Catalytic Pyrolysis of Biomass

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I declare that this document is an original work of my own authorship and that it fulfils all the requirements of the Code of Conduct and Good Practices of the *Universidade de Lisboa*.

Aknowledgements

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Abstract

The aim of this thesis was to examine hydrotalcites as catalysts for the process of catalytic pyrolysis of biomass, which was portraited as a representative of renewable sources and as an alternative for fossil fuels in the future. Pyrolysis is originally carried out for biomass in order to transform it into bio-oil. Hydrotalcites were chosen, because the perfect catalyst for this type of process is natural, cheap, economically efficient. In this work *Arthrospira platensis* algae was representing the biomass, and was mixed separately with four different hydrotalcites: MgAlFe, MgAl, NiZn and ZnAl, in this way that the amount of catalyst in each sample was equal to 5% of amount of biomass. Thermal analysis was carried out for all samples in was TA Instruments SDT 2960 simultaneous TGA/DSC apparatus in order to study the catalytic performance of all hydrotalcites on microalgae in the process of pyrolysis. The obtained results, were shown on TGA, DTG and DSC graphs and all samples were compared on them to each other and to the reference sample, which was pure algae. The results showed, that the samples containing MgAlFe and MgAl catalyst performed the best compared to reference sample and other catalysts. After pyrolysis, combustion was carried out to burn the residuals. The results were shown on the same types of graph, which can be analysed in further studies. 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 by resorting to a least-squares fitting methodology values of weight fractions, energy activation and reaction rate constant were obtained. 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. Results obtained in this thesis may be the base for wide range of scientific studies in the future examining the catalytic nature of hydrotalcites and further analysis of catalysts obtained in that work in the synthesis of bio-oil from algaes and different biomass feedstocks.

Keywords: Biomass, hydrotalcites, pyrolysis, catalysis, TGA/DSC

Resumo

O objetivo desta tese foi examinar catalisadores à base de hidrotalcites para a pirólise catalítica de biomassa, que é apresentada como representativa das fontes de energia renováveis e como uma alternativa aos combustíveis fósseis no futuro. A pirólise é efetuada sobre a biomassa no sentido de a transformar em bio-óleo. As hidrotalcites foram escolhidas porque os catalisadores ideais para este processo devem ser naturais, baratos e eficientes do ponto de vista económico. Neste trabalho foi utilizada a alga *Arthospira platensis* como fonte de biomassa, tendo sido misturada, separadamente, com quatro hidrotalcites diferentes: MgAlFe, MgAl, NiZn e ZnAl. As misturas foram feitas para que o catalisador correspondesse a 5 % da quantidade de biomassa. Foi feito um estudo de termo-análise para todas as amostras num aparelho SDT 2960 com TG/DSC simultâneos para analisar o desempenho catalítico de todas as hidrotalcites sobre as microalgas no processo de pirólise. Os resultados obtido, representados sob a forma dos sinais de TG, DTG e DSC e todas as amostras foram comparadas entre si com a a amostra de referência, constituída pela biomassa algal sem catalisador.

Os resultados mostraram que os catalisadores contendo MgAlFe e MgAL tiveram o melhor desempenho quando comparados com o material de referência e também com os outros catalisadores, embora não tenham tido um efeito muito profundo sobre a decomposição térmica da biomassa. Depois da pirólise foi realizada uma combustão do resíduo. Os resultados foram analisados de forma semelhante. Os resultados foram ainda analisados recorrendo a modelação cinética para todas as amostras no que diz respeito à pirólise e à combustão do resíduo para a amostra com MgAlFe. Foram realizados ajustes do modelo cinético e, utilizando uma técnica de mínimos quadrados relativamente às frações de massa, foram estimadas as energias de ativação e as constantes cinéticas. Apesar de os resultados não terem sido completamente discutidos mas são apresentados como base para trabalho futuro que permita uma maior compreensão da pirólise catalítica de biomassa utilizando estes catalisadores. Os resultados obtidos nesta tese podem servir de base a um conjunto de estudos científicos para analisar o comportamento catalítico de hidrotalcites e posterior análise dos catalisadores obtidos neste trabalho na produção de bio-óleo a partir de algas ou de outras fontes de biomassa.

Palavras-chave: Biomassa, hidrotalcites, pirólise, catálise, TGA/DSC

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Introduction and aim of work

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 are 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 the problems portrayed above.

Biomass is one of the renewable energy sources that could be able to fulfil the modern demand for energy, while being safe for the environment and profitable. In many countries, various sectors produce significant amount of waste, which also includes biomass. By merging waste to energy principle with seeking for new energy source, the biomass becomes even more indispensable. [3] From various types of this source, come different categories of products:

- Chemicals
- Energy
- Electricity
- Transportation fuel

In order to obtain this products, a specific biomass conversion must be carried out. [4] The pyrolysis of biomass produces liquid oil (pyrolysis oil), gas (pyrolysis gas) and solid (char) products and all of these may be the target products of biomass pyrolysis [3]. Raw pyrolysis oil consists mainly of oxygenated compounds, which has a bad impact on fuel properties. Such product has high viscosity, low heating value, is corrosive and thermally unstable. But apart from these it is at the same time less toxic, has better lubricity and is more biodegradable in comparison to petroleum fuels. In order to obtain fuels with adequate properties and get rid of the oxygenated compounds, it is very important to upgrade the raw oil. One process that can help with achieving such goal is catalytic pyrolysis. [3]

There are various types of different kinds of catalyst, that have the ability to improve the pyrolysis process and the quality of the raw pyrolysis oil in different way. The aim of this work is to contribute to the development of catalysts and study the kinetics of catalytic pyrolysis of biomass. In this research double layered hydroxides (hydrotalcites) were used. It is very important, while focusing on improving fuel properties and finding economically and ecologically beneficial way to do it, that the catalysts used are also profitable and friendly for the environment.

1. Layered double hydroxides

Layered materials are being often used in adsorption and catalytic technologies, thanks to their properties and structure. As it is known, that these kind of materials can make interesting catalysts and adsorbents, for the last century the research on them has been developing, which led to a large number of modifications, both compositional and structural, of layered materials. Because of these modifications it is possible to create and improve their properties, which results in a large spectrum of applications. [5]

All layered solids can be divided by depending on the charge of their layers [5]:

- Natural layer materials - graphite, hydroxides (such as brucite), phosphates, metallic oxides (V2O5);
- Positively charged layers with compensating anions in their interlayer space – anionic clays, such as hydrotalcite-like materials (HTs). This kind of material is very rare to be found in natural environment, so they have to be prepared in the laboratory;
- Negatively charged layers with compensating cations – cationic clays like montmorillonite and vermiculite, are the type of materials which, in comparison to anionic clays, occur widely in nature.

This work and chapter is focused mostly on hydrotalcite-like materials as a catalyst. Another name for this kind of materials is layered double hydroxide (LDH). These solids have a wide range of application, not only are they have a potential to be great catalysts but also can be used in medicine, electrodes, anion exchangers and as PVC stabilisers. [6]

Hydrotalcite was discovered in Sweden 1842 and more practically speaking is a hydroxycarbonate of magnesium and aluminium. It is a mineral, that when crushed, looks similar to talc and that resemblance is the reason of the name “hydrotalcite”. If found in nature, it occurs in fibrous masses or foliated and contorted plates. [7]

HTs are mainly used after being calcinated, which leads to obtaining oxides. They give the minerals interesting properties, such as [7]:

- High surface area;
- Basic properties;
- “Memory effect”;
- Thermal stability thanks to formation of homogeneous mixtures of oxides with small crystal size.

After obtaining such properties, it became clear, that hydrotalcites can be easily modified in order to use them in different fields. They can be the starting point for many catalytic or acid-basic materials, which can be used as catalysts in a wide range of reactions. [8] Apart from that LDHs have ionic exchanged capacity ad this ability to capture and exchange inorganic and organic anions makes them even more unique. The variety of their applications, modifications and properties can be seen on fig.1. They are often chosen over other compounds due to their simplicity, versatility, low cost and their ability to be easily modified. [9]

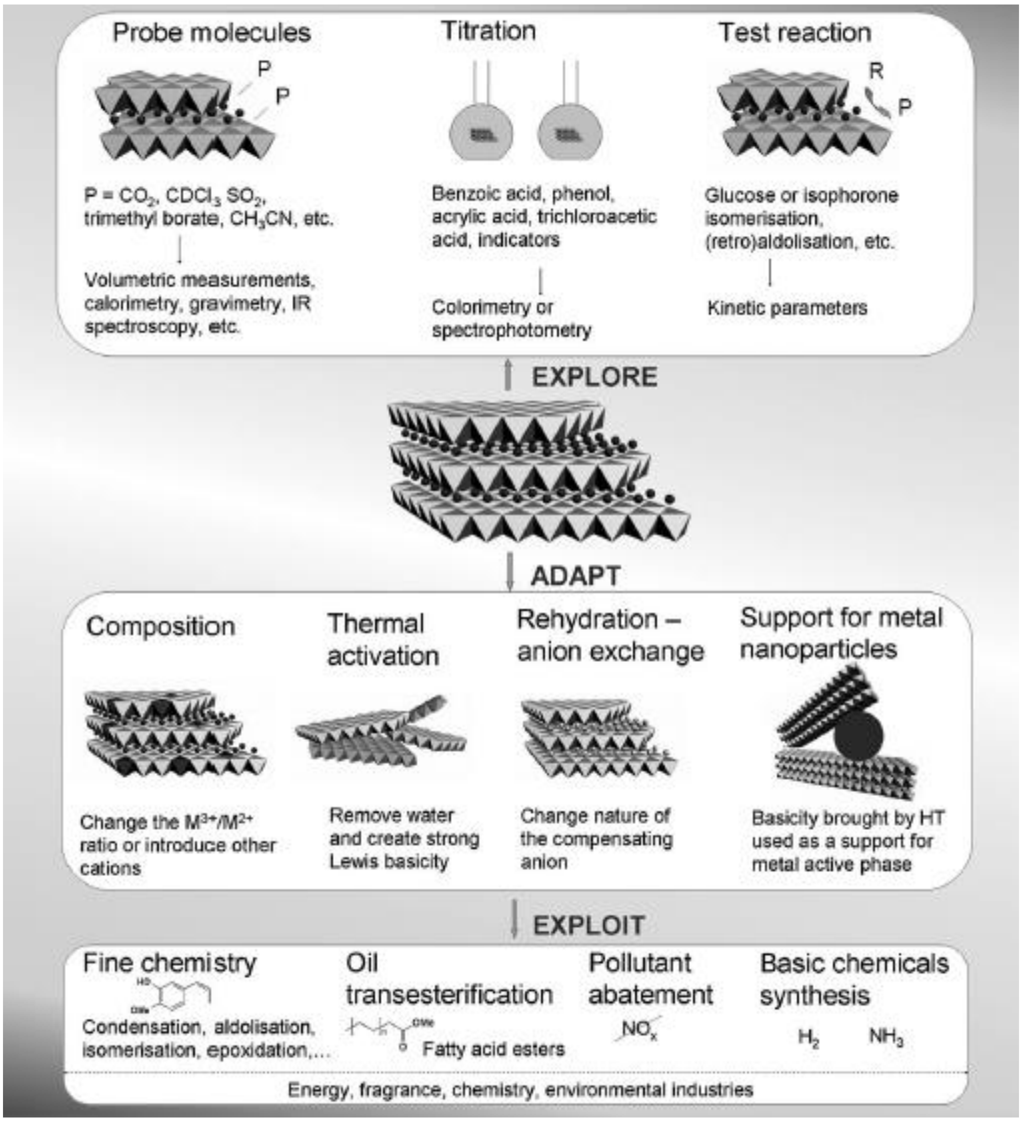


Fig. 1 The variety of properties, applications and modifications of HTs [8]

1.1 Structure and composition

Hydrotalcites are natural or synthetic layered materials, which consist of positively charged two-dimensional surfaces of hydroxides mixed with water exchangeable anions. [8] They are basically mixed aluminium and magnesium hydroxycarbonate with a structure of brucite. [5] So in order to understand the structure of these materials, it is important to first learn about the structure of brucite-like compounds. For example Mg(OH)2, where octahedra of magnesium cations share edges, creates infinite sheets, which are put on top of each other and stick together thanks to hydrogen bonding. [7] The octahedral unit, that can be seen in fig. 2 and from which HTs layers consist of, has a specific structure, in which divalent or trivalent cation is in its center and six OH- groups are placed in its corner. The structure of hydrotalcite depends on the arrangement of layers, which decides on their symmetry: [5]

- Rhombohedral symmetry – more common, build up from three layers;
- Hexagonal symmetry – build up from two layers.

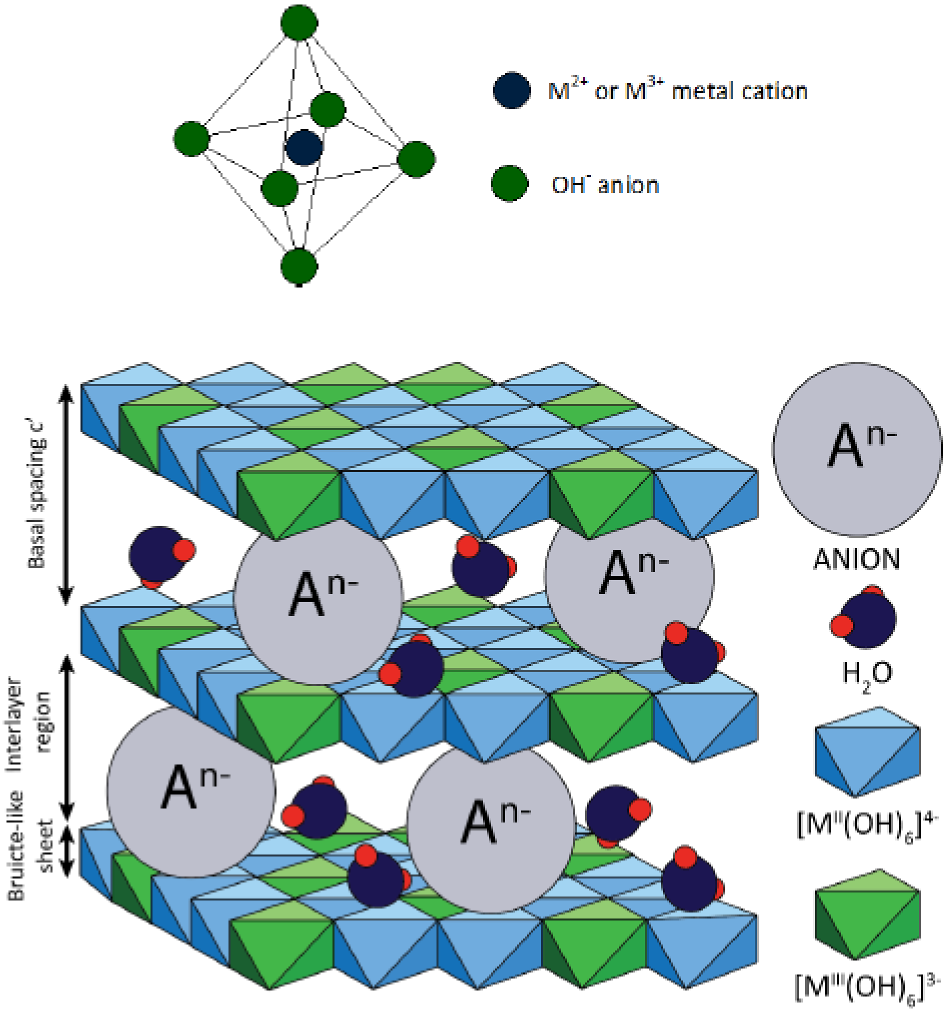


Fig. 2 Octahedral unit of brucite-like layers in the structure of HT and the schematic representation of the whole hydrotalcite structure. [5]

The most general formula for hydrotalcites is:

$$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$$ [10]

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;
- $[(A^{n-})_{x/n}\cdot mH_2O]$ – describes composition of the interlayer spaces.

The basic structure of LDH may be obtained by substituting the fraction of divalent cations in the brucite lattice with trivalent cations, so that layers turn out to have positive charge. This change is being balanced by intercalation of anions, and sometimes water, between the layers. Thanks to being able to vary the nature and the proportions of divalent cations, trivalent cations and interlayer ions, the formula

$[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$ can be applies to most materials in the LDH group. There is also a possibility to obtain and preprare tenary and quaternary LDHs, which contain different mixtures of M(II) and M(III) cations. A prerequisite for a correct hydrotalcite structure is the introduction of metals with a similar ion beam. Metal cations that can be introduced into the hydrotalcite structure together with their ionic rays are given in Table 1. An important factor is also the molar fraction of the trivalent metal - x. A pure hydrotalcite structure can be obtained only for: $0.2 < x < 0.33$. [10]

M (II)	Mg^{2+} (0,65)	Zn^{2+} (0,74)	Co^{2+} (0,74)	Ni^{2+} (0,72)	Cu^{2+} (0,69)	Mn^{2+} (0,80)	Fe^{2+} (0,76)
M (III)	Al^{3+} (0,50)	Cr^{3+} (0,69)	Co^{3+} (0,69)	Fe^{3+} (0,64)	V^{3+} (0,74)	Mn^{3+} (0,66)	

Table 1: Ion rays of selected metals [7]

There may be various types of anions in the inner space of the hydrotalcite. Depending on the type of salt used for the synthesis of the hydrotalcite, compounds with different types of anions can be obtained. Carbonate hydrotalcites are most often obtained. Due to its properties, by leaving the hydrotalcite in a solution containing appropriate anions or using the memory effect, virtually any type of anion can be introduced into the interlayer space, for example simple inorganic anions, organic anions or complexes.

LDHs interlayer galleries have in their structure both interlayer anions and water molecules. Apart from that there is also a complex network made from hydrogen bonds between water molecules, anions and layer hydroxyl groups. Hydrogen bonds in this kind of structure are constantly fluxed and the interlayer itself is substantially disordered, which leads to conclusion, that their nature is very complex. [11] Octahedral layers are connected by bonding with the interlayers, which is made of hydrogen bonding and electrostatic effects. Hydroxyl groups, especially the ones, which are connected to trivalent cations have the tendency to being strongly polarized and they are able to interact with interlayer anions. Every anion must balance the overabundance of positive charges on both octahedral layers, which are balanced by two interlayers being in their neighbourhood. Another important property of LDHs is that in most cases, there are only weak bonds between interlayer anions and the structure of the host. Thanks to that, a big variety of different anions can be put between the layers, while forming new layered structure or during anionic exchange that may occur in the future for this material. Examples of such anions are: [11]

- Organic anions (carboxylates, phosphonates, alkyl sulphates)
- Oxo-anions (carbonate, nitrate, sulphate, bromate)
- Oxo and polyoxo-metallates (chromate, dichromate, $(Mo7O24)^{6-}$,$(V10O28)^{6-}$)
- Halides (fluoride, chloride)
- Anionic complexes (ferro- and ferricyanide, $(PdCl4)^{2-}$)

The layer rigidity is also one very important aspect of LDHs, because it has a strong effect on its properties. [10]

1.2 Properties

LDHs physicochemical properties are mainly based on their chemical composition and the method with which materials were prepared. It has been proven in many studies that the preparation method strongly influences the HTs morphology and texture. Even though many LDHs have different properties, there are some that they all have in common, like memory effect or basic character. HTs are also able to form homogeneous mixtures, which contain well dispersed elements in layer and interlayer domains. [12]

1.2.1 Memory effect

This property in other words can be explained as the reconstruction of hydrotalcites. It basically means that calcinated HTs can go back to their layered structure, if they are put in contact with water and desired anions. It can also be called the retro-topotactical transformation. Memory effect depends highly on the temperature in which base HT was calcined, for example if this temperature was too high, than the memory effect of the whole structure is lower. [8] It means, that in order to obtain such property, hydrotalcite must be calcined in moderate temperature, as higher may even lead to the material loosing its ability to reconstruct layered structure. [5] The memory effect is one of LDHs best features, if they are being used as sorbents for anionic species. By calcining the adsorbents there is a possibility for them to being recycled and reused with elimination of the harmful molecules. [10] Fig. 3 represents reconstruction of Mg-Al CO_3 hydrotalcite by the memory effect. First, there is the thermal decomposition of mentioned HT and after its immersion in water, without contact to air. As the result of such actions a hydrotalcite-like structure is being formed by presenting OH^- anions to the interlayer spaces. [5]

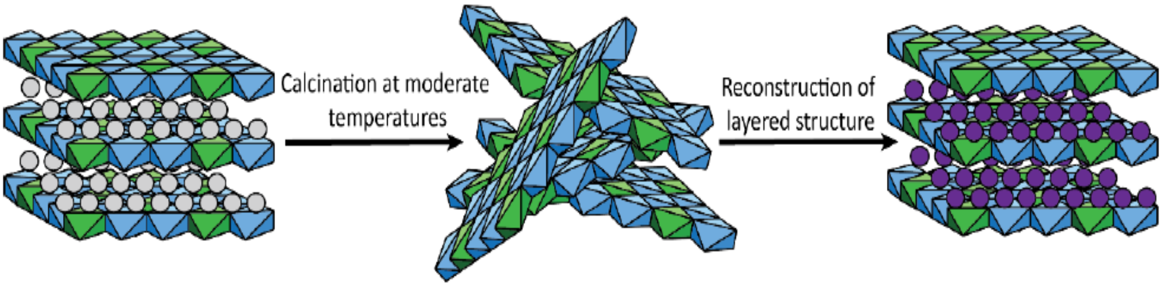


Fig.3 Schematic representation of the memory effect. [5]

1.2.2 Thermal stability

The thermal stability of HTs is a very important feature, when it comes to application in a wide range of industry branches of products obtained from thermal decomposition of LDHs. Even though there are many different types of hydrotalcite like materials, because they can be built from various elements, they all have similar thermal decomposition behaviour. [13] The nature of the layer cations, interlayer anions and conditions during heating have big influence on LDHs thermal decomposition. Usually the process of this kind of decomposition can be pictured in four steps: [6]

- Removal of water, under the temperature below 100°C, that was physically adsorbed on the external surface of crystallites;
- Removal of interlayer water in the temperature under 250°C;
- Removal of hydroxal groups in the form of water vapour, from the layers;
- Removal of interlayer anions in the temperature under 500°C.

Removal of hydroxil groups and interlayer anions usually overlap. When thermal treatment is being carried out under the temperature up to 500°C it comes with a consequence of obtaining loss of 40 wt.% initial weight. These values are the same for many HTs with different composition. [5] The result of thermal decomposition of HT is the collapse of its layered structure, so that new phase of periclase-like mixed nano-oxides is obtained. [13]

Water and gas products obtained from anion decomposition, after being released, are able to create channels in brucite like layers, which leads to formation of a mesoporous structure and additional porosity. It can be deduced, that mixed oxides, which were obtained with HT calcination, have higher specific surface area than basic material. [7]

1.2.3 Anion Exchange Capacity

HTs are able to exchange their interlayer anions. This property is connected with non-divalent layer cation and can be expressed by formula: [13]

$$ACE = \frac{x\ 10^5}{FW}$$

Where:

- FW – formula weight of HT;
- x – amount of trivalent cations.

HTs anion exchange capacity is higher than the one presented by cationic clays. This property strongly depends on the type of anion that is in interlayer spaces. Many anions behave differently but in general, the monovalent anions are more exchangeable the divalent ones. [5]

1.2.4 Acid-base properties

HTs and HT-like materials are generally basic, because hydrotalcites contain basic surface hydroxyl groups. Chemical composition of brucite-like layers have strong influence on the basicity of the material. Acid-base HT properties may be adjusted to certain level, for example by substituting some cations with different higher basicity cations, similar to basicity of HTs containing carbon, which depend on electronegativity of brucite-like layer cations. [12]

The products obtained from HT calcination show strong acidic-basic character. There are three types of basic sites - that can occur on the surface of HT-like materials, which are also represented on Fig.4: [5]

- Weak basic sites (Brønsted sites) – surface hydroxyl groups;
- Intermediate-strength Lewis metal-oxygen pairs;

- Strong basic sites – low coordinated O^{2-} anions

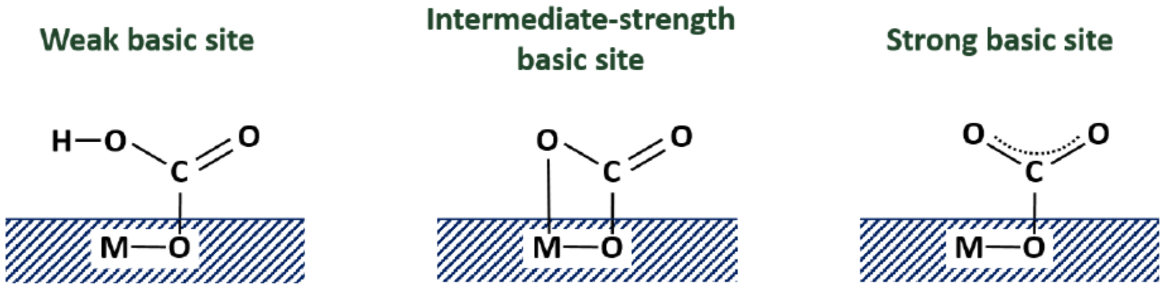


Fig.4 Types of basic sites based on adsorption of CO_2 on HT-like material. [5]

Basicity of thermal decomposition products of HTs (mixed oxides), strongly depend on the composition on layer composition and material precursor in general or, in case of catalysts, it depends on the presence of additional species (promoters) and the types of anions in HT interlayer spaces. [5]

1.3 Preparation methods

There are many methods for obtaining hydrotalcites. The choice of the appropriate method is conditioned by the material to be obtained. LDHs are very easy to synthesize in laboratory, although not every time it is possible to obtain pure phases. [10] The best and most widely used method ist he co-precipitation method, followed by urea, sol-gel or salt-oxide methods. Obtained products may be modified later by anion exchange, reconstruction, microwave or hydrothermal treatments. [5]

1.3.1 Co-precipitation synthesis

It is the most common method of HT preparation. It consists in slowly adding a solution containing divalent and trivalent metal salts to the reactor containing water (often an aqueous solution of sodium carbonate is used instead). At the same time, a solution of the base (most commonly NaOH) is added to the reactor to maintain a constant pH. The pH range in which the synthesis takes place should be selected so that both metals precipitate in the form of hydroxides. If the process would be carried out at variable pH, than it would lead to formation of hydroxides or hydrous oxides. [5] This type of synthesis may be portraited in the form of equation: [13]

$$(1\text{-}x)M^{2+}A_{2/n}^{n-} + xM^{3+}X_{3/n}^{n-} + 2NaOH + mH_2O \rightarrow [M^{2+}_{1-x}M^{3+}_{x}(OH)_2][(A^{n-}_{x/n})\cdot mH_2O] + 2NaA^{n-}_{1/n}$$

Selection of the appropriate pH value is a key parameter that can affect the chemical, structural and textural properties of the product. In addition, competitive reactions may be able to have an influence on coprecipitation process, so, the method itself may sometimes have limitations. However, it gives an opportunity to produce a wide range of HTs with halogen, nitrate or carbonate anions in the interlayer spaces, which can be later modified by ion exchange, reconstruction or hydrothermal treatment, so that structure and composition of the material would be modified. [7]

By using the co-precipitation method, the scientists are able to obtain HTs and HT-like materials with high crystallinity, high average pore diameter, high specific surface area and small particle size, which makes the very suitable for industrial use. [5, 13]

1.3.2 Urea method

It is an alternative method for preparing of HTs and is not as common as the co-precipitation synthesis, but due to the fact that this technique does not need as much alkaline as that required by other methods, it is sometimes preferred, especially in industrial processes. [8] Urea method can also be called urea hydrolysis. Urea is being used as agent for precipitation, because of its various properties; it is a very weak Bronsted base, it can be controlled by watching the temperature of the solution and finally it dissolves easily in water. [9,10] The reaction of this kind of hydrolysis is carried out at pH=9 (depending on temperature). Thanks to this value, large amount of metal hydroxides is being precipitated. [10] The reaction scheme of this method, based on Mg and Al solution is represented below: [9]

$$\begin{aligned}
&\mathrm{Mg(H_2O)}_n{}^{2+} + \mathrm{H_2O} \longrightarrow \mathrm{Mg(OH)(H_2O)^{+}}_{n-1} + \mathrm{H_3O^{+}} \\
&\mathrm{Al(H_2O)}_n{}^{3+} + \mathrm{H_2O} \longrightarrow \mathrm{Al(OH)(H_2O)^{2+}}_{n-1} + \mathrm{H_3O^{+}} \\
&\mathrm{Mg(OH)(H_2O)^{+}}_{n-1} + \mathrm{Al(OH)(H_2O)^{+}}_{n-1} + \mathrm{OH^{-}} \\
&\quad + \mathrm{CO_3}^{2-} \longrightarrow \mathrm{MgAl(OH)_3CO_3H_2O}
\end{aligned}$$

Using urea method, helps to obtain pure hydrotalcite single phase, at the same time it is the only method which allowes to do so. [9] Otherwise from that, HTs synthesized with this technique have high crystallinity, homogenous particle size and large crystallites. [5]

1.3.3 Sol-gel method

This technique is very cost effective and results in very pure materials. The whole process looks like this: the desired metal precursors are hydrolysed in water solution and particulate or polymeric sol is thus created. By giving heat to sol mixture or by using good solvent there is a possibility of hydrolysing insoluble salts. In order to obtain highly dispersed metals in the solution, a certain amount of base or acid must also be added. HTs produced by this technique have thermal stability up to 550°C and high specific surface area, which makes them more distinguishable then natural HTs. [9]

1.3.4 Ion-exchange method

If there is a situation, where co-precipitation method cannot be used, then usually ion-exchange technique is picked. As shown on fig.5, the ions are exchanged with the anions, which occurs in the structure of preformed HTs, so that specific anion pillared HT is created. [10] The ion exchange itself depends on the electrostatic interaction between host sheets and exchanging ions, and on free energy, which is involved in hydration change. [14]

Fig.5 Schematic representation of the ion-exchange method [10]

The best precursors for this method are chloride and nitrate HTs. [5] Basically, this method is used to introduce selected anions into the interlayer space of hydrotalcites. It consists in mixing hydrotalcite with a solution containing an excess of anions that we want to enter into LDH.

1.3.5 Salt-oxide method

Called differently as induced hydrolysis, depends on the reaction between the oxide and the salt of the corresponding metals. Most commonly, nitrates or chlorides are used in it. Metal oxides dissolve progressively, which leads to co-precipitation of HT-like materials. The reaction below represents the process, which occurs in this technique: [15]

$$M^{2+}O + xM^{3+}A^{n-}_{3/n} + (m+1)H_2O \rightarrow [M^{2+}_{1-x}M^{3+}_{x}(OH)_2][(A^{n-}_{x/n})\cdot mH_2O] + 2M^{2+}A^{n-}_{2/n}$$

1.3.6 Hydrothermal method

This method allows to obtain good yields of well crystallized HT, which is not that as easy when using techniques of co-precipitation. The process is being carried out in the presence of water vapour and it must remain in a certain temperature , which cannot be higher than the decomposition temperature of LDHs. [9] In short, the hydrothermal method involves “aging of hydrotalcite mineral suspension at desired temperatures and pressures” [5] Similar techniques are microwave and ultrasound treatments.

1.4 Use and application of LDHs

HT-like materials have many and varied practical applications, as shown on fig.6. HT are usually calcinated before their use. Thanks to properties like high surface area, basicness and ability to create thermally stable mixtures with very small particle size, HTs can be used in heterogeneous catalysis. The memory effect allows HTs find use in purification of water, which contains organic and inorganic waste anions. [7]

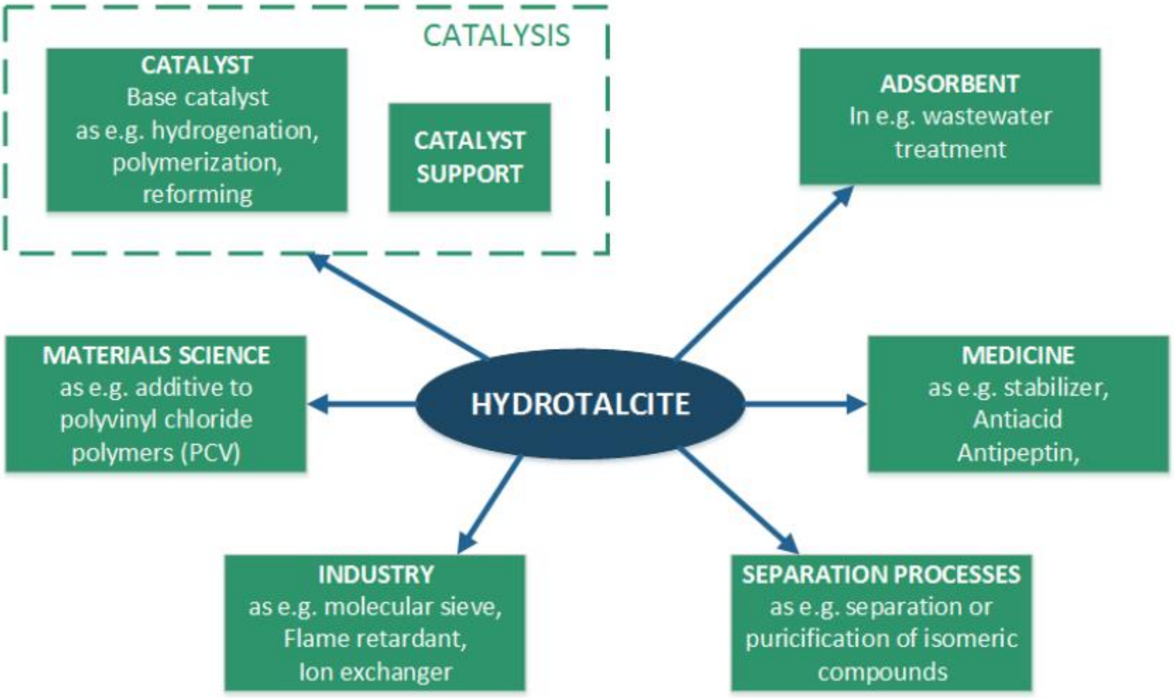


Fig.6 Application of HTs [5]

Hydrotalcites thanks to their low cost, and easily modified properties are promising materials for catalysis, adsorption, electrochemistry, pharmaceutics, photochemistry and so on. [10] Their versatile properties are visible even before thermal treatment, but they seem to react better after calcination. As this paper focuses on LDHs as catalysts, most of examples presented in this chapter will be focused on catalytic applications of HTs.

1.4.1 HTs in catalysis

Synthesis of layered double hydroxide is relatively easy, they are inexpensive and may be recycled, which influenced their development in catalytic areas, which are: [16]

- Catalyst supports;
- Catalyst precursors;
- Catalysts.

Thanks to basic properties of HTs, they can be used as solid base catalyst; moreover it is possible to introduce new active sites by many different modifications, like for example anion exchange. LDHs also have high specific surface area (100-300 m^2/g) which is useful in catalysis. Lamellar structure of these materials, as well as strong metal support interactions result in anti-sintering properties of the reduced metal species on the surface of catalyst. Base catalyst from HT-like materials are mainly used in organic chemistry, for example in aldol condensation or acetone aldolization. The route of creating an catalyst from HT is shown on fig.7 [5,17]. It shows how HTs can be applied as precursors of supported metal catalyst. This kind of materials have contain metal and acidic and basic sites. As seen on fig.7 there are three ways to creating such product: by synthesizing HT precursor with desired metal ions in their layers; by performing ion exchange with anionic metal precursor, which contains certain metal; by calcining and then deposition of metal precursor, and finally reconstructing of HT structure. [5]

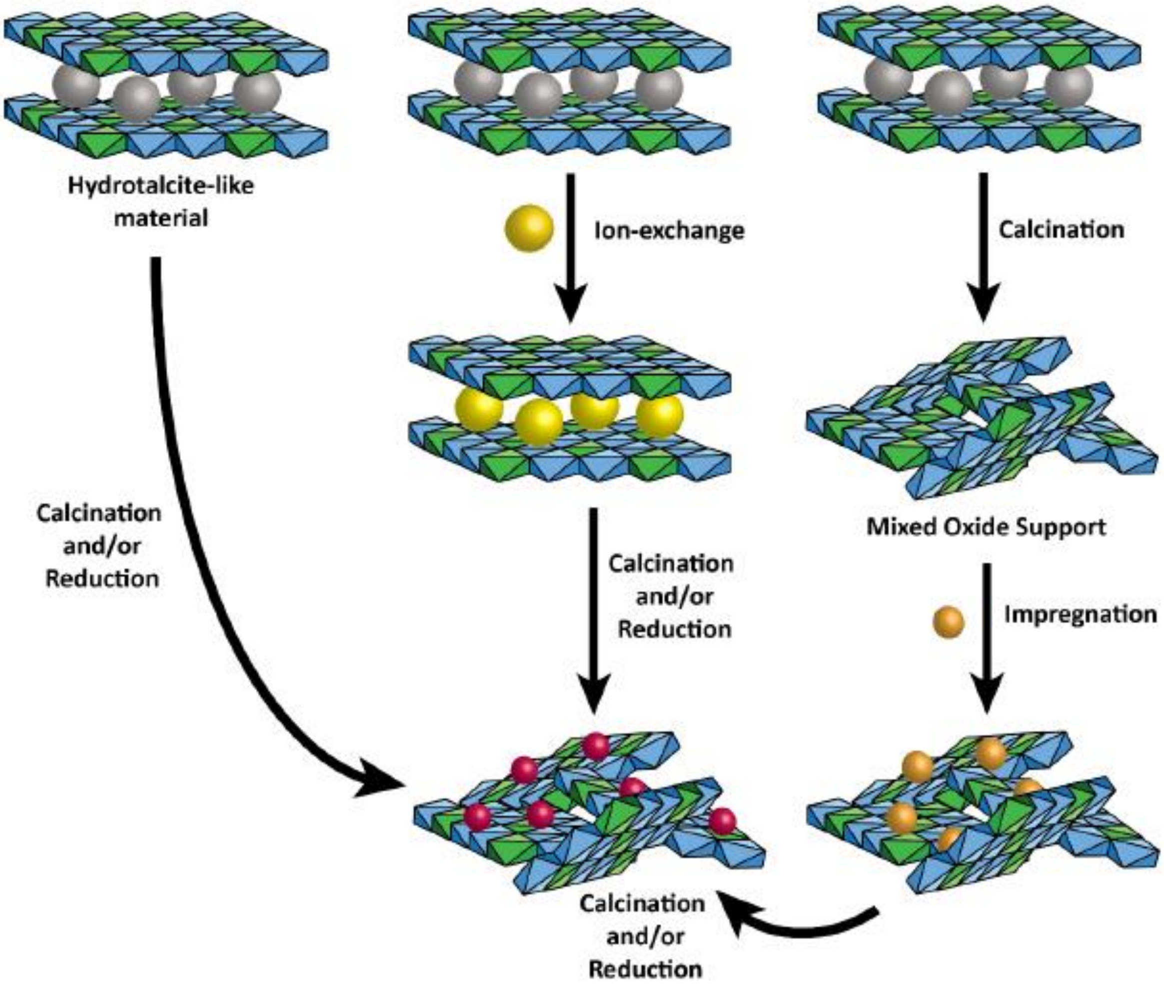
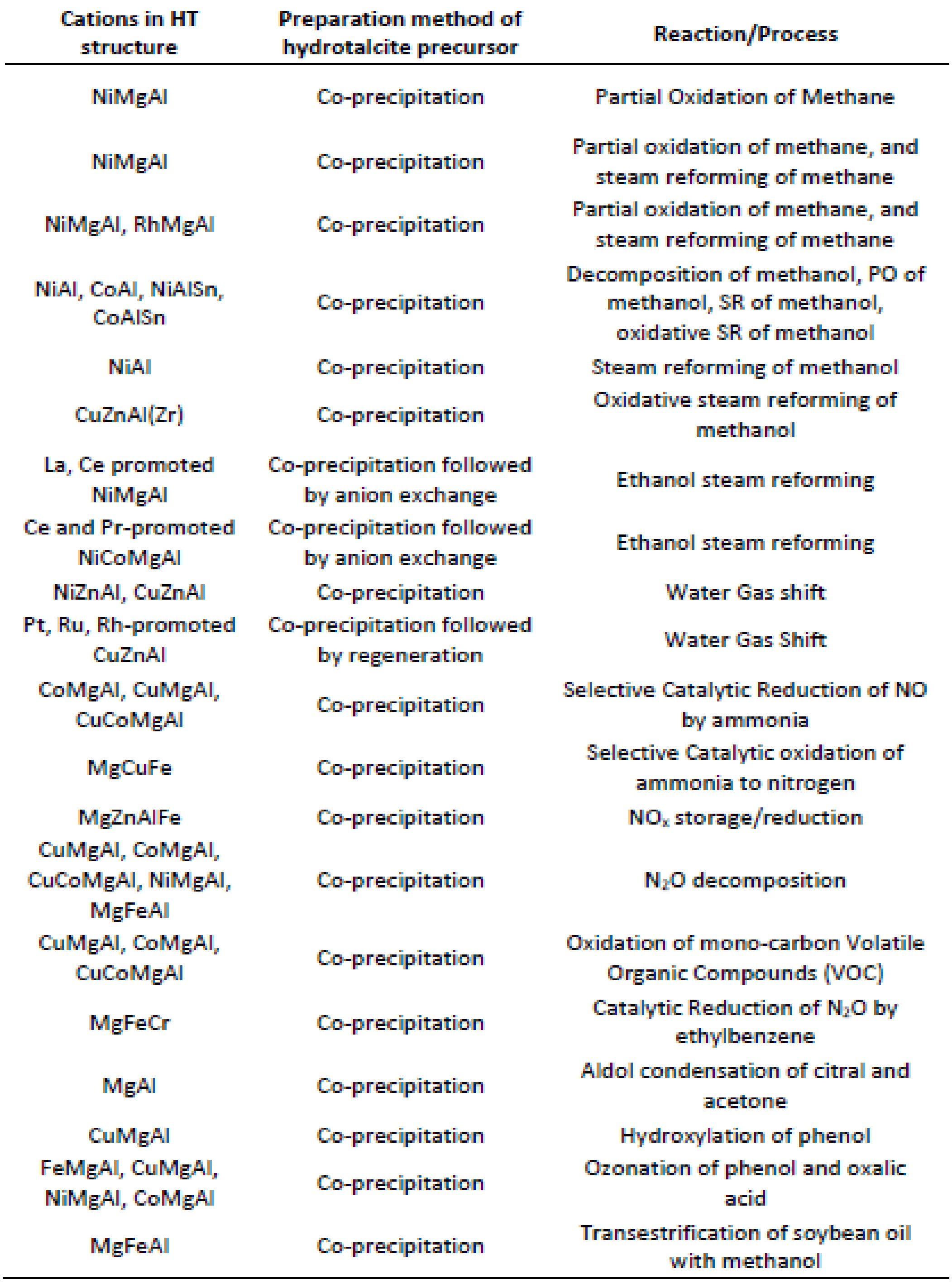


Fig. 7 Representation of obtaining supported metal catalyst from HT [17]

Examples of application of HT-like materials in catalytic processes are presented in the table 2 below [5] and it shows that HT precursors are effective in many environmental processes.



Cations in HT structure	Preparation method of hydrotalcite precursor	Reaction/Process
NiMgAl	Co-precipitation	Partial Oxidation of Methane
NiMgAl	Co-precipitation	Partial oxidation of methane, and steam reforming of methane
NiMgAl, RhMgAl	Co-precipitation	Partial oxidation of methane, and steam reforming of methane
NiAl, CoAl, NiAlSn, CoAlSn	Co-precipitation	Decomposition of methanol, PO of methanol, SR of methanol, oxidative SR of methanol
NiAl	Co-precipitation	Steam reforming of methanol
CuZnAl(Zr)	Co-precipitation	Oxidative steam reforming of methanol
La, Ce promoted NiMgAl	Co-precipitation followed by anion exchange	Ethanol steam reforming
Ce and Pr-promoted NiCoMgAl	Co-precipitation followed by anion exchange	Ethanol steam reforming
NiZnAl, CuZnAl	Co-precipitation	Water Gas shift
Pt, Ru, Rh-promoted CuZnAl	Co-precipitation followed by regeneration	Water Gas Shift
CoMgAl, CuMgAl, CuCoMgAl	Co-precipitation	Selective Catalytic Reduction of NO by ammonia
MgCuFe	Co-precipitation	Selective Catalytic oxidation of ammonia to nitrogen
MgZnAlFe	Co-precipitation	NO_x storage/reduction
CuMgAl, CoMgAl, CuCoMgAl, NiMgAl, MgFeAl	Co-precipitation	N_2O decomposition
CuMgAl, CoMgAl, CuCoMgAl	Co-precipitation	Oxidation of mono-carbon Volatile Organic Compounds (VOC)
MgFeCr	Co-precipitation	Catalytic Reduction of N_2O by ethylbenzene
MgAl	Co-precipitation	Aldol condensation of citral and acetone
CuMgAl	Co-precipitation	Hydroxylation of phenol
FeMgAl, CuMgAl, NiMgAl, CoMgAl	Co-precipitation	Ozonation of phenol and oxalic acid
MgFeAl	Co-precipitation	Transestrification of soybean oil with methanol

Table 2: Examples of different HTs used in catalysis processes [5]

1.4.2 Other applications of HTs

Apart from catalysis, there are many more areas, in which LDHs find use. Their application in adsorption and ion-exchange is used for removal of negative charged species. HTs are able to adsorb inorganic and organic contaminants with anionic character from solutions, using three mechanisms: [17]

- Surface adsorption;
- Interlayer anion-exchange;

- Reconstruction of calcined HT precursor, thanks to “memory effect”.

A different, very interesting area, where HTs find application is their use in pharmaceutics, like in medicine and biochemistry. The interlayer of LDH works like a microvessel, where a drug can be stored, so that it is able to maintain active for a long period, while it is protected from light and oxygen. After its use, the drug can be deintercalated. By this kind of drug delivery system it is possible to reduce side effects of certain drugs, while at the same time prolong its active time. When it comes to biochemistry, DNA or ATP may be intercalated into certain types of HTs, where they are protected from degradation. [17]

LDH can find use I photochemistry as well by, for example acting like infrared absorbing materials in plastic films in agricultural area. It results in higher temperatures in greenhouses at night hours. HTs also upgrade organic dyes, especially by improving their UV, oxygen and thermal stability. [18]

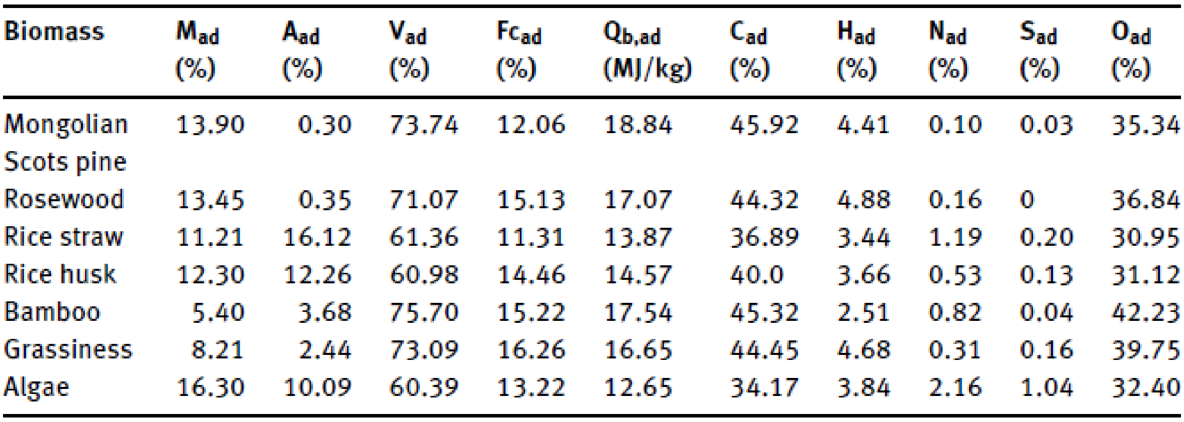
Electrochemistry is another area which benefits from layered double hydroxides, because such materials can replace organic polymers, which are often used in modified electrodes. LDHs are better in this field because of their stability, chemical inertness and tolerance to oxidizing conditions and high temperatures. [19]

2. Biomass

2.1 Biomass characteristics

Biomass is an organic matter, which comes from living organisms. Speaking differently it is an material, that can be formed by direct or indirect photosynthesis and includes plant materials, all animals, microbes and agricultural crops. The composition of biomass and the organic matter, from which it is derived, has an influence on processing operations and its handling. It is treated as renewable source of energy and usually refers to plant-based elements, which are not meant for eating, for example forest wastes, like woodstrip. [20,21]

Biomass is generally composed of three elementary bodies: carbon, hydrogen and oxygen, which in total gives more than 95% of content. It can also have small amounts of other elements, like sulfur and nitrogen in its structure. Various kinds of biomass have different percentage of elements that its made of, which is shown in table 3. Different types of biomass, even if they are very similar in chemical composition, may differ in behaviour during reactions and processes. [20]



Biomass	M_{ad} (%)	A_{ad} (%)	V_{ad} (%)	Fc_{ad} (%)	$Q_{b,ad}$ (MJ/kg)	C_{ad} (%)	H_{ad} (%)	N_{ad} (%)	S_{ad} (%)	O_{ad} (%)
Mongolian Scots pine	13.90	0.30	73.74	12.06	18.84	45.92	4.41	0.10	0.03	35.34
Rosewood	13.45	0.35	71.07	15.13	17.07	44.32	4.88	0.16	0	36.84
Rice straw	11.21	16.12	61.36	11.31	13.87	36.89	3.44	1.19	0.20	30.95
Rice husk	12.30	12.26	60.98	14.46	14.57	40.0	3.66	0.53	0.13	31.12
Bamboo	5.40	3.68	75.70	15.22	17.54	45.32	2.51	0.82	0.04	42.23
Grassiness	8.21	2.44	73.09	16.26	16.65	44.45	4.68	0.31	0.16	39.75
Algae	16.30	10.09	60.39	13.22	12.65	34.17	3.84	2.16	1.04	32.40

Table 3. Elemental analysis of different types of biomass. [20]

Main components of biomass are cellulose, lignin and hemicelluse, which are formed on plant's cell wall, where they are dispensed unevenly. Together they build a scaffolding by linking materials, which can be seen on fig. 8. Cellulose appears usually in the form of pipes, while the space between them is filled by lignin and hemicellulose. These three components are connected by hydrogen and covalent bonds. [22] Biomass may also contain nonstructural compounds, like paraffin, fat, pigment, starch or tannin, called extractives. These compound may be extracted by organic solvents. [23] Few inorganic metal salts may also be present in the structure. Main compounds, as well as extractives and inorganic salts have a big impact on physical and chemical behaviour of biomass. [20]

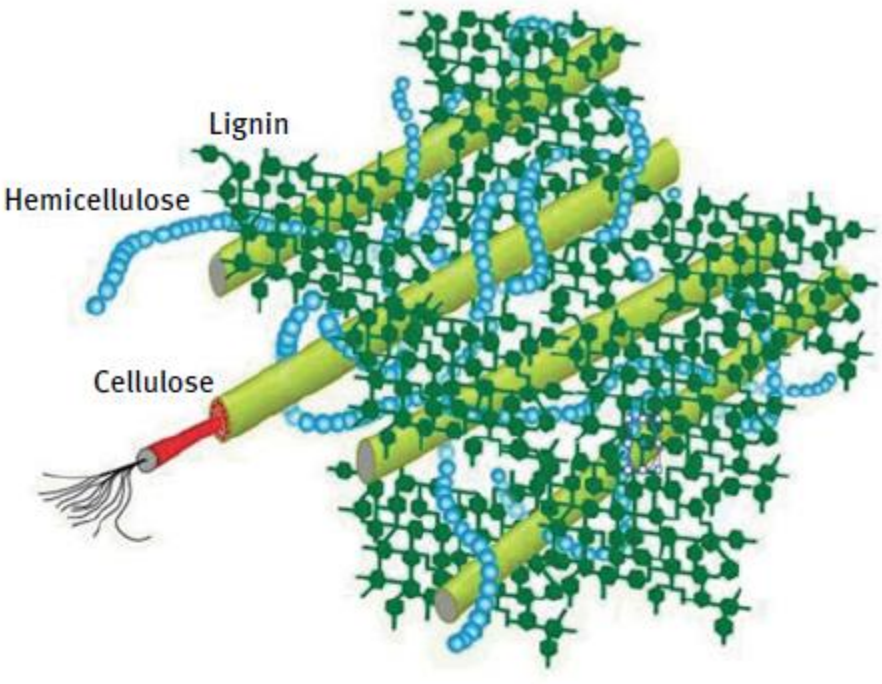


Fig 8 Components of biomass [20]

2.2 Biomass as a renewable fuel

Biomass is considered to be a renewable source of energy, because the elements that its made of can reproduce (eg. plants grow by using sunlight for photosynthesis). It grows by absorbing carbon dioxide from the atmosphere during the process of photosynthesis. During the burning of biomass CO_2 is released but only in the amount that was absorbed not a long time ago, which results in not adding any additional carbon dioxide into the atmosphere, which makes it carbon neutral fuel. [4]

2.2.1 Types of biofuels and motivations for the conversion of biomass

As stated earlier, biomass can be converted to different types of fuels in order to produce bioenergy. There are three primary types of such fuels: [4]

- Liquid – pyrolysis and vegetable oil, biodiesel, methanol, ethanol;
- Gaseous – syngas, biogas, producer gas, substitute natural gas;
- Solid – charcoal and torrefied biomass.

Conversion of biomass methods were known for a long time, but recently there has been rising interest in obtaining this renewable fuel due to three benefits: [4]

- Environmental;
- Renewability;
- Sociopolitical.

In past few years environment has become a major issue. People are more aware of the air pollution and global warming effect and fighting it became very important. Biomass is a great solution for this issue, as it does not make net contribution to CO_2 emission; and is economically applicable in many countries. Apart from that, fuels obtained from biomass when used, may help with reducing carbon dioxide, sulfur and nitrogen emissions. Also toxic pollutants like furans or dioxins are not released in combustion system of biomass in contrast to fossil fuels. [4] Renewability of biomass has been discussed above. When it comes to sociopolitical benefits of converting biomass into biofuels, they are substantial, because it is a resource that is grown locally. Biomass power plants must be located in a certain distance from where the biomass itself comes from, which means, that if a biomass power plant were to be built, it would start development of industries for growing, collecting and transporting the biomass. This kind of situation could create approximately twenty times more job vacancies the coal or oil based power plants. [25] Another very important sociopolitical aspect of biomass, is that it can reduce the reliance in imported fossil fuels and locally grown, it is relatively free from uncertainties connected to prices. [4]

2.2.2 Conversion of biomass

Biomass can be converted to biofuels by using different processes, which is shown in fig. 9. There are three types of such processes: physical, thermochemical and biochemical. In physical processes, densification methods are used for the biomass conversion. When it comes to biochemical processes, the elements that help create biofuels from this renewable source are enzymes and microorganisms. Finally, thermochemical processes use chemical catalysts and, of course heat energy for the same results. [24]

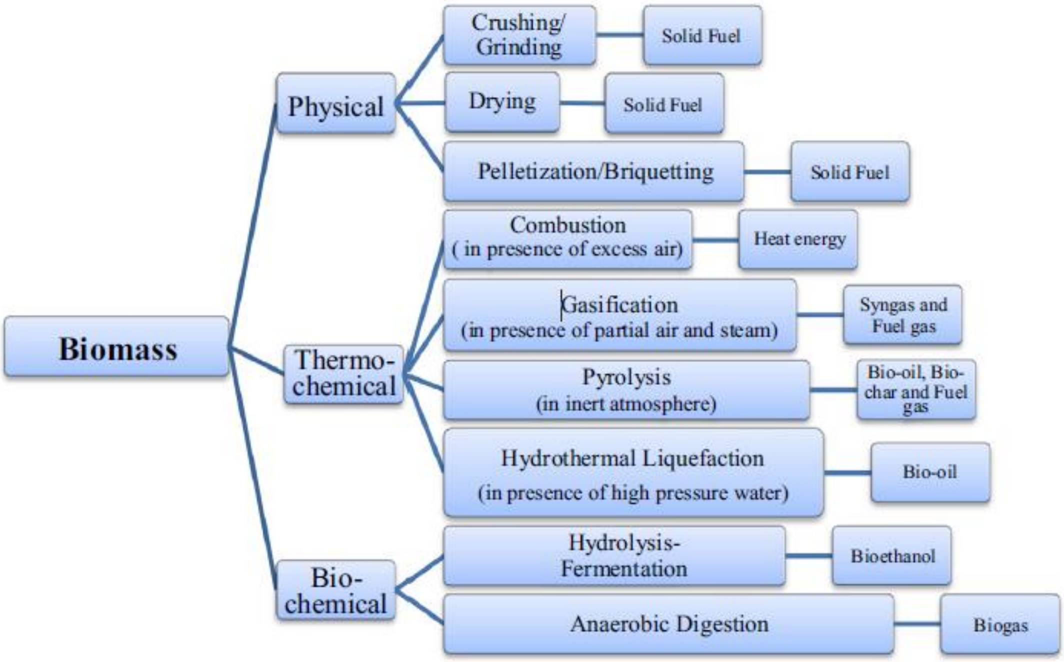
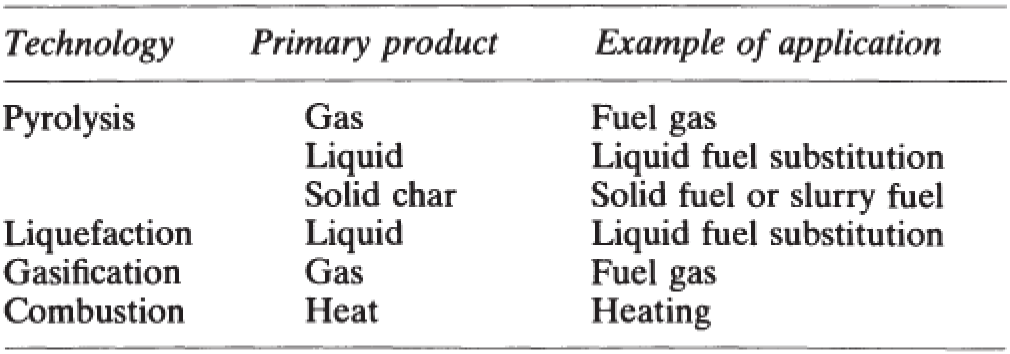


Fig. 9 Paths of converting biomass to bioenergy [24]

Biochemical conversion consist on molecules of biomass breaking into smaller ones with the use of enzymes and bacteria. It is a slower process then thermochemical conversion, but on the other hand it requires less external energy. As seen on fig. 9, the routes of obtaining fuels by converting biomass biochemically, are digestion, fermentation and hydrolysis. Fermentation converts biomass into sugars thanks to acid or enzymes. Then, the obtained sugar converts into ethanol by using yeast. [4] Physical conversion of biomass produces solid fuels and the routes for obtaining it are drying, crushing, grinding and briquetting.

When it comes to thermochemical conversions, the four routes are pyrolysis, combustion, gasification and hydrothermal liquefaction. As pyrolysis is the topic of this thesis, it will be described in another chapter. Each of these methods give different range of products and need different type of operating configurations, which is presented in table 4 below: [26]



Technology	*Primary product*	*Example of application*
Pyrolysis	Gas	Fuel gas
	Liquid	Liquid fuel substitution
	Solid char	Solid fuel or slurry fuel
Liquefaction	Liquid	Liquid fuel substitution
Gasification	Gas	Fuel gas
Combustion	Heat	Heating

Table 4: Thermochemical conversion technologies and its products [26]

Primary products may be used directly or in further chemical processing in order to upgrade the value of fuel and give it higher quality. There is also a possibility obtaining secondary products of such biomass conversions, like: hydrocarbon and oxygenate transport fuels, bulk chemicals, power and chemical specialities. [26]

The combustion of biomass is one of the oldest processes of its conversions known to mankind. In other words, it is a simple burning of biomass in order to produce heat and sometimes light. Along with this energy, CO_2 and water are produced. Complete combustion consist of three processes: incineration, direct firing and burning. It is a rapid reaction of biomass and oxygen called oxidation, which results in radiant or thermal energy release. [27]

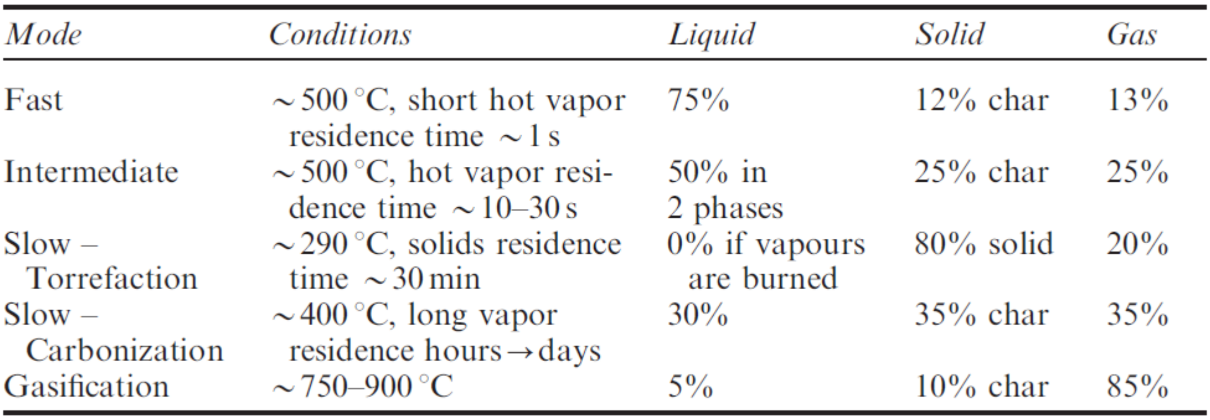
Gasification of biomass is usually designed to produce low or medium energy fuel gases, hydrogen or synthesis gases. There are three types of biomass gasification: pyrolysis, partial oxidation and reforming. Under idealized conditions, they all have the same primary products: carbon dioxide and water. Under certain different conditions, CH_4 and light hydrocarbon gases are formed. Based on cellulose as a feedstock, the three processes have equations: [27]

$$\begin{array}{ll} \text{Pyrolysis:} & C_6H_{10}O_5 \rightarrow 5CO + 5H_2 + C \\ \text{Partial oxidation:} & C_6H_{10}O_5 + O_2 \rightarrow 5CO + CO_2 + 5H_2 \\ \text{Steam reforming:} & C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2. \end{array}$$

2.3 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. [28]

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. [26] 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 5: [21]



Mode	*Conditions*	*Liquid*	*Solid*	*Gas*
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 5: Different types of pyrolysis [21]

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): [4]

- Slow pyrolysis: $t_{heating} >> t_r$
- Fast pyrolysis: $t_{heating} << t_r$

2.3.1 Conventional (slow) pyrolysis

This process consist of carbonization, destructive and dry distillation, and resorting. It is a thermal decomposition, which is slow and irreversible an, of course happens in the absence of oxygen. The product usually obtained by this model of pyrolysis process is charcoal. [29] Slow pyrolysis is the oldest form of this process, where biomass is being slowly heated to 400°C (which is relatively low temperature) for a long time (thousands of years ago this period of time may have even lasted for couple of days). In fig. 10 a sketch of typical oven, where the slow pyrolysis takes place has been presented. It is in the form of beehive, where a fire at the bottom produced heat, which stayed closed and insulated chamber. Slow pyrolysis helps obtaining gaseous, liquid and char products. [4]

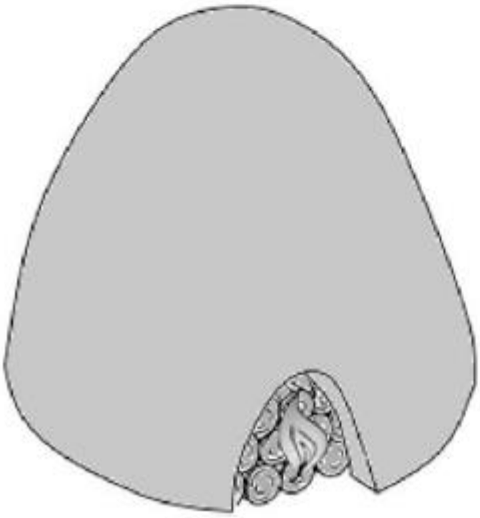


Fig.10 Scheme of beehive oven in which conventional pyrolysis takes place [4]

2.3.2 Fast pyrolysis

This kind of pyrolysis process has been developed and applied in renewable energy field, and is thought to be an advance technology. [20] The main goal of it is to maximize the production of fuel. The biomass in this process is being heated very rapidly in order for it to reach a peak temperature before its decomposition. Heating rate in fast pyrolysis is very high, the biggest one even up to 10000°C, but the peak temperature should not go over 650°C if the process is used for bio-oil. The residence time of vapor in reactor is very short (less then 3 seconds). [4] The basic concepts of fast pyrolysis are that the biomass must be heated rapidly in a very short period of time; its products must be removed very fast from the zone of reaction and then cooled down, also in very short time; and finally the temperature of reaction itself must be between 400-500°C [30]

The reaction process of fast pyrolysis starts when biomass goes through hot field so that heat is being transferred through radiation and convection to its surface and to the inside by conduction. Next, the biomass particle gets rid of water and by increasing the temperature the pyrolysis begins, coke is being formed and volatiles are released. [20] By quenching of vapours and aerosols obtained in the process of fast pyrolysis, bio-oil is being produced. In order to have as large bio-oil yields as possible, the products of such pyrolysis are removed and cooled down rapidly, so that no secondary reactions takes place. It can be done by, for example, spraying cold liquid hydrocarbon. [30]

After biomass decomposition by fast pyrolysis, aerosol, vapors and char are generated, then after vapor condensation, a liquid substance called bio-oil is obtained. The oil itself is a dark brown and free flowing liquid substance. The color may vary due to different feedstock composition. Bio-oil is the most attractive product of biomass pyrolysis, because it is easy to transport and utilize, and has increased energy density. [31]

Fast pyrolysis can be performed by various types of reactors, which is a very important feature when it comes to efficiency of bio-oil production. The reactor should: [31]

- Be able to coordinate pressure, temperature and residence time;
- Have low implementation risk;
- Have economical size, while maintaining a lot of energy.

Reactors that have those features are: bubbling fluidized beds, circulating fluidized beds and rotating cone reactors.

Fast pyrolysis is thought to be a zero waste process, because both liquid bio-oil and char can be used in further processes and have commercial value. [31]

3. Catalytic biomass upgrading – reasons and examples.

Summing up what was written in the previous chapters about hydrotalcites, biomass and its ability to turn into renewable fuel by pyrolysis process, in this chapter a connection between all those things will be discussed and presented in certain examples as this is a key to this work about catalytic pyrolysis of biomass.

3.1 Catalytic pyrolysis of microalgae

As explained earlier, biomass is a attractive renewable source and a great replacement for fossil fuels, due to increased world energy demand. There are several articles describing the process of pyrolysis of microalgae, which uses hydrotalcites as catalysts. Fuels based on algae are potentially one of the most environment friendly energy sources, as they come from renewable source and do not generate as much negative impact as crop fuels; although the process of conversion of microalgae to energy needs to be investigated, so it will be cost effective and the obtained fuel will have desirable properties. [32] Microalgae called Chlamydomonas Reinhardtii, can be very usefull in that case, because they have high growth rate and can be found even in difficult conditions . The main problem with this type of biomass, is that the bio-oil produced from it, tends to have high nitrogen compounds content, which has a bad influence on its efficiency and on the environment (NOx emissions). That is the reason, why such biofuel has to be upgrated. In the article “Characterization and product formation during the catalytic and non-catalytic pyrolysis of the green microalgae Chlamydomonas Reinhardtii” [32], the scientists decided to use hydrotalcite in the process of pyrolysis of Chlamydomonas Reinhardtii and compare the fuel properties with the one obtained from non-catalytic pyrolysis. HT was chosen because of its basic characteristics and thanks to its high dispersion, large surface area and high stability. The experiment showed, that the pyrolysis in which HT was used as a catalyst had increased formation of hydrocarbons, decreased formation of oxygenated compounds and most importantly, significantly low content of nitrogen compounds, which are better results than for the non-catalytic pyrolysis. Thus, despite microalgae having tendencies to create a lot of nitrogen containing compounds, with use of hydrotalcite it can be used to produce bio-fuel with good properties. [32]

In the article created by Brazilian scientists, the process of catalytic solar pyrolysis of the same microalgae was being examined. [33] This kind of pyrolysis process takes its energy from the sun, in order to convert biomass into biofuel. The fuel obtained by such route needs to be upgraded, as it contains many unwanted components, which was mentioned before. The goal of this experiment was to check different variables of solar pyrolysis of Chlamydomonas Reinhardtii, catalized with HT and their influence on bio-oil properties. Scientists again chose hydrotalcite due to its beneficial properties, like low cost, high surface area and acid-based character. The results proved the point, that hydrotalcites improve performance of solar pyrolysis and in the end give biofuel with high content of hydrocarbon and low formation of nitrogen compounds. [33]

In the “A review on the production of nitrogen-containing compounds from microalgal biomass via pyrolysis” by Chinese scientists, the production of nitrogen-containing compounds (NCC’s) was being discussed. [34] In the article, the goal was to obtain NCCs from the microalgae, in order to use them in pharmaceutical or polymer industries. The microalgae used in this study was Chlamydomonas Reinhardtii. It turns out, that using hydrotalcite as catalyst in biomass pyrolysis process has a bad effect on the generation of NCCs, so if biofuel would be produced using the same method, it would have better properties, as the NCCs lowers the efficiency of the fuel. [34]

3.2 Role of hydrotalcites in the process of steam reforming of biomass tar

Gasification of biomass has recently become very attractive way to transform this renewable fuel into energy, but the problem with this method is, amongst others, that the obtained products usually contain tar. Tar is a "complex mixture of condensable organic compounds" [35] which can lead to condensation of downstream equipments and therefore needs to be removed from the products. It turns out that steam reforming combined with pyrolysis of biomass over catalysts derived from hydrotalcites may be a solution to the presence of tar in biofuels.

In the article "Steam reforming of tar from pyrolysis of biomass over Ni/Mg/Al catalysts prepared from hydrotalcite-like precursors" [35], Japanese scientists investigate the catalytic performance of Ni/Al/Mg hydrotalcite in the process of steam reforming of tar obtained from pyrolysis of biomass. The biomass used in this study was cedar wood, which was rapidly pyrolized in the presence of steam, which resulted in tar creation and then was introduced to the catalyst. The Ni/Al/Mg catalysts was produced by the co-precipitation method. Such hydrotalcite was used because Ni catalysts have low cost and high activity, Al is a good support, but with connection to Ni it may lead to coke deposition and later to deactivation, so presence of Mg is needed, as it has the ability to prevent that process. [35] MgO supported Ni and Al_2O_3 supported catalysts are known for their catalytic abilities as well in the steam reforming of tar, but the result of studies showed that the combination of Ni/Al/Mg elements in HT catalyst give better results, as it has higher performance in catalytic activity, suppression of coke deposition and is more stable. [35]

As mentioned earlier, gasification of biomass may lead to producing tar as a by-product, which is a big disadvantage. It has been proven, that high temperature of reaction can decrease the production of tar. Because in addition the products of gasification may be diluted with nitrogen, a different method had to be investigated in order to reduce unwanted compounds in biofuels to the minimum. In another study by the same scientists a different hydrotalcite catalyst was investigated the steam reforming of tar. They decided to combine catalytic steam reforming of tar with the pyrolysis of biomass. The hydrotalcite used in this study was Ni-Cu/Mg/Al, as many studies showed, that combination of Ni and Cu makes HT catalysts characterized with high activity and coke resistance. [36] The results of this experiment proved these statements as the catalyst performed successfully in the steam reforming and turned out to give better results then Ni/Mg/Al catalyst, because of better long term stability. [36]

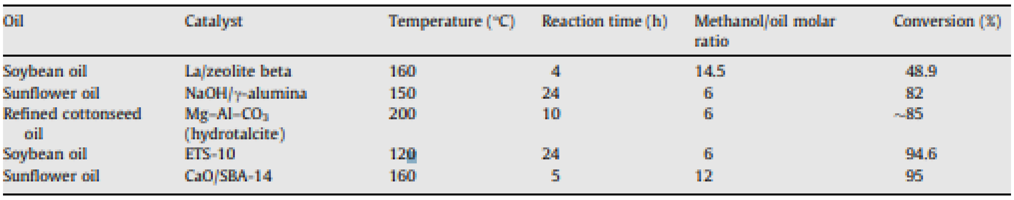
In the study "Promoting effect of trace Pd on hydrotalcite-derived Ni/Mg/Al catalyst in oxidative steam reforming of biomass tar" [37] the combination of biomass pyrolysis with steam reforming of tar catalized by hyrotalcite material was once again examined. This time the influence of noble metal (such as Pd) on the catalytic performance of HT was examined. Pd was added to the Ni/Mg/Al catalyst (used later as a reference) by the impregnation method. The goal of this experiment was to compare reference catalyst with the one containing a noble metal and to check its catalytic performance. The biomass used in the study was, once again cedar wood. The results proved, that hydrotalcite based catalysts containing Pd have improved catalytic performance when it comes to steamed reforming of tar obtained from biomass pyrolysis in comparison to Ni/Mg/Al catalyst. [37]

3.3 Other examples of biomass pyrolysis catalized by hydrotalcite-like materials

There are many examples of using different types of hydrotalcites in the process of pyrolysis of various types of biomass. In this section some of these examples are presented.

In the article “Catalytic fast pyrolysis of biomass over Mg-Al mixed oxides derived from hydrotalcite-like precursors: Influence of Mg/Al ratio” [38] the upgrading of biooils is being discussed. As mentioned before, thermochemical conversion of biomass (such as fast pyrolysis) is a very attractive method for generating renewable energy, but the bio-oil obtained from lignocellulosic biomass has high content of oxygenated compounds, which may result in thermal instability, corrosiveness and non-volatility of the fuel. [38] In order to produce efficient biofuel with this method, the oxygen must be removed, which is possible by performing catalytic pyrolysis. In this study the Mg/Al HT catalyst was used and was successful, but the results derived for different Mg/Al ratio. It turns out that the catalyst that gave the best performance in decarboxylation capacity and had the biggest gas production, was the one that had the lowest Al concentration. [38]

Various types of hydrotalcites have different catalytic influence on the pyrolysis of many types of biomass feedstock. For example in the review called “Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery” [39] many kinds of catalysts were examined and compared to each other in the production of biofuel from palm oil. As palm oil is a cheap and environmental friendly feedstock, there has been a big interest in using it to produce energy. The main issue was in finding a suitable catalyst for the pyrolysis process, which had to be cost efficient, thermally stable and effective. Figure 11 below represents how hydrotalcite would performe in that process in comparison to different types of catalyst, based on results obtained on various vegetable oils.



Oil	Catalyst	Temperature (°C)	Reaction time (h)	Methanol/oil molar ratio	Conversion (%)
Soybean oil	La/zeolite beta	160	4	14.5	48.9
Sunflower oil	NaOH/γ-alumina	150	24	6	82
Refined cottonseed oil	$Mg–Al–CO_3$ (hydrotalcite)	200	10	6	~85
Soybean oil	ETS-10	120	24	6	94.6
Sunflower oil	CaO/SBA-14	160	5	12	95

Fig. 11: Various catalysts used for transesterification of vegetable oils [39]

The article “Investigation on catalytic pyrolysis of pine sawdust: Catalyst screening by Py-GC-MIP-AED” [40] also examined different catalysts in the process of pyrolysis. In this case, where the feedstock was pine sawdust, in order to see which one would lead to abtaining the best biooil. Hydrotalcite was compared to montorillonites and zeolites. The HT catalyst decreased the heavy matter yields, which is a very good thing, but at the same time the reduction of biofuel yield occurred. [40]

Experimental Section

4. Experimental method

4.1 Preparation of the catalysts: the co-precipitation method

Four hydrotalcite-like materials were prepared by the co-precipitation method, in order to use them later as catalysts in the process of biomass pyrolysis.

The prepared hydrotalcites were:

- Mg/Al/Fe
- Ni/Zn
- Mg/Al
- Zn/Al

The method used 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.

First, the solutions of 1M NaOH and 0,05M Na_2CO_3 had to be prepared and the pH-meter needed to be calibrated using buffers of pH equal to 7 and 9. The exact amount of Na_2CO_3 depends on the hydrotalcite.

Based on the $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$ [10] equation, explained in the chapter about hydrotalcites, and knowing that the salt solution need to be equal to 1M, the amount of substrates needed to create certain hydrotalcites was delivered, which is represented below:

- **Mg/Al/Fe** – 24.27g of magnesium nitrate hexahydrate, 5.93g of $Al(NO_3)_3$*$9H_2O$ and 6.38g of $Fe(NO_3)_3$ 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 methos with divalent to trivalent cations ratio equal 3;
- **Mg/Al** – 25.43g of magnesium nitrate hexahydrate and 12.42g of $Al(NO_3)_3$*$9H_2O$ 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 $Zn(NO_3)_2$*$6H_2O$ and 12.42g of $Al(NO_3)_3$*$9H_2O$ 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 figure 12 below:

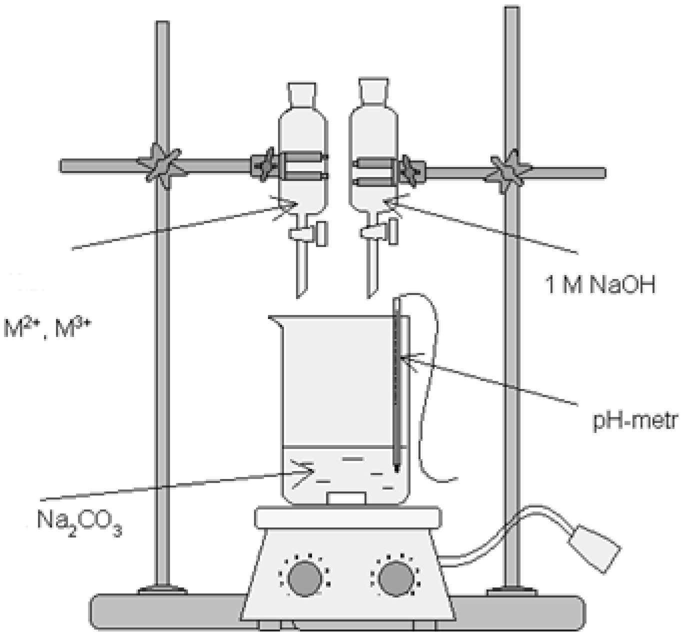


Fig. 12: Scheme of HT synthesis kit [5]

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 was dropwise added in it at the same time. The dropping needed to be very carefuly monitored, so that the solution was constant and 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 as shown on Fig. 13

Fig. 13 Magnetic stirrer used for preparation of HT

After this time the obtained precipitate was filtered using a Bunchner funnel (Fig. 14) and later washed with about 1.5l of warm distilled water to prevent cracking. The solid remaining was the hydrotalcite, which was transferred to a Petri glass and dried in the oven for 24h. Fig. 15 shows how hydrotalcites looked after being dried.

Fig. 14 Bunchner funnel

Fig. 15 Hydrotalcites obtained through co-precipitation method after being dried – Zn/Al (left) and Mg/Al.Fe (right)

When the preparation of HTs ended, they had to be grinded and calcinated for 6h in 500 ^{o}C.

4.2 Preparation of samples

The biomass used in this study was an algae called *Arthrospira platensis*. The goal of this work was to pyrolize the biomass with different hydrotalcites. Five samples were prepared: four with catalysts and one with pure biomass for reference. The proportion of catalyst to the biomass sample needed to meet the requirement of 5% of HT of the whole weight, as it was decided by the supervisor. 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 TGA/DSC apparatus, which allowed measurement of the kinetics of devolatilization and the thermicity of the process.

4.3 Equipment

The equipment used in this study was TA Instruments SDT 2960 simultaneous TGA/DSC apparatus. The device has the ability to perform pyrolysis and combustion needed for the experiment. It contains a furnace, which can work in the temperature up to 1500°C, thermoelectric disks used to measure the heat flow and finally, a balance, thanks to which the weight of samples can measured during the analysis. The apparatus is connected to three separate lines that provide air, nitrogen and/or carbon dioxide. It is also equipped in a digital flow meter, which guarantees constant flow of all experiments. A computer, which is connected to the device, processes and stores data from the TA analysis made with this equipment, like time, temperature, heat flow, weight, etc. Among these, this apparatus creates graphs of the data. In this particular case, two pans will be introduced into the equipment and be held by the disks. First one will be empty, for reference, while the second one will contain the sample. Fig. 16 shows the photo of the equipment.

Fig. 16: TA Instruments SDT 2960 simultaneous TGA/DSC apparatus with computer and samples.

4.4 Experiment

The experimental part of this study contained of thermogravimetric analysis and differential scanning calorimetry test (TGA/DSC). 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.

Before starting the experiment, preparation of the device had to be made. Nitrogen was selected as a gas, so it had to be connected to the equipment. The flow rate of nitrogen was 54.1 through whole analysis for every sample. Also the apparatus had to be balanced, so in order to achieve that two empty pans were placed in the disks and then the equipment was tarred. After this preparation, TGA/DSC instrument was ready to perform the analysis of different samples. 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 and heat flow of pyrolysis and combustion processes could be carried out.

4.5 Data processing and calculations

In this chapter the equations and methods used to analize obtained results of the experiment will be described. All calculations were made in Excel software.

4.5.1 Obtained data

The data obtained from the TS Instrument were:

- Temperature [°C]
- Heat Flow [mW]
- Weight [mg]
- Derivative weight [mg/min]

All of these variables were assigned to appropriate time [min] duration of the experiment.

4.5.2 Raw data analysis

The data obtained was used to draw the graphs representing changes in heat flow, weight and derivative weight vs temperature in Excel Software, respectively called DSC, TGA and DTG analysis, during the pyrolysis and combustion of each sample in order to analyse thermal decomposition of biomass and check the influence of each catalyst on it. Fig. 17 [41] represent examples of TGA and DTG graphs obtained from TA instrument during the pyrolysis of biomass in comparison to catalytic pyrolysis of the same feedstock.

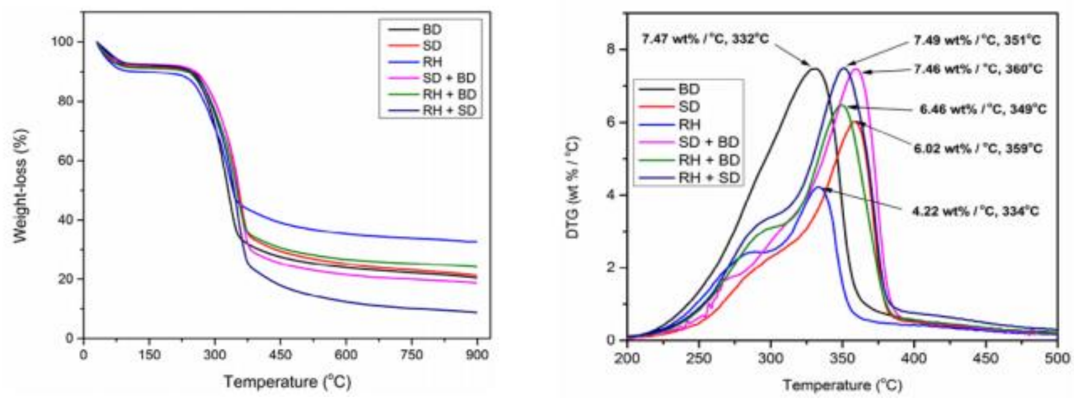


Fig. 17 Example of TGA and DTG curves for catalytic pyrolysis of biomass [41]

4.5.3 Kinetic modelling

In order to analyse kinetic parameters of examined samples, curve fitting has been applied to the received results of the experiment. Kinetic models in this work were used to simulate the weight loss in the pyrolysis of biomass.

The whole method of kinetic model for weigh loss stimulation is based on Arrhenius equation, presented by Eq.(1), for the rate of product's transition changes with temperature, which is presented below:

$$k(T) = A \cdot e^{-\frac{E_a}{RT}} \qquad (1)$$

Where:

- K(t) – reaction rate constant
- A – frequency factor [1/min]
- Ea – activation energy [J/mol]
- R – gas constant 8.314 [J/mol*K]
- T – temperature [K]

The biomass in this case was considered to contain three pseudocomponents that decomposed independently. Their kinetic parameters obtained from thermochemical conversion were estimated separately, following these steps:

1. Masses of pseudocomponents were estimated by TGA graphs representing weight at given time to temperature.
2. The rates of decomposition of components were estimated by using Arrhenius equation, presented as Eq.1, showed below:

$$\frac{dwi}{dt} = kref(T) \times e^{\frac{-Ea}{R} \times (\frac{1}{Tt} - \frac{1}{Tref})} \times wi_t \quad (2)$$

Where,

- w – weight [mg]
- Tref – assumed referenced temperature 300[K]

The equation was obtained from dividing Arrhenius equation by Arrhenius equation for the decomposition of component in reference temperature.

3. After obtaining weight, the least-square method approach was used to fit model data to the experimental data, which was done by comparison of given and created data. In order to achieve it the Eq. (3), presented below, was used:

$$f(W)_m = (W_{experimental,m} - W_{total,m})^2 \quad (3)$$

Where,

- $f(W)_m$ – squared error between experimental and model data substraction at given time, m

A final error sum, showed as Eq. 4, is done for all the time steps to get a final error comparing the experimental and the model data:

$$Error = \sum_{J=1}^{N} f(W) \quad (4)$$

Where,

- Error - total error of the difference between the experimental data and the model data
- N - Number of time steps that were present on the experimental data provided by the software

The total error was used in solver tool in Excel software to make an objective function and minimize the error to fit the curve on the the grapf through changing values of k, w and Ea parameters.

In this work low square residual value and correlation coefficient (R^2) were used. Correlation coefficient shows how close the model data is to the experimental data through the percentage of the response variable variation. R^2 has to be greater then 0.99 between the model data and the experimental data, so that for model data would be considered reliable.

5. Results and discussion

In this chapter, results of experiment, based on obtained data, are presented. DTG, TGA and DSC curves are shown or graphs created with excel software. Kinetic modelling and curve fitting of pyrolysis of biomass results for all samples, as well as kinetic model and curve fitting of combustion of biomass for one sample will also be shown in this part of work.

In the graphs, the curves names refer to exactly:

- Biomass – pure biomass sample
- MgAlFe – Biomass sample containing MgAlFe catalyst
- MgAlHT or MgAl – biomass sample containing MgAl catalyst (HT stands for hydrotalcite, but both names refer to the same catalyst)
- NiZn – biomass sample containing NiZn catalyst
- ZnAl – biomass sample containing ZnAl catalyst

5.1 TGA results

The weight data obtained from TA Instrument apparatus, was used to draw the graph representing weight loss to temperature dependence, which can also be referred to as TGA graph. This activity was applied to all samples, in order to compare how catalysts influence the thermal decomposition of biomass. In Fig. 18, which refers to pyrolysis process, the curves representing all 5 samples were drawn. It is important to know, that the weight data used in these graphs, was normalised for all samples, in order to make comparison more clear, and that regarding samples with catalysts, the weight of catalyst itself was subtracted from the original weight data obtained from the apparatus, in order to represent the decomposition of pure biomass.

In Fig. 18 it is very clear, that catalyst MgAlFe had the biggest influence on biomass, when it comes to thermal decomposition in the pyrolysis process. It's curve is the most different in comparison to curve representing pure biomass sample. When it comes to the rest of the samples, the one containing ZnAl catalyst, had the least different curve in comparison to pure biomass, which means, that the catalyst had minor influence on thermal decomposition of biomass in the pyrolysis process. The sample with NiZn catalyst, had bigger impact on the process performance than ZnAl and biomass containing MgAl catalyst was the next, when it comes to differences in comparison to non-catalytic sample. The decomposition of biomass can be seen from 150 to 600°C, where nearly 75% of weight loss occurs. After 600°C there is no significant visible reduction in weight loss, which may be referred to formation of residual ash. [42]

TG curves can be divided into three phases of thermal degradation [43]:

- 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

Major degradation of algae was noticed for all samples it phase 2 (degradation of cellulose and hemicellulose) and that is why it is important to maximize the weight loss in this phase, by selecting the right catalyst. [43] As mentioned before, MgAlFe catalysed sample, differs the most from the pure biomass reference sample. The curve representing this sample has the biggest drop in the phase 2 of thermal degradation and leaves the least solid residue in comparison to all other samples, which means that in case of TGA analysis, this catalyst performed the best, followed respectively with MgAl, NiZn and ZnAl catalysts.

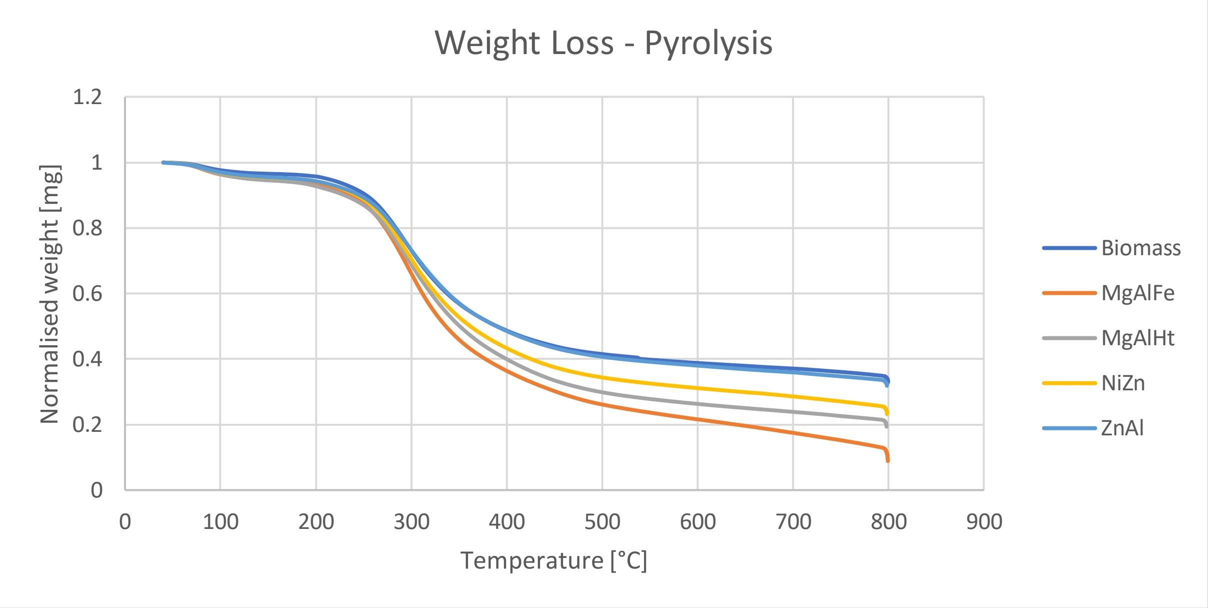


Fig.18 Comparison of weight loss to temperature dependence for all samples in the pyrolysis process

5.2 DTG results

DTG analysis is the comparison of dependence of derivative weight and temperature, which is represented in this chapter. Unlike in TGA and DSC analysis, the data to draw graphs here, is the pure data obtained from thermal analysis apparatus and is not normalised. Like before, fig.19 show comparison of four biomass samples catalysed with different hydrotalcites to reference pure biomass in process of pyrolysis, presented as DTG curves.

DTG curves, similar to TG curves may be divided into three phases of thermal degradation. The same rules apply for both types of analysis. As seen on fig. 20 the effect of different catalyst on algae, has slight influences on peak temperature of DTG curves. For all samples, it is very similar. However, when it comes to degradation rate, the highest value was registered for the sample containing MgAl catalyst (~0.45 mg/min), while the lowest value was observed for MgAlFe catalysed sample, which was very similar to the value observed for reference sample (~0,25 mg/min). Biomass catalysed by NiZn and ZnAl catalysts had comparable values of degradation rate (~0,3 mg/min). The peak occurred for all samples in phase 2 of thermal degradation, which suites the biggest drop of the TGA curve in the same phase. However, neither of the catalyst changes the position of the peaks in terms of reducing the temperature of occurred peaks, which means that studied in this work hydrotalcites, do not have a major influence on reducing the temperature degradation. First peak around 100°C represents the water evaporation from the biomass. [44] The other big peak occurring around 300°C, which is the highest for MgAl containing sample, as mentioned above, may come from released CO_2 or CO from cellulose, according to the scientists [45]. Although the peak looks much different then the one representing the reference sample, it is not that relevant for the study in this work.

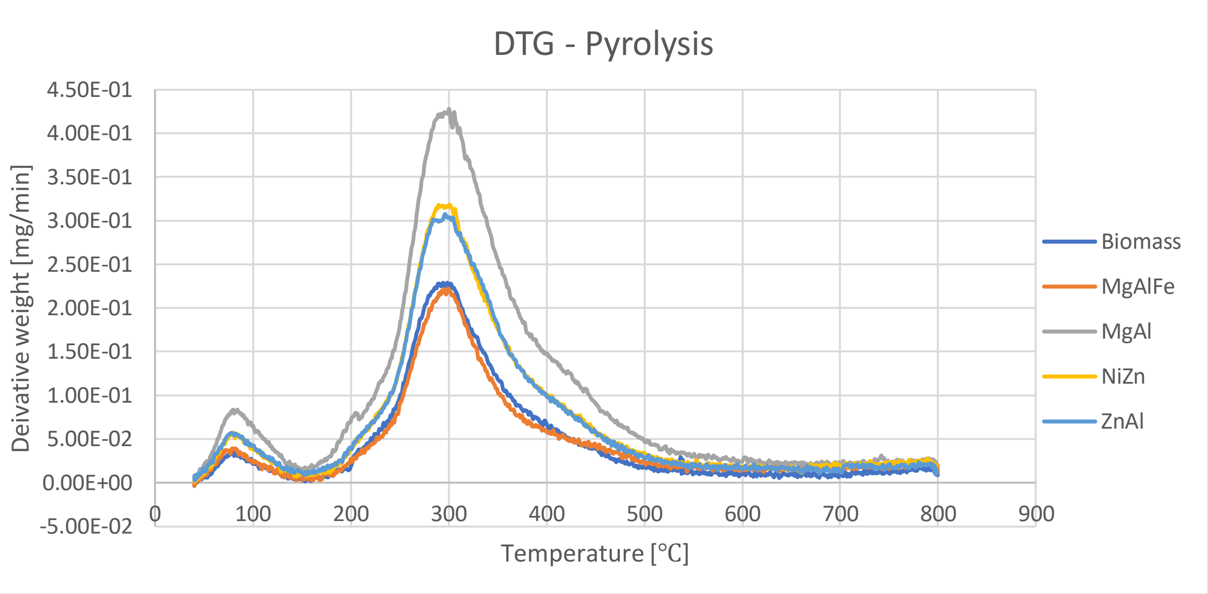


Fig. 19 Comparison of derivative weight to temperature dependence for all samples in the pyrolysis process

5.3 DSC results

Heat flow, next to weight, is the other very important data obtained from thermal analysis of pyrolysis and combustion processes. In this chapter, the changes of heat flow vs temperature are represented on the graphs comparing 4 samples containing different catalysts with reference sample, which is pure biomass, in processes mentioned above. The analysis performed in this way is also called DSC analysis. It can be seen in Fig 20. Similar to TGA analysis, the values of heat flow are normalised in order for comparison being as clear as possible.

In Fig. 20 DSC analysis was carried out for the pyrolysis process. The curves representing samples catalysed with MgAlFe, NiZn and ZnAl, were not that different from the reference sample. The one that was the least similar to pure biomass representation, was biomass catalysed with MgAl. This curve had the biggest drop of all samples and was the furthest from reference curve. DSC represents the amount of heat that was absorbed or released at the moment of time and in certain temperature. By looking on graph presented on fig.20, it is clear, that most samples show endothermic behaviour after reaching the temperature of around 400°C. The only slight exothermic activity can be noticed in the curve representing the MgAFe catalysed sample, which after reaching around 500°C also becomes endothermal. The temperature of degradation is not reduced in any of the curves in comparison to the reference sample. The biggest difference is in the sample containing MgAl, but it is not relevant action, when it comes to purposes of this study.

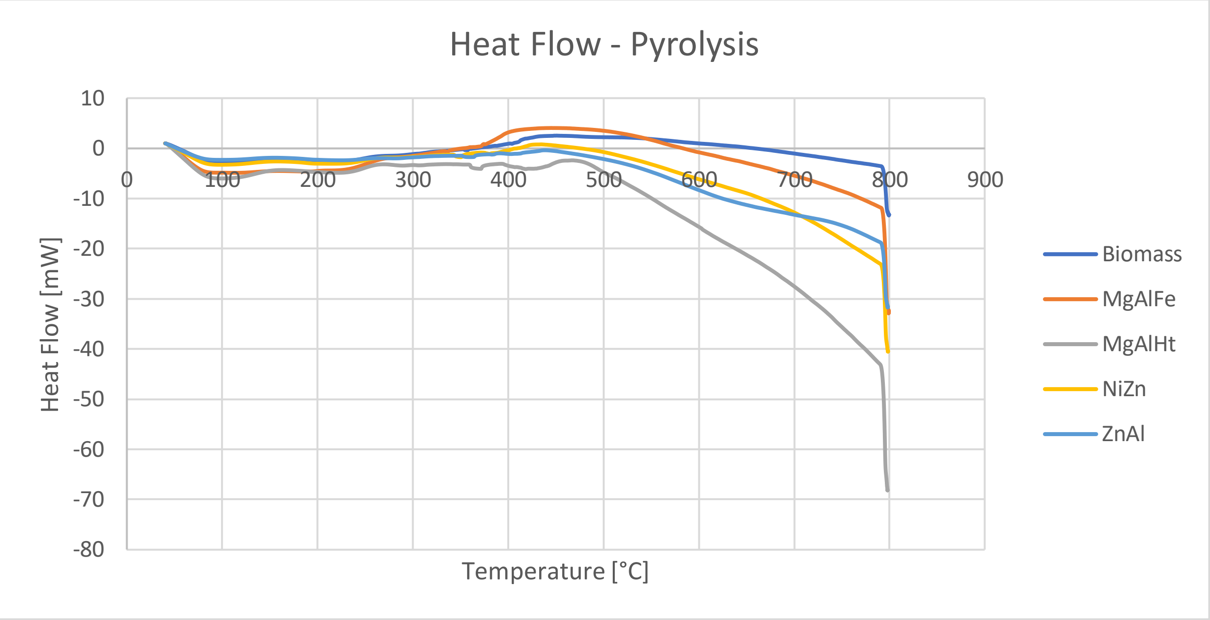
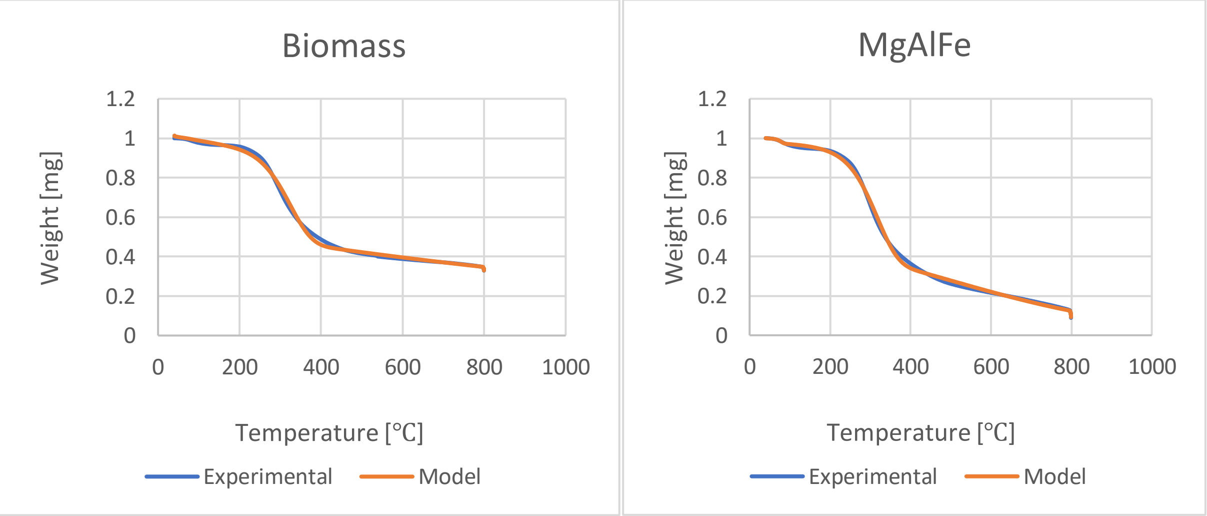


Fig. 20 Comparison of heat flow to temperature dependence for all samples in the pyrolysis process

5.4 Kinetic modelling of weight loss to temperature dependence for pyrolysis process

Kinetic modelling was carried out for weight loss to temperature dependence in the pyrolysis process of biomass for all samples. The results are presented above, but will not be analysed in this work, as the main focus is put on the thermal analysis and may be used in further investigation on influence of hydrotalcites as catalysts in the pyrolysis of biomass.

Curve fitting was applied to weight loss representing graphs in the biomass pyrolysis process. The results of the fitting for all samples are represented in fig. 21



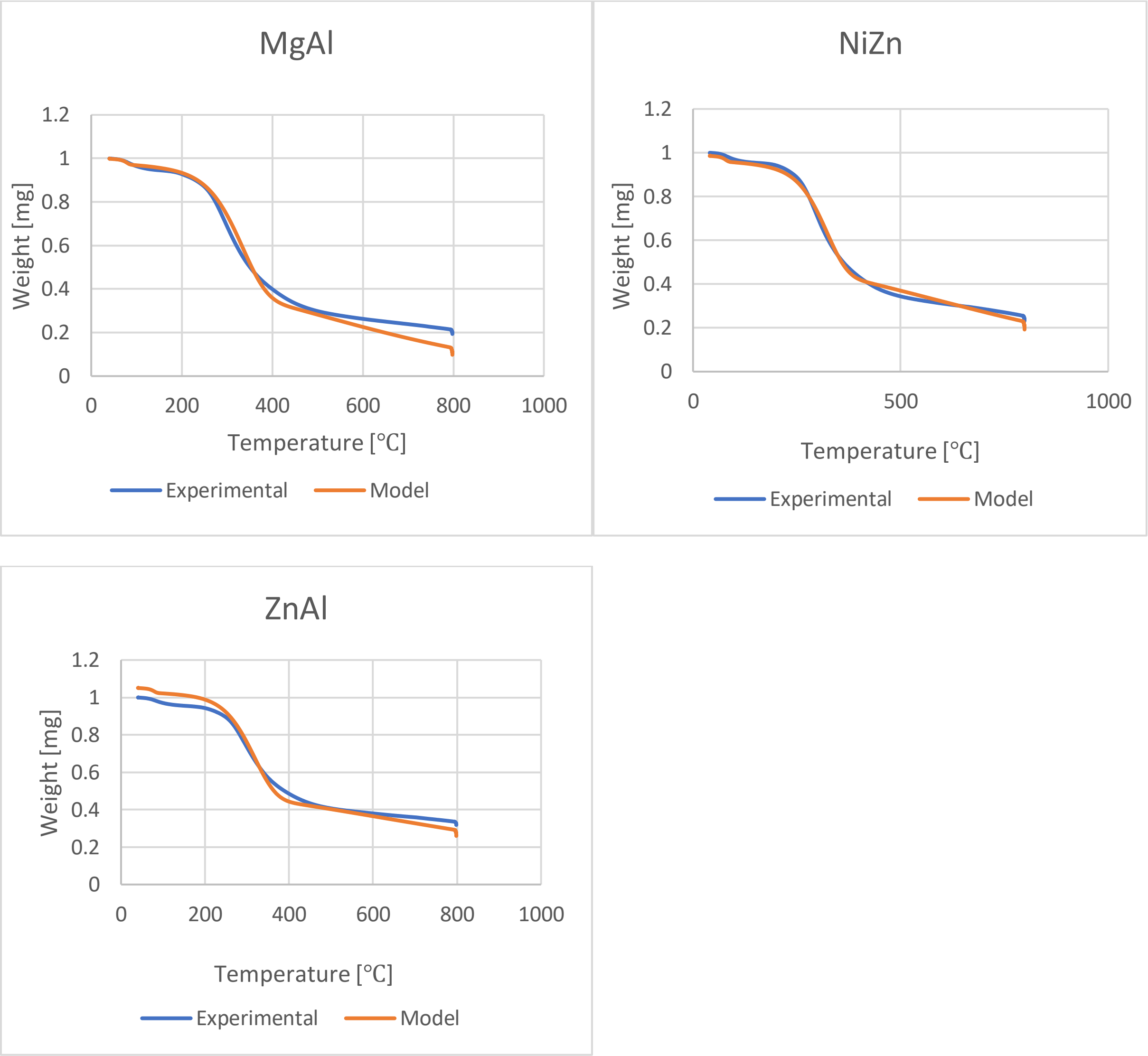


Fig. 21 Model fitting for weight loss to temperature dependence in the pyrolysis process for all samples

In table 6 below, the 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, even if in some graphs, like ZnAl and MgAl, there are visible differences. If R^2 has value higher than 0.994, it means that the curve is fits. As explained in chapter 4.5.3 “Kinetic modelling”, the biomass in this case is considered to have three pseudocomponents (hemicellulose, cellulose and lignin, represented by numbers 1, 2 and 3 respectively), which decomposed independently. Letters w, Ea and k refer to weight fraction, activation energy and reaction rate constant respectively, referring to different pseudocomponents of biomass. Because analysis of kinetic modelling in this work was not carried out, the table represents hypothetical results, which are very likely to change after more precise calculations and curve fitting in Excel Software.

	Biomass	MgAlFe	MgAl	NiZn	ZnAl
w1 [mg]	0,441319	0,518856	0,516918	0,444521	0,509521
w2 [mg]	0	0,022026	0,022026	0,022019	0,022026
w3 [mg]	0,572076	0,459969	0,46055	0,520265	0,519802
Ea1 [J/mol]	56692,19	56926,5	57677,06	60366,16	57092,71
Ea2 [J/mol]	0	121584,2	121584,1	121598,3	121579,9
Ea3 [J/mol]	0	10179,99	10055,34	8577,992	7307,96
k1 [1/min]	0,483626	2,62E-06	1,56E-06	1,25E-06	2,52E-06
k2 [1/min]	1	9,64E-04	9,64E-04	9,64E-04	9,64E-04
k3 [1/min]	0	0,001722	0,001713	0,001588	0,001511
R^2	0,997974	0,99885	0,994049	0,996045	0,997772

Table 6: 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

5.5 Combustion process results - TGA, DTG, DSC curves and kinetic modelling

A mentioned before, the combustion of all samples was carried out after the pyrolysis pyrolysis in order to burn materials that pyrolysis did not degrade. Because the main objective of this work is catalysed pyrolysis of biomass, the thermal analysis of combustion of the samples will not be carried out, however, the TGA, DTG and DSC curves will be presented, (respectively fig. 22, 23, 24) so that the obtained results can be investigated and analysed in further studies of influence of hydrotalcite catalyst on biomass pyrolysis. Kinetic modelling of one catalysed sample (MgAlFe) will also be presented here, for the reasons mentioned above.

Fig. 22 represents comparison of all 5 samples, when it comes to changes in weight to temperature dependence. Here again, The sample catalysed with MgAlFe has curve that is the most dissimilar than the one representing pure biomass. In this case the curve practically does not have a drop in comparison to all other samples. The next ones are, respectively the samples containing catalysts ZnAl and NiZn. The least different curve to the reference one is catalysed with MgAl.

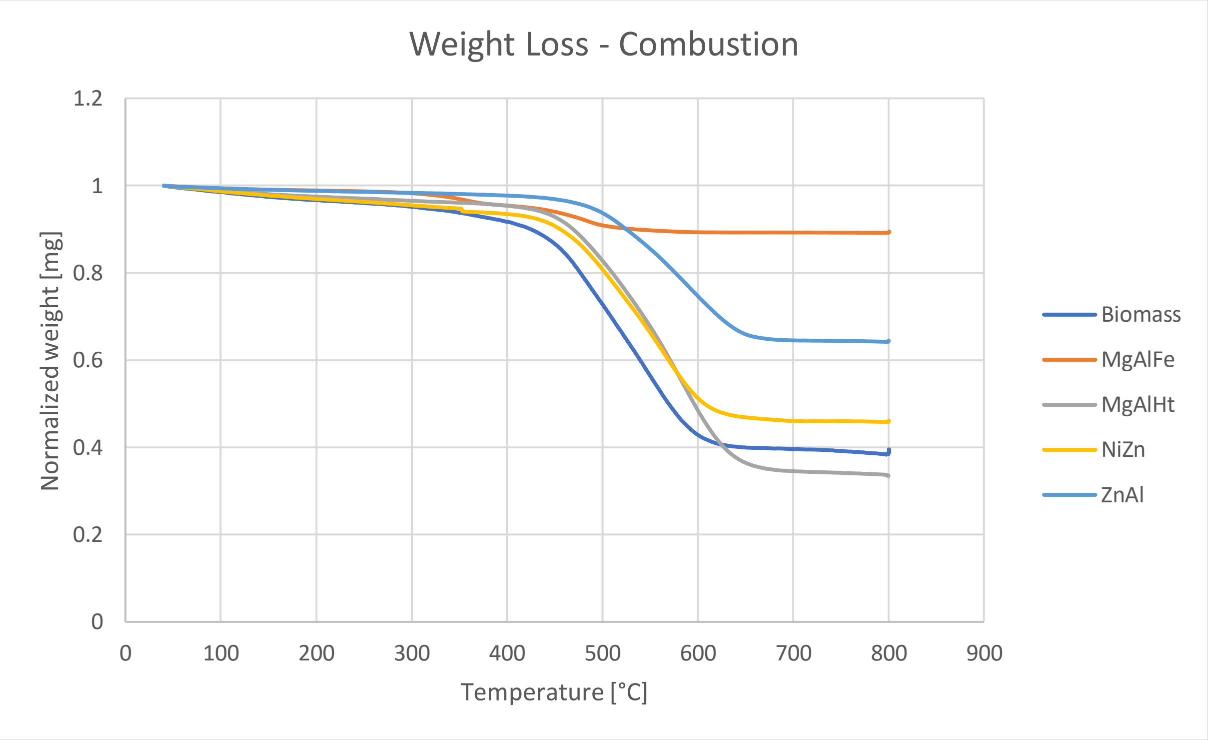


Fig. 22 Comparison of weight loss to temperature dependence for all samples in the combustion process

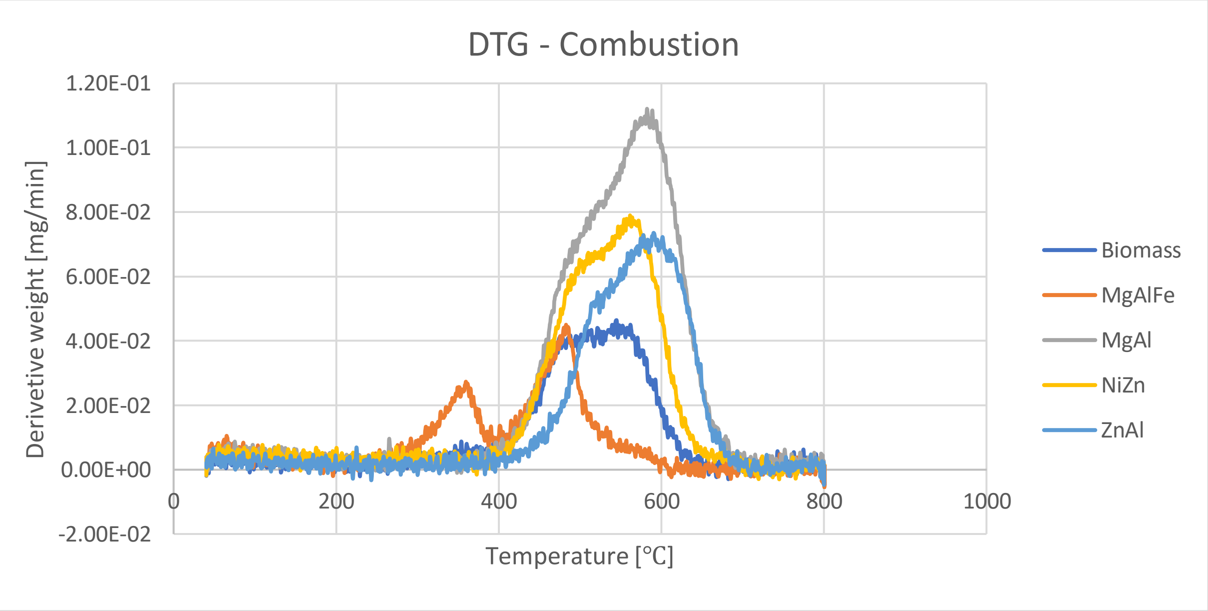


Fig. 23 Comparison of derivative weight to temperature dependence for all samples in the combustion process

Fig. 23 represents DSC analysis for combustion process. The reference curve and samples catalysed with MgAl, NiZn and ZnAl, look quite similar to each other in comparison to curve representing MgAlFe catalyst. The other four samples have one wide peak, while MgAlFe gives two separate peaks. Similar situation occurs in the DSC graph represented in fig. 24. Curves of all samples have one wide peak, except for the MgAlFe containing sample, which again, shows two separate peaks.

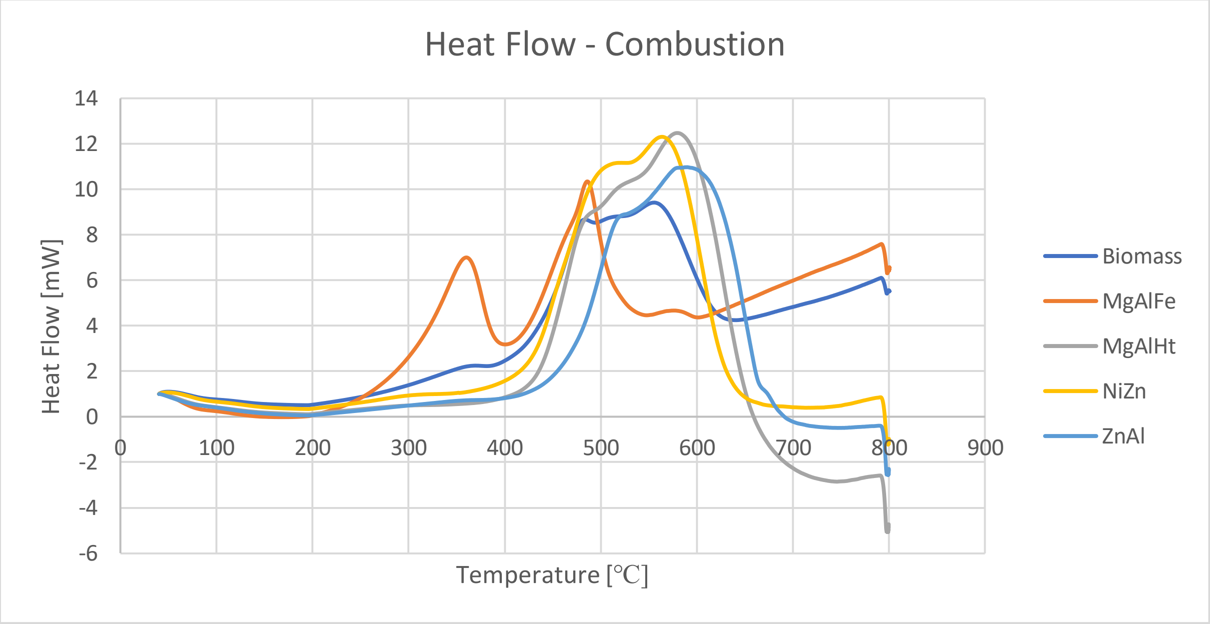


Fig. 24 Comparison of heat flow to temperature dependence for all samples in the combustion process

Kinetic modelling fitting was applied to the sample containing the most promising catalyst of all examined in this work – MgAlFe in the process of combustion. The graph representing curve fitting is represented in fig. 25, while table 7 represents obtained from this action values of weight fractions, energy activation and reaction rate constant, as well as correlation coefficient. Here, similar to chapter 5.4 "Kinetic modelling of weight loss to temperature dependence for pyrolysis process", the analysis of kinetic modelling in this work was not carried out and the table represents hypothetical results, which may vary from the correct results obtained after more detailed calculation in Excel Software.

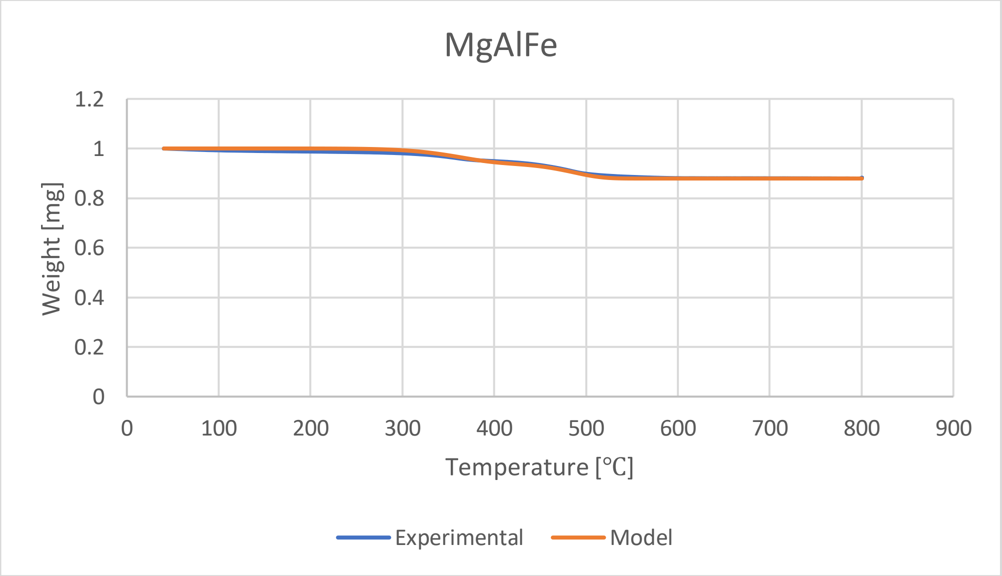


Fig. 25 Model fitting for weight loss to temperature dependence in the combustion process for sample containing MgAlFe catalyst

	MgAlFe
w1 [mg]	0,057655
w2 [mg]	0,063355
w3 [mg]	0,87899
Ea1 [J/mol]	85000
Ea2 [J/mol]	150000
Ea3 [J/mol]	0
k1 [1/min]	4E-09
k2 [1/min]	5E-17
k3 [1/min]	0
R^2	0,993708

Table 7: Values of weight fractions, Ea, k and correlation coefficient for sample containing MgAlFe for model fitting for weight loss to temperature dependence in the combustion process.

6. Outlook and conclusions

To sum up everything, that has been presented in this work on experiment carried out for the purpose of Master's thesis, this chapter is dedicated to brief reviews of all chapters, the drawn conclusions, as well as the outlook for the future experiments.

Biomass as a feedstock for biofuel, has been examined for the past few years, as it is a very good alternative for fossil fuels, which are obviously not renewable and the world's demand for energy increases. The other issue, why biomass is a good replacement, is that it lowers emissions of carbon dioxide and other pollutants, which for now is a big problem. Biomass can be used to produce bio-oil, which can be used as fuel, but for now it is not a very efficient one. In some cases, depended on which kind of biomass was used, pollutants like NO_X can be produced. The fuel itself can be seen as low-quality liquid. That is why catalytic pyrolysis has become widely studied , as it is a good strategy for high efficiency energy utilization of biomass. In this work catalysts were derived from hydrotalcites.

Hydrotalcites are natural and economic layered materials, which can be used as catalysts in pyrolysis process of biomass, which was carried out in this thesis. There are many ways to synthesise HTs and it turns out that co-precipitation method, which was performed in this experiment, is a fast and easy way to produce these materials. It is also very efficient, because big amount of HTs were obtained, which can be used in further experiments.

In order to check influence of catalysts on algae pyrolysis, the process was carried out in TGA/DSC apparatus, so that thermal analysis for all samples would be carried out. Four hydrotalcites, prepared earlier, were mixed with algae in the same proportions, which made four samples. The fifth samples was pure biomass for reference.

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 refence one (around 300°C).

DSC analysis represents the amount of heat that was absorbed or released I 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 endothermal behaviour, except for MgAlFe catalyst, which had slight exothermal performance, but then after few degrees went back to its endothermal 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 catalyst 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 this 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 degradated 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 obtained. 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 algaes, where the hydrotalcite's performance as catalysts may be examined with more details.

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