# DOCTORAL (PhD) DISSERTATION REVIEW

## Dissertation title: Hydrogen Production by Waste Plastics Pyrolysis-Gasification Using Transition Metal-Containing Catalysts

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**Subject:**

Plastics have been become part of the daily life of the modern society. They can be found in the households, transportation, workplaces and so on. Production quantity of plastics was dynamically increased in the last decades and it will continue in the future, too. This results in formation of large amount of plastic waste, too, which causes serious environmental problems. Recycling of the plastics are important both from environmental and economic aspects. One of the promising solutions is the chemical recycling of the plastics. *Therefore, the selection of the topic of the PhD dissertation is actual and forward-looking.*

**Review of the state of the art:**

The literature survey contains 30 pages and it was built up on 186 sources. The author introduced the challenges of the utilization of the plastic wastes. It was shown that composition of the generated plastic wastes is varied with the industrial sectors, and different approaches are required to utilize them. The author summarized the commonly used waste utilization methods and they were critically evaluated, too.

The hydrogen/syngas production as a possible method for the waste plastic utilization was described in detail. The author summarized the most important information about the "classical" hydrogen/syngas production based on the steam reforming or partial oxidation of methane, and the waste gasification technology was also discussed.

Connecting to the topic of the PhD dissertation the waste plastics utilization with pyrolysis-reforming process was discussed in detail. Author summarized the process conditions and main findings of several scientific papers prepared on this research area. Based on this information the effect of the process conditions e.g. temperature, pressure and residence time on the product distribution was discussed. Catalysts those had been investigated to improve the product distribution and economy of the process were also described. The author also reviewed the effect of the reaction atmosphere on the product yield. Kinetic parameters of the plastic pyrolysis processes were also summarized and discussed. Various types of reactors were applied to investigate the pyrolysis of the plastic wastes, which were also reviewed and evaluated by the author.

The author gave detailed description about the products formed during the pyrolysis of waste plastics, e.g. pyrolysis oil, gases, char. The possible production of carbon nanotubes was also discussed.
The author briefly reviewed the economics of the process, the challenges of the sale-up from the laboratory scale to pilot scale were also discussed.
Based on the literature review the author determined the gaps in the present knowledge and direction of his experimental work.

**Experimental**

Mixture of real plastic waste originated from municipal source was selected as feedstock. The feed contained 45% PET, 50% polyolefines (PP, LDPE, HDPE) and 5% others. The detailed description of the feed was presented.
The author prepared various metal/zeolite type catalysts. Both single and double metal catalysts were synthetized. The detailed description of the catalysts, for example metal content, surface area, Si/Al ratio of the support etc., were given.
The applied reactor systems and the experimental procedures were also discussed. Additionally, methods, those were applied for qualifying the products, were introduced.
The presented methods were adequate to obtain the aims of the research plan.

**Results and discussion**

*Chapter 3.1.* displayed the results of the experiments aimed at investigating the effect of the various zeolite support on the yield and composition of the products. The selected zeolites were the following: natural zeolite, β-zeolite, ZSM-5 and Y-zeolite, the applied metal was Ni. The catalysts were tested at 600, 750 and 900°C in order to determine the effect of the temperature. Based on the results author determined that overall the most favorable catalyst was the Ni/ZSM-5 taking into account the hydrogen formation. Differences in the efficiency of the catalysts were attributed to their different surface areas. However, the different pore structure of the studied catalyst supports can also contribute to the efficiency. Additionally, it was not clearly explained what was the source of the water(steam) whose presence was presumed by the author.
The author selected ZSM-5 as catalyst support for the further investigation.
*Chapter 3.2.* summarized the results of experiments carried out with using various metals e.g. Ni, Co, V, Zn, Fe supported on ZSM-5 zeolites of different Si/Al ratios (22.5, 41.9 and 65.5). The experiments were performed at temperature of 700°C.
Huge amount of data was presented regarding to the catalytic properties of the selected catalysts. The author presented detailed discussion about the effect of the type of the metal and the Si/Al ratio of the catalysts on yield and composition of products. However, the author did

not define what catalyst was the most favorable taking account the yield and composition of the products.

*Chapter 3.3.* showed the results of experiments aimed at to determine the effect of the ratio of the Ni/second metal supported ZSM-5 zeolite of Si/Al=30. The second metal was Ce, La, Ca, Mg, Mn, and the Ni/second metal ratios were 0.1, 0.5 and 2.0.
Based on the results of the experiments author determined, that La and Ce provided the greatest positive effect, additionally it was shown that increase in the second metal/Ni ratio over 0.5 did not gave further advantage. It would have been expected to discuss the correlation between the properties of second metals (electron structure, size etc.) and the yields/properties of the reactor product.

*Chapter 3.4.* summarized the results of TGA experiments using bimetallic catalysts supported on ZSM-5 zeolite in order to determine apparent kinetic parameters supposing first order kinetics for the reactions were taken place. Results of variation in the catalyst/raw material were also introduced and discussed in this chapter.
Based on the results author determined that the studied catalyst decreased significantly the apparent activation energy, especially the Ni, NiCe, NiLa /ZSM-5 ones. The author also discussed the effect of the catalyst/raw material ratio, he stated that there was not advantageous effect of the high ratio (over 1:1).

*Chapter 3.5.* displayed the results of experiment carried out in gas flow of different compositions applying bimetallic catalysts supported on ZSM-5 zeolite. Investigation of carbon nanotube formation on the surface of the catalyst was also discussed in this chapter.
The author showed that the higher oxygen content of the reaction atmosphere resulted higher gas yield and lower carbon deposition on the catalyst. The reasons of these were discussed in detail. Valuable part of this chapter the investigation of the carbon nanotube formation on the surface of the catalyst (TPO and TEM measurements).

*Chapter 3.6.* summarized the results of experiments of steam reforming of waste plastic. Effect of variation in the steam/raw material ratio on the product yields and compositions was investigated using Ni, NiLa and NiCe supported on ZSM-5. These experiments were carried out both vertical and horizontal reactor. Additionally, introducing dolomite into the reactor as carbon dioxide source was also investigated and the results were summarized in this chapter.
Author determined that increase in the steam rate resulted higher gas yield and lower carbon deposition on the surface of the applied Ni/ZSM-5 catalyst. Author showed that using bimetallic catalysts (La, Ni, Ce, Ni) high gas yield can be obtained and the carbon formation can be

suppressed at the applied process conditions, the most advantageous results was obtained by using Ni,La/ZSM-5 catalyst and dolomite as carbon dioxide source.
Author obtained different results in vertical and horizontal reactors, but the reason of the differences was not explained.

**Style, logic and structure of the thesis:**
Thesis has been written in English language, where applied terminology is up to current engineering standard. The thesis is result of a massive work done – what is expressed in its lengths as well. There are some edition mistakes in the dissertation, but they are not misleading. Structure of the thesis is in accordance with the requirement.

**Thesis points**
The most important scientific results were summarized in 6 thesis points. Thesis point 3.1 a) is accepted as new scientific result. Thesis points 3.2 a) and 3.2 b) are accepted as new scientific results. Thesis points 3.3 a) and 3.3 b) are accepted as new scientific results. Thesis points 3.4 a) and 3.4 b) are accepted as new scientific results. Thesis points 3.5 a) and 3.5 b) are accepted as new scientific results. Thesis point 3.6 is accepted as new scientific result.

**Publication activity**
The publication activity of the author meets with the requirements of the Doctoral School of Chemical Engineering and Materials Science (University of Pannonia). The Impact Factor of 22.23 is well supports the author's readiness.

**Concluding:**
Based on the presented results and their evaluation the dissertation can be accepted.

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