THESIS OF PHD DISSERTATION

IMPROVING IN CORROSION, TRANSPORTATION AND STORAGE PROPERTIES OF REAL WASTE DERIVED PYROLYSIS OIL

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1. INTRODUCTION AND OBJECTIVES

Since the synthesis of the first plastic in the early 1900s, plastics have replaced many other materials such as wood, metals and ceramics, owing to their lightness, durability, resistance to corrosion, ease of production, their low cost and their variety of applications. Thermoplastics represent 80% of the total consumption of plastics and they are found in many sectors, but mainly in packaging. On the other hand, the recycling of used plastic items is still unsolved question. However, the mechanical and chemical recycling of plastic wastes looks attractive for their long term utilization. Among the energy recovery techniques, pyrolysis is promising, which is an endothermic decomposition in a reducing atmosphere under the effect of heat (over 300°C). This process allows the decomposition of solid organic matter into three phases: solid (pyrolysis coke or char), liquid (consisting of heavy condensable - pyrolysis oils or tars, light oil and water) and gaseous (CO, H_2, CO_2, CH_4, C_2H_4, C_2H_6). One of the most important question which has to be solved the further utilization of products obtained from waste pyrolysis. Thus the composition of pyrolysis oils is affected by many factors (e.g. raw materials, process, catalysts, etc.); they should be containing many of components deteriorating their long term properties. The long term properties of the pyrolysis oils can be improved by in-situ and the selection of catalyst, reaction parameters or operation unit is important aspect of both the process and product development. In general, the long term properties of the waste derived pyrolysis oils are investigated by accelerated aging test, when the change in many properties of the products are followed before and after the aging.

The main aim of this study is to investigate the effect of different raw materials, reactor configurations and catalysts for the in-situ upgrading of pyrolysis oil. Furthermore the possibility for improving in corrosion, transportation and storage properties of real waste derived pyrolysis oil is investigated to obtain valuable hydrocarbons for energetic, refinery or even petrochemical application. Pyrolysis of different polymeric waste (paper, biomass, plastic and chlorinated plastic) were taken in batch and tubular reactors with the use of different catalyst (Ni/SAPO-11, Ni/ZSM-5, $Ca(OH)_2$, red mud). The products yield and the yield composition were investigated, the longer-term utilization of the pyrolysis oils were followed by corrosion and different accelerated aging tests.

2. EXPERIMENTAL

Three different kinds of real wastes were used as raw materials: chlorinated polyolefin rich plastic waste, plastic waste containing biomass and plastic waste containing paper. Raw

materials had been cut and crashed by a laboratory miller and dried at 80°C until 5h before the experiments.

Mixtures of different Ni/ZSM-5 and Ni/SAPO-11, $Ca(OH)_2$ and red mud were used with different ratios to enhance the waste polymer decomposition, modify the product properties and enhance their long term application.

Two different reactors were used to investigate the thermal and thermo-catalytic decomposition of wastes: a laboratory scale batch reactor testing 50g of raw material at 510-520°C and a tubular reactor using 750g/h raw material feed at 550-560°C. In case of thermo-catalytic pyrolysis, 5% of catalyst was used.

The composition of gases and pyrolysis oil was investigated mainly by GC-FID, GC-TCD, HPLC and FTIR methods. The long-term properties (e.g. density, viscosity, solid deposition and the total acid number) of waste derived pyrolysis oil were followed by both accelerated and non-accelerated aging tests. During the accelerated test, the pyrolysis oil was stored for 7 days at 80°C. The corrosion properties of the pyrolysis oil were followed via copper plate storage at room temperature till 60 days. Regarding the cellulose derived products, especially the effect of oxygenated compounds (alcohols, aldehyde, ketones, carboxylic acids or phenol and its derivative) to the properties was concluded.

3. NEW SCIENTIFIC RESULTS

3.1. Effect of Ni/ZSM-5 and Ni/SAPO-11 based catalysts to the product properties using any raw materials

a) Comparing the three raw materials, the amount of char decreased in the order of wastes containing paper, biomass and PVC.
b) It was stated, that due to the larger pore areas and higher Si/Al ratio, the ZSM-5 supported catalysts resulted higher gas yields, can more significantly isomerize the main carbon frame of compounds and promote the production of unsaturated hydrocarbons than SAPO-11 based in gases. Furthermore, synergetic property of Ni/catalyst and red mud was found the hydrogen production which increases the concentration of hydrogen in gases.
c) The TAN values decreased in the order of plastic waste/paper > plastic waste/biomass > plastic waste/PVC, independently from the reactors used.

3.2. Thermo-catalytic pyrolysis of waste HDPE and PVC in batch and tubular reactors for in-situ product improvement

a) The concentration of unsaturated branched hydrocarbons, especially isobutene, trans-but-2-en and cis-but-2-en were high in case of SAPO-11 containing catalyst, while the ZSM-5 based catalysts show high efficiency in aromatization reaction. High amount of $Ca(OH)_2$ in catalyst mixture can led to significantly less yields of volatiles and chlorinated monoaromatic.

b) The presence of red mud and $Ca(OH)_2$ was highly preferred for the reduction of the chlorine content in the pyrolysis oil. However, the chlorine could be transformed mainly into gaseous products and the chlorine concentration in pyrolysis oils can further decreased and the aromatic, branched and unsaturated hydrocarbon content increased by the using of catalysts. By comparing between the two catalysts, catalyst mixtures with Ni/SAPO-11 showed better properties for chlorine reduction than Ni/ZSM-5 based catalyst mixture.

c) In terms of chlorine and dechlorination, catalysts can decrease the chlorine content of the gases and light oil, which was in the form of chloromethane and chloroethane as organic chlorinated hydrocarbons. The chlorine content of the solid residue increased significantly. Ni/SAPO-11 based catalysts showed advanced properties in dechlorination, and reduced significantly the weight loss of copper plate during the aging test.

d) With regards to the stability and longer-term utilization, the catalysts can decrease the rate of aging comparing to the catalyst free thermal pyrolysis. On the other hand, Ni/ZSM-5 containing catalyst aging has slower rate than that of Ni/SAPO-11. Ni/SAPO-11 based catalysts (especially with high red mud and $Ca(OH)_2$ content) showed better corrosion (TAN and corrosion rate) properties, than Ni/ZSM-5 based catalysts.

3.3. Thermo-catalytic co-pyrolysis of waste plastic and paper in batch and tubular reactors for in-situ product improvement

a) More hydrogen and less CO_2 were found in tubular reactor, than that of using batch reactor in gases. By using a tubular reactor, the catalysts can promote the yield of hydrogen and methane, and decrease the concentration of CO_2. It was also found, that the yield of water was not affected significantly by the different catalysts.

b) Regarding the light oil, it was concluded, that the yield of oxygenated compounds has significantly decreased by the use of catalysts. Products obtained from the tubular reactor had better transportation and storage characteristics than those acquired from the batch reactor. Particularly, the alkaline catalysts had a positive effect on the TAN and corrosion properties and in term of the density and viscosity of the products, the use of high synthetic zeolite-containing catalysts can significantly reduce it value, which could improve the long-term use of light oils.

3.4. Fuels by Chemical Recycling of Waste Plastic and Biomass Mixture and Utilization of the Products

a) It was concluded, that under the same conditions, more water was produced using tubular reactor than the batch reactor. Contrary as result of waste plastic containing paper pyrolysis, the water content of the products was slightly higher for both reactor designs using Ni/SAPO-11 based catalyst mixtures. Regarding gases less C_2-C_5 hydrocarbon and more hydrogen, CO, CO_2 and CH_4 was found than in case of waste plastic containing paper raw material, which was independent from the reactor configuration. The catalysts can reduced the n-paraffin/n-olefin ratio in pyrolysis oil and opposite effect was observed in the presence of catalysts, than absence, since the former had a higher n-paraffin/n-olefin ratio in the light oils from the batch reactor. Oxygenated compounds in light oil can significantly decrease using tubular reactor, whereas only a slight decrease was observed regarding the batch reactor by the using of Ni/SAPO-11 based catalysts. The yield of mono-aromatic hydrocarbons and poly-aromatics can nearly double by Ni/ZSM-5 type catalyst mixtures in case of batch reactor, while catalysts synthesized by SAPO-11 based catalyst mixtures can increase the concentration of poly-aromatics.

4. PUBLICATION IN THE FIELD OF THE PHD THESIS

4.1. Publication in foreign journal

1. **B. Fekhar**, N. Miskolczi, T. Bhaskar, J, Kumar, V. Dhyani, 2018. Co-pyrolysis of biomass and plastic wastes: investigation of apparent kinetic parameters and stability of pyrolysis oils. IOP Conference Series: Earth and Environmental Science, 154, p.012022. Available at: http://dx.doi.org/10.1088/1755-1315/154/1/012022.
2. **Fekhar, B**., Zsinka, V., Miskolczi, N., 2019. Value added hydrocarbons obtained by pyrolysis of contaminated waste plastics in horizontal tubular reactor: In situ upgrading of the products by chlorine capture. Journal of Cleaner Production, 241, p.118166. Available at: http://dx.doi.org/10.1016/j.jclepro.2019.118166.
3. **Fekhar, B**., Miskolczi, N., Zsinka, V. 2019. Fuels by Chemical Recycling of Waste Plastic and Biomass Mixture and Utilization of the Products. Chemical Engineering Transactions 76, p 1447. Available at: http://dx.doi.org/10.3303/CET1976242.
4. **Fekhar, B**., Gombor, L., Miskolczi, N., 2019. Pyrolysis of chlorine contaminated municipal plastic waste: In-situ upgrading of pyrolysis oils by Ni/ZSM-5, Ni/SAPO-11, red mud and $Ca(OH)_2$ containing catalysts. Journal of the Energy Institute, 92(5), pp.1270–1283. Available at: http://dx.doi.org/10.1016/j.joei.2018.10.007.
5. **B. Fekhar**, V. Zsinka, N. Miskolczi. 2020. Thermo-catalytic co-pyrolysis of waste plastic and paper in batch and tubular reactors for in-situ product improvement, Journal of Environmental Management 269, pp. 110741. Available at: https://doi.org/10.1016/j.jenvman.2020.110741

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

1. **B. Fekhar**, N. Miskolczi, T. Bhaskar, J, Kumar, V. Dhyani: Co-pyrolysis of biomass and plastic wastes: investigation of apparent kmetic parameters and stability of pyrolysis oils, 7th International Conference on Clean and Green Energy (ICCGE 2018), 7-9 February, Paris, France, 2018.
2. **B. Fekhar**, N. Miskolczi: Stability and Storage Properties of Hydrocarbons Obtained by Pilot Scale Pyrolysis of Real Waste HDPE-PVC in Tubular Reactor, 21st Conference on Process Integration, Modelling and Optimization for Energy Saving and Pollution Reduction, PRES 2018, 25-29 August, Prague, Czech Republic, 2018.
3. **B. Fekhar**, N. Miskolczi, V.Zsinka: Thermo-catalytic pyrolysis of waste plastic and paper using synthetic zeolites: quality increasing of pyrolysis 14th Conference on Sustainable Development of Energy, Water and Environment Systems (SDEWES) Dubrovnik, Croatia;1-6 October 2019
4. **B. Fekhar**, N. Miskolczi, V.Zsinka. Fuels by Chemical Recycling of Waste Plastic and Biomass Mixture and Utilization of the Products; 22nd Conference Process Integration, Modelling and Optimization for Energy Saving and Pollution Reduction (PRES'19) Crete, Greece; 20-23 October 2019.

4.3. International, foreign language conference presentation with abstract publication

1. **B. Fekhar**, V. Zsinka, N. Gao, C. Quan, J. Sója, N. Miskolczi: Thermo-catalytic pyrolysis of waste plastics and biomass mixtures using Ni/ZSM-5 and Ni/SAPO-11 based catalysts: a kinetic approach, 6th International Conference on Biomass Energy (ICBE 2018), Wuhan, 16-19 October, China, 2018.

2. **B. Fekhar**, L Gombor, N. Miskolczi: Hydrocarbons obtained by waste pyrolysis: improving in corrosion stability by in-situ upgrading, 22nd International Symposium on Analytical and Applied Pyrolysis, 3-8 June, Kyoto, Japan, 2018.
3. **B. Fekhar**, N. Miskolczi: Comparison of different aging test for the investigation of the long-term properties of pyrolysis oils, The10th International Symposium on Feedstock Recycling of Polymeric Materials (ISFR) 26-29 May, Budapest, Hungary, 2019
4. **B. Fekhar**, N. Miskolczi: Improving in product quality of waste derived hydrocarbons over modified SAPO-11 catalysts, Chemical Engineering Conference, 24-26 April, Veszprem, Hungary, 2018
5. **B. Fekhar**, N. Miskolczi, Z Eller. Catalytic co-pyrolysis of waste polymers to obtain value added products. The Chemical Engineering Conference. Veszprem, Hungary, April 2019.

4.4. International Hungarian language conference presentation with abstract publication

1. Zsinka V., **Fekhar B**., Miskolczi N.: Hulladék polimerek alacsony hőmérsékletű termo-katalitikus hőbontása: a termékek in-situ minőségjavítása, XXIV. Nemzetközi Vegyészkonferencia, október 24-27., Szovátafürdő, Románia, 2018.

5. SCIENTOMETRIC DATA

Number of publications which are base of the PhD thesis:	5
Total impact factor:	14.998
Foreign language peer reviewed in foreign journal:	5
Publication in conference proceeding:	10
Foreign language international conference proceeding:	4
Abstract in international conference proceeding:	5
Abstract in Hungarian language international conference proceeding:	1
Number of citation (Scopus):	18
h-index:	3

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