Answers to Dr György Pölczmann

Firstly, I express my gratitude for the Reviewer's work and the questions/comments, which help to improve the scientific content of the PhD thesis.

1. What is the biggest accumulation points of waste plastics?

   The municipal solid waste (household waste) and the industrial waste.

2. In the chapter 1.4.1.1 the experiment described in the text, do not present in the table. Why?

   The experiment described in the text, was not presented in the table in order to avoid redundancy and verbosity.

3. Is there any literature about co-pyrolysis of plastic and paper?

   The co-pyrolysis of paper and plastic was also investigated in the last paragraph of Chapter 1.4.2. Other results were found in references from 178 to 183.

4. How the water content of pyrolysis oil can affect the corrosion properties?

   The presence of water in the pyrolysis oil fraction can increase the rate of internal corrosion, which is the most costly type of corrosion. It has been mentioned in the literature part page 35 "Aubin et al. [224] found that the corrosion rate of pyrolysis oil would be boosted with its water content."

5. What are the usual olefin and aromatic content of pyrolysis oils from thermal-only processes? How do these values change with in-situ catalytic upgrading?

   Typically the waste plastic derived pyrolysis oil contained 20-70% unsaturated hydrocarbons, depending on the raw materials and conditions. The biomass derived bio oils had less (20-60%) unsaturated hydrocarbons. In general, catalysts can decrease the amount of unsaturated hydrocarbons. One of the another role of the zeolite catalysts led to aromatization reactions, therefore synthetic zeolites (e.g. ZSM-5, Y-zeolite) can increase the aromatic content of the liquid products. The aromatic concentration of pyrolysis products is low using low temperature without catalyst. Pyrolysis product with high aromatic content (30-90%) could be obtained only from raw materials, with aromatic ring in the monomer structure (e.g. PET, PS, ABS, cellulose, etc.) without catalysts. However, the mostly investigated waste fractions resulted considerably less aromatics in pyrolysis/bio oils (10-30%).

6. Does the pyrolysis oil fulfil the European diesel fuel standard (Figure 1.7)?

   No, it does not fulfil. It needs to be upgraded (reduce the viscosity, eliminate the contaminants, reduce the water content, etc.)

7. How could the producing of pyrolysis oil be economically viable?

Costs to produce pyrolysis oil/bio-oil can be considerably different depending on the capacity, the used raw materials, the location (national laws, operating surroundings) or even the optimal product structure. In general, large-scale plant has lower production costs. One of the most difficulties regarding the large-scale commercialization of the pyrolysis plants are the product quality [187]. Especially the contaminants and the missing standardization of the products are the most problem that have to be solved, against the economic operation of the plants.

8. What are the quality limits of pyrolysis oil regarding using it as transportation fuels?

   Pyrolysis oil has lower H/C ratio, more oxygenated compounds, less calorific value, lower pH, more water content, higher viscosity and density than fuel oil. It should be contaminated and it is unstable.

9. What are the origins of the wastes which are the raw materials, and why they are the chosen ones?

   The raw materials were real wastes supplied from waste collection. Plastic waste was chosen, because their recycling is unsolved problem, especially in their contaminated form. The chlorine contamination can cause serious problem during recycling. On the other hand in the form of wastes, the plastics are mixed with other constitutes, e.g. paper and biomass. Therefore, the effect of the paper and biomass presence was also investigated.

10. What were the inspirations for using these catalysts, especially the red mud?

    The ZSM-5 catalyst is widely used for the pyrolysis of wastes, however less information is available about the SAPO-11 catalyst supporting the pyrolysis reaction. The two catalysts have different structure and elemental composition. By this way, I would to compare the applicability a widely used catalyst with the rarely used one. Catalysts were also modified by nickel. It is well known that the nickel has activity in hydrogenation-dehydrogenation reaction. By modifying the catalysts with nickel, I wanted to investigate the possibility for quality improvement due to in-situ hydrogenation-dehydrogenation reactions. The $Ca(OH)_2$ looks attractive for decreasing the acidity of the products, furthermore, it is cheap and widely available. Some papers mentioned the positive effect of the red mud to dechlorinating reactions. However, the iron can catalyze the contaminant reduction. This was the reason that I would to investigate the applicability and the effect of the red mud for the in-situ quality improving reactions. On the other hand, the red mud is hazardous waste, so it further application can help the problem of their disposal and further treating.

11. Based on what experience were the catalyst treat rates 5% in every case?

    Based on the results of previous experiments at the MOL Department of Hydrocarbon and Coal Processing, it has been observed that more than 5% of catalysts are difficult to introduce into the tubular reactor, and abrasive problems already occur in that case. For this reason, I did not increase the catalyst concentration above 5%. I did not *choose a lower amount of catalyst, because I would have picked up if there were clearly visible differences between result of thermal and thermo-catalytic pyrolysis. Of course, for economically reason, the catalyst concentration should be reduced as low as acceptable.*

12. If the TAN are not applicable to unique polymers, can it be used generally in aging tests?

    The reviewer is right, the TAN can predict the changes in case of acidic compounds; especially cellulose sourced bio-oil, however, there are some polymers, from which acidic compounds should be obtained (e.g. PET).

13. If the solid deposition measurement is correlates on the 3rd day already, is the 7 day/80 °C aging is good for forecasting storage properties?

    The reviewer is right. However, in that chapter, the correlation between the two aging test results was investigated using different raw materials. On the other hand, the correlation also depends on the composition of the raw materials. There are different correlations for different raw material derived hydrocarbon fractions. In my experimental work, I used the 80°C, 7 day accelerated aging test because it is used mainly in literature. Thus, the generally obtained results based on my work and the results in the literature can be compared.

14. Comparing the batch and tubular reactor product yields: residue equals heavy oil+char?

    Residue was the remaining fraction after the pyrolysis in case of batch reactor, however the two pyrolysis reactor are totally different, because the pyrolysis was taken till the volatiles come from the reactor in case of batch process. Virtually, the appearance of the residue was solid, which is closer to the char appearance.

15. If the red mud and the $Ca(OH)_2$ are reducing the catalytic active sites, why are they needed?

    In one hand the aim of my work was to modify the product yield and composition by zeolite catalysts. On the other hand, the possibility for in-situ contaminant reduction (e.g. chlorine) was also investigated. Many of the references mentioned the advanced properties of the alkaline and red mud. Red mud is hazardous waste, therefore I would to investigate the possibility for its value added utilization.

16. Light oil means two very different fractions in case of only thermal and in case of thermocatalytic results: could the different chain length environment had any effect in corrosion and accelerated aging tests?

    The aim of my research was to investigate the largest amount of fractions obtained by the pyrolysis. According to the literature, the liquid product produced during pyrolysis is in most cases not separated into further fractions, but attempts are made to utilize it in the given form. The stability of naphtha and diesel-like products produced from light oil will differ significantly in case if the amount of components causing difficulties (e.g.

olefins, chlorine, acidic components, etc.) in one fraction differs significantly from the other.

17. Based on accelerated results does any light oil need filtering?

    After a given density or viscosity increase, the light oil should be needed to filter. However, it is depending on the further application aim of the fraction.

18. Did the water cause any problem during paper-plastic pyrolysis?

    From energetic viewing point, water needs additional energy to heat up and evaporate, however the small water/steam bubbles can mix the degrading polymer, resulting better homogeneity. From chemical aspect, the water is undesired, because of the corrosion problems and phase separation.

19. Is the forming of CO_2 during paper-plastic pyrolysis a problem regarding the environment? Is hydrogen forming positive or dangerous?

    Yes, the CO_2 production can cause environmental and sustainable problems, because of the limited emission of CO_2 into the atmosphere. For chemically viewing point, due to the possibility for in-situ hydrogenation, the hydrogen has rather positive effect to the pyrolysis products.

20. Where can the pyrolysis oil of this research be applied based on its quality?
    a) Diesel engines
    Slow and medium speed diesel engines are well-known for their capability to carry on low quality fuels. The complications encountered with corrosion seems to be solvable with the appropriate selection of materials and enhanced particulates elimination from the pyrolysis oil. On the other hand, blended methanol with pyrolysis oils has demonstrated performance characteristics comparable to the conventional diesel fuel. [Gros, S. "Pyrolysis Liquid as Diesel Fuel, "Seminar on Power Production from Biomass II, 27.0-28.3, 1995, Espoo, Finland. 1995.]

    b) Combustion turbines
    Combustion turbines are a well-known technology that used for producing heat and electricity at reasonably high efficiencies. They are mainly powered on natural gas or petroleum distillates but if suitably designed, in combination with proper fuel specifications, they must be able to function on any fuel comprising pyrolysis oil. One of the crucial concerns of using pyrolysis oils in combustion turbines is the effective elimination of char from the pyrolysis oil. The higher viscosity, low heating value, and acidic nature properties of pyrolysis oil can be arranged by material selection and appropriate design in the turbine. Strenziok et al. established a smaller (75 kW) commercial turbine on pyrolysis oils. In his experiment, the combustion chamber was adjusted to enable a dual fuel process with pyrolysis oil and diesel. The ratio was 40% pyrolysis oil and 60 % diesel. [Strenziok, R.; Hansen, U.; Künster, H. "Combustion of Bio-oil in a Gas Turbine," Bridgewater, A.V., ed.

Progress in Thermochemical Biomass Conversion. Oxford: Blackwell Science, 2001; pp. 1452-1458.].

c) *Boiler*
Pyrolysis oil can be used for the combustion in boiler for electricity and heat production.

d) *The production of chemicals*
Pyrolysis oil can be used for the invention of chemicals. Such as tars, acetic acid, methanol, at an inferior cost comparing to other feedstock's derived from crude oil, natural gas, or coal. The substances that can be extracted from pyrolysis oil are: additives applied in the fertilizing industry, or fiber synthesizing. E.g. phenols should be used for the production of resins.

21. Is it possible to use medical wastes in polymer pyrolysis process?

Medical waste is produced by clinics, hospitals, and other associated health-care establishments. Which has characteristically high potential infectious and toxic materials. Medical waste is mainly composed of 50% plastic, 16% paper, 10% textile fiber, 1% metal, 23% other (wood; glass; cotton, etc.). Since it contains high proportion of organic matters that has the characteristics of high volatiles and high energy density it can be used for pyrolysis process. [E.S. Windfeld, M.S. Brooks, Medical waste management – a review, J. Environ. Manag. 163 (2015) 98–108.]