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# HYDROTHERMAL CARBONIZATION: PRODUCTION OF ENERGY THROUGH THE THERMOCHEMICAL TREATMENT OF BIOMASS

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**Abstract - Hydrothermal carbonization (HTC) is characterized by simplicity and relatively low reaction temperature and pressure (subcritical water conditions). It is also capable of processing organic material with high moisture content. The combination of the above justifies the growing interest around this specific pre-treatment method of biomass. However, the properties of hydrochar, the main product of HTC, are significantly affected by the process conditions (temperature, residence time, water-to-biomass ratio, feedstock composition etc.). In addition, the exact reaction mechanism is currently partially understood. That is the reason why only the hydrothermal carbonization of specific types of biomass under distinct conditions has been investigated. The purpose of this paper is to highlight the advantages of hydrothermal carbonization, describe the general reaction mechanism and examine the dependence of the products to the process parameters. Representative cases of reaction kinetics modeling based on experimental data were selected for demonstration. The paper concludes with an overall evaluation along with suggestions to improve the efficiency of the process.**

**Keywords:** renewable energy, hydrothermal carbonization, HTC, biomass, thermochemical treatment, reaction kinetics

## 1. INTRODUCTION

Humanity is faced with an imminent energy crisis. The exponential growth of the human population and the consequential increase of the required energy on a global scale, the dramatic climate change and the exhaustibility of natural resources combined, force us to strive towards a sustainable future. The majority of energy is being produced by fossil fuels, carriers of high density of primary energy. Their reserves, however, are finite and the rate at which they are physically replenished is extremely slow. Alternatives are available in the form of renewable energy sources (RES). RES, such as photovoltaic systems, wind turbines, biofuels etc., share a series of common characteristics. They are practically inexhaustible, produce little to no emissions and pose no threat to the environment. At the same time they are characterized by low energy density, increased cost and intermittent nature. Biofuels (i.e., fuels produced by biomass) and geothermal power are excluded from the latter [1-2]. The shares of total final consumption per fuel type between the years 1973 and 2014 are depicted in Fig. 1. It is quite evident that fossil fuels are still dominant even after the lapse of almost 40 years [3].

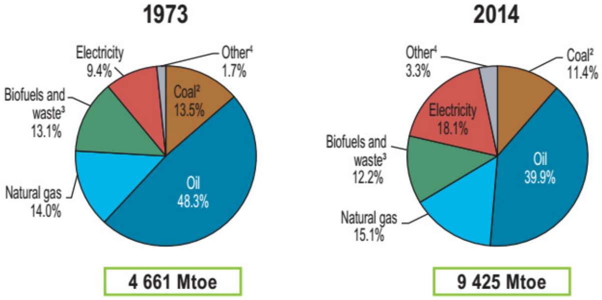

**Fig. 1. International Energy Agency. 1973 and 2014 fuel shares of total final consumption. Other includes geothermal, solar, wind, heat etc [3].**

The use of biomass as an energy source, despite its current status, is an increasingly attractive option. According to the International Energy Agency: "Biomass is any organic, i.e. decomposable, matter derived from plants or animals available at a renewable basis. Biomass includes wood and agricultural crops, herbaceous and woody energy crops, municipal organic wastes as well as manure [4]."

Biomass consists mostly of cellulose, hemicellulose and lignin. The three chemical components exist in various proportions, depending on the type of biomass. Cellulose is a glucose homopolymer (pollysaccharide, a linear chain of glucose units) and is the most common organic compound on earth since it participates in the formation of cell walls in plants. Hemicellulose is a heteropolymer that consists primarily of xylose, mannose, glucose and galactose, with xylose being the most abundant component. Lignin is a complex heteropolymer consisting of three different phenyl-propane monomer groups. Out of the three chemical components that comprise the biomass, lignin has the highest calorific value. Biomass is abundant and generally available at a renewable basis. Biomass feedstock includes a wide variety of organic materials that ranges from specifically cultivated crops and harvested wood products to agricultural and industrial waste. It is the only renewable energy resource that can be converted into any fuel form (solid, liquid or gaseous). In addition, biomass does not contribute to the increase of carbon dioxide ($CO_2$) in the atmosphere. It emits the same amount of carbon that was sequestered through photosynthesis during the plant's growth [5-8].

The use of biomass as a fuel, however, faces a series of challenges. Despite its abundance, it is characterized by low energy density, a fact tantamount to high cost of transportation and storage [9]. High moisture content, hydrophylic behaviour, heterogeneous nature and poor grindability further increase the cost of biomass applications. Therefore, pre-treatment processes need to take place in order to improve the physicochemical properties of the biomass fuel [10-11].

Currently, the conversion of biomass takes place mainly through two process technologies: biochemical and thermochemical [7-8, 12-13].

Biochemical conversion of biomass employs the use of microorganisms and enzymes for the production of liquid or gaseous fuels. The most common biochemical processes are fermentation and anaerobic digestion [12-14].

Thermochemical processes aim to valorize biomass by converting it into an energy carrier of higher density. They take place under heat and in the presence of a catalyst. As seen in Fig. 2, combustion, gasification, pyrolysis and liquefaction summarize the thermochemical processes used for biomass conversion [8-9, 12-14]. Despite being connected to the production of environmentally detrimental gases, combustion is considered to be the most technologically mature method for the valorization of biomass.

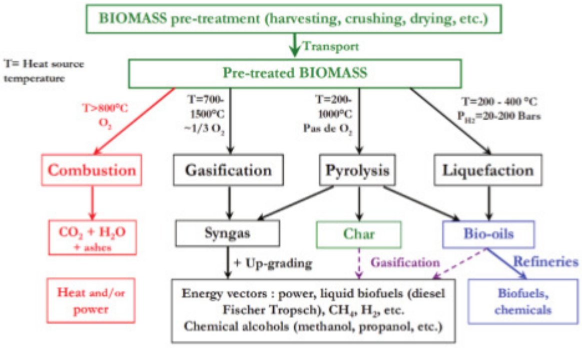

**Fig. 2. Main thermochemical processes of biomass conversion [9].**

Thermochemical processes, when compared with the biochemical, possess several advantages that affect their potential commercialization greatly. The duration of thermochemical processes is much shorter, spanning from seconds to several hours, while biochemical processes require up to several days. In addition, themochemical processes utilize a wider range of feedstock including biomass with high moisture content. In the case of biochemical conversion, the microorganisms are extremely sensitive to the organic input and the conversion of biomass may even be impossible, depending on the organic input [14]. Finally, thermochemical processes are characterized by higher conversion efficiency [5].

The focus of the present paper is the hydrothermal carbonization (HTC) of biomass. The process, the effect of its conditions on the properties of the resulting hydrochar and the general reaction mechanisms are discussed in the respective sections. The mathematical modeling of selected cases of HTC follows. The paper concludes with a discussion on the results and on possible ways to maximize the efficiency of the process.

## 2. HYDROTHERMAL CARBONIZATION

### 2.1. Definitions, conditions and products

The direct use of biomass as fuel faces many challenges (e.g. low energy density, high moisture content, biological instability etc.). Pre-treatment processes that improve the characteristics of the organic materials in use are necessary. Hydrothermal carbonization (HTC), also known as wet pyrolysis, emulates the natural process of coalification [5-6, 16-17]. Biomass in the presence of water is heated in a closed environment. The process takes place at subcritical water conditions (below 374 $^{o}$C and 22 MPa, usually within 150-250 $^{o}$C and 2-6 Mpa). Usually, the reaction pressure is not controlled. It is autogenous and ideally corresponds to saturated values for a specific reaction temperature. HTC, apart from liquid and gaseous by-products, results in the production of a solid material rich in carbon. The percentage and composition of the end products are directly tied to the process parameters, with reaction temperature, residence time and water-to-biomass ratio being the most significant. With a further increase in temperature, the processes of hydrothermal liquefaction (above 250 $^{o}$C) and hydrothermal gasification (supercritical water conditions) take place, both of which are beyond the scope of the present paper [5-6, 10-11]. The classification of hydrothermal processes of biomass as a function of temperature and pressure is depicted in Fig. 3.

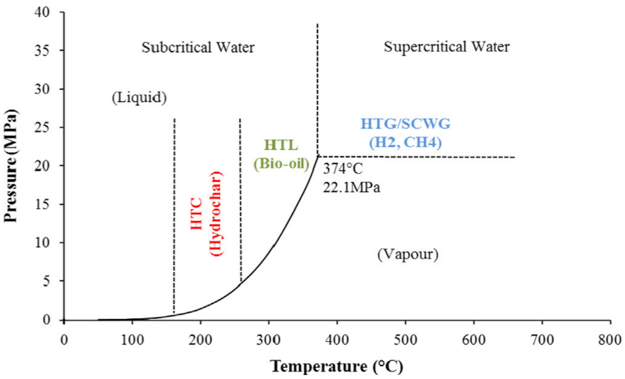

**Fig. 3. Classification of hydrothermal processes [5].**

At this junction, the distinction between hydrochar and the common term biochar has to be made. Biochar is the organic charcoal material produced mainly from pyrolysis (thermochemical process of biomass in an oxygen-deprived envinronment) and its main purposes are to be used in carbon sequestration and as soil amendment. Solid products similar to biochar may be achieved by other processes, though they cannot be classified as biochar for reasons specific to the process in question. For instance, the process of liquefaction produces a small yield of solid material that contains high amount of alkali and alkaline earth metals as well as polyaromatic hydrocarbons (PAHs), compounds that are formed in high-temperature reactions. PAHs are extremely toxic pollutants, while the high alkali content is responsible for corrosion, fouling and other adverse effects during combustion [5, 9, 12-13, 18-21].

The solid carbonaceous material, which is the main product of HTC, when compared with unprocessed biomass, displays superior fuel characteristics. Its content is lower in oxygen and higher in carbon. It produces lower emissions of greenhouse gases and displays increased hydrophobicity. Hydrochar, above all, possesses a calorific value comparable to that of lignite. Unlike biochar, which is the product of a dry carbonization process, hydrochar is produced as a solid-liquid mixture (slurry) [5, 10, 17, 22-25].

The physicochemical properties of hydrochar in combination with the advantages that HTC offers (simplicity, low cost, solid yield percentage, ability to process wet biomass) render hydrochar a more appealing product [6]. In a recent detailed comparison between biochar and hydrochar, hydrochar was found to be superior in specific ways and HTC was characterized as a highly promising method of treating biomass. However, the interest around hydrothermal carbonization is relatively new and, therefore, extensive research has to take place before any conclusions about the feasibility of the process are to be reached [5].

## 2.2. Definitions, conditions and products

The hydrothermal carbonization process results in the production of solid, liquid and gaseous outputs with solid hydrochar being the main product. The percentage at which these products are formed and their respective properties are directly linked to the process conditions. It has been generally observed that, by increasing reaction severity, i.e. increasing temperature and/or residence time, the solid products exhibit higher carbon content and, at the same time, lower solid yield [5, 24]. The effect of each parameter is described in the following sections.

### 2.2.1 Reaction temperature

Reaction temperature is regarded as the most significant among the process conditions that affect the properties of the final products [5-6, 26]. Usually the temperature range lies between 180-250 °C. Temperatures above 260 °C correspond to other hydrothermal processes (hydrothermal liquefaction and hydrothermal gasification), while temperatures below a lower limit have proven to be insufficient for the initial hydrolysis of biomass. These actual limits are directly linked with the consistency of the organic materials in use. For instance, in the case of hydrothermal carbonization of coniferous biomass a lower boundary temperature of 150 °C was reported [5-6, 10]. Beyond that, almost no degradation takes place.

It has been found that by elevating the temperature of the process the calorific value of the produced hydrochars improves. Among the reactions that take place during HTC, dehydration and decarboxylation are responsible for the reduction of oxygen and hydrogen content of the initial organic material. These reactions are promoted by temperature increase. Thus, an energy densification of the end product occurs since the fixed carbon content in the produced hydrochar is increased. At the same time, however, higher temperatures have a negative effect on the solid yield. This is attributed to the liquefaction and gasification reactions, which are parallel to the hydrothermal carbonization and their impact grows with increasing reaction severity (both temperature and residence time) [5, 11, 15, 24, 27].

In addition, the temperature affects the properties of water, which plays the roles of solvent and catalyst for organic compounds [24]. More details on the respective section.

### 2.2.2 Residence time

An additional parameter, which governs the properties of the end products of hydrothermal carbonization, is residence time. Typical residence times span from a few hours to days, although durations of a few seconds have been reported as well. The correlation between residence time and hydrochar properties has not been systematically studied yet. Nevertheless, it has been experimentally observed that the effect of residence time on the solid yield and heating value of hydrochar is much weaker than that of reaction temperature [24, 28-32].

Naturally, longer residence times ensure a more complete hemicellulose and cellulose decomposition and thus, provide a higher carbonization degree. As a direct result, prolonged reaction times lead to higher mass losses and, consequently, increased energy densification.

However, several studies have shown that for constant reaction temperatures, the effect of residence time in the solid yield is significant at the lower regions of the HTC temperatures and diminishes at higher temperatures. In other words, as the reaction temperature increases, the actual attainable solid yield can be achieved in shorter retention times after which the temporal effect becomes marginal. Lastly, the impact of residence time on the resulting hydrochar HHV (higher heating value) was also found to be less significant than that of carbonization temperature [6, 10-11, 29-32].

The combined effect of reaction temperature and residence time on the solid yield and energy densification can be exploited towards to a more energy efficient process.

### 2.2.3 Water-to-biomass ratio

An additional process parameter that affects the final products of HTC is the water-to-biomass ratio, although it has not been examined consistently [24, 33]. Whether it is more or less influential than residence time is currently debatable [33-35].

The mass of the process water is typically 3-10 times greater than that of the dry feedstock [5]. It has been reported that with increasing the water-to-biomass ratio the acceleration of the carbonization process is achieved. At the same time the produced solid yield decreases. This is attributed to the greater impact of hydrolysis reactions caused by the increase in water quantity [10, 30, 34]. On the other hand, the carbon content and HHV of the final product was found to be affected by water-to-biomass ratio at a negligible degree [34].

### 2.2.4 Hydrous conditions

In hydrothermal carbonization, biomass submerged in water is heated in a closed environment. It has been observed that, biomass above the water surface does not undergo carbonization [24, 35].

Under subcritical conditions (below 374 $^{o}$C and 22,1 MPa), the physicochemical properties of water (density, dielectric constant, ion products) are affected in ways that are beneficial to the decomposition of organic compounds [36-38]. Subcritical water acts as solvent, reactant and catalyst that enhances several of the involved carbonization reactions, with hydrolysis being the most intensified [17, 24, 28-29, 36, 39]. In more detail, the hydrolysis of cellulose and hemicellulose at the presence of subcritical water initiates at the range 160-180 $^{o}$C. Lignin, being a thermo-chemically stable polymer, remains unaffected. Thus, HTC results in a product rich in lignin, which displays the highest HHV among biomass polymers. At the same time, elevated temperatures promote the solvent character of water. Moreover, water being an adequate heat transfer medium with relatively high heat capacity ensures a degree of thermal homogeneity [5-6, 10, 24].

In conclusion, the fact that water is an integral part of the hydrothermal processes renders the preliminary drying of wet feedstock redundant. Hydrothermal processes in general and hydrothermal carbonization specifically, are suitable for the conversion of biomass with high moisture content [5-6, 10-11, 16, 25-26, 28-29, 31, 36, 39-42].

## 2.3. Chemical mechanism

During hydrothermal carbonization several chemical reactions take place. These reactions are not consecutive but instead, have been aptly characterized as a parallel network of reactions [24, 29]. Detailed information about the exact reactions is currently available only for specific types of biomass, i.e. cellulose [16, 23]. The main reaction pathways in HTC process consist of hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization [10, 16-17, 24, 29, 35, 37].

Hydrolysis involves the cleavage of chemical bonds (predominantly ester and ether bonds) by the addition of water. In the case of HTC, it is the first step towards biomass degradation during which, cellulose and hemicellulose are converted into water-soluble monomers and oligomers. Lignin, being a more complex component, remains relatively unaltered under the standard HTC conditions [5, 26, 36, 41-42]. It has been found that, because the main organic compounds are more unstable under HTC conditions, hydrolysis requires less activation energy compared to other decomposition reactions. This allows hydrothermal carbonization to be performed under lower reaction temperatures while achieving similar conversion efficiencies [55-56]. In addition, below a certain temperature threshold (175 $^{o}$C), apart from a partial decomposition of hemicellulose, hydrothermal carbonization is not possible since the ionization constant of water is unsuitable for the hydrolysis of organic compounds [6]. Generally, elevated temperatures and increased water-to-biomass ratios work in favor of HTC by promoting the effect of hydrolysis and accelerating the carbonization rate. Lastly, hydrolysis has been defined as a decisive step for the properties of hydrochar. It provides the components that will be used later for the formation of the solid products [44].

Decarboxylation involves the removal of a carboxyl group and the consequent release of $CO_2$. Dehydration is a condensation reaction in which two functional groups combine to form a larger molecule. This reaction is accompanied by the removal of a water molecule. The dehydration and decarboxylation reactions are responsible for the energy densification of the initial feedstock by reducing the hydrogen and oxygen content. Thus, a portion of biomass with no calorific value is removed and the production of a carbon-rich product is promoted. It has also been established that both of these reactions are favored by an increase in temperature [11, 16, 22, 36, 43-46].

The products of decarboxylation and dehydration are unsaturated water-soluble compounds that can readily be polymerized due to the anterior removal of hydroxyl and carboxyl groups. Polymerization is a process where reacting monomers join to form polymer chains. It has been speculated that, condensation polymerization, specifically aldol condensation, may be critical in the formation of aromatic compounds and the hydrochar itself. Condensation polymerization is a form of step-growth polymerization. Two smaller molecules form a larger one releasing condensates. In organic reactions, condensates are usually water molecules [36, 47-49]. Aromatization is the conversion of aliphatic components into aromatic compounds. The most common aromatic compounds are derivatives of benzene. Aromatic structures are cyclic, planar organic compounds that display high stability (low reactivity). The increased stability of these compounds has led to their consideration as the main constituent for the development of the solid product. The formation of carbonaceous spherical particles through a burst nucleation process and the consequent growth of the nuclei ensue when the concentration of aromatic compounds reaches a critical point. Both polymerization and aromatization are favored by elevated reaction temperatures [24, 27, 32, 42, 50-51].

## 3. MATHEMATICAL MODELING

The modeling of the process of HTC employs the field of chemical kinetics, which deals with the rate of chemical reactions. The development of a mathematical model for the rates of chemical reactions, one of the basic aims of applied reaction kinetics, provides elucidating information about the reaction mechanisms and the factors that influence these rates. This fundamental understanding of chemical reactions enables their manipulation in order to achieve products with desirable properties [52-60].

Due to the complex nature of the process and the varying composition of biomass, detailed information are available only for the hydrothermal carbonization of specific types of biomass [17, 24]. In some cases, a detailed kinetics modeling was proposed while in others, a more simplified approach was adopted. In the present paper two distinct research efforts to model and predict the process of hydrothermal carbonization will be presented.

### 3.1. Hydrothermal carbonization of grape marc

In [61], D. Basso et al. proceeded with the modeling of the hydrothermal carbonization of grape marc, a waste product of the wine-making industry. Experimental data were acquired by repeating the process nine times, for three distinct temperatures (180, 220 and 250 $^oC$) and for three different residence times (1, 3 and 8 h). The water-to-biomass ratio was kept at 10:3 (6.1 g of biomass, 20.4 g of deionized water). The initial heating and final cooling times where not considered to be a part of the residence time.

The reaction model that was used is based on the scheme for the thermal degradation of xylan proposed by C. Di Blasi and M. Lanzetta [62]. According to the adopted two-step reaction mechanism, the initial feedstock A forms an intermediate compound B which, in turn, forms the final product C. At each step the formation of the volatiles $V_1$ and $V_2$ takes place in parallel to the A-B-C transformation.

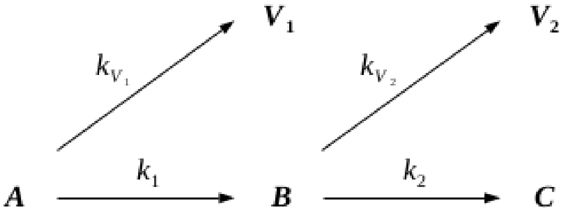

**Fig. 4. Two-step reaction mechanism for the hydrothermal carbonization of grape marc [61].**

Rate laws of the first order were assumed to describe the involved reactions, while the temperature dependence of the rate constant was described by the original form of the Arrhenius equation:

$$k = k_0 e^{-\frac{E_a}{RT}} \tag{1}$$

where:

$k_0$, the pre-exponential or frequency factor [appropriate units]

$E_a$, the activation energy [J/mol or cal/mol]

R, the universal gas constant [8.314 J/mol·K or 1987 cal/mol·K]

T, the absolute temperature [K]

The equations that describe the model are thus:

$$\frac{\vartheta m_A}{\vartheta t} = -k_1 m_A - k_{V_1} m_A \tag{2}$$

$$\frac{\vartheta m_B}{\vartheta t} = k_1 m_A - k_{V_2} m_B - k_2 \tag{3}$$

$$\frac{\vartheta m_C}{\vartheta t} = k_2 m_B \tag{4}$$

$$\frac{\vartheta m_{V_1}}{\vartheta t} = k_{V_1} m_A \tag{5}$$

$$\frac{\vartheta m_{V_2}}{\vartheta t} = k_{V_2} m_B \tag{6}$$

where:

$m_A$, $m_B$, $m_C$, are the masses of the initial feedstock, the intermediate product and the final hydrochar respectively [g]

$m_{V1}$. $m_{V2}$, are the masses of the volatile products of the first and second reaction respectively [g]

$k_1$, $k_2$, are the kinetic constants of the A→B and B→C transformations respectively [$s^{-1}$]

$k_{V1}$, $k_{V2}$, are the kinetic constants of the A→$V_1$ and B→$V_2$ transformations respectively [$s^{-1}$]

Apparently, at the beginning of the process $m_A=m_0$ with $m_0$ being the mass of the initial sample. All other masses are equal to zero $m_B=m_C=m_{V1}=m_{V2}=0$.

Fitting the model parameters to the experimental data using least square optimization gave the following table of pre-exponential factor and activation energy values.

**Table 1. Values of the Arrhenius parameters ($k_0$, $E_a$) for the hydrothermal carbonization of grape marc according to D. Basso et al. [61].**

| $k_{0,1}$ [$s^{-1}$] | $k_{0,2}$ [$s^{-1}$] | $k_{0,V1}$ [$s^{-1}$] | $k_{0,V1}$ [$s^{-1}$] |
|---|---|---|---|
| $3.34 \cdot 10^{7}$ | $1.10 \cdot 10^{10}$ | $9.15 \cdot 10^{6}$ | $1.55 \cdot 10^{10}$ |
| **$E_{a,1}$ [kJ/mol]** | **$E_{a,2}$ [kJ/mol]** | **$E_{a,V1}$ [kJ/mol]** | **$E_{a,V2}$ [kJ/mol]** |
| 94.5 | 139.7 | 93.7 | 146.2 |

With the Arrhenius parameters and the initial masses known, the system of differential equations (2)-(6) was solved using a fourth-order Runge-Kutta method (Gill's method).

### 3.2. Hydrothermal carbonization of coniferous wood

Another noteworthy research was conducted by E. Sermyagina et al. [10]. The effect of the process conditions on the hydrochars produced by coniferous wood chips was investigated. The tested water-to-biomass mass ratios were 6:1 and 8:1 while the tested residence times were 3 and 6 hours. The process temperature was within 180-250 °C. The anticipated mass and energy yield of the final products were expressed as functions of reaction temperature, residence time and water-to-biomass ratio. The mass yield was defined as:

$$MY = \frac{m_{hydrochar}}{m_{biomass}} \tag{7}$$

where:
MY, the mass yield [-]
$m_{hydrochar}$, the dry mass of hydrochar [kg]
$m_{biomass}$, the dry mass of biomass hydrochar [kg]

The energy yield was defined by the following equation:

$$EY = MY \frac{HHV_{out}}{HHV_{in}} \tag{8}$$

where:
EY, the energy yield [-]
$HHV_{out}$, the higher heating value of dry hydrochar [MJ/kg]
$HHV_{in}$, the higher heating value of dry biomass [MJ/kg]

The following correlations for mass and energy yield were developed:

$$MY = 1 - 0.04079 (T - 150)^{0.0337} t^{0.2142} w^{0.3055} \tag{9}$$

$$EY = 1 - 0.05632 (T - 150)^{0.062} t^{0.2846} w^{0.4405} \tag{10}$$

where:
T, the reaction temperature [°C]
t, the residence time [h]
w, the water-to-biomass ratio [-]

The form of equations (9) and (10) was found to describe the experimental data with acceptable accuracy while the constants were determined by minimizing the residual sums of squares (RSS). Such mathematical postulations, that reveal the dependence of the process on the operating conditions, can be beneficial in terms of modeling and optimization of the HTC process.

## 4. RESULTS

### 4.1. Hydrothermal carbonization of grape marc

Another noteworthy research was conducted by E. Sermyagina et al. [10]. The effect of the process conditions on the hydrochars produced by coniferous wood chips was investigated. The solution of the system of equations (2)-(6) leads to distribution of mass yield versus time for the three experimental temperatures (180, 220 and 250 °C) and for residence times up to 8 hours.

The examination of Fig. 5, 6 and 7 leads to several observations:

- The reactions of the first step (A→B and A→$V_1$) progress much more rapidly. This general behavior was anticipated since the activation energies are significantly lesser that those of the second step.
- The effect of residence time diminishes over time. As reaction temperature increases, the carbonization of the feedstock into hydrochar occurs faster and, therefore, residence time becomes less significant. At the same time, this is an affirmation of the reaction temperature as the dominant parameter.
- The relatively low temperature of 180 °C is proven to be insufficient to facilitate the second reaction step (B→C and B→$V_2$). As a direct result, insignificant quantities of hydrochar are produced at the lowest experimental temperature.

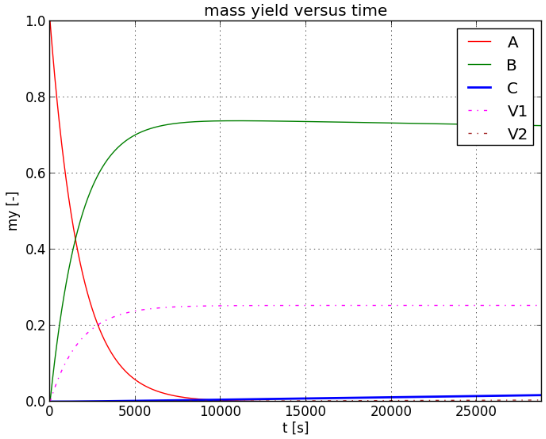

**Fig. 5. Mass yield versus time of the hydrothermal carbonization of grape marc according to D. Basso et al. for temperature 180 °C and residence times up to 8 hours.**

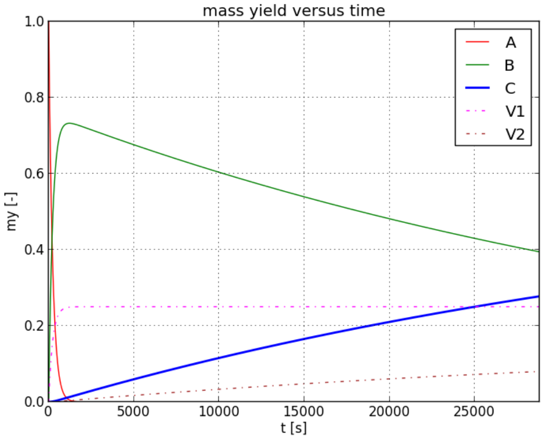

**Fig. 6. Mass yield versus time of the hydrothermal carbonization of grape marc according to D. Basso et al. for temperature 220 $^oC$ and residence times up to 8 hours.**

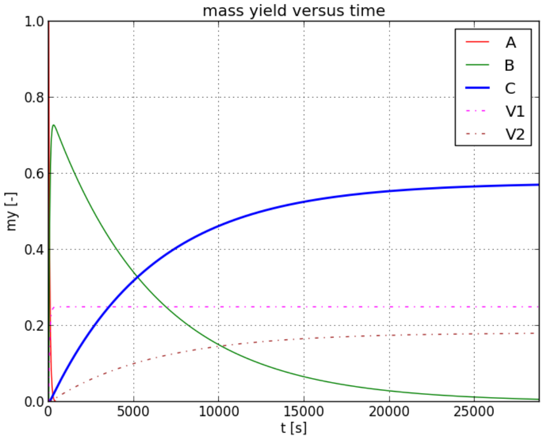

**Fig. 7. Mass yield versus time of the hydrothermal carbonization of grape marc according to D. Basso et al. for temperature 250 $^oC$ and residence times up to 8 hours.**

### 4.2. Hydrothermal carbonization of coniferous wood

In Fig. 8 and 9 the distribution of mass and energy yield versus temperature are depicted. The water-to-biomass ratio and the residence time were treated as parameters. Generally, an increase in temperature, residence time or water-to-biomass ratio leads to increased mass losses and higher energy yields. However, the effect of temperature as the dominant process parameter was verified. Comparing hydrochars produced at 180 and 250 $^oC$, the hydrochar produced at the latter displayed on average 20 % lower mass yield and 40 % increased energy yield. The use of greater quantities of water caused higher carbonization rates due to the enhancement of hydrolysis. Also, prolonged HTC process revealed that the effect of residence time on the properties of hydrochar was minor.

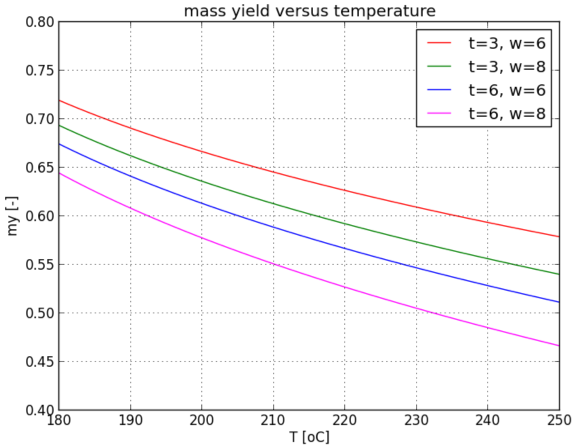

**Fig. 8. Correlation curves for the hydrochar mass yield of coniferous wood chips according to E. Sermyagina et al.**

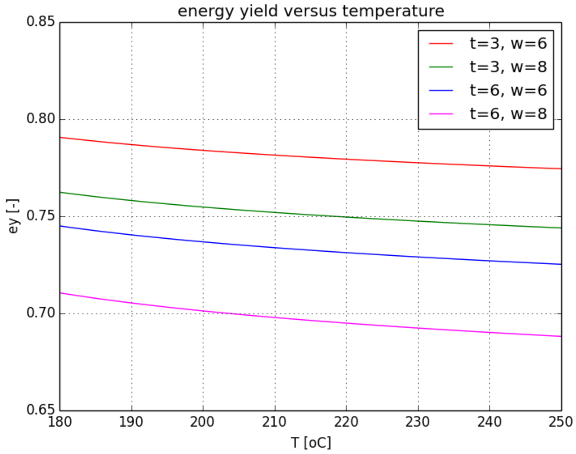

**Fig. 9. Correlation curves for the hydrochar energy yield of coniferous wood chips according to E. Sermyagina et al.**

## 5. CONCLUSION

Hydrothermal carbonization stands out among other thermochemical processes. It is based on a simple principal, which is the immersion of organic feedstock in water within a sealed vessel and heating under relatively mild conditions. The capacity to handle feedstock with high moisture content makes it even more appealing. However, in terms of commercial application HTC faces a series of challenges.

The reaction mechanism is highly complex and partially understood. A detailed reaction model that is capable of accurately describing the process, the effect of its parameters and the properties of the products is currently unavailable. Simplified reaction kinetics models have been developed experimentally to predict the solid and energy yield of the produced hydrochar but the actual mechanism is still under investigation [10, 24, 38, 41, 44, 61-62]. Gases and an aqueous solution are produced alongside the hydrochar. The distribution of products depends highly on the process parameters and the composition of the feedstock. The gaseous products are a mixture of gases consisting mainly from $CO_2$ and traces of CO, $H_2$ and $CH_4$. It has been found that the amount of gaseous products is favored by elevated temperatures. The liquid products are rich in organic and inorganic compounds and, therefore, constitute a potential source of useful chemicals. The separation and handling of these byproducts is an additional design difficulty [6, 24, 27, 46, 61]. Even though the initial energy-intensive removal of moisture from the organic feedstock is redundant, the need for drying steps is not entirely bypassed. The product leaves the reactor in a state of slurry and, thus, a drying process still needs to take place before it can be utilized properly. Nevertheless, compared to the initial biomass, hydrochar displays much less moisture content [5, 10]. Another cause for concern is the reaction pressure. At high temperatures, the pressure inside the reactor is also very high. Therefore, in a commercial application of HTC, the high pressure requirement would increase the complexity of the process [26]. The required water-to-biomass ratios are typically high in a HTC process. That would mean that an industrial application should be capable of handling large quantities of water, a fact that further increases the cost and complexity of a hypothetical HTC installation [24, 36].

Several concepts that would improve the conversion method have been proposed. An important degree of heat recovery can be achieved by recirculating process water and using it to preheat the submerged feedstock. It has also been speculated that the organic substances contained in the process water may be able to participate in the process, thus increasing the energy yield of the products [24, 40, 63]. The use of additives that facilitate the conversion (lower required reaction temperature and pressure) is also being explored, though a relative verification is still pending [16, 24]. The development of a highly accurate reaction kinetics model would allow to optimize the reaction conditions towards a more energy-efficient process [66].

In some cases, HTC has been scrutinized as a possible preliminary step for other conversion methods with promising results [63, 65-66]. Its process water, rich in specific nutrients, is being investigated as a possible soil amendment [67]. Other researchers regard HTC as an effective method for urban waste management [22, 68-69]. Its main product, hydrochar, can be used as fuel, soil amendment, sorbent and in carbon dioxide sequestration [24, 29]. Combining HTC with other renewable technologies, interesting sustainable applications may arise [70]

In conclusion, despite its drawbacks, hydrothermal carbonization is an auspicious conversion method especially for decentralized applications [24, 72-74].

## NOMENCLATURE

| | | |
|---|---|---|
| $E_a$ | [J/mol] | Activation energy |
| EY | [-] | Energy yield |
| HHV | [J/kg] | Higher heating value |
| k | [$s^{-1}$] | Reaction rate constant |
| $k_0$ | [$s^{-1}$] | Pre-exponential factor |
| M | [g or kg] | Mass |
| MY | [-] | Mass yield |
| R | [8.314 J/mol·K] | Universal gas constant |
| t | [s or min or hour] | Time |
| T | [K or °C] | Reaction temperature |
| w | [-] | Water-to-biomass ratio |

## REFERENCES

[1]. K. Mertens. Photovoltaics. Fundamentals, Technology and Practice. New Jersey: Wiley & Sons. 1st edition.

[2]. N. L. Panwar et al. Role of renewable energy source in environmental protection: A review. Renewable and Sustainable Energy Reviews 15 (2011) 1513-1524.

[3]. International Energy Agency. Key world energy statistics. 2016 Link: https://www.iea.org/publications/freepublications/publication/KeyWorld2016.pdf

[4]. International Energy Agency. Definition of Biomass and Bioenergy. Link: https://www.iea.org/topics/renewables/subtopics/bioenergy/

[5]. H. S. Kambo, A. Dutta. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. Renewable and Sustainable Energy Reviews 45 (2015) 359-378.

[6]. A. Alvarez-Murillo et al. Generation of biofuel from hydrothermal carbonization of cellulose. Kinetics modelling. Energy 94 (2016) 600-608.

[7]. P. McKendry. Energy production from biomass (part 1): overview of biomass. Bioresource Technology 83 (2002) 37-46.

[8]. P. McKendry. Energy production from biomass (part 2): conversion technologies. Bioresource Technology 83 (2002) 47-54.

[9]. A. Dufour. Thermochemical Conversion of Biomass for the Production of Energy and Chemicals. New Jersey: Wiley & Sons. 2016. 1st edition.

[10]. Sermyagina et al. Hydrothermal carbonization of coniferous biomass: Effects of process parameters on mass and energy yields. Journal of Analytical and Applied Pyrolysis 113 (2015) 551-556.

[11]. S. E. Elaigwu, G. M. Greenway. Microwave-assisted hydrothermal carbonization of rapeseed husk: A strategy for improving its solid fuel properties. Fuel Processing Technology 149 (2016) 305-312.

[12]. R. Wei et al. Current status and potential of biomass utilization in ferrous metallurgical industry. Renewable and Sustainable Energy Reviews 68 (2017) 511-524.

[13]. A. Kumar et al. Thermochemical Biomass Gasification: A review of the current status of technology. Energies 2009, 2, 556-581; doi:10.3390/en20300556.

[14]. R. Singh et al. Strategies for the selection of thermo-chemical processes for the valorisation of biomass. Renewable Energy 98 (2016) 226-237.

[15]. R. Mehrabian et al. Application of numerical modelling to biomass grate furnaces. Journal of Thermal Engineering. Yildiz Technical University Press, Istanbul, Turkey, Vol. 1, Special Issue 3, No. 6, pp. 550-556, May, 2015.

[16]. M. A. Rather et al. Hydrothermal carbonization of macrophyte Potamogeton lucens for solid biofuel production. Eng. Sci. Tech., Int. J. (2016), http://dx.doi.org/10.1016/j.jestch.2016.08.015

[17]. D. Schneider et al. Characterization of biochar from hydrothermal carbonization of bamboo. International Journal of Energy and Environment, Volume 2, Issue 4, 2011 pp.647-652.

[18]. A. Demirbas. Combustion of biomass, Energy Sources, Part A: Recovery, Utilization and Environmental Effects, 29:6, 549-561, DOI: 10.1080/009083190957694.

[19]. T. Nussbaumer. Combustion and Co-combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction. Energy & Fuels 2003, 17, 1510-1521.

[20]. P. McKendry. Energy production from biomass (part 3): gasification technologies. Bioresource Technology 83 (2002) 55-63.

[21]. C. Quan et al. Pyrolysis of biomass components in a TGA and a fixed-bed reactor: Thermochemical behaviors, kinetics, and product characterization. Journal of Analytical and Applied Pyrolysis 121 (2016) 84-92.

[22]. D. Kim et al. Upgrading the characteristics of biochar from cellulose, lignin and xylan for solid biofuel production from biomass by hydrothermal carbonization. Journal of Industrial and Engineering Chemistry 42 (2016) 95-100.

[23]. W. Yang et al. Fuel properties and combustion kinetics of hydrochar prepared by hydrothermal carbonization of bamboo. Bioresource Technology 205 (2016) 199-204.

[24]. A. Funke, F. Ziegler. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. Biofuels, Bioprod. Bioref. 4:160-177 (2010), DOI: 10.1002/bbb.198;

[25]. J. Cai et al. Hydrothermal carbonization of tobacco stalk for fuel application. Bioresource Technology 220 (2016) 305-311.

[26]. H. S. Kambo. Strength, storage, and combustion characteristics of densified lignocellulosic biomass produced via torrefaction and hydrothermal carbonization. Applied Energy 135 (2014) 182-192.

[27]. C. Falco et al. Morphological and structural differences between glucose, cellulose and lignocellulosic biomass derived hydrothermal carbons. Green Chem., 2011, 13, 3273.

[28]. M. Makela et al. Hydrothermal carbonization of lignocellulosic biomass: Effect of process conditions on hydrochar properties. Applied Energy 155 (2015) 576-584.

[29]. P. Gao et al. Preparation and characterization of hydrochar from waste eucalyptus bark by hydrothermal carbonization. Energy 97 (2016) 238-245.

[30]. S. Roman et al. Hydrothermal carbonization as an effective way of densifying the energy content of biomass. Fuel Processing Technology 103 (2012) 78-83.

[31]. Y. Gao et al. Effect of residence time on chemical and structural properties of hydrochar obtained by hydrothermal carbonization of water hyacinth. Energy 58 (2013) 376-383.

[32]. X. Lu et al. Influence of reaction time and temperature on product formation and characteristics associated with the hydrothermal carbonization of cellulose. Bioresource Technology 138 (2013) 180-190.

[33]. L. Li et al. Investigating the role of feedstock properties and process conditions on products formed during the hydrothermal carbonization of organics using regression techniques. Bioresource Technology 187 (2015) 263-274.

[34]. S. Guo et al. Influence of reaction conditions and feedstock on hydrochar properties. Energy Conversion and Management 123 (2016) 95-103.

[35]. S. Guo et al. Characteristic evolution of hydrochar from hydrothermal carbonization of corn stalk. Journal of Analytical and Applied Pyrolysis 116 (2015) 1-9.

[36]. K. Tekin et al. A review of hydrothermal biomass processing. Renewable and Sustainable Energy Reviews 40 (2014) 673-687.

[37]. B. Weiner et al. Potential of the hydrothermal carbonization process for the degradation of organic pollutants. Chemosphere 92 (2013) 674-680.

[38]. A. Kruse et al. Hydrothermal conversion of biomass to fuels and energetic materials. Current Opinion in Chemical Biology 2013, 17:515-521. http://dx.doi.org/10.1016/j.cbpa.2013.05.004

[39]. Q Bach et al. Hydrothermal pretreatment of fresh forest residues: Effects of feedstock pre-drying. Biomass and Bioenergy 85 (2016) 76-83.

[40]. S. S. Toor. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. Energy 36 (2011) 2328-2342.

[41]. M. K. Hrncic et al. Hydrothermal treatment of biomass for energy and chemicals. Energy 116 (2016) 1312-1322.

[42]. K. Nakason et al. Characteristics of hydrochar and liquid fraction from hydrothermal carbonization of cassava rhizome. Journal of the Energy Institute xxx (2017) 1-10, http://dx.doi.org/10.1016/j.joei.2017.01.002

[43]. N. D. Berge et al. Hydrothermal carbonization of municipal waste streams. Environ. Sci. Technol. 2011, 45, 5696-5703, http://dx.doi.org/10.1021/es2004528

[44]. J. A. Libra et al. Hydrothermal carbonization of biomass residuals: A comparative review of the chemistry, processes and applications of wet and dry pyrolysis. Biofuels (2011) 2(1), 89-124.

[45]. G. K. Parshetti et al. Chemical, structural and combustion characteristics of carbonaceous products obtained by hydrothermal carbonization of palm empty fruit bunches. Bioresource Technology 135 (2013) 683-689.

[46]. D. Basso et al. Agro-industrial waste to solid biofuel through hydrothermal carbonization. Waste Management 47 (2016) 114-121.

[47]. A. M. Smith, A. B. Ross. Production of bio-oil, bio-methane and fertilizer from seaweed via hydrothermal carbonization. Algal Research 16 (2016) 1-11.

[48]. G. Ying et al. Characterization of products from hydrothermal liquefaction and carbonation of biomass model compounds and real biomass. J Fuel Technol, 2011, 39(12), 893-900.

[49]. X. Cao et al. Chemical structures of swine-manure chars produced under different carbonization conditions investigated by advanced solid-state 13C nuclear magnetic resonance (NMR) spectroscopy. Energy Fuels 2011, 25, 388-397, http://dx.doi.org/10.1021/ef101342v

[50]. M. Sevilla, A. B. Fuertes. Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonization of saccharides. Chem. Eur. J.

2009, 15, 4195-4203, http://dx.doi.org:/10.1002/chem.200802097

[51]. M. Sevilla, A. B. Fuertes. The production of carbon materials by hydrothermal carbonization of cellulose. Carbon 47 (2009) 2281-2289.

[52]. R. W. Missen et al. Introduction to chemical reaction engineering and kinetics. New Jersey: John Wiley & Sons. 1999. 1st edition.

[53]. C. G. Hill Jr., T. W. Root. Introduction to chemical engineering kinetics and reactor design. New Jersey: John Wiley & Sons. 2014. 2nd edition.

[54]. M. E. Davis, R. J. Davis. Fundamentals of chemical reaction engineering. New York: McGraw-Hill. 2003. 1st edition.

[55]. O. Levenspiel. Chemical reaction engineering. New Jersey: John Wiley & Sons. 1999. 3rd edition.

[56]. T. Turanyi, A. S. Tomlin. Analysis of kinetic reaction mechanisms. New York: Springer. 2014. 1st edition.

[57]. M. R. Wright. An introduction to chemical kinetics. New Jersey: John Wiley & Sons. 2004. 1st edition.

[58]. H. S. Fogler. Elements of Chemical reaction engineering. New Jersey: Prentice Hall. 1999. 3rd edition.

[59]. L. Masgrau et al. The curvature of the Arrhenius plots predicted by conventional canonical transition-state theory in the absence of tunneling. Theor Chem Acc (2003) 110:352-357.

[60]. D. G. Truhlar, A. Kohen. Convex Arrhenius plots and their interpretation. PNAS, January 30, 2001, vol. 98, no. 3, 848-851.

[61]. D. Basso et al. (2014) Modeling the reaction kinetics during hydrothermal carbonization of waste biomass. 22nd European Biomass Conference & Exhibition, Stockholm, Sweden. http://dx.doi.org/10.5071/22ndEUBCE2014-3DV.1.4

[62]. C. Di Blasi, M. Lanzetta. Intrisic kinetics of isothermal xylan degradation in inert atmosphere. Journal of Analytical and Applied Pyrolysis 40-41 (1997) 287-303.

[63]. J. Stemann, F. Ziegler. Assessment of the energetic efficiency of a continuously operating plant for hydrothermal carbonisation of biomass. World Renewable Energy Congress 2011, 8-13 May 2011, Linkoping, Sweden.

[64]. D. Jung, A. Kruse. Evaluation of Arrhenius-type overall kinetic equations for hydrothermal carbonization. Journal of Analytical and Applied Pyrolysis 127 (2017) 286-291.

[65]. B. Erlach et al. Combined hydrothermal carbonization and gasification of biomass with carbon capture. Energy 45 (2012) 329-338.

[66]. C. R. Correa et al. Evaluation of hydrothermal carbonization as a preliminary step for the production of functional material from biogas digestate. Journal of Analytical and Applied Pyrolysis 124 (2017) 461-474.

[67]. Y. Fawaz et al. Characterization of biocoal from hydrothermal carbonization of pine needles and palm leaves. Journal of Multidisciplinary Engineering Science and Technology (JMEST). ISSN: 3159-0040. Vol. 2, Issue 11, November-2105.

[68]. E. Danso-Boateng et al. Kinetics of faecal biomass hydrothermal carbonization for hydrochar production. Applied Energy 111 (2013) 351-357.

[69]. X. Xu, E. Jiang. Treatment of urban sludge by hydrothermal carbonization. Bioresource Technology 238 (2017) 182-187.

[70]. A. Ghasemi et al. Exergy based optimization of a biomass and solar fuelled CCHP hybrid seawater desalination plant. Journal of Thermal Engineering, Vol. 3, No. 1, pp. 1034-1043, January, 2017.

[71]. O. V. Marchenko, S. V. Solomin. Efficiency of hybrid renewable energy systems in Russia. International Journal of Renewable Energy Research, Vol. 7, No. 4, 2017.

[72]. Q. Wu et al. Characterization of products from hydrothermal carbonization of pine. Bioresource Technology 244 (2017) 78-83.

[73]. A. M. Patel, S. K. Singal. Economic analysis of integrated renewable energy system for electrification of remote rural area having scattered population. International Journal of Renewable Energy Research, Vol. 8, No. 1, March, 2018.

[74]. D. D. Guta. Assessment of biomass fuel resource potential and utilization in Ethiopia: Sourcing strategies for renewable systems. International Journal of Renewable Energy Research, Vol. 2, No. 1, 2012.