

REVIEW OF PHD THESIS

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Title of thesis: Hydrogen production by waste plastics pyrolysis-gasification using transition metal-containing catalysts

General review of thesis

The thesis investigates waste-to-energy conversion technology using pyrolysis-gasification of waste plastics. The topic to produce renewable energy from real polymer waste is modern and very important considering the huge environmental problem caused by the used plastics.

Various catalysts have been applied for the pyrolysis and gasification of waste plastics. Considering economic conditions, cheap zeolite supported Ni catalysts with high catalytic activity were selected and improved by second metal promoters (Ca, Ce, La, Mg, and Mn). The influence of main process parameters (temperature, type of carrier gas), catalyst type and plastic/catalyst ratio was studied on the product yield from real waste plastic mixture. The influence of modified catalysts and second metal promoters on the catalyst performance was also studied. The decomposition reaction pathways were also investigated via the kinetic parameters.

All of the thesis sections are structured in suitable proportion.

The section “Introduction” describes the background and state-of-the-art appropriately and contains the relevant literature aspect of the research. The scientific literature survey is based on up-to-date references. PhD candidate studied an enormous number of relating papers and collected suitable and most related information to his work.

The experimental methods are modern and fit to the aims. The “Experimental part” is well-structured and contains every important data on the experiments. However, I might have added the main properties of catalysts summarized also in tables into the section “Results and discussion”.

In “Results and discussion” the candidate’s findings, which contain huge data, have been arranged logically, although maybe some results could have been neglected. Candidate cited some literature data in order to compare his results with the state-of-the-art, nevertheless, some more discussion would have been interesting, e.g. on how the branched/non-branched hydrocarbon and H₂/CO ratios are correlated with the expectations.

The number and quality of the figures and tables are appropriate, although some diagrams contain commas instead of decimal points (e.g. Figures 3.6 and 3.7).

The section “Conclusion” summarizes the most important findings correctly.

The reference list is up to date and includes the references with sufficient detail.

The new scientific results are summarized adequately in six points, however, the 3rd and 4th point could have been shortened slightly. I accept each of the points as new scientific results.

The results have been published in journals of high quality (especially two manuscripts), and the quantity and quality of publications exceed the requirement of doctoral school to a high extent.

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.
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”.
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/γ-zeolite and Ni/β-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.

4. The thesis contains neither statistics nor information on the reproducibility of the investigations.
5. In section “Results and discussion”, the titles should not contain “investigation” (e.g. 3.1., 3.2. and so on)
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.
7. It would have been interesting to read some consideration on that syngas or pyrolysis oil formation was more preferable in this 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.

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?
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?

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?
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.
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?
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.
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?
8. Page 80, paragraph 2, line 3: “When 100 %/0 % of N_2/O_2 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?

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 H_2/CO ratio (page 54, line 6 and line 9; page 59, line 6 and line 9).

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.
3. Page 14, 2nd paragraph, the reference number should be in the same sentence, where the authors of reference are cited.
4. Page 22, line 11: „Al-asadi et al. [106] reported 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.
5. I would have involved subsection 1.5.1 in 1.5.
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...”
7. Page 58, line 1: “increasing of second promoters to 2.0” In fact, the ratio of second promoters was increased to 2.0.
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”
9. Page 60, paragraph 2, line 2: “were the main compositions” components not compositions.
10. Page 66, title of section 3.5.1. should be read as “Pyrolysis in nitrogen and partial...”
11. Terminology errors:
 - Page 33, paragraph 3, line 4: „dissolution” must be corrected to „solution”, dissolution is the process, solution is the product of the process.
 - Catalyst supporter is used several times, however, the correct terminology is catalyst support not supporter.
12. There are a lot of mistyping and grammatical errors in the text. Some typical examples are shown in minor comments. The most typical grammatical errors:
 - Predicate is missing from the sentence, e.g. page 74, line 3; page 97, last sentence

- A lot of mistakes in conjugation, e.g.: page 22, paragraph 3, line 3: „can significantly influenced the decompoaiton” (mistyping as well); page 22, paragraph 3, line 4: „can promoted”; page 24, paragraph 3, line 3: „can affects”; page 30, paragraph 2, line 2: „this type of energy have many serious problems which can affects”; page 41, paragraph 2, line 4: „to set and controlled...”; 49, line 7: “it can produces”; page 63, paragraph 2, line 6: “to mentioned” instead of “to mention”; page 65, line 1: “important to means” must be corrected to “important to mean”, “can increased” instead of “can increase” page 98, line 3: “did not influenced”; page 98, last but one line: „could promoted”;
- Carbon-monoxide and carbon-dioxide instead of carbon monoxide and carbon dioxide in several sites in the thesis.
- Mixing of nouns with verbs: e.g. “effected” instead of “affected” several times.
- Plural instead of singular and vice versa: e.g. page 17, last paragraph line 1: „a regular particle size of waste plastics are feed”; page 25, paragraph 3, „The syngas are formed”; page 25, paragraph 2, line 1: Char is a carbonaceous materials

13. The most typical mistyping errors:

- Frequent mistyping: “concenteration”
- Cumulative mistyping in one sentence: e.g. page 22, line 4: The authors demonistrtd that the higer rate input of CO2 led to significant increasing of syngas production [59].
- Word repetitions, e.g. front board: “Made in the the framework”; page 22, paragraph 3, line 6: „throw the the reforming”; page 97, paragraph 2, line 7: “the maximum yield was obtained (14.67 %) was obtained”
- Mixing of letters e.g. page 23, line 4: „suffiecnt”; page 25, last paragraph, line 1: „sutided” instead of studied; page 30, paragraph 2, line 5: „by secnitiest and reserachers” instead of „by scientists and researchers”

Most of my major remarks concern the catalyst properties which contain interesting results, though they are not the most important findings of the work. In summary, the thesis contains



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well-based and important findings in an extremely challenging and important topic. I keep the thesis suitable for public dispute and I suggest to accept the thesis.

Veszprém, 24 November, 2021

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