Answers to Dr Tivadar Feczkó

First of all, I would like to thank you for the revision, and the very useful comments and suggestions. Please see the responses to the comments and remarks in the following

Major remarks:

1) The title of thesis emphasizes hydrogen production; however, the thesis does not focus mainly on hydrogen production, but the production of gases (including hydrogen) and oils gets similar emphasis in the work. Hence, in my opinion the title starting with Pyrolysis of waste plastics… would have better represented the content of the study

   In one hand, our main aim was to produce hydrogen rich syngas over the different modified catalysts, but since the products from the pyrolysis-gasification have also oil and other hydrocarbons. Therefore, we also investigated the influence of the used catalysts on the product yields to give more sight and information about the reaction pathway. On the other hand, I would to follow the terminology used in pyrolysis-gasification. However, I can accept the suggestion.

2) The first paragraph of "Experimental part" contains partly the description of the aims. This has been already done at the end of the introduction, and it should have been combined there and not included in "Experimental part

   Thank you very much for the remark. The purpose of the paragraph was to keep the readers connecting with the main aims of study.

3) In section 2.1.2.2. the following is written: "Based on the results of catalyst supporter selection, ZSM-5 synthetic zeolite was selected for further investigation." However, Table 2.2 shows that two of the other three catalysts had higher surface area than ZSM-5; thus, it would have been reasonable to give other explanation to the choice. Later, in the section "Results and discussion" it is given, but in 2.1.2.2. the reader has got some feeling of lack of information. Moreover, in page 35, paragraph 2, line 1 author writes: "As shown in Table 2.2, Ni/ZSM-5 catalyst has the highest surface area among the other used catalysts." This can be seen in Table 2.3 and not in Table 2.2, since Table 2.2. shows that Ni/y-zeolite and Ni/b-zeolite have higher surface area. That is why it would have been important to give some more reason here for the choice of Ni/ZSM-5

   Thank you very much for the remark. The sentence quoted is indeed about Tables 2.3-2.5 and not Table 2.2. Several aspects had to be considered when selecting the catalyst support, e.g. surface area, catalytic effect, activity, degree of coking or deactivation, literature and experimental data. ZSM-5 zeolite is a widely used and tested catalyst or catalyst support in pyrolysis and pyrolysis-gasification experiments mainly due to high gas yield of products, favourable product composition, longer-term applicability and economic downturns. In my case the selection of Ni/ZSM-5 catalyst was based on both literature data and experimental results as the presence of this catalyst generated the maximum gas and hydrogen yield among the various catalyst supports.

4) The thesis contains neither statistics nor information on the reproducibility of the investigations

This step was earlier investigated by another student and the relative standard deviation (RSD%) value of the pyrolysis-gasification experiment was between 3.5-6.1%. $RSD\% = \frac{SD}{\bar{x}_i}100$ *, The SD is the standard deviation and* $\bar{x}_i$ *is the mean of measurements "i".*

5) In section "Results and discussion", the titles should not contain "investigation" (e.g. 3.1., 3.2. and so on)

Thank you for the remark, I will avoid such term in the future

6) Page 46, last line: "The order can be attributed to the difference in surface areas of the catalysts." Ni/ZSM had the second lowest surface area, but it was the best or the second best catalyst depending on the condition. Hence, the described relation does not exist.

Thank you very much for the remark. I will revise this sentence. The sentence should be confused, because I just wanted to explain that in general larger surface areas tend to cause more cracking.

7) It would have been interesting to read some consideration on that syngas or pyrolysis oil formation was more preferable in this study

Perhaps there was not enough reference to this, but the main goal of the dissertation was to increase the amount of hydrogen and synthesis gas. The syngas formation was the more preferable in my study.

8) Page 48, line 2: "Acidic zeolite catalysts promoted the formation of hydrogen, CO…" Some explanation on the gas formation as a function of acidic character would have been interesting from the chemical point of view.

In general, the higher acidity of catalyst promotes the more cracking of C-C bond leading to more decomposition of raw materials and increasing in gas yield. Based on earlier results, it was found, that both Lewis and Brønsted acid sites of the catalyst play roles in the cracking mechanism which is initiated by the abstraction of the hydride ion from the polymer structure by Lewis acid sites of the catalyst, or the addition of a proton to the C–C bonds by Bronsted acid sites of the catalyst. Moreover, the higher amount of Brønsted acid sites on the surface of the catalyst provides more hydrogen ions for double bond cleavage and further propagation steps.

Questions:

1) Page 35, paragraph 2, line 4: "At Si/Al ratio of 41.9, Fe/ZSM-5 catalyst had the highest average grain diameter (38.2)." What is its significance? Does it add some additional value e.g. better handleability? Or why is this result emphasized here?

With this sentence, I just wanted to mention the difference among the average particle sizes of the catalysts.

2) I would have expected a clearer description on catalyst selection. Which is the most important parameter of catalysts among the investigated ones? Which parameter was

considered during the catalyst selection? What were the expectations towards the catalyst parameters?

During pyrolysis gasification, the most important catalyst characteristics are the pore structure, the surface area, the acidity, and the presence of other elements which have a beneficial effect on the reaction. E.g. the nickel and other transition metals has beneficial role on hydrogenation-dehydrogenation reactions. The addition of nickel to ZSM-5 increased the catalyst stability. Moreover, ZSM-5 has advanced pore structure and advanced Si/Al ratio. Therefore, Ni/ZSM-5 catalyst showed good activity towards the decomposition reaction of waste polymers. On the other hand, the addition of metals to Ni-based catalyst introduces more active sites by improving the Ni dispersion and Ni particle size. Regarding to the expectations, since the cracking reaction prefers the acidic catalysts. Hence, I used acidic zeolite to promote the more cracking of raw materials due to the presence of Lewis and Brønsted acid sites.

3) Page 37, paragraph 2, line 2: "For further investigations the Ni^{2+} was selected, and ZSM-5 catalyst with Si/Al ratio of 30 was used." So far Si/Al ratios of 22.5; 41.9 and 65.5 were used. From where did the ratio 30 come?

   *For this step the purpose was to investigate the influence of different Si/Al ratios (22.5, 41.9 and 65.5) and to see their influence on the product compositions. So the main aim was to figure out the performance of catalysts with various Si/Al ratios and to provide clear sight about the role of Si/Al ratio. In one hand, the use of Me/ZSM-5 catalysts with higher Si/Al ratio resulted in higher gas yields and less pyrolysis oil yield. Furthermore, the amount of synthesis gas increased slightly with the Si/Al ratio of the catalyst. However, the formation of surface coke deposition, which also caused catalyst deactivation, was significantly higher and faster at higher Si/Al ratios. Therefore, I try to choose an optimum value between two existing points (*22.5; 41.9*), and I wanted to do a significant part of the experimental work with that completely new value.*

4) In Tables 2.6-2.8 metal contents "on catalyst grain" and "between catalyst grains" are shown. What is the difference between them? Does applicant mean "on grain" as present on the surface and "between grain" as in the inner pores of the grain or outside the grains? The expression "between" is definitely false

   Thank you very much for the remark. The term "on catalyst grain" means on the surface, while, "between grain" means in the bulk of catalyst outside the grains.

5) Page 38: The concentration of metal salt solutions is not provided. Concentration ranges for the second metals are given, however, it is not clear which belongs to each of them. What was the reason for choosing these ranges?

   The reason for choosing these ranges was to study the effect of second metal on the catalyst performance at low and high concentration. Based on the literature, concentrations below 20% have been used in previous work. However, the effect of high concentrations is more significant, but they are economically problematic. Therefore I would to use the concentration of nickel below 5%, and that of second metal up to 10%. The 0.41%-0.48% means the second metal concentration range in case of Me/Ni=0.1, the 1.97%-2.11% and 7.70%-8.51% concentration ranges represent the second metal concentrations in case Me/Ni=0.5 and Me/Ni=2.0, respectively.

6) The Ni/ZSM-5 average grain diameter was between 12.1 μm and 16.8 μm. How is it possible that after second metal immobilization it decreased to 0.56-1.28 μm? My expectation would be the impregnation increases and does not decrease the size. It should also have been mentioned that the BET surface increased significantly after impregnation. An explanation to this would have also been desirable

   The catalysts shown in Tables 2.3-2.5 and the catalysts shown in Tables 2.6-2.8 were not the same. The catalysts shown in Tables 2.6-2.8 had different Si/Al ratios and other characteristics than the catalysts shown in Tables 2.3-2.5. Basically, this was the reason for the anomaly mentioned above. However, the decreasing in the average grain diameter should be due to the crashing step after the impregnation and drying.

7) Page 50, last line: “Gasification was behind that phenomena as the oil yield was only 1.1 %". I do not understand this sentence, and neither the previous text environment helps in understanding. What does candidate mean under phenomena here?

   It means that the oil product transformed to gases due to the high reaction temperature and that’s why lower yield of oil was reported.

8) Page 80, paragraph 2, line 3: “When 100 %/0 % of N2/O2 atmosphere was used, darker spots were visible on the image.” What are the darker spots in the image? Why do they decrease and then increase after the enhancement of oxygen content?

   The darker spots are belong to the amorphous carbon and oxidation due to the presence of oxygen was beyond the decreasing. It is also important to mentioned, that the image showed one given area of the catalyst. Therefore, the decreasing or increasing in the darker spots in the picture should be not same on the whole catalyst surface. That is why the amorphous/filamentous ratio of the catalyst was followed via their temperature programmed oxidation.

Minor remarks:

1) Branched/non-branched hydrocarbon ratio is given in molar ratio and not in percentage as written in the text (Page 53, last line; page 54, first line). The same is true for H2/CO ratio (page 54, line 6 and line 9; page 59, line 6 and line 9).

   Thank you for comment, it was mistyping.

2) Page 11, line 8 “The calorific value of the product gas may decline when the air introduced to the gasifier due to the presence of air which dilutes the gas yield.” This is a meaningless sentence

   With this sentence, I would like to point out that the nitrogen used during the gasification can significantly affect the further use of the gas product, because, for example, the energy content of the product is significantly reduced.

3) Page 14, 2nd paragraph, the reference number should be in the same sentence, where the authors of reference are cited

   Thank you very much for the remark. I will avoid such mistake in the future.

4) Page 22, line 11: „Al-asadi et al. [106] re-ported that positive effect in the gas and liquid yields was found by increasing the ratio of oxygen atmosphere for the gasification process of HDPE, LDPE, PP and PET" It is completely unusual and incorrect to cite an own work in the literature review, when the results of thesis is based on these findings.

   Thank you for the remark, I will avoid such mistake in the future.

5) I would have involved subsection 1.5.1 in 1.5

   Thank you very much for the remark.

6) Page 48, line 1: "Hydrogen and other hydrocarbons are also affected by the presence of catalysts." should be corrected to "Formation of hydrogen and other hydrocarbons are also affected…"

   Thank you for the suggestion.

7) Page 58, line 1: "increasing of second promoters to 2.0" In fact, the ratio of second promoters was increased to 2.0.

   Thank you very much for the correction.

8) Figures 3.11 and 3.17 have got double titles. Figure 3.17 title should be ended as following "using La/Ni/ZSM-5 catalyst"

   Thank you very much for the remark.

9) Page 60, paragraph 2, line 2: "were the main compositions" components not compositions.

   Thank you for the correction.

10) Page 66, title of section 3.5.1. should be read as "Pyrolysis in nitrogen and partial…"

    Thank you very much for the suggestion.

11) 11,12,13- Terminology errors, mistyping and grammatical errors:

    Thank you very much for the corrections, I will give more attention to avoid such a mistakes in the future.