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Overview of BTX (Benzene, Toluene, Xylene) Production from Polyethylene Pyrolysis over Ga and Zn Modified HZSM-5 Catalyst

Shafira Hakim Yanewati[1] **and Dijan Supramono**[1*]

[1]Chemical Engineering Department, Faculty of Engineering, Universitas Indonesia, Kampus UI, Depok, 16424, Indonesia

[*]*E-mail*: dsupramo@che.ui.ac.id

Abstract

The increase in Indonesia's BTX chemical production was carried out to keep pace with global demand trends. The raw material for alternative production is household waste in Indonesia, of which 36% is plastic. Polyolefins make up 76% of the composition of household plastic waste. The rapidly developed BTX production process is the depolymerization of polyolefin plastics by pyrolysis and catalyst modification for catalysis. Polyolefin plastic in the form of polyethylene produces the highest aromatic yield and selectivity among other types of plastic in plastic waste. This study compared two scenarios with the highest yield of aromatics using different catalysts as base literature with an additional overview regarding the topic related. The process scenarios being compared are polyethylene pyrolysis over CaO with Ga/ZSM-5 catalyst and Zn-ZSM-5 catalyst. Literature overview obtained the overall BTX production progress over time and the potential of polyethylene catalytic pyrolysis for further study.

Keywords: *BTX; polyolefin plastic; pyrolysis; catalyst; overview.*

Introduction

The chemical industry is one of the main contributors to the performance of the non-oil and gas processing industry in Indonesia. Globally, it is estimated that the need for BTX (Benzene, Toluene, Xylene) will increase by 10% annually for a decade after 2020 with Indonesia planning to increase production to reduce the burden of imports (Warsito, 2022). In the process, there are various alternatives to produce BTX apart from the commonly used petroleum such as naphtha, namely from triglycerides in vegetable oils and polyolefin plastics in plastic waste. The potential in Indonesia for polyolefin plastics can be obtained from waste where there is 36% of total household waste in Indonesia in 2021 (SIPSN, 2022). Previous research related to BTX production includes process variations, feed types, catalysts, and operating conditions but has not obtained high yields or selectivity (Zhu, Wang, & Li, 2013), and the energy consumption is still high (Chen, et al., 2021). Thus, research to enhance further understanding of the BTX production process, as well as global industry needs and potential plastic waste reduction solutions, is needed.

The production of BTX generally uses the principle of the Diels-Alder reaction to produce aromatic compounds. One of the rapidly developed processes is the depolymerization of polyolefin plastics by pyrolysis (Damayanti, et al., 2022) and catalyst modification (Akubo, Nahil, & Williams, 2019) to cut the reaction pathway so that energy consumption is reduced (Yansaneh & Zeins, 2022). Polyolefin plastics which undergo pyrolysis to form char (solid fraction), hydrocarbons, and pyrolysis oil (liquid fraction) with polyethylene produce the highest yield and aromatic selectivity among other types of plastics (Radhakrishnan, et al., 2022). Various studies have been carried out to support the development of catalyst modification and optimization of pyrolysis in catalytic pyrolysis to obtain Monocyclic Aromatic hydrocarbons (MAHs) such as BTX. Research that has been carried out includes modification of the catalyst into a mixture of CaO with Ga/ZSM-5 (Fu, et al., 2022) and Zn-ZSM-5 (Wang, et al., 2022) under various operating conditions which managed to obtain yields of MAH by 90%.

A literature study was conducted to define an overview of the overall potential and picture of BTX production from certain catalysts as a reference for Indonesia’s industrial development. References from this study then could be further used for techno-economic analysis with reactor and process design or application in industrial processes. Techno-economic research, for example, is specific and there is no simultaneous research on process simulation and techno-economic analysis of BTX production from polyethylene pyrolysis. This research will analyze works of literature regarding polyolefin, preferably polyethylene, pyrolysis over Ga/ZSM-5 and Zn/ZSM-5 catalysts as a comparison with control reference using ZSM-5 or HZSM-5 catalysts. A brief simulation to support overview analysis will use Aspen Hysys.

Research Methodology

The literature review approach used in this study is semi-systematic. Evaluated research areas of qualitative and quantitative analysis are grouped based on catalyst modified on ZSM-5 which progresses over time. The literature researched may obtain experimental data or offer either bulk or microkinetic modelling of reactions related to catalytic pyrolysis. The relationship analysis between the two types of analysis can also be added to the literature studied because it is generally part of the topic as a missing link of explanation.

In mathematical modeling for kinetic properties and phenomena prediction, various kinetic models are used to describe the relationship between the rate r_l for reaction l and concentration of reactant i where concentration can be interchangeable with partial pressure p, mole fraction, etc. Standl and Hinrichsen (2018) listed several basic kinetic models for catalysts such as power law, Langmuir (L), Langmuir-Hinshelwood (LH), Eley-Rideal (ER), and Higen-Watson (HW). A common approach is L-isotherm in Equation (1) with relative coverage θ_i of species i on the catalyst surface and specific adsorption equilibrium constant K_i^{ads}.

$$\theta_i(T) = \frac{K_i^{ads}(T)\, p(i)}{1+K_i^{ads}(T)p(i),} \tag{1}$$

The simplest way to construct a kinetic model is using power law expression as shown in Equation (2). Rate constant k_l and reaction order κ are obtained by fitting the model to experimental data.

$$r_l = k_l p\ (i)^{\kappa} \tag{2}$$

For monomolecular reactions, the reactant adsorption can be described via Langmuir isotherm in Equation (3).

$$r_l = \frac{k_l K_i^{ads} p(i)}{1+\sum_j K_j^{ads} p(j)} \tag{3}$$

A similar expression was obtained for bimolecular reactions where both reactant i and v must be adsorbed before the reaction referred to as the Langmuir-Hinshelwood mechanism shown in Equation (4).

$$r_l = \frac{k_l K_i^{ads} p(i) K_i^{ads} p(v)}{\left(1+\sum_j K_j^{ads} p(j)\right)^2} \tag{4}$$

Lastly, the temperature dependence of the rate constants is expressed via the Arrhenius approach in Equation (5) using activation energy Ea.

$$k = A \exp\left(-\frac{Ea}{RT}\right) \tag{5}$$

Potential reaction components of aromatization towards BTX production simulated through polyethylene general thermal cracking mechanism presented by Selvaganapathy, Muthuvelayudham, and Kumar (2018) as shown in Equation (6). Simple conversion will be using Aspen Hysys's pyrolytic reactor at atmospheric pressure, 450^{o}C temperature, 95% conversion, and 100 kg/h of polyethylene feed.

$$36C_2H_4 \rightarrow H_2 + CH_4 + C_2H_6 + C_2H_4 + C_3H_6 + C_3H_8 + C_4H_{10} + C_8H_{16} + C_{16}H_{32} + C_{28}H_{56} + 5C \tag{6}$$

Result and Discussion

Zeolites and related nanoporous materials are widely used as adsorbents, ion exchangers, and catalysts. Zeolite is a mineral consisting of hydrated alumina silicate crystals containing alkaline or alkaline earth cations. The structure of the zeolite is an inorganic polymer crystal with a tetrahedral framework of AlO_4 and SiO_4. In the zeolite structure, all Al atoms are in a tetrahedral form so that the Al atom will be negatively charged because it coordinates with the oxygen atom. Zeolites can be manipulated by inserting certain metals so that they have certain catalytic properties (Haslego, 1999). Zeolite Socony Mobil-5 (ZSM-5) is a part of silica pentacle zeolite whereas one of the most common heterogeneous catalysts used for various applications. Zeolite has a high content of silicon and low content of aluminum, which makes the framework hydrophobic. H-ZSM-5 is the protonic type or H form of ZSM-5 and has been widely used in industrial chemical processes catalyzed by acid catalysts (Shaikh, 2015).

The use of a Zeolite catalyst (HZSM-5) in plastic cracking results in a concentration of aromatic compounds reaching 83% wt so that it can be used for polyethylene pyrolysis. HZSM-5 Zeolite is acidic in which the acid site or Bronsted acid site on the HZSM-5 catalyst can form coke which reduces the performance of the catalyst. Accumulation of coke on the catalyst site, if left unchecked, can form accumulations on the surface of the catalyst leading to catalyst deactivation. Catalyst deactivation occurs within a certain period due to the accumulation of short carbon in pores or sites that are too active so that there are carbon deposits. Catalyst deactivation can be prevented by regeneration through combustion (Shemfe, Gu, & Fidalgo, 2017). Because the need for repeated catalyst regeneration is not sustainable for the process, an alternative is to modify the HZSM-5 catalyst, such as adding support or a modifier.

The HZSM-5 derivative used needs to be microporous in size because the catalyst used is Bronsted acid and Lewis acid catalyst and the product target is short carbon chain olefins (MAH) (Rane, Kersbulck, Santen, & Hensen, 2008). Akubo, Nahil, & Williams (2019) found a greater concentration of MAH and a high yield percentage of aromatic hydrocarbons with a deficiency in the formation of carbon deposits on the HZSM-5 derivative catalyst with a modified transition metal support. The problem of carbon deposits is handled by further research on the preparation and effective composition of the catalyst. Notation after modification for catalyst usually writes off as Ga/ZSM-5 and Zn/ZSM-5. Fu, et al. (2022) and Wang, et al. (2022) succeeded in obtaining carbon deposits below 1 wt% from catalyst, a mixture of CaO with Ga/ZSM-5 and Zn/ZSM-5 respectively where there were variations in composition and process operating conditions such as temperature and pressure.

Various studies related to Ga and Zn/ZMS-5 catalysts have been carried out in which this study will only evaluate a few in each group. The research evaluated includes but is not limited to the aromatization of polyolefin or their cracking products such as alkanes and alkenes. The sequence of studies evaluated is based on the year the research results were published. Evaluation results in general can then be analyzed. Table (1) shows an overview of catalytic pyrolysis research for aromatic production over the Ga/ZSM-5 catalyst.

Table 1. Review of Ga/ZSM-5 Catalyst Research

Reference	Feed	Process	Result
Fu, et al. (2022)	Linear Low-Density Polyethylene (LLDPE) with a combination of Cao and Ga/ZSM-5 catalysts.	Three catalytic modes, CaO before the catalyst layer Ga/ZSM-5, CaO after Ga/ZSM-5 catalyst, and mixed mode, done for catalytic pyrolysis LLDPE. Ratio variation molar Ga with ZSM-5. Temperature 240-440^{o}C and atmospheric pressure with heating rate 5^{o}C/minute at fix-bed reactor.	1. The selectivity to MAH increased from 70.35% of the time using pure HZSM-5 to 94.02% with 7% weight Ga modified HZMS-5. A mixture of CaO and Ga/ZSM-5 gave the best results high with 90% MAH on the product.
Liu, et al. (2015)	Propane with Ga-modified-HZSM-5	Aromatization in a stainless-steel at 550°C and WHSV of 1.0 h–1 (pure propane) under atmospheric pressure.	1. Ga species improved the aromatics selectivity and inhibited cracking reactions. After being reduced in hydrogen, Ga2O3 was most likely transformed into Ga^+ and GaH^{2+} species, and migrated into the zeolite channels. Subsequent air-oxidation treatment of the reduced (Ga,H) ZSM-5 led to formation of GaO^+ species, thus greatly increasing the aromatization activity. 2. A kinetic model for ethene and propene aromatization over HZSM-5 and GaHZSM-5 is developed. 3. About 85% of dienes and 55 % of aromatics are formed on gallium active species. In the case of propene conversion, these species are responsible for the formation of 70 % of dienes and 25% of aromatics.
Lukyanov, Gnep, and Guisnet (1994)	Ethene and Propene over Ga/HZSM-5	Kinetic modelling with parameters from Gnep et al. (1988) and Doyemet (1989) where parameters were obtained on catalyst time on stream was 2-3 min in a flow reactor at 530"C and hydrocarbon pressure of 1 bar. Aromatization over HZSM-5 and Ga/HZSM-5.	1. Aromatics formation accelerates olefin conversion due to the olefin consumption, on one hand, and inhibits olefin conversion due to the partial blocking of the zeolite catalytic sites, on the other hand. Because of this, both the increase and the decrease in olefin conversion over GaHZSM-5 can be observed (in comparison with HZSM-5), depending on the feed olefin and on the reaction conditions.

Table (2) shows an overview of catalytic pyrolysis research for aromatic production over the Zn/ZSM-5 catalyst.

Table 2. Review of Zn/ZSM-5 Catalyst Research

Reference	Feed	Process	Result
Wang, et al. (2022)	Linear Low Density Polyethylene (LLDPE) with Zn/ZSM-5 catalyst.	Using a high-pressure reactor. Variations in pressure, temperature, and loading percentage Zn on ZSM-5 catalyst. There are three stages research namely stage -1 (340ºC; 1 bar; 1 wt%), 0 (380ºC; 4 bar; 3 wt%), and 1 (420ºC; 7 bar; 3 wt%).	1. The proportion of aromatics in the liquid product reaches 90%, and the yield aromatic monocyclic by mass of reactants is 51% at optimal conditions. 2. The production of carbon deposits on the catalyst is low (only about 1%), which allows for a higher liquid yield. 3. Parameter pairing mechanism of several factors in the reaction depolymerization/aromatization is proposed.
Liang, et al. (2019)	Ethane with Zn-HZMS-5 catalyst	Aromatization was performed in a home-built flow reactor system. The reaction was initiated by abrupt switching of the influent gas from Ar to C_2H_6 (20 mL/min) at 550°C under atmospheric pressure at a gas hourly space velocity (GHSV) of 8000 h^{-1}.	1. The early-stage ethane conversion and BTX selectivity both increased with decreasing Si/Al_2 ratios. Specifically, the space−time yields of BTX increase linearly with increasing Brønsted acidity, indicating Brønsted acids as the main active sites for BTX.
Chen, et al. (2015)	Ehylene with Zn-modified-HZMS-5 catalyst.	Aromatization in a continuous flow fixed bed reactor with N_2 (30 ml/min) where ethylene was pumped into the reactor with a weight hourly space velocity (WHSV) of 0.9 h^{-1}. The reaction was carried out at 480°C and 0.1 MPa. Zn-containing HZSM-5 zeolites with different Zn contents were prepared by ion exchange and physically mixing methods and were characterized.	1. The preparation method has a significant influence on the distribution of the Zn species. The catalytic behavior of Zn-containing HZSM-5 with different Zn contents showed that the $Zn(OH)^{+}$ and ZnO species were responsible for aromatic formation from ethylene.

Thus, Ga and Zn modified catalyst studies have progressed over years where active applications are also a big interest especially for industrial process. The newest references could be used for main source of further study in implementing simulation for industrial scale because the high MAH yield where Fu et al. (2022) achieved higher percentage.

Extensively, thermal cracking conversion was conducted in a pyrolytic reactor with Aspen Hysys based on Selvaganapathy, Muthuvelayudham, and Kumar's (2018) steady-state simulation for polyethylene. The result was evaluated to predict the feasibility and information needed to simulate the process. Simulation under inert gas nitrogen obtained that simulation converges. Further study of process and catalyst can be done by simulation using a kinetic model of each catalyst for monocyclic aromatic hydrocarbons as BTX production study over polyethylene catalytic pyrolysis. Catalyst specification also needed to be specified along with process optimal operation condition. Table (3) shows Migliori, et al. (2017) kinetic parameters for Ga/ZSM-5 of propane aromatization at optimal temperature.

Table 3. Ga/ZSM-5 Kinetic Parameters for BTX Production

Reaction Class	k [h^{-1}]	Reaction T [ºC] 525ºC	Ea [kJ/mol]	R^2
	k_p	1.564 ± 0.046		
Cracking	k_C	1.028 ± 0.039	143.9 ± 27.1	0.966
Benzene formation	k_b	0.071 ± 0.004	145.3 ± 41.4	0.925
Toluene formation	k_T	0.128 ± 0.004	141.2 ± 41.4	0.911
Xylene formation	k_X	0.031 ± 0.05	120.4 ± 34.7	0.923

Table (4) shows Zn/ZSM-5 kinetic parameters presented by Liang, Toghiani, and Xiang (2018) for BTX formation from ethylene and ethane at optimal temperature. Both data can be used as a starting point for further topic study.

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Table 4. Zn/ZSM-5 Kinetic Parameters for BTX Production

T [°C]	**Feed**	**Rate Constant *k* ($10^{-3}s^{-1}$)**		
		Benzene (C_6H_6)	**Toluene (C_7H_8)**	**Xylene (C_8H_{10})**
525	C_2H_6	8.6	10.0	/
550	C_2H_6	12.4	14.0	/
575	C_2H_6	14.0	18.0	/
600	C_2H_6	19.0	27.0	/
425	C_2H_4	5.6	5.6	5.8
450	C_2H_4	7.9	8.0	6.9
475	C_2H_4	11.0	9.6	8.0
500	C_2H_4	13.4	12	10.7
Feed		**Arrhenius plot gradient**		
Ethane (C_2H_6)		-8808.1	-6825.4	/
Ethylene (C_2H_4)		-6825.4	-5346.5	-4266.1

Conclusion

This study aims to review overall BTX production progress over time and the potential of polyethylene catalytic pyrolysis over Ga and Zn modified HZSM-5 catalyst for further study. Mainly, this study compared two scenarios with the highest yield of aromatics using different catalysts as base literature with an additional overview regarding the topic related. The process scenarios being compared are polyethylene pyrolysis over CaO with Ga/ZSM-5 catalyst and Zn-ZSM-5 catalyst. Literature review conducted not only the progression of usage but also the kinetic models of related catalyst for process to set the groundwork of simulation. The result of overview shows that there is a potential of using Ga and Zn modified HZMS-5 catalyst for industrial polyethylene pyrolysis process through operation and catalyst properties optimization.

Notation List

A = Pre-exponential factor [L.s/mol]
Ea = Activation Energy [kJ/mol]
k = Rate constant [s^{-1}]
P = Pressure [atm]
R = Gas constant [8.314 $Jmol^{-1}K^{-1}$]
T = Temperature [°C]

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