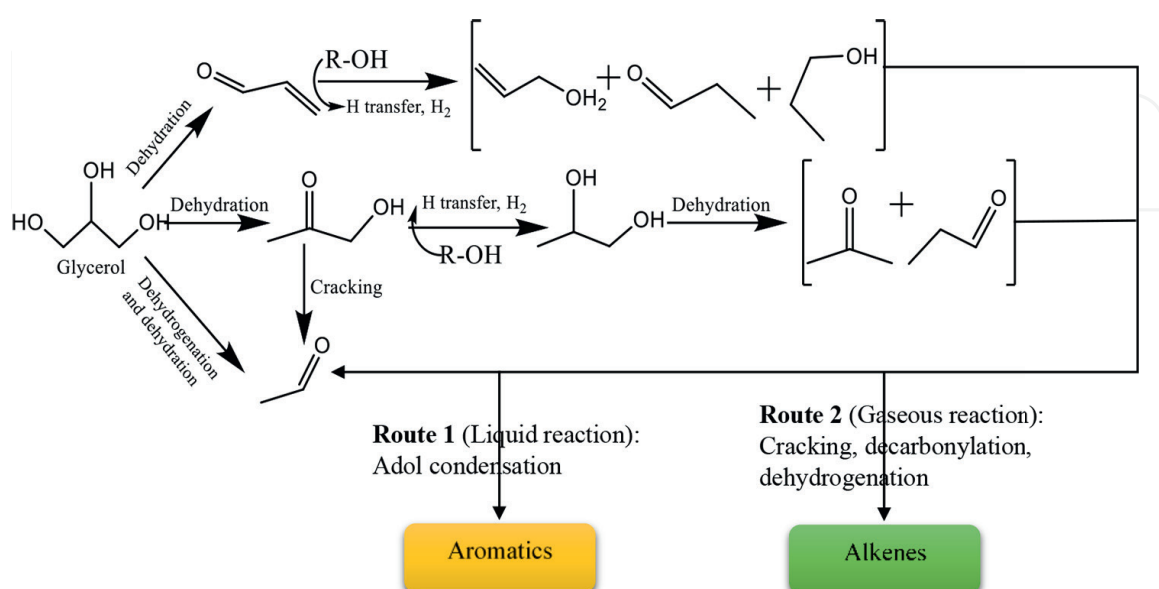
To promote this reaction, zeolites of ZSM-5 or protonated ZSM-5 have been widely used. However, the yield over these catalysts is generally low. To increase the catalytic activity, noble metals or transition metals have been functionalized on the ZSM-5 and used with remarkable performance [28, 29]. The noble metals of Pt, Pd, and Rh, promote the cleavage of C – O bonds of glycerol, which enhances the formation of hydrocarbons from polyols instead of H<sub>2</sub> and CO<sub>2</sub> gases [24, 30]. Another problem encountered

when ZSM-5 or H-ZSM-5 is used is rapid deactivation due to sintering, coking from reaction products, and attrition. This can be minimized by using a binder such as  $\text{Al}_2\text{O}_3$  [31]. The binder stops irreversible deactivation and prolongs the catalyst life. In all these, control of the reaction conditions such as the temperature, catalyst amount, and sometimes the atmosphere, greatly influence the yield of bio-based aromatics. The operating reaction conditions also determine the operating cost of the process.

In this study, catalytic glycerol conversion to liquid hydrocarbon and bio-based aromatics are investigated with emphasis on the reaction mechanistic pathway and the influence of the reaction conditions such as temperature, time, and catalyst weight. The catalyst design, challenges, and deactivation mechanism are discussed. Prospects on bio-based aromatics are presented to reveal the knowledge gap and provide future guidelines for researchers and industries.

## 2. Mechanism of glycerol conversion to biobased BTX and BTEX

The mechanism of glycerol to liquid hydrocarbon follows two main routes namely hydrodeoxygenation (HDO), followed by aromatization reaction. Hydrodeoxygenation is an established method of removing oxygen from biomass. Glycerol hydrodeoxygenation is usually carried out to synthesize 1,2-propanediol, which is an oxygenate compound used in pharmaceutical, tobacco, and cryogenic industries. This pathway occurs through simultaneous C-O bond cleavage and hydrogen addition [27]. Usually, hydrogen is added from an external source, however, recent studies have shown that *in situ* hydrogen generation from hydrogen donors such as methanol, formic acid, 2-butanol, ethanol, etc. could eliminate the need for external hydrogen [25]. The hydrodeoxygenation also follows two parts of hydration-hydrogenation and dehydrogenation-hydration-hydrogenation, which is the most common pathway. The dehydration happens on the acid catalyst sites, whereas the hydrogenation is catalyzed by the noble metals or Cu, Zn, Ni, Sn, etc. This is because these metals promote the aqueous phase reforming of glycerol to



**Figure 1.** Reaction pathways for glycerol dehydration-hydrogenation and dehydrogenation-hydration-hydrogenation reaction to produce aromatics [17].

produce hydrogen that is consumed during the hydrogenation stage. **Figure 1** shows the liquid and gaseous steps for glycerol dehydration and dehydrogenation pathways.

Hydroxyacetone can be produced via dehydration or via another route that involves dehydration to obtain glyceraldehyde, followed by hydrogenation to hydroxyacetone [25, 27]. Also, there are other hydrocarbon mixtures of acetone, propenal, alcohols, ketone, paraffins, and olefins of ethylene and propylene. Both liquid and gaseous routes produce a hydrocarbon pool, which in the presence of a catalyst could be upgraded to benzene, toluene, and xylene (BTX) or benzene, toluene, ethylbenzene, and xylene (BTEX) and other oxygenate compounds [17]. Also, the hydrocarbon pool can be further cracked to light paraffin or olefins. Generally, the presence of strong acid sites results in the build up of heavy aromatics such as trimethylbenzene and tetra- methylbenzene, whereas the reduction in the strong catalytic sites that propagates cracking and cyclization reaction, inhibit the gas route. The liquid route however, is unaffected since the aldol condensation reaction requires weak acid sites [16, 17].

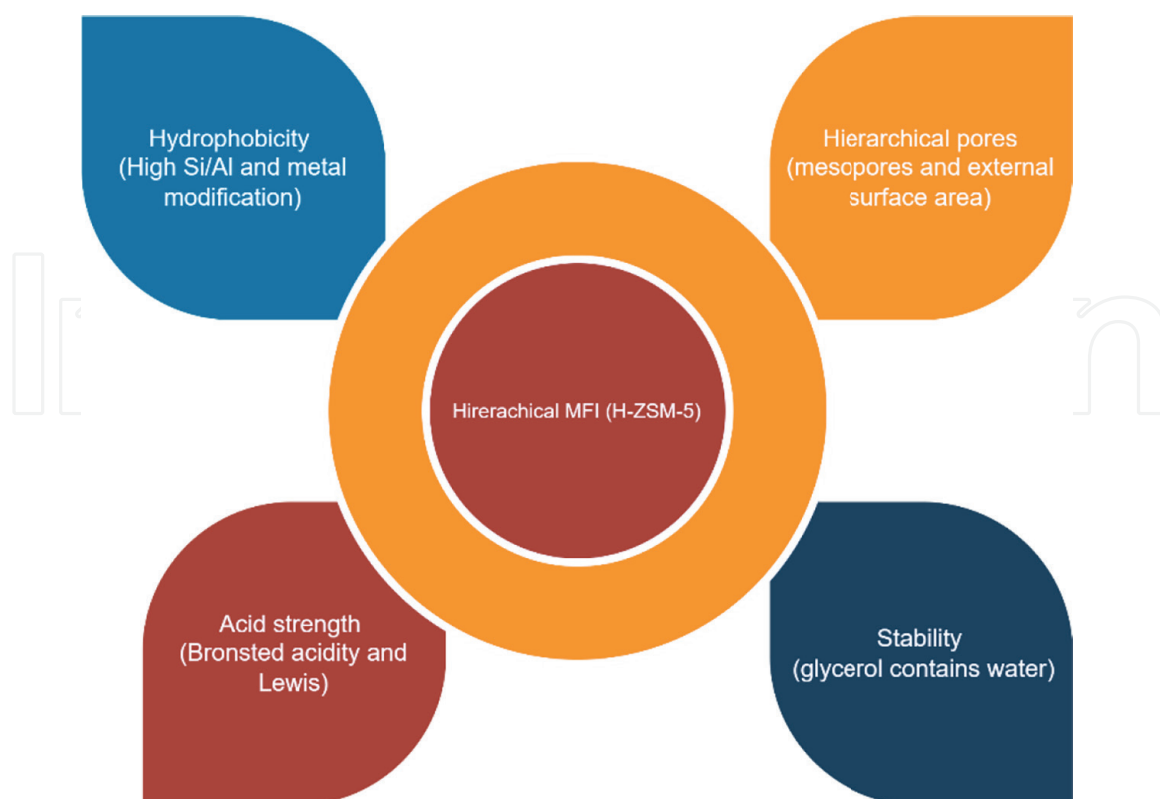
### **3. Effect of HZSM-5 acidity, metals addition, and reaction conditions**

The unique three-dimensional cage-like crystalline structure and tunable acid properties of ZSM-5 render it a choice catalyst for many reactions including isomerization reaction, alkylation reaction, and aromatization reaction. Also, this catalyst possesses an appreciably high surface area and has been extensively used successfully to drive the reaction of methanol to aromatics. Studies on the glycerol to aromatics synthesis revealed that protonated ZSM-5 (H-ZSM-5) has been effective for BTX and BTEX production due to its acidity and shape-selective characteristics [32]. The H-ZSM-5 contains sinusoidal channels ( $0.51 \times 0.5 \text{ nm}$ ) that are crossed with straight channels of the dimension ( $0.53 \times 0.56 \text{ nm}$ ) with intersection channel of  $0.9 \text{ nm}$  size [33, 34]. However, the relatively large micropores of the catalysts limit the mass transport of large molecules and present a diffusion barrier, which ultimately results in undesired bulkier aromatics and cokes and eventual deactivation of the catalysts [35]. To correct this, hierarchical porous H-ZSM-5 catalysts with macro-meso-and micropores have been developed to ensure hitch-free diffusion of reactants. In the synthesis of hierarchical H-ZSM-5 catalyst, several factors should be considered (see **Figure 2**). These factors are the hydrophobicity of the catalyst since the reaction most times produce water, concentration, and strength of acid sites, presence of mesopores, and shape selectivity of the catalyst. Also, several metals have been added to stabilize the H-ZSM-5 and increase its acidity and efficiency [36]. This section presents the effect of acidity and the effects of metals used to functionalize H-ZSM-5 catalysts. Also, the influence of reaction conditions such as time on stream and reaction temperature was presented.

#### **3.1 Effect of catalyst acidity**

The acidity of the ZSM-5 and MFI (H-ZSM-5) is vital to promoting the aromatization or hydrodeoxygenation of glycerol. To determine the influence of the catalyst acidity, several analytical characterizations can be performed. A notable characterization technique employed is temperature desorption programming (TPD) using ammonia as a probe molecule [37]. Ammonia is used because it is basic and can easily interact with acid sites. The TPD can also be used to determine the number of active sites in mmol/g by deconvolution of the peaks using gamma distribution or the gaussian model [12]. The





**Figure 2.**  
*Considered factors in the application of hierarchical porous H-ZSM-5 [34].*

TPD peaks could be classified as weak, moderate, and strong peaks. The weak peak can be appreciated from 150 to 220°C, the moderate acid sites are around 300–350°C and the strong sites are from 400°C and above [38]. For zeolites, only weak and strong acid sites are usually identified [39]. Although weak and moderate peaks contribute to the deoxygenation and aromatization, mainly the strong acidity favors a higher yield of aromatics.

For instance, the yield of aromatics over catalyst of Zn/P/Si/ZSM-5 was lower than Zn/P/ZSM-5 catalyst by about 14.3% because the SiO<sub>2</sub> impregnation reduced the amount of the total acid sites by about 7.02% [38]. Also, the concentration of the surface acid sites is more vital than the total acid sites, because it is largely a surface dominated reaction. A similar study on atomic layer deposition (ALD) of Zn species on Sn/HZSM-5 zeolite revealed that above 20 cycles of ALD of Zn, precisely 40Zn, the interaction between the HZSM-5 and deposited Zn species were limited. Also, the strong acid sites reduced significantly, resulting in a reduction of BTX yield from close to C. 39% (for Sn/HZSM-5@20Zn) to C. 31% (for Sn/HZSM-5@40Zn) based on carbon yield [17]. Dealumination of HZSM-5 by steaming and acid leaching could produced different results. For instance, using 6 M nitric acid to remove extra-framework aluminum from the surface and channels of HZSM-5 and steaming to achieve the same purpose revealed significantly lower Brønsted acidity in steam treated HZSM-5. Whereas the concentration of the strong acid sites for the acid treated HZSM-5 remained almost unchanged. However, the weak acid sites decreased significantly, resulting in reduced total acidity. Likewise, BTX aromatic yield was higher for acid treated HZSM-5 (C. 28.1%) compared to the steam treated zeolite (C. 18.3%) [16].

To evaluate the type and concentration of the acid site, Fourier transforms infrared (FTIR) of adsorbed pyridine are normally used [40]. The pyridine IR is usually conducted by heating a known mass of the catalyst at around 150°C for 3 h, followed

by pyridine adsorption for 2 h and subsequent desorption of the pyridine at 200°C under vacuum [41–43].

From pyridine DRIFTS analysis, the types of acid sites normally encountered with ZSM-5 zeolites are Brønsted and Lewis acid sites. Due to high pressure and temperature conditions of the glycerol to liquid fuels and aromatics compounds, high coke selectivity and consequent deactivation often occur for this type of catalyst. Particularly, the strong acid sites, which are mainly Brønsted acids promote the undesired coke formation, because the coke deposits preferentially on these sites through different proton transfer steps that occur on the Brønsted acid sites [26]. It is important to mention that understanding of acidity types of the zeolite catalyst can be appreciated from the Si/Al ratio [44]. Tuning of the acid strength [41] and reduction in the acid density [45] are two notable strategies to reduce coke deposits. The tuning of the acid strength and concentration can be achieved by modifying the zeolite tetrahedral framework Al content of the H-ZSM-5 or exchanging the protons that compensate for the negative charge of the Al sites tetrahedral framework. The strategy adopted over the years to accomplish these are either post-synthesis modification (top-down) or in situ modification during synthesis (bottom-up) [26, 32]. For instance, the synthesis of H-ZSM-5 with different Si/Al ratios is a common bottom-up strategy to evaluate the effect of acidity. For the bottom-up strategy, the total acid sites increase when the Si/Al ratio decreases. Top-down strategies include dealumination by acid extraction or steam treatment and isomorphic substitution of Al or Si atom with Zr, Fe, Ga, In, etc. [21, 46–48], other metals, heteroatoms of phosphorus, sulfur, and alkali metals, and alkaline earth metals [16, 40, 43]. Although these substitution strategies, which focus on the framework tetrahedral sites have been successful, however, they often result in the damage of the framework or defects of the crystalline structure, which adversely impacts the reactants and products diffusion to and from the cage-like zeolite structure. Also, the accurate introduction of these metals could be very problematic and can lead to uncertainty in the pore dimension [26].

Evaluation of the H-ZSM-5 acidity after dealumination via washing with HNO<sub>3</sub> and steaming revealed that the weak acid sites decreased, whereas the strong acid sites were unaffected. It is important to note that ZSM-5 zeolites have amorphous extra framework aluminum, which contributes significantly to the weak acid sites (although it could contribute slightly to the medium and strong acid sites with other silanols (Si-(OH)-Al) species), whereas the framework aluminum species are more related to the strong acid sites. Hence, the reduction in weak acid sites after dealumination can be attributed to the removal of the extra framework aluminum. The steaming treatment, however, resulted in a remarkable reduction of the acid concentration and strength, which shows the dealumination of the framework and extra-framework aluminum [16].

### **3.2 Effect of metal addition**

Metal addition on H-ZSM-5 is bifunctional to provide stability as well as promote the dehydration/dehydrogenation reaction of glycerol to aromatics. A conducted study using only H-ZSM-5 reveal that predominantly oxygenates namely acrolein were obtained with about 11% of C<sub>6</sub> – C<sub>9</sub> compounds [30]. In this same study, the addition of metals (platinum and palladium), provided bifunctional properties, which promoted the C – O, C – H, O – H, and C – C bonds cleavages to achieve deoxygenation of the oxygenates [24]. Palladium however showed better performance in the conversion of the oxygenates to aromatics because of the higher H/metal ratio.

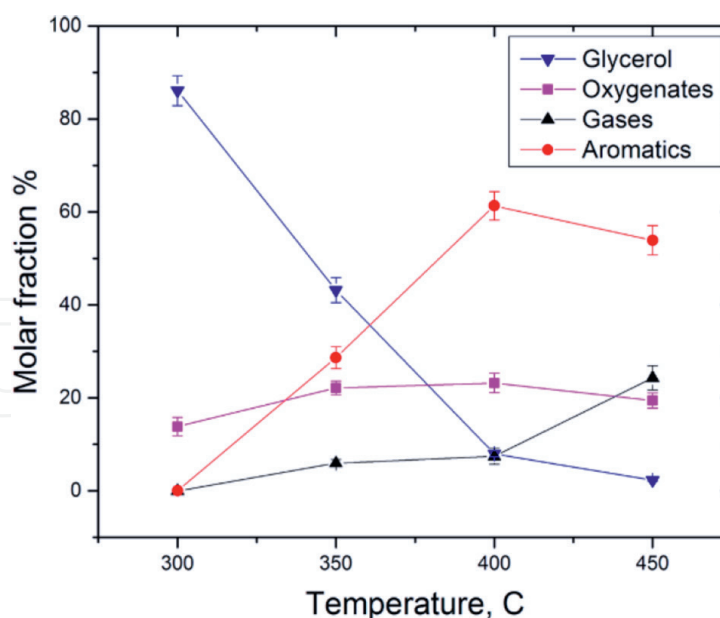
Notably, noble metals are preferred for fast kinetic activation of hydroxyl groups of glycerol and hydrogen dissociative adsorption [49]. Depending on the operating temperature they generally promote the hydrocarbon formation instead of the CO and H<sub>2</sub> pathway.

Apart from noble metals, which are usually expensive and can impact the overall production cost of liquid hydrocarbon and biobased aromatics from glycerol, other metals have been used with appreciable performance. Binders such as Al<sub>2</sub>O<sub>3</sub> have been used to prolong the H-ZSM-5 catalyst life. The mesopores of the Al<sub>2</sub>O<sub>3</sub> provided a higher capacity to store coke deposits in amorphous form. Also, the binder promoted a high total BTX yield compared to H-ZSM-5 [31]. Another study investigated the incorporation of tin (Sn) species in ZSM-5 catalysts. The composite catalysts were treated hydrothermally using sodium hydroxide, followed by ion exchange with ammonium chloride. The H[Sn, Al] ZSM-5/0.3AT composite catalysts after ion exchange reaction showed a slight decrease in crystallinity, a decrease in total Bronsted acid sites with an increase in Lewis acid sites [36]. Also, the Sn incorporation replaced some medium and strong acid sites and new acid sites were formed. The addition of the Sn did not destroy the H-ZSM-5 morphology, and the composite catalyst showed intra-mesopores and micropores, which benefits mass transfer of reactants and products. Overall, the catalyst showed a higher carbon yield of BTX (C 32.1%) compared to H-ZSM-5 (C 17.8%). The H[Sn, Al] ZSM-5/0.3AT could sustain about 13 h of time on stream reaction (H-ZSM-5 sustained the reaction for only 3 h with severe deactivation due to coke deposits), which was attributed to the mesopores and tuned Lewis acid and Bronsted acid sites due to alkali post-treatment. Similar studies have demonstrated the effect of binary material of Sn, Zn incorporated on H-ZSM-5 with appreciable BTX yield and longer catalyst life [17]. The Zn has been reported to promote high BTX formation by suppressing H-transfer reactions and light paraffins [29].

### 3.3 Effect of temperature

Catalytic pyrolysis is employed to achieve glycerol to aromatics and liquid hydrocarbons conversion. The operating temperature is very vital because glycerol to aromatics is a consecutive reaction steps that involves dehydration, oligomerization, cyclization, aldol condensation, cracking, and dehydrogenation. Since these reaction pathways occur simultaneously and parallel, different product distributions could be obtained at different reaction temperatures. An effect of reaction temperature on glycerol to aromatics shows that at a low temperature of ~200°C, O – H and C – H bonds could be easily broken due to their lower activation energy. This activation could be prevented by a possible hydrogenation reaction that is propagated by high H<sub>2</sub> content. An increase in temperature in the range of 300–400°C facilitated the bond cleavages of C – C and C – O species, which could happen simultaneously due to their similar activation energy [24]. However, breaking of the C – C bond at this temperature results in the formation of coke deposits, which could be graphitic or amorphous. Hence, the temperature should be tuned properly with the right amount of catalyst acidity to achieve the breaking of C – O bonds, while minimally avoiding the C – C bond. At 450°C, more of the liquid products are further cracked to gases, and syngas formation and methanation reactions are promoted [30]. Hence, the aromatics yield decreases, whereas the gaseous product increases as shown in **Figure 3** [30]. Most studies adopted 400°C as the optimum temperature to achieve the glycerol to aromatic conversion [18, 32, 50].





**Figure 3.**

Effect of pyrolysis temperature using Pd/H-ZSM-5 catalyst. Conditions: 1 atm,  $H_2$ /glycerol molar ratio of 10, and 6 g cat-h/g glycerol (copyright obtained <https://pubs.acs.org/doi/full/10.1021/acsenergylett.6b00421>).

### 3.4 Effect of time on stream

Time on stream for glycerol conversion to bio-based aromatics could be categorized into induction time, steady-state reaction time, and deactivation time [16]. Selectivity of the products is a clear function of the reaction time on stream; hence, it is important to optimize this factor. This has been generally established based on the yield of the aromatic intermediates in the cage structure of the H-ZSM-5 zeolite during aromatization. A study revealed that polymethyl benzenes and olefines, which is a very vital active hydrocarbon pools, were formed over the H-ZSM-5 cages as a product of the dehydration of the glycerol (oxycarbides) in the induction period [17]. This results in improved aromatic yields with a decrease in oxycarbides. After the induction period in a continuous reaction set-up, aromatization of glycerol proceeds via multiple steps of autocatalytic non-stop reaction of alkylation/dealkylation, oligomerization, and H-transfer. This stage usually has a relatively constant BTX and BTEX yield because the consumed hydrocarbon species are replenished. As the reaction time on stream is prolonged, the dealkylation step is suppressed with a corresponding decrease in lighter aromatic yield (toluene) and a buildup of heavier hydrocarbon species [38]. This was attributed to the coverage of the strong active sites by the heavier autocatalytic species, which suppresses the cracking and cyclization pathways propagated by the strong acid sites [51]. Hence, the gaseous route is mitigated allowing for the liquid synthesis. Further extension of the time on stream for continuous reaction set-up facilitates the conversion of the heavier intermediates (heavier hydrocarbon species) into carbon by a condensation reaction [52]. Eventually, the carbon formed blocks the micropores and the acid sites resulting in the catalyst deactivation. In the deactivation phase, the BTX and BTEX yields drop drastically, however, unconverted glycerol, acetol, acetaldehyde, and acrolein remained in the product [15]. **Table 1** shows the reported catalysts for glycerol conversion to aromatics and reaction conditions with selectivity towards BTX.

Catalyst	Conditions	Glycerol conv. (%)	Selectivity of aromatics (%)	Ref.
Dealuminated H-ZSM-5 (MFI) with initial Si/Al = 25	T = 400°C, glycerol/methanol = 40 wt.%, P = 0.1 MPa, WHSV: 0.71 h <sup>-1</sup> .	Ca. 98	ca.32 (C% BTX)	[16]
ZSM-5 (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 30)	T = 400°C, WHSV = 0.8 h <sup>-1</sup> .	100	>30 (C% BTX)	[18]
H-ZSM-5 (Si/Al <sub>2</sub> = 200)	T = 400°C, WHSV = 0.9 h <sup>-1</sup> .	100	18	[36]
Hierarchical Sn-ZSM-5	T = 400°C, WHSV = 0.9 h <sup>-1</sup> .	100	32 BTX	[36]
H-ZSM-5/Al <sub>2</sub> O <sub>3</sub> (60/40 wt%)	T = 550°C, WHSV = 1 h <sup>-1</sup> , TOS = 0–12 h.	—	19.5 (C% BTX)	[31]
H-ZSM-5/Al <sub>2</sub> O <sub>3</sub> catalysts (60/40 wt%)	T = 550°C, glycerol/oleic acid = 30/70 wt.%, TOS = 12 h, catalyst = 10 g.	—	26.7 (C% BTX)	[53]
H-ZSM-5 (SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> = 23)	T = 400°C, WSHV = 1 h <sup>-1</sup> , TOS = 5 h, 0–5 mbar.	—	28.1 (C% BTX)	[50]
Nano-sized H-ZSM-5 modified with carboxymethylcellulose sodium, NaCl, and sodium alginate	T = 400°C, WHSV = 0.9 h <sup>-1</sup> , catalyst = 1.2 g, glycerol/methanol = 40 wt.%.	—	35 (C% BTX)	[33]
Nano-sized H-ZSM-5 produced with sodium alginate (S-HZSM-5–0.75)	T = 400°C, WHSV = 0.96 h <sup>-1</sup> , catalyst = 1.2 g, glycerol/methanol = 40 wt.%.	100	35.06 (C% BTX)	[39]
Zn and Sn modified H-ZSM-5 (Si/Al = 25)	T = 400°C, WHSV = 0.71 h <sup>-1</sup> , glycerol/methanol = 40 wt.%, TOS = 1.5 ~ 2 h.	—	Ca. 35.7 (C% BTX)	[17]

**Table 1.**  
 Reported catalysts for glycerol conversion to aromatics.

#### 4. Deactivation of catalysts

Deactivation of catalyst is the loss of performance over time, and the difference in catalyst life depends on the contaminant and application. There are several mechanisms by which a catalyst can be deactivated including fouling, poisoning, sintering, leaching of active surface, and mechanical attrition. Thermal degradation deactivation could be found with catalysts used in petroleum cracking or polymers [54]. Poisoning is a deactivation mechanism whereby a contaminant is loosely or strongly adsorbed on the active sites of the catalyst, which prevents access to the reactant species. This type of deactivation could be reversible or irreversible. A notable poisoning mechanism is coking, which results in carbon deposits, which could mask the surface of the active sites or even block the catalyst pores (pore mouth-filling). Coke formation can be investigated by temperature gravimetric analysis and visual inspection to observe a color change, usually from off-white to black. In general, catalyst deactivation is inevitable, however, careful catalyst design and operation under mild conditions could prolong the catalyst life in any given application. The design of a suitable shape-selective catalyst with tunable acid properties could increase the peak BTX yield, and total productivity and prolong the catalyst life.

Aromatization reaction occurs through a series of consecutive reaction steps that involves aldol condensation, oligomerization, cracking, cyclization, dehydrogenation, dehydration, aromatization, etc. The strength and concentration of the acid sites influence the yield of BTX and BTEX; specifically, the amount of Bronsted and Lewis acids could propagate the deactivation of the catalysts. The Bronsted acid sites promote cracking, H-transfer, and oligomerization reaction and it is principally responsible for coke generation since it promotes the C – C bond breaking. A Survey of the literature shows that coke deposition is the main deactivation mechanism of the H-ZSM-5. The coking deactivation is considered reversible because the coke can be removed by oxidative treatment. The spent catalyst is subjected to high-temperature calcination in the air to decompose the coke deposits. For instance, the stability analysis for H-ZSM-5/Al<sub>2</sub>O<sub>3</sub> and H-ZSM-5 catalysts used in the synthesis of BTX showed that the Al<sub>2</sub>O<sub>3</sub> binder had more coke accommodation capacity than only H-ZSM-5. This was attributed to the mesoporous nature of Al<sub>2</sub>O<sub>3</sub>. Besides, the coke formation on the H-ZSM-5/Al<sub>2</sub>O<sub>3</sub> was amorphous, whereas that of H-ZSM-5 was graphitic [50, 55]. This implies that the decomposition temperature would vary widely and the graphitic coke obviously would result in irreversible deactivation [31].

There are other forms of deactivation of H-ZSM-5 related to the deformation of the structure, reduction of crystallinity, acid strength, and reduction of microporosity. As stated before, this type of structural defect can manifest during the top-down approach. A situation whereby the acidity is reduced by chemical treatment or steaming. In particular, the hydrophobicity and spatial constraints of some chemical agents such as CH<sub>3</sub>ONa and NaOH, in high concentrations could promote rapid desilication of the H-ZSM-5, which results in the damage of the catalyst microporous structure, diminished cage-like walls of the H-ZSM-5, and a drastic reduction in the crystallinity [52]. This situation presents a deformed H-ZSM-5 catalyst with low catalytic

Catalyst	Total acidity ( $\mu\text{mol NH}_3$ $\text{g}^{-1}$ cat fresh sample)	Total coke content (wt.%)	No. of reuse	catalyst lifetime (h)	Ref.
H-ZSM-5/Al <sub>2</sub> O <sub>3</sub> (60/40 wt%)	1051	16.0	5	8.5	[31]
ZSM-5	—	—	—	8	[19]
H-ZSM-5	1466	12	1	4	[15]
3 h 500°C/HZSM-5	413	—	—	8.5	[16]
H-ZSM-5/Al <sub>2</sub> O <sub>3</sub>	1051	16.8	5	12	[53]
3 h 450°C/0.3 M NaOH/ HZSM-5	615	22.82	—	3	[35]
S-HZSM-5-0.75	1240	1123.90*	3	11.5	[39]
Sn/HZSM-5@20Zn	878	—	3	11	[17]
H-ZSM-5/ Al <sub>2</sub> O <sub>3</sub>	1238	15	1	5.3	[56]
H-ZSM-5/SiO <sub>2</sub>	1286	9	1	3.66	[56]
H-ZSM-5/ Kaolinite	1318	13	1	4	[56]

\* is the peak area of the coke determined by the TPO method at 395°C.

**Table 2.**  
Reported H-ZSM-5-based catalysts, coke content, acidity, and number of reuse.

performance towards the aromatization reaction of glycerol. Another study reported in situ deactivation due to the conditions of the pyrolysis and reaction intermediates. He et al. [56] in their study to produce bio-based aromatics from glycerol revealed that dealumination of H-ZSM-5 occurred, which severely affected the crystallinity and acidity of the catalyst. This dealumination was attributed to catalyst exposure to steam generated by glycerol dehydration and the framework interaction with intermediate oxygenates. These types of deactivation are irreversible and eventually result in the complete deactivation of the catalyst. **Table 2** shows the total acidity of some reported catalysts, total coke content, and catalyst lifetime.

## 5. Prospects of catalytic glycerol to bio-aromatics

The conversion of glycerol to liquid fuels and aromatics is a notable research effort towards the production of “green” drop-in fuels that can be used as aviation fuel or bio-based chemicals. The glycerol is subjected to pyrolysis and sometimes in situ hydrotreating to reduce the oxygenates under heterogeneous catalysts. Zeolites of MFI (ZSM-5) have been widely applied because of the shape-selective nature, tunable acidity, and structure of the catalyst that promotes dehydration and hydrodeoxygenation reaction to produce hydrocarbon pools. In particular, protonated ZSM-5 (H-ZSM-5) has been synthesized for this synthesis with different modifications to evolve hierarchical pores and moderate the Bronsted acidity. However, there are continuous improvements to this strategy to increase the yield of BTX and BTEX from glycerol pyrolysis.

Notable about this is the modification of the H-ZSM-5 with metals and steaming to dealuminate the catalyst or alkaline treatment. These techniques are deployed to stabilize the zeolite and achieve higher selectivity of BTX. Conducted studies have evidenced that most strategies used to achieve dealumination or functionalization with metals are invasive, i.e., the crystallinity is sometimes affected significantly [44]. Hence, it is pertinent to look for non-invasive methods, such as low-temperature plasma techniques and isomorphous substitution methods [46, 48]. These methods are capable of achieving grafting metals on the H-ZSM-5 with minimal damage to the crystallinity or the framework structure. Also, the synthesis of the zeolite with pore-templating agents to evolve hierarchical pores would benefit the mass transport of reactants and products from the catalyst active sites. Another aspect that needs further insights is the optimization of reaction conditions such as the temperature, time on stream, weight hourly space velocity (WHSV), and methanol/glycerol ratio. Optimization of these reaction influencing parameters will result in minimal operation cost and provide insights into the mechanistic pathways involved.

Wholistic study of the deactivation mechanism of the unmodified H-ZSM-5 based on time and spaced resolved analysis suggested that coke deposit increases with the time on stream. The longer time on stream, the more coke accumulation. The mechanism proposed for this scenario posits that initially, coke is formed at the microporous channel of the H-ZSM-5 catalyst, followed by accumulation on the external surface of the zeolite as the time on stream increases [15]. The primary cause of the coke formation is the strong acid sites of the H-ZSM-5 catalysts, which have been improved by the design of shape-selective catalysts [35], metals, additive addition [33], and dealumination [43]. It is important to search for more binders that are capable of accumulating coke in amorphous form as opposed to the graphitic form, which is energy-intensive to regenerate.



## 6. Conclusions

Conclusively, the aromatization of glycerol via pyrolysis methods could be promoted using MFI zeolites (HZSM-5 and ZSM-5) catalysts. The acid form of ZSM-5 (H-ZSM-5) possesses appropriate crystallinity and acidity to tailor the reaction to produce benzene, toluene, and xylene (BTX) and/or benzene, toluene, ethylbenzene, and xylene (BTEX) with some oxygenates. The crystalline cage-like structure, acidity, pore size, and channel of the H-ZSM-5 catalysts influence the product's yield and distribution. Also, the reaction conditions such as temperature, time on stream, weight hourly space velocity significantly influence the product distribution and the carbon yield (BTX and BTEX). Also, these factors impact the coke formation mechanism, especially the time on stream and reaction temperature. The addition of metals like Zn, noble metals, Sn, binders ( $\text{Al}_2\text{O}_3$ ), and additives (heteroatoms) influence the H-ZSM-5 acid concentration, acid strength, and acid type. These chemical modifications of the H-ZSM-5 catalysts substitute the framework aluminum responsible for high Bronsted acidity, which promotes coke formation and stabilizes the catalysts. Deactivation caused by dealumination techniques and *in situ* reaction conditions destroys the crystalline cage-like zeolite framework and is irreversible. Whereas reversible coke deposition is removed by energy-intensive oxidation that could impact the porosity and crystalline structure of the catalyst.

Hence, it is recommended that further studies should be conducted on the synthesis of shape-selective and hierarchical porous H-ZSM-5 catalyst with moderate Bronsted acidity to minimize coke formation and promote mass transport. Non-invasive modification methods such as plasma techniques should be adopted to achieve metal and heteroatoms incorporation into the cage-like structure of the H-ZSM-5 without damage to the framework. An in-depth study on the techno-economic analysis and life cycle analysis of the aromatization reaction will provide insights on the associated costs for comparison and the environmental impact of this process. Also, machine learning methods should be deployed to optimize the reaction conditions.

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## Conflict of interest

The authors declare no conflict of interest.

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