

Catalytic pyrolysis of biomass

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1. Introduction

The global demand for energy is constantly growing, due to the growth of economy all over the world. Current social needs in the field of fuels and chemicals are strongly dependent on fossil fuels. This dependence can lead to uncertainty in the economy, political affiliation and supply insecurity. What is more, increased CO₂ emissions and global warming are associated with the use of fossil fuels and is a collateral damage that destroys the future of Earth. [1] Considering environmental and social issues, the use and creation of new renewable sources becomes necessary. This solution should also be directed at fixing the problem with decreasing reserves of fossil fuels and reducing the CO₂ emissions produced by their burning processes. Basically, it is crucial to find economically and environmentally beneficial way to satisfy modern society's energy needs using renewable energy sources. [2] In this work the main focus will be put on biomass, as a solution to problems portrayed above.

In order to obtain the biofuel, pyrolysis of biomass must be carried out. Raw pyrolysis oil is unstable and can be toxic, catalyst have to be studied, so that this process is improved. In this work new catalyst were developed and examined in the process of catalytic pyrolysis of biomass. The catalysts were double layered hydroxides (hydrotalcites), which were chosen because they fulfill all guidelines for perfect catalysts as they are economically and ecologically efficient.

1.1 Hydrotalcites

Layered double materials (LDHs) are natural or synthetic layered materials, which consist of positively charged two-dimensional surfaces of hydroxides mixed with water exchangeable anions. [3] They are basically mixed aluminum and magnesium hydroxycarbonate with a structure of brucite. It was discovered in Sweden 1842. It is a mineral, which when crushed, looks similar to talc and that resemblance is the reason of the name "hydrotalcite" (HT). If found in nature, it occurs in fibrous masses or foliated and contorted plates. HTs are mainly used after being calcinated, which leads to obtaining oxides. They give the minerals interesting properties, such as [4]:

- High surface area;
- Basic properties;
- "Memory effect";

- Thermal stability thanks to formation of homogeneous mixtures of oxides with small crystal size

The variety of application of HTs is presented on fig.1:

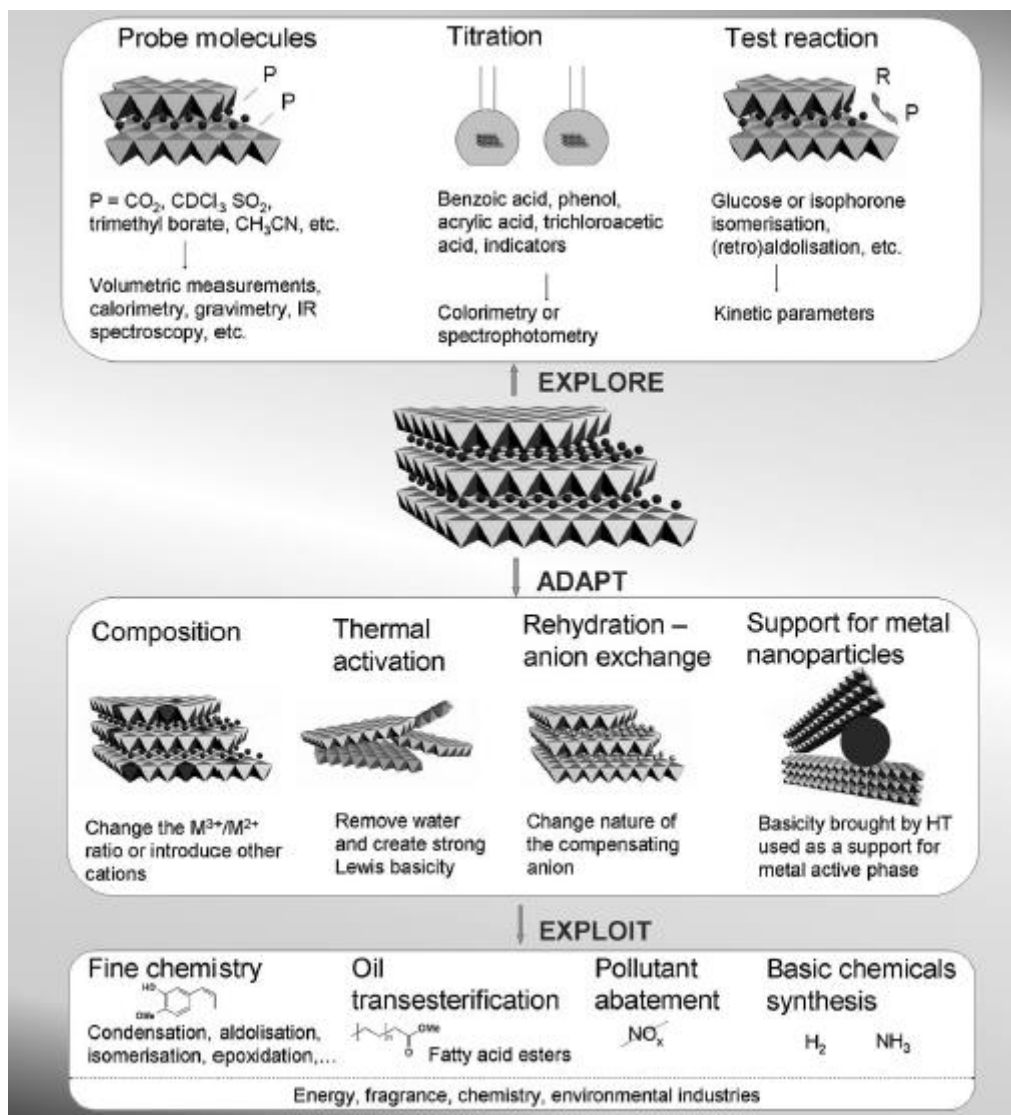
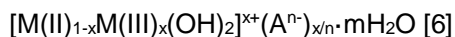


Fig.1 The variety of properties, applications and modifications of HTs [3]

The structure of LDH is presented in fig.2, while the most general formula is shown below:



Where:

- x – mole fraction of trivalent cations;
- M(II), M(III) – divalent and trivalent cations;
- A – interlayer anions;
- [M(II)_{1-x}M(III)_x(OH)₂] – describes composition of the brucite-like layers;
- [(Aⁿ⁻)_{x/n}·mH₂O] – describes composition of the interlayer spaces.

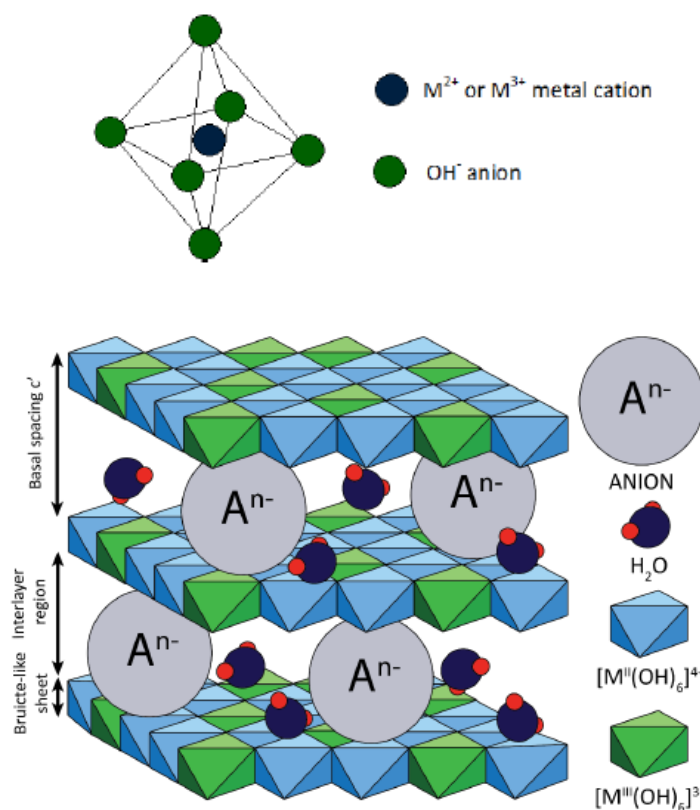


Fig.2 Octahedral unit of brucite-like layers in the structure of HT and the schematic representation of the whole hydrotalcite structure. [5]

Because of all properties of LDHs mentioned above, they became very interesting alternatives for catalysts in the biomass pyrolysis process.

1.2 Pyrolysis of biomass

The reason why pyrolysis of biomass has been studied is that scientist would understand better how the process of combustion would control the flammability of biomass and (which is more relevant to this work) to improve processes of biomass conversion in order to obtain more useful energy forms. [7] The process of pyrolysis is basically a thermal degradation under absence of oxygen or with limited supply of that element, so that the gasification would not be able to occur. It is usually carried out in relatively low temperatures of 500-800°C and as a result, most of the time, three products are obtained: gas, liquid and char, which depends on method of the pyrolysis process and parameters of the reaction. [8] Pyrolysis in other words is a thermal decomposition, which is always a first step in combustion and gasification. There are different models of pyrolysis, which occur in different conditions and give various proportions of products, which is illustrated in the table 1 [9]

When it comes to pyrolysis of biomass, what is important, is to remember that its components react differently to the thermal decomposition and that is why the composition of biomass has a major influence on products obtained and thus is a really important feature. In this work the main focus is put on slow and fast pyrolysis. The main difference between those two is the time required to heat biomass to the temperature of pyrolysis ($t_{heating}$) in comparison to the time of reaction of pyrolysis (t_r): [10]

- Slow pyrolysis: $t_{heating} \gg t_r$
- Fast pyrolysis: $t_{heating} \ll t_r$

<i>Mode</i>	<i>Conditions</i>	<i>Liquid</i>	<i>Solid</i>	<i>Gas</i>
Fast	~ 500 °C, short hot vapor residence time ~ 1 s	75%	12% char	13%
Intermediate	~ 500 °C, hot vapor residence time ~ 10–30 s	50% in 2 phases	25% char	25%
Slow – Torrefaction	~ 290 °C, solids residence time ~ 30 min	0% if vapours are burned	80% solid	20%
Slow – Carbonization	~ 400 °C, long vapor residence hours → days	30%	35% char	35%
Gasification	~ 750–900 °C	5%	10% char	85%

Table 1: Different types of pyrolysis [9]

2. Methodology

2.1 Catalyst preparation

Four hydrotalcites were prepared with co-precipitation method, which consists in adding solutions of metal salts to the sodium carbonate solution in the same time with NaOH in order to maintain constant pH. The process is carried out in constant temperature. The obtained precipitate is the first form of the HT. Amounts of different solutions, pH and temperature depends on the types of hydrotalcites:

- **Mg/Al/Fe** – 24.27g of magnesium nitrate hexahydrate, 5.93g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 6.38g of $\text{Fe}(\text{NO}_3)_3$ were mixed with 126ml of water, while the solution of Na_2CO_3 was created by mixing 2.09g of solid salt with 395ml of water;
- **Ni/Zn** – obtained with coprecipitation method with divalent to trivalent cations ratio equal 3;
- **Mg/Al** – 25.43g of magnesium nitrate hexahydrate and 12.42g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed with 132ml of water, while the solution of Na_2CO_3 was created by mixing 2.19g of solid salt with 414ml of water;
- **Zn/Al** – 30.54g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 12.42g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed with 94ml of water, while the solution of Na_2CO_3 was created by mixing 1.56g of solid salt with 294ml of water.

After creating all the solutions, the hydrotalcite synthesis kit needed to be assembled, as in fig. 3. The synthesis was carried out in temperature of 60 °C and pH=10. The process started when the solution of Na_2CO_3 reached the 60 °C and metal salt with 1M NaOH solutions began to be dropped in it at the same time. The dropping needed to be set very carefully, so that the solution was constantly equal to pH=10±0,2. All amount of obtained solutions were dropped into the Na_2CO_3 and after were left on a magnetic stirrer for 1h at 60°C. After this time the obtained precipitate had to be filtered on a Buchner funnel and later washed with about 1.5l of warm distilled water to prevent cracking. The left residue was the hydrotalcite, which was transferred to a Petri glass and dried in the oven for 24h. When the preparation of HTs ended, they had to be grinded and calcinated for 6h in 500 °C.

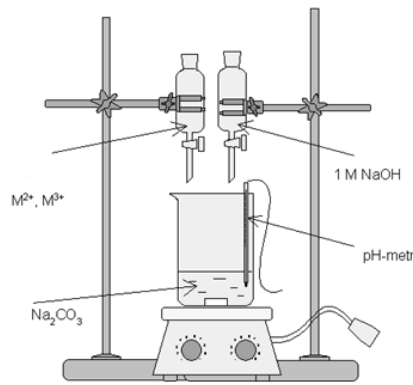


Fig. 3 Scheme of HT synthesis kit [5]

2.2 Experiment

Firstly, the samples were prepared: four with catalysts and one with pure *Arthrospira platensis* algae. The proportion of catalyst to the biomass sample needed to meet the requirement of 5% of HT of the whole weight. The proportions for different hydrotalcites were:

- Mg/Al/Fe – 5.1mg of biomass and 0.6mg of catalyst
- Ni/Zn – 8.1mg of biomass and 1mg of catalyst
- Mg/Al – 11mg of biomass and 1.2mg of catalyst
- Zn/Al – 7.6mg of biomass and 0.7mg of catalyst

The sample with pure biomass, contained 5.5mg of the feedstock. All of the samples were analysed using TA Instruments SDT 2960 simultaneous TGA/DSC apparatus, which allowed measurement of the kinetics of devolatilization and the thermicity of the process. The samples introduced into the apparatus went through controlled heating program in controlled environment in order to achieve the pyrolysis and combustion process. The combustion of the samples was carried out after pyrolysis in order to burn materials that pyrolysis did not degrade. TGA/DSC analysis in this case provided information about weight loss and heat flow of both processes. The experiment starts when one reference pan and one pan with a sample (5-11mg) are placed in the apparatus and then it is followed by the same steps:

- Equilibrate at 40°C
- Isothermal for 10min
- Ramp 10°C/min to 800°C
- Isothermal for 10min
- Air cool: On
- End of experiment

After computer processed the data from the experiment, analysis of weight loss, derivative weight and heat flow of pyrolysis and combustion processes was carried out as well as kinetic modelling was performed.

3. Results

Results of the pyrolysis process of all five samples were presented and analysed on DTG, TGA and DSC graphs. Same was done for the process of combustion, although the results were not analysed, just presented on the graphs, in order to be used in future studies of catalytic pyrolysis of biomass. The similar situation is applied for kinetic modelling of weight loss dependence to temperature in the pyrolysis process for all samples, and combustion process for MgAlFe containing sample. The curves were fitted, and thanks to that the values of weight fractions, energy activation and reaction rate constant were estimated. The results were not discussed, but were shown in order to make use for them in future experiments, examining catalytic pyrolysis of biomass with the same catalysts as used in this work. Figures 4,5 and 6 represent thermal analysis of pyrolysis. TA curves can be divided into three phases of thermal degradation [11]:

- Phase 1 in temperature below 150°C representing vaporisation of moisture and light components
- Phase 2 between 150-450°C representing devolatilization of hemicellulose and cellulose
- Phase 3 in temperature above 450°C until 700°C representing lignin decomposition

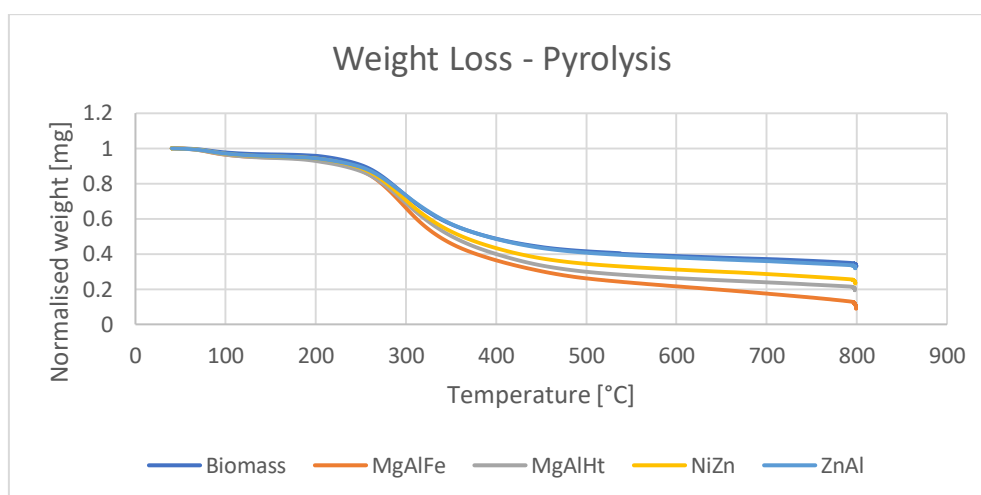


Fig.4 Comparison of weight loss to temperature dependence for all samples in the pyrolysis process

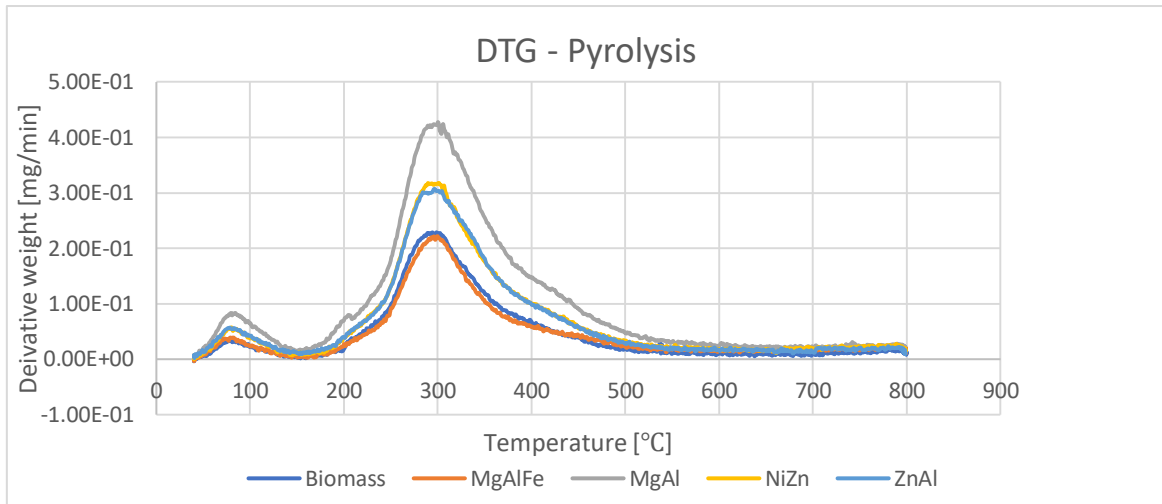


Fig. 5 Comparison of derivative weight to temperature dependence for all samples in the pyrolysis process

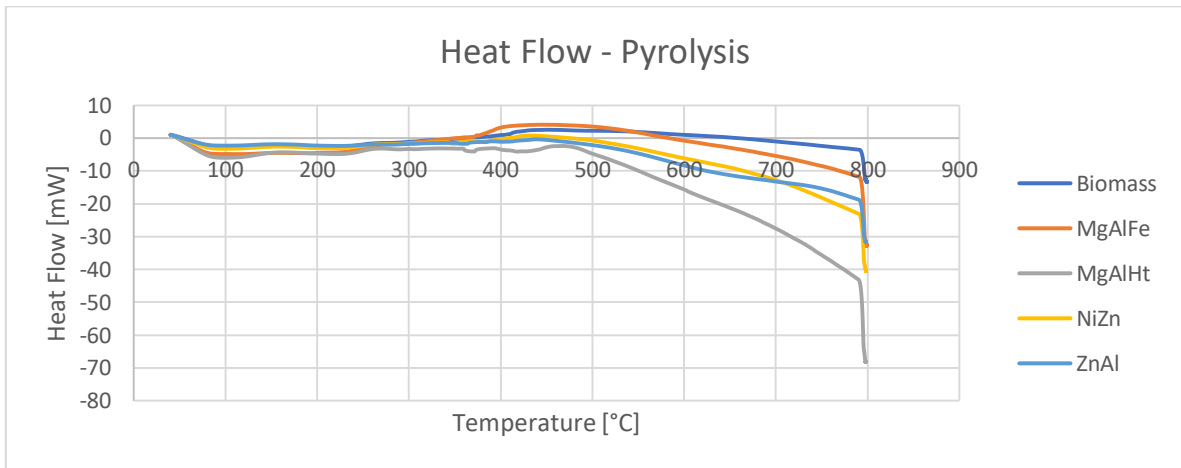


Fig. 6 Comparison of heat flow to temperature dependence for all samples in the pyrolysis process

As mentioned above, kinetic modelling and fitting curve were carried out for certain samples and purposes. Below, the fitted curves are presented for the process of pyrolysis in TGA graph for pure biomass and MgAlFe containing samples (Fig. 7) as well as the table 2 containing obtained values from curve fitting of weight fractions, energy activation and reaction rate constant are presented for all samples. Also the correlation coefficient R^2 is presented, in order to show, that all the curves are fitted correctly. If R^2 has value higher than 0.994, it means that the curve is fits.

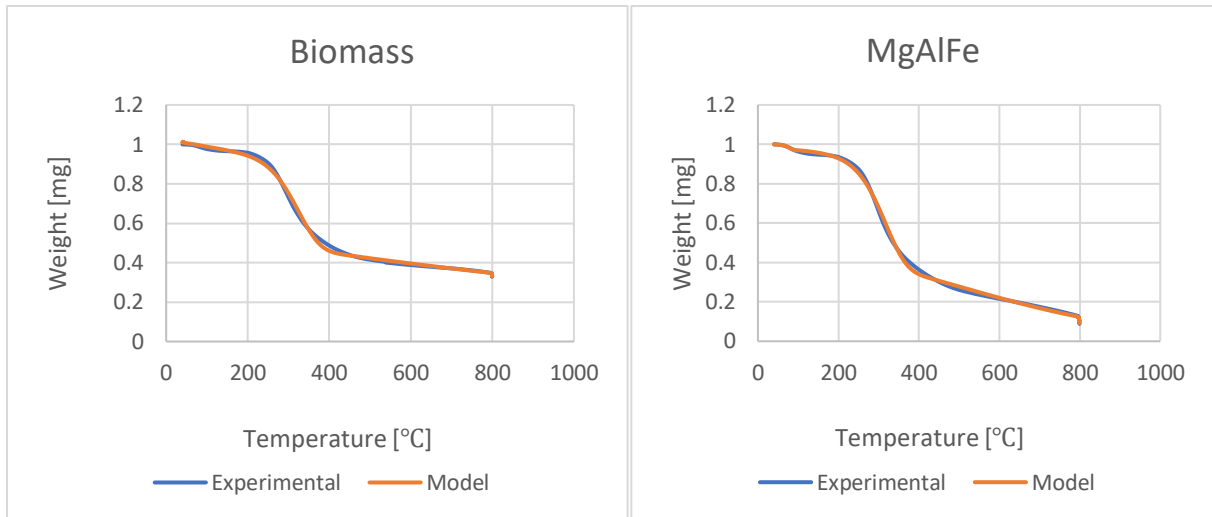


Fig. 7 Model fitting for weight loss to temperature dependence in the pyrolysis process

	Biomass	MgAlFe
w1 [mg]	0,441319	0,518856
w2 [mg]	0	0,022026
w3 [mg]	0,572076	0,459969
Ea1 [J/mol]	56692,19	56926,5
Ea2 [J/mol]	0	121584,2
Ea3 [J/mol]	0	10179,99
k1 [1/min]	0,483626	2,62E-06
k2 [1/min]	1	9,64E-04
k3 [1/min]	0	0,001722
R²	0,997974	0,99885

Table 2: Values of weight fractions, Ea, k and correlation coefficient for all samples for model fitting for weight loss to temperature dependence in the pyrolysis process

4. Conclusions and outlook

After thermal analysis, results showed that the catalyst do not have a major influence on the biomass performance in pyrolysis process. There have been many experiments and articles examining other economic catalysts, like zeolites, montmorillonites and even other hydrotalcites, that performed better in similar tests. One catalysts examined in this work, stood out of the rest samples, and performed the best. This hydrotalcite was MgAlFe.

TGA analysis showed that the curve representing MgAlFe catalyst had the biggest drop in phase 2 of pyrolysis process in comparison to the performance of non-catalysed biomass, which means that this catalyst maximized the weight loss of algae thermal degradation the most out of all other studied catalysts, which makes it the best one in this study. Other catalysts had similar weight loss to pure biomass sample. The worst result was obtained from the sample catalysed with ZnAl, which was almost identical to the reference sample. The thermal degradation for all samples, began around 250°C.

In DTG analysis the biggest peak, which occurred around 300°C is connected to the biggest drop of the curves in TGA analysis, which was presented for similar temperature. Both of these results occurred in the phase 2 of pyrolysis process. DTG in this case represent the amount of biomass that was lost in specific amount of time and its dependence to temperature. The results, however, do not differ that much from the reference sample. The amount of weight lost in DTG analysis are different from each other, but the values are so small, that it would not have a greater impact in bigger scale. In this case MgAl had the biggest weight loss in specific amount of time. Unfortunately neither of catalysts examined in this work, lowered the degradation temperature. It was the same for all samples, including the reference one (around 300°C).

DSC analysis represents the amount of heat that was absorbed or released in the moment of time and in certain temperature. Here, similar to DTG analysis none of the catalysts shown to lower the degradation temperature. Each sample, including the one containing pure algae had endothermic behaviour, except for MgAlFe catalyst, which had slight exothermic performance, but then after few degrees went back to its endothermic nature. The catalyst that differed the most from reference sample was MgAl. The curve representing it had the biggest heat flow drop, but it does not influence the conclusions for this type of study.

In conclusion, the catalysts do work, but are not the best ones available, when it comes to price, renewability and economic approach. From these four catalysts examined in this thesis MgAlFe and MgAl had the biggest influence on the algae's performance in the pyrolysis process. It means that with the use of these catalysts in the pyrolysis of biomass, the bio-oil synthesis would be more efficient, in comparison to non-catalytic pyrolysis.

In the future, scientists may check the performances of other hydrotalcites containing magnesium and aluminium, as these had the best performance in this work. Also the obtained catalyst may be studied in catalysis of different processes or different biomass feedstocks. There is still a lot to be discovered in this area.

Apart from pyrolysis, the combustion process after pyrolysis was carried out for all samples in order to burn not degraded materials. The result of thermal analysis of this process was presented on TGA, DTG and DSC graphs, which may also be examined in future studies, but were not the goal in this thesis. The similar situation is applied for kinetic modelling of weight loss dependence to temperature in the pyrolysis process for all samples, and combustion process for MgAlFe containing sample. The curves were fitted, and thanks to that the values of weight fractions, energy activation and reaction rate constant were estimated. The results were not discussed, but were shown in order to make use for them in future experiments, examining catalytic pyrolysis of biomass with the same catalysts as used in this work.

This thesis may be analysed further in the production of bio-oil from the algae, where the hydrotalcite's performance as catalysts may be examined with more details.

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