THESIS OF PHD DISSERTATION

HYDROGEN PRODUCTION BY WASTE PLASTICS PYROLYSIS-GASIFICATION USING TRANSITION METAL-CONTAINING CATALYSTS

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1. INTRODUCTION AND OBJECTIVES

Nowadays, the global municipal solid waste has high a proportion of plastic waste and continues to rising due to high demand of plastics. From environment point of view, it would be not appropriate to disposal waste plastic to the landfill due to the non-degradable property. Hence, the recycling of plastic waste can decreasing the disposal of these wastes and save the environment from their impacts. Furthermore, plastic are materials with high energy content due to the hydrocarbon base as it is produced by petroleum products. Therefore, from energy aspect, it would be worthy to recover the hidden energy of waste plastic by the application of a suitable recycling method.

Waste to energy technology through pyrolysis-gasification of waste plastics is considered as an attractive and feasible way to produce renewable energy from the unwanted or even contaminated waste. Regardless of the feedstock type, the valuable products from pyrolysis process can be utilized as fuel or feedstock for other petrochemical processes. Hence the structure and properties of these products can be differ based on the type of raw materials that feed to the process. However, various catalysts have been applied for the catalytic pyrolysis and gasification of waste plastic in order to improve the product selectivity. Catalysts have a great influence on the decomposition rate of these polymers as the needed temperature for maximum degradation can be reduced by introducing the catalyst to the process.

The main aim of the current study is to investigate the influence of process parameters (temperature, type of carrier gas), catalyst type and plastic/catalyst ratio on the products yield from real waste plastic mixture. The influence of modified catalysts and second metal promoters on the catalyst performance was also studied. Furthermore, the pathway for the decomposition reaction was also investigated by studying the kinetic parameters to obtain more information about pyrolysis process. The current study can provide more understanding about the role and effect of second promoter in the degradation of waste plastics mixtures.

2. EXPERIMENTAL

A mixture of real waste plastics of 45% PET, 19% PP, 17% LDPE, 14% HDPE and 5% others (polystyrene, ethylene-propylene copolymer) were used as raw materials. Raw materials had been cut and crashed into small particles (<5mm) by a laboratory grinder. A group of various active metals and different supports were used as catalyst in order to enhance the decomposition reaction of waste plastics and obtained high value products. The catalysts

were: Ni/ZSM-5, Ni/y-zeolite, Ni/natural zeolite, Ni/β-zeolite, Co/ZSM-5, V/ZSM-5, Fe/ZSM-5, Zn/ZSM-5, Ce/Ni/ZSM-5, La/Ni/ZSM-5, Mg/Ni/ZSM-5, Ca/Ni/ZSM-5, Mg/Ni/ZSM-5 and Mn/Ni/ZSM-5.

One-stage and two-stages tubular reactor were used to pyrolyzed the feedstock of waste plastics at temperature range of 550-900°C with a heating rate of 25 °C/min. 10g of the raw material was investigated in case of the one-stage reactor, while, 5 g was used for the two-stages reactor. The reaction time was 20 minutes at the set temperature.

BET, SEM, TEM, and TPO were used to characterize the catalysts. On the other hand, the composition of gases and pyrolysis oil was investigated mainly by GC-TCD and GC-FID. Based on the obtained results, the best catalyst with best support was chosen for further investigation. Additionally, TG-FTIR was used to the analysis of raw materials in order to determine the main reaction kinetic parameters. The chosen catalyst was further modified by five different promoters and examined for the decomposition reaction of waste plastic. To optimize the product yields, different reaction atmosphere have been used which include; nitrogen, oxygen and carbon dioxide.

3. NEW SCIENTIFIC RESULTS

3.1. Effect of catalyst supporters and temperature on the product compositions from the decomposition of waste plastics

a) Among the different supporters, Ni supported by ZSM-5 catalyst produced the maximum gas yield. While, the lowest yield was obtained in the presence of natural zeolite supporter. Acidic zeolite catalysts promoted the formation of hydrogen, CO, CO_2 and light hydrocarbons due to their activity for increasing the decomposition rate of raw materials. The maximum hydrogen yield was reported over Ni/ZSM-5 catalyst. The presence of catalyst resulted in more intermolecular hydrogen transfer and isomerization reactions which explain the increasing of branched hydrocarbons.

3.2. The effect of active metals and Si/Al ratio on the catalyst performance for the decomposition reaction of waste plastics

a) Among the different active metals, Ni/ZSM-5 produced the highest amount of gases for the various Si/Al ratios due to the ability of Ni catalyst for speed up the reaction rate and resulted in lighter compounds (gases). On the other hand, the maximum oil yield was reported over the lowest Si/Al ratio.

b) The maximum hydrogen yield was obtained in the presence of Ni/ZSM-5 catalyst with high Si/Al ratio of 65.5 which was attributed to the high surface area and due to the more hydrogen transfer reaction. Ni has the ability to increase the conversion rate compared to other active metals. In contrast, V/ZSM-5 catalyst produced the lower yields of hydrogen. The maximum oil yield was produced over Zn/ZSM-5 catalyst at the lowest Si/Al ratio (22.5).

3.3. Effect of second metal/catalyst ratio on the high temperature pyrolysis of municipal plastic waste

a) It was found, that the incorporation of a second metal into the catalyst structure can support the higher decomposition of polymer main chain. The gas yield decreased with increasing concentrations of the second metal. The highest gas yields were obtained with Ce, La and Mn catalysts at 0.1 Me/Ni ratios. In contrast, yields of pyrolysis oil increased by increasing the concentration of the second metal content; a ratio of 2.0 yielded the maximum pyrolysis oil. At the same time, the amount of char and carbon deposited on the catalyst surface increased by increasing the content of the second metal, which explains decreasing gas yields at high ratios (2.0).

b) A ratio of 0.5 Me:Ni was the best among all other ratios in terms of syngas and hydrogen production. The highest hydrogen and syngas yields were observed using ceria- and lanthanum-covered catalysts. The maximum production of syngas and hydrogen was found in the presence of Ce/Ni/ZSM-5 catalyst with a 0.5 Me/Ni ratio. However, raising the concentration of second promoters resulted in more coke formation on the catalyst surface, which leads to active site blockage. Higher concentrations of second metals can block the catalyst pore channels due to the more coke formation, which leads to smaller surface area.

3.4. The effect of different ratio of nitrogen/oxygen on the syngas production from pyrolysis-gasification of waste plastics

a) Results demonstrated that using of O_2 in carrier gas can enhancing the production of syngas due to the increasing reaction rate of partial oxidation. Increasing in both temperature and oxygen in the atmosphere led to higher n-paraffin/n-olefin ratio and more multi-ring aromatic hydrocarbons in pyrolysis oils. The highest gas yield was obtained with the Ni/ZSM-5 catalyst at 850 °C independently from the pyrolysis gasification atmosphere, while the La and Mg promoted Ni/ZSM-5 catalyst resulted the

highest gas yield at 550 °C. The addition of second metal on the Ni/ZSM-5 based catalyst retained their effect on reducing the cracking reactions at both temperatures.

b) Less carbon depositions was found at 850 °C or even by the using of catalyst and more oxygen in the carrier gas. Significant increase in hydrogen concentration was the main effect of the increased oxygen content in the carrier gas. Furthermore, more significant methanization reactions in the presence of higher oxygen contents were primarily due to the higher partial carbon dioxide content in the reactor. The using of higher oxygen content, significantly higher carbon dioxide contents in the gas product could be measured without catalyst. Regarding to the oil composition, the higher oxygen concentration in the carrier gas can reduce the formation of phenolic compounds in the presence of Ni containing catalysts.

3.5. The effect of Me/Ni-catalysts combined with dolomite and the CO_2 atmosphere on the hydrogen and syngas yield from waste plastics

a) At low temperature of 550 °C, the presence of dolomite did not affect the gas formation, while, more CO_2 can be generated from the dolomite at higher temperatures which led to more gas product (syngas). Hence, the results demonstrated that the presence of dolomite before the catalyst bed can transform the carbonaceous deposition to gases. Furthermore, the carbon deposition on the catalyst surface can be reduced by using dolomite, which was attributed to the gasification of char with carbon dioxide. The dolomite had a negative role in the production of filamentous carbons, especially at the higher temperature.

b) The result suggests that the presence of catalysts is essential for the positive effect of CO_2 in the carrier gas on synthesis gas production; e.g. the increase in hydrogen and carbon monoxide was attributed to the reforming reactions in the carbon dioxide atmosphere. The dray reforming reaction required elevated temperature to occur, thus, Ce/Ni/ZSM-5 catalyst produced the maximum yield of hydrogen and carbon monoxide.

3.6. The effect of steam rate on the product compositions from waste plastics mixture

a) The highest steam rate of 10 g/h produced the maximum gases yield, in both vertical and horizontal reactors. La/Ni/ZSM-5 produced the maximum gas product for the various atmosphere reaction. Regarding to the reactor type, syngas over horizontal reactor was relatively higher, than in case of vertical reactor.

4. PUBLICATION IN THE FIELD OF THE PHD THESIS

4.1. Publication in foreign journal

1. **M. Al-asadi**, N. Miskolczi: Pyrolysis of polyethylene terephthalate containing real waste plastics using Ni loaded zeolite catalysts, *IOP Conf. Series: Earth and Environmental Science* 154, 2018, 012021
2. **M. Al-Asadi**, L. Gombor, N. Miskolczi: Production of hydrogen rich products from mixture of HDPE and PET over different Ni/ZSM-5 catalysts, *Chemical Engineering Transaction 70*, 2018, 1663-1668
3. **Mohammed Al-asadi**, Norbert Miskolczi, Linda Gombor: Dry Reforming of Waste Polymers in Horizontal Reactor to Syngas Production, Chemical Engineering Transaction 76, 2019, 1429-1434
4. **Mohammed Al-asadi**, Norbert Miskolczi: High Temperature Pyrolysis of Municipal Plastic Waste Using Me/Ni/ZSM-5 Catalysts: The Effect of Metal/Nickel Ratio, Energies 2020, 13, 1284; doi:10.3390/en13051284
5. **M. Al-asadi**, N. Miskolczi, Z. Eller: Pyrolysis-gasification of wastes plastics for syngas production using metal modified zeolite catalysts under different ratio of nitrogen/oxygen, Journal of Cleaner Production, 271 (2020) 122186, https://doi.org/10.1016/j.jclepro.2020.122186
6. Ningbo Gao, Cui Quan, Zoltán Eller, Orsolya Toth, Nobert Miskolczi, **Mohammed Al-asadi**: Thermo-catalytic pyrolysis of wastes using bimetal-modified ZSM-5 catalyst: investigation of the reaction kinetic parameters, Energy Research, 2021; https://doi.org/10.1002/er.6406
7. **Mohammed Al-asadi**, Norbert Miskolczi, Hydrogen rich products from waste HDPE/LDPE/PP/PET over Me/Ni-ZSM-5 catalysts combined with dolomite, Journal of the Energy Institute 96 (2021) 251-259; https://doi.org/10.1016/j.joei.2021.03.004

4.2. International, foreign language conference presentation with full text publication

1. **M. Al-asadi** and N. Miskolczi: Pyrolysis of polyethylene terephthalate containing real waste plastics using Ni loaded zeolite catalysts, 7th International Conference on Clean and Green Energy (ICCGE 2018), 7-9 February, Paris, France, 2018
2. **M. Al-Asadi**, L. Gombor, N. Miskolczi: Production of hydrogen rich products from mixture of HDPE and PET over different Ni/ZSM-5 catalysts, *21st Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction, PRES 2018*, 25-29 August, Prague, Czech Republic, 2018
3. **Mohammed Al-asadi**, Norbert Miskolczi: Effect of metal/catalyst ratio to the syngas production from real waste plastics 10th International Symposium on feedstock recycling of polymeric materials Conference 2019 Budapest, Hungary 26-29 May 2019
4. **Al-asadi M.**, Miskolczi N., Z. Eller: Waste HDPE/LDPE/PP/PET pyrolysis to obtaining syngas over ZSM-5 supported bimetallic catalysts, 14th Conference on Sustainable Development of Energy, Water and Environment Systems (SDEWES), Dubrovnik, Croatia, 1-6 October 2019
5. **Al-asadi M.**, Miskolczi N., L. Gombor: Dry Reforming of Waste Polymers in Horizontal Reactor to Syngas Production: 22nd Conference on Process Integration. Modelling, and Optimisation for Energy Saving and Pollution Reduction, (PRES'19), 20-23 October 2019, Greece

4.3. International, foreign language conference presentation with abstract publication

1. **Mohammed Al-asadi**, Linda Gombor, Norbert Miskolczi: Syngas production from real plastic waste by metal loaded ZSM-5 catalysts, *Chemical Engineering Conference*, 24-26 April, Veszprém, Hungary, 2018
2. N. Miskolczi, **M. Al-asadi**: High temperature thermo-catalytic pyrolysis of municipal plastic waste for hydrogen production: the effect of residence time, *22nd International Symposium on Analytical and Applied Pyrolysis*, 3-8 June, Kyoto, Japan, 2018
3. N. Miskolczi, **M. Al-asadi**: Hydrogen production from municipal plastic wastes over metal loaded synthetic zeolite catalysts, *22nd International Symposium on Analytical and Applied Pyrolysis*, 3-8 June, Kyoto, Japan, 2018
4. **M. Al-asadi**, L. Gombor, Mao Qiaoting, Zou Jun, Yang Haiping, Chen Hanping, J. Sója, N. Miskolczi: Production of valuable hydrocarbons by the pyrolysis of waste polymers: optimization in raw material/catalyst ratio, *6th International Conference on Biomass Energy (ICBE 2018)*, Wuhan, 16-19 October, China, 2018
5. **M. Al-asadi**, N. Miskolczi, V. Zsinka: High temperature pyrolysis of real wastes polymers for hydrogen rich syngas production, Chemical Engineering Conference 2019(CEC 2019) Veszprém, Hungary, 16-18 April 2019
6. Eller, **M. Al-asadi**, N. Gao, C. Quan, Y. Duan, N. Miskolczi: Catalytic gasification of PET containing biomass for in situ CO2 reduction, 2019 Science and Technology Annual Conference: Biomass Thermochemical Conversion Sub-branch, August 23-25, Xi'an, China, 2019

4.4. International Hungarian language conference presentation with abstract publication

1. Gombor L., **Al-asadi M**., Miskolczi N.: Átmenetifémekkel módosított katalizátorok alkalmazása műanyaghulladékok pirolízise során: szintézisgáz előállítása, XXIV. Nemzetközi Vegyészkonferencia, október 24-27., Szovátafürdő, Románia, 2018

5. SCIENTOMETRIC DATA

Number of publications which are base of the PhD thesis:	7
Total impact factor:	22.23
Foreign language peer reviewed in foreign journal:	7
Abstract in international conference proceeding:	6
Abstract in Hungarian language international conference proceeding:	1
Number of citation (Scopus):	21
h-index:	3

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