Production of Hydrocarbons from Bioethanol: A Review

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Abstract: Bio-ethanol can be used to produce a number of chemicals that are important to industries. Extensive research has been done for the production of valuable chemicals from ethanol in recent years. Acetaldehyde is produced at basic sites of catalyst, whereas ethylene is produced on the acidic sites. Ethylene can be produced through the dehydration of ethanol. Ethylene can be used as raw material for polymers' production (e.g., polyethylene, polyvinylchloride, and polystyrene), ethylene glycol, ethylene oxide, ethylbenzene, etc.

Keywords- Bio-ethanol, Selectivity, Yield, Ethylene, Propylene.

I. INTRODUCTION

Fossil fuels are the major energy sources used in the world today. The increasing energy and fuel demand and the declining sources of fossil fuels are necessary to look for alternative renewable sources of energy [1].

Biomass, a renewable energy source has several significant advantages: its use reduces the dependence of the chemical industry on non-renewable resources, considered as CO_2 neutral, and also methanol, ethanol, dimethyl ether (DME), synthetic natural gas (SNG), hydrogen, etc. are produced[2,3]. The most prominent biofuel worldwide is ethanol (EtOH), which accounted for 86% of biofuels produced in the United States in 2018 [4].

Ethanol can be produced in two ways: Fermentation of plant sugars and petroleum feedstock. The low-cost, renewable chemical-derived bioethanol is produced by fermenting non-edible lignocellulose obtained from biomass [5,6,7](**Figure. 1)**. The alcohol obtained in this way is usually called bio-ethanol [8]. This route is unsustainable to satisfy the increasing ethanol demand for a world with a growing population [9]**.**In the production of olefins and aromatics, ethanol is a green alternative to petroleum [10].
Due to the petrochemical industry's development and oil processing, more than half a million products are produced today using a catalyst [11]. Ethanol is converted into various chemicals such as ethylene, propylene, hydrogen,1,3-butadiene, acetaldehyde, n-butanol, acetic acid, etc. [12,13,14].

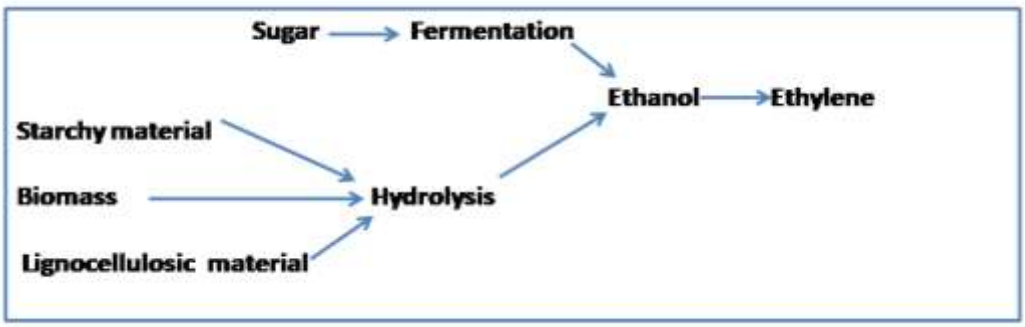

Figure 1. The production of ethanol from various materials.

Naptha or liquefied petroleum gas has used as raw material for ethylene production using steam thermal cracking [6,15,16]. Fossil fuel depletion has created interest in the researcher to produce ethylene from renewable energy sources such as biomass, agricultural waste, etc. The essential raw material in the chemical sector industry is ethylene in the generation of plastics, rubbers, ethylene glycol, vinyl chloride resin, acetic acid, styrene, and other chemicals [17].

Fluid catalytic cracking of naphtha and steam cracking help in the production of propylene [18]. The basic material for propylene is polypropylene resin, acrylonitrile, acrylic acid, propylene oxide, isopropyl alcohol, acetone, etc. Production of propylene from ethanol with the help of renewable biomass is a carbon-neutral process[19].

The reaction network for ethanol's catalytic transformation includes the parallel formation of ethylene and acetaldehyde via dehydration or dehydrogenation. Ethanol conversion to propylene pathway can be shown as Ethanol → Ethylene and Ethanol → Acetaldehyde → Acetone →Propylene [20].
Arenamnart and Trakarnpruk 2006 [21] produced ethylene from ethanol by modified Mordenite catalyst with the Zn, Mn, Co, Rh, Ni, Fe, and Ag metals. Zr-Ag modified modernite catalyst showed a 100% conversion with 98% maximum ethylene yield with the reaction condition of T =350°C, P = 1atm, and WHSV = $1hr^{-1}$. Bi et al. 2011 [22] investigated Ce-modified ZSM-5 for ethylene production. 98.8% maximum ethanol conversion and 68.9% maximum ethylene selectivity was achieved at T=400°C, P = 1atm and WHSV = $3hr^{-1}$ reaction condition. Xin et al. 2014 [23] investigated HZSM-5 and produced 76% ethanol conversion

and 18.9% ethylene selectivity [T = 200°C, and P = 1atm]. Garcia et al. 2018 [24] investigated the mesoporous γ-Al_2O_3 catalyst for ethanol's transformation to ethylene. 99.7% conversion of ethanol achieved along with 97% selectivity of ethylene [T= 723K, and P= 4torr]. Banzaraktsaeva et al. 2019 [25] investigated alumina catalysts for 94.2% ethanol conversion and 93.35% selectivity of ethylene at 400°C temperature and 1atm pressure.

Sugiyama et al. 2010 [26] studied Ni/MCM-41N catalyst for propylene production from ethanol. 96% ethanol transformed to produce 13% selectivity of propylene at 673K temperature and 1atm pressure. Song et al. 2013 [27] investigated the ZSM-5 catalyst modified over zirconium and phosphorus for ethanol to propylene production. The maximum propylene yield was 29.2% with 100% conversion of ethanol [T = 823K, and P=0.1MPa]. Tsunoji et al. 2013 [28] investigated the TON type zeolite catalyst for converting ethanol into propylene production. The conversion of ethanol achieved was 100% with 25.8% maximum propylene yield production [T= 550°C, and P = 0.1MPa]. Xia et al. 2016 [29] showed a zeolite (HZSM-5) catalyst for propylene production. The maximum propylene yield production was 25.4% at temperature 773K and pressure 0.1MPa. Xia et al. 2019 [30] investigated La modified zirconia for ethanol transformation to propylene. 93.6% transformation of ethanol was achieved along with 42.3% propylene yield [T = 450°C, P = 1atm, and W/F = 0.045g/ml/min]. Duan et al. 2011 [18] studied the HZSM-5/SAPO-34 catalyst for the conversion of ethanol to propylene. 100% ethanol transformation with 28% maximum propylene yield was achieved [T= 550°C, and P = 0.1MPa]. Duan et al. 2013 [19] also showed HZSM-5/SAPO-34 catalyst for propylene production from ethanol. The conversion of ethanol achieved was 100% with 34.5% maximum propylene yield [T= 500°C, and P = 0.1MPa].

Inaba et al. 2006 [31] investigated Mg, Cr, Fe, Co, Ni, Cu, Ga, Ru, Rh, Pd, Ag, Re, Ir, Pt, and Au promoted HZSM-5 for ethanol transformation to hydrocarbon. Pt modified HZSM-5 catalyst showed 98% transformation of ethanol and 91.89% hydrocarbon selectivity at T = 400°C, and WHSV = 0.158 mol/gcat/h. Ramasamy et al. 2014 [32] also investigated HZMS-5 catalyst for hydrocarbon production from ethanol and showed 100% ethanol conversion and 68% hydrocarbon yield [T = 360°C, P = 300psig, and WHSV = 4.73 h^{-1}]. Astafan et al. 2016 [33] studied HZSM-5 catalyst produced 98% conversion of ethanol along with 82% maximum hydrocarbon yield [T = 350°C, P = 3 MPa, GHSV = 5.3hr]. Abdullah and Zaidi 2016 [5] investigated over ZnO and NiO modified ZSM-5 catalyst for ethanol transformation into hydrocarbon. The transformation of ethanol was 100% and hydrocarbon yield was 55% at (1.5 Zn/4 Ni)/ZSM-5 catalyst [T = 410°C, P 1atm, and WHSV = 3.5h^{-1}]. Liu et al. 2020 [34] investigated Ni/ZSM-5 catalyst for ethanol transformation into hydrocarbon. 90% ethanol transformed, and 50% selectivity of hydrocarbon was achieved at temperature 623K and WHSV 1.8 h^{-1}. **Table 1** shows the literature overview of catalysts used for ethanol transformation along with reaction condition, conversion, selectivity, and yield of the product.

Table 1 The literature overview of the catalysts used in ethanol conversion to major products (ethylene and propylene).

S.NO.	Reaction	Catalyst	Reaction Condition	Conversion	Selectivity	Yield	References
1.	Ethanol→Ethylene	Zn-Ag/DM	T = 350°C, P = 1atm WHSV = 1 hr^{-1}	100%	–	98%	[21]
2.	Ethanol→Ethylene	Ce -HZSM −5	T=400°C, P = 1atm WHSV = 3hr^{-1}	98.8%	68.%	–	[22]
3.	Ethanol→Ethylene	HZSM-5	T = 200°C, P = 1atm	76%	18.9%		[23]
4.	Ethanol→Ethylene	γ-Al_2O_3	T = 723K P = 4 torr	99.7%	97%	-	[24]
5.	Ethanol→Ethylene	Al_2O_3	T =400°C P = atm. press	94.2%	93.5%	-	[25]
6.	Ethanol→Propylene	Ni/MCM-41N	T = 673K P = 1atm	96%	13%	-	[26]
7.	Ethanol→Propylene	P/Zr/ZSM-5	T = 823K P = 0.1MPa	100%	-	29.2%	[27]
8.	Ethanol→Propylene	St/HTON	T = 550°C P = 1atm W/F=0.05gmin/mL	100%	-	25.8%	[28]

9.	Ethanol→Propylene	HZSM-5	T = 773K P = 0.1MPa W/F = 0.0025g/ ml/min	-	-	25.4%	[29]
10.	Ethanol→Propylene	La/ZrO_2	T= 450°C, P=1.11MPa, W/F=0.045g/ml/min	93.6%	-	42.3%	[30]
11.	Ethanol→Propylene	HZSM-5/SAPO-34	T = 500°C P= 0.1MPa	100%	-	28%	[18]
12.	Ethanol→Propylene	HZSM-5/SAPO-34	T = 500°C P= 0.1MPa	100%	-	34.5%	[19]
13.	Ethanol→Hydrocarbon	HZSM-5	T = 360◦C, P = 300 psig, WHSV= 4.73hr^{-1}	100%	99%	68%	[32]
14.	Ethanol→Hydrocarbon	HZSM-5	T = 350°C, P = 3.0 MPa, GHSV = 5.3hr^{-1}	98%	–	82%	[33]
15.	Ethanol→Hydrocarbon	1.5Zn/4Ni/ZSM-5	T = 410 °C, P = 1 atmospheric, WHSV = 3.5hr^{-1}	100%	–	55%	[5]
16.	Ethanol→Hydrocarbon	Ni/HZSM-5	T = 623K WHSV = 1.8hr^{-1}	90%	50%	-	[34]
17.	Ethanol→Hydrocarbon	Pt/HZSM-5	T = 400 °C, WHSV = 0.158 mol/gcat/h,	98%	91.89%	–	[31]

II. CONCLUSION

Presently, there is a hike in the prices of petroleum products due to high demand. Also, stringent laws are formed related to pollution; thus, waste biomass can be used as a possible substitute for biofuel biochemical production. Bioethanol, which is obtained from renewable waste materials, can be used in the automobile and industrial sector. Bioethanol is produced due to thermochemical and biological conversion processes.

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REFERENCES

[1] Li, S., Li, M., Zhang, C., Wang, S., Ma, X., and Gong, J., 2012. Steam reforming of ethanol over Ni/ZrO_2 catalysts: Effect of support on product distribution. *International journal of hydrogen energy*, 37, 2940-2949.

[2] Molino, A., Larocca, V., Chianese, S., and Musmarra, D., 2018. Biofuels Production by Biomass Gasification: A Review. *Energies*, 11, 1–31.

[3] Godova, N. and Horvath, B., 2018. Catalytic conversion of ethanol into alkenes and acetaldehyde. *Acta Chimica Slovaca*, 11, 11—20.

[4] Eagan, N.M., Kumbhalkar, M.D., Buchanan, J.S., Dumesic, J.A., and Huber, G.W., 2019. Chemistries and processes for the conversion of ethanol into middle- distillate fuels. *Nature reviews chemistry*, 3, 223–249.

[5] Abdullah, T.A. and Zaidi, H.A., 2016. Effect of ZnO and NiO Modified HZSM-5 Catalyst for Ethanol Conversion to Hydrocarbons. *International Journal of Chemical Engineering and Applications*, 7, 151–155.

[6] Mohsenzadeh, A., Zamani, A., and Taherzadeh, M.J., 2017. Bioethylene Production from Ethanol: A Review and Techno-economical Evaluation. *ChemBioEng Reviews*, 4, 75–91.

[7] Zhang, M. and Yu, Y., 2013. Dehydration of ethanol to ethylene. *Industrial and Engineering Chemistry Research*, 52, 9505–9514.

[8] Hansen, J.R., Falsig, H., Jorgensen, B., and Christensen, C.H., 2007. Bioethanol : fuel or feedstock. *Journal of chemical technology biotechnology*, 82, 329–333.

[9] Li, X., Deng, Y., Yang, Y., Wei, Z., Cheng, J., Cao, L., Mu, D., Luo, S., Zheng, Z., Jiang, S., and Wu, X., 2017.

Fermentation Process and Metabolic Flux of Ethanol Production from the Detoxified Hydrolyzate of Cassava Residue. *Frontiers in Microbiology*, 8, 1–12.

[10] Oliveira, T.K.R., Rosset, M., and Perez-Lopez, W.O., 2018. Ethanol dehydration to diethyl ether over Cu-Fe/ZSM-5 catalysts. *Catalysis Communications*, 104, 32–36.

[11] Makshina, E. V., Dusselier, M., Janssens, W., Degreve, J., Jacobs, P.A., and Sels, B.F., 2014. Review of old chemistry and new catalytic advances in the on-purpose synthesis of butadiene. *Royal society of chemistry*, 43, 7917–7953.

[12] Zabed, H., Sahu, J.N., Suely, A., Boyce, A.N., and Faruq, G., 2017. Bioethanol production from renewable sources: Current perspectives and technological progress. *Renewable and Sustainable Energy Reviews*, 71, 475–501.

[13] Xue, F., Miao, C., Yue, Y., Hua, W., and Gaoa, Z., 2017. Direct conversion of bio-ethanol to propylene in high yield over the composite of In_2O_3 and zeolite beta. *Green chemistry*, 19, 5582–5590.

[14] Rana, P.H. and Parikh, P.A., 2020. Catalytic Transformation of Ethanol to Industrially Relevant Fine Chemicals. *In*: *Biorefinery of Alternative Resources: Targeting Green Fuels and Platform Chemicals*. 49–74.

[15] Ren, T., Patel, M., and Blok, K., 2006. Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes. *Energy*, 31, 425–451.

[16] Zacharopoulou, V. and Lemonido, A.A., 2018. Olefins from Biomass Intermediates: A Review. *Catalysts*, 8, 1–19.

[17] Harmsen, P.F.H., Hackmann, M.M., and Bos, H.L., 2014. Green building blocks for bio-based plastics. *Biofuels Bioproducts Biorefineries*, 8, 306–324.

[18] Duan, C., Zhang, X., Zhou, R., Hua, Y., Chen, J., and Zhang, L., 2011. Hydrothermally Synthesized HZSM-5/SAPO-34 Composite Zeolite Catalyst for Ethanol Conversion to Propylene. *Catalysis Letters*, 141, 1821–1827.

[19] Duan, C., Zhang, X., Zhou, R., Hua, Y., Zhang, L., and Chen, J., 2013. Comparative studies of ethanol to propylene over HZSM-5/SAPO-34 catalysts prepared by hydrothermal synthesis and physical mixture. *Fuel Processing Technology*, 108, 31–40.

[20] Xia, W., F. Wang, X. Mu, K. Chen, A. Takahashi, I. Nakamura, and T. Fujitani. 2017. Highly Selective Catalytic Conversion of Ethanol to Propylene over Yttrium-Modified Zirconia Catalyst. *Catalysis Communications* 90: 10–13.

[21] Arenamnart, S. and Trakarnpruk, W., 2006. EthanolConversiontoEthyleneUsing Metal-Mordenite Catalysts. *International Journal of Applied Science and Engineering*, 4, 21–32.

[22] Bi, J., Liu, M., Song, C., Wang, X., and Guo, X., 2011. C_2- C_4 light olefins from bioethanol catalyzed by Ce-modified nanocrystalline HZSM-5 zeolite catalysts. *Applied Catalysis B: Environmental*, 107, 68–76.

[23] Xin, H., Li, X., Fang, Y., Yi, X., Chu, Y., Zhang, F., Zheng, A., Zhang, H., and Li, X., 2014. Catalytic dehydration of ethanol over post-treated ZSM-5 zeolites. *Journal of Catalysis*, 312, 204–215.

[24] Garcia, M.V., Garbarino, G., Finocchio, E., Busca, G., Del Hoyo Martinez, C., and Escribano, V.S., 2018. Characterization of a mesoporous γ-Al_2O_3catalyst: Influence of their properties on ethanol conversion. *Materials Today: Proceedings*, 5, 17515–17524.

[25] Banzaraktsaeva, S.P., Ovchinnikova, E.V., Danilova, I.G., Danilevich, V.V., and Chumachenko, V.A., 2019. Ethanol-to-ethylene dehydration on acid-modified ring-shaped alumina catalyst in a tubular reactor. *Chemical Engineering Journal*, 374, 605–618.

[26] Sugiyama, S., Kato, Y., Wada, T., Ogawa, S., Nakagawa, K., and Sotowa, K.-I., 2010. Ethanol Conversion on MCM-41 and FSM-16, and on Ni-Doped MCM-41 and FSM-16 Prepared without Hydrothermal Conditions. *Topics in catalysis*, 53, 550–554.

[27] Song, Z., Liu, W., Chen, C., Takahashi, A., and Fujitani, T., 2013. Production of propylene from ethanol over ZSM-5 co-modified with zirconium and phosphorus. *Reaction Kinetics, Mechanisms and Catalysis*, 109, 221–231.

[28] Tsunoji, N., Furumoto, Y., IDE, Y., Sadakane, M., and Sano, T., 2013. Conversion of Ethanol into Propylene over TON Type Zeolite. *Journal of the Japan Petroleum Institute*, 56, 22–31.

[29] Xia, W., Chen, K., Takahashi, A., Li, X., Mu, X., Han, C., Liu, L., Nakamura, I., and Fujitani, T., 2016. Effects of particle size on catalytic conversion of ethanol to propylene over H-ZSM-5 catalysts—Smaller is better. *Catalysis Communications*, 73, 27–33.

[30] Xia, W., Wang, F., Wang, L., Wang, J., and Chen, K., 2019. Highly Selective Lanthanum-Modified Zirconia Catalyst for the Conversion of Ethanol to Propylene: A Combined Experimental and Simulation Study. *Catalysis letters*, 2, 1–9.

[31] Inaba, M., Murata, K., Saito, M., and Takahara, I., 2006. Ethanol conversion to aromatic hydrocarbons over several zeolite catalysts. *Reaction Kinetics and Catalysis Letters*, 88, 135–141.

[32] Ramasamy, K.K., Zhang, H., Sun, J.M., and Wang, Y., 2014. Conversion of ethanol to hydrocarbons on hierarchical HZSM-5 zeolites. *Catalysis Today*, 238, 103–110.

[33] Astafan, A., Benghalem, M.A., Pouilloux, Y., Patarin, J., Bats, N., Bouchy, C., Daou, T.J., and Pinard, L., 2016. Particular properties of the coke formed on nano-sponge BEA zeolite during ethanol-to-hydrocarbons transformation. *Journal of Catalysis*, 336, 1–10.

[34] Liu, C.Y., Struwe, K., Lee, C.H., Chuang, H.Y., Sauer, J., Yu, J.C.C., Nguyen, V.H., Huang, C.W., and Wu, J.C.S., 2020. Ethanolconversion to selective high value hydrocarbons over Ni/ HZSM-5 zeolite catalyst. *Catalysis Communications*, 144, 1–17.