Reaction kinetics modeling of hydrothermal carbonization

P. Kladisios, A. Sagia

Laboratory of Heat Transfer and Thermal Processes, School of Mechanical Engineering, National Technical University of Athens, Greece.

Abstract
Hydrothermal carbonization (HTC) is a thermochemical pretreatment process suitable for the valorization of biomass. It emulates the natural coalification and its main product, hydrochar, is a solid carbon-rich product that has a calorific value similar to that of lignite. The relatively low reaction conditions, the capability of the process to handle organic materials with high moisture content and the appealing properties of hydrochar render HTC a highly promising field. However, the reactions that take place are complex and partially understood. Several attempts have been made to develop reaction kinetics schemes in order to model the carbonization of specific types of biomass. In the present paper, two proposed models are examined and suggestions are made for the advancement of the process.

Keywords: Hydrothermal carbonization; HTC; Pretreatment; Reaction kinetics.

1. Introduction
Biomass is becoming increasingly attractive as a potential source for the production of fuel and valuable chemicals. Its direct use as a fuel, however, faces a series of challenges (low-density energy, high moisture content, biological instability etc.) [1]. Pretreatment processes are necessary to improve the characteristics of the organic feedstock. Hydrothermal carbonization (HTC), also known as wet pyrolysis, emulates the natural process of coalification. During hydrothermal carbonization, biomass in the presence of subcritical water (below 374 ºC and 22 MPa) is heated in a closed environment [2].
The main product of HTC, apart from liquid and gaseous by-products, is hydrochar, a solid material rich in carbon. The solid product displays superior fuel characteristics compared to the organic feedstock. 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. It can be used as fuel, in soil amelioration, in carbon sequestration and for the production of chemicals [2-5].
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 [6]. Due to the complexity of the reaction mechanism, detailed information about the exact reactions is currently available only for specific types of biomass, i.e. cellulose. The main reaction pathways in a HTC process consist of hydrolysis, dehydration, decarboxylation, condensation polymerization and aromatization [2, 3, 6, 7].
The percentage and composition of the end products are directly tied to the process conditions with reaction temperature, residence time and water-to-biomass ratio being the most important. Reaction temperature is

regarded as the governing parameter of the process. Elevated temperatures have a beneficial outcome on the calorific value of the solid output, but, at the same time, the solid yield decreases [4-7]. Typical residence times in HTC span from a few hours to days. Similar to reaction temperature, longer retention times lead to higher energy and lower mass yields. In addition, it has been experimentally observed that as the temperature increases the effect of residence time becomes less significant [1, 5, 6]. The water-to-biomass ratio was found to accelerate the carbonization process with a simultaneous decrease in solid yield. This is attributed to the greater impact of hydrolysis reactions caused by the increase of water quantity [6, 7].

The physicochemical properties of the latter in combination with the advantages that HTC offers (simplicity, low cost, solid yield percentage, ability to process wet biomass, lack of preliminary drying) justify the recent research activity around the process [5, 6]. Nevertheless, 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.

2. Mathematical modeling

The complex nature of the process combined with the necessity to predict its outcome has led to the development of reaction kinetics models. 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. In both cases, the system of partial differential equations was solved using COMSOL's reaction engineering module.

2.1 Hydrothermal carbonization of grape marc

In [8], 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 °C) 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 [9]. 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 (Figure 1).
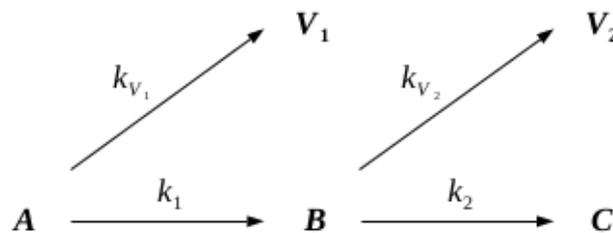

Figure 1. Two-step reaction mechanism for the hydrothermal carbonization of grape marc [8].

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 [10]:

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

(1)

where: k_0, the pre-exponential or frequency factor [appropriate units], E_a, the activation energy [J/mol] R, the universal gas constant [8.314 J/mol·K], T, the absolute temperature [K].
The equations that describe the model are thus:

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

(2)

$$\frac{\partial m_B}{\partial t} = k_1 m_A - k_{V_2} m_B - k_2 m_B$$

(3)

$$\frac{\partial m_C}{\partial t} = k_2 m_B$$

(4)

$$\frac{\partial m_{V_1}}{\partial t} = k_{V_1} m_A$$

(5)

$$\frac{\partial m_{V_2}}{\partial t} = k_{V_2} m_B$$

(6)

where: m_A, m_B, m_C, are the mass yields of the initial feedstock, the intermediate product and the final hydrochar respectively [-], m_{V1}, m_{V2}, are the mass yields of the volatile products of the first and second reaction step respectively [-], 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 a least squares algorithm (trust-region-reflective algorithm) gave the Table 1 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. [8].

$k_{0,1}$ [s^{-1}]	$k_{0,2}$ [s^{-1}]	$k_{0,V1}$ [s^{-1}]	$k_{0,V2}$ [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

2.2 Hydrothermal carbonization of soft rush

M. Jatzwauk and A. Schume [11] proposed a model to describe the hydrothermal carbonization of soft rush in the temperature range of 180-240 °C. According to the proposed scheme, the initial solid substrate A is hydrolyzed into intermediate products B which, in turn, form the hydrochar C and gaseous and dissolved byproducts D. The formation of hydrochar was found to be favored by the intermediate product concentration. This was expressed by a higher reaction order degree of the reaction B→C (n=1.53). The remaining two reactions were assumed to be of the first order (Figure 2).
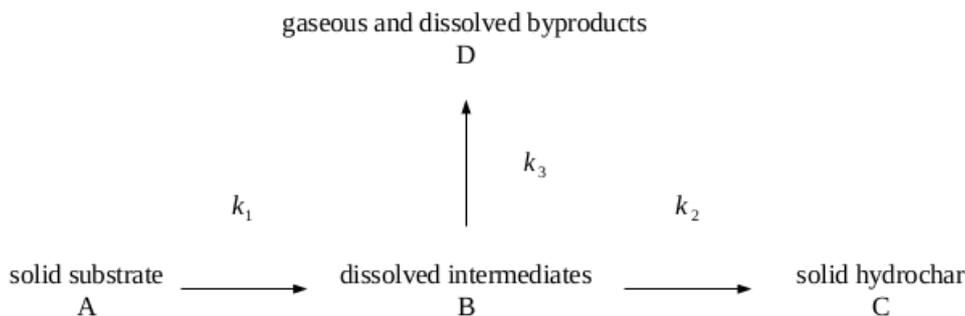

Figure 2. Proposed reaction mechanism for the hydrothermal carbonization of soft rush [11].

The system of equations that describe the proposed reaction mechanism are:

$$\frac{dC_A}{dt} = -k_1 C_A \tag{7}$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B^n - k_3 C_B \tag{8}$$

$$\frac{dC_C}{dt} = k_2 C_B^n \tag{9}$$

$$\frac{dC_D}{dt} = k_3 C_B \tag{10}$$

where: C_A, C_B, C_C, C_D, are the carbon content yield for the initial substrate, the intermediate products, the hydrochar and the gaseous/dissolved byproducts [-].

The temperature dependence of the rate constant was expressed by the classical Arrhenius equation, Equation (1), while the Arrhenius parameters are given in Table 2. The value 1.53 for the order of the reaction B→C was found to fit the experimental data accurately.

Table 2. Values of the Arrhenius parameters (k_0, E_a) for the hydrothermal carbonization of soft rush according to M. Jatzwauk and A. Schumpe [11].

$k_{0,1}$ [h^{-1}]	$k_{0,2}$ [g$^{-0.53}$·h^{-1}]	$k_{0,3}$ [h^{-1}]
1.89·10^{14}	1.15·10^7	1.89·10^7
$E_{a,1}$ [kJ/mol]	$E_{a,2}$ [kJ/mol]	$E_{a,3}$ [kJ/mol]
141	75	74.3

The use of citric acid was also investigated as a potential catalyst that enhances the hydrolysis. Its effect on hydrochar carbon content, however, was proven to be negligible.

It is important to mention that the degradation of lignin was assumed. This has to be tested against substrates with higher lignin content since it the most thermo-chemically stable organic component found in biomass [2].

3. Results

3.1 Hydrothermal carbonization of soft rush

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 ºC) and for residence times up to 8 hours.

The examination of Figures 3, 4 and 5 leads to the following 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, reaction temperature is being highlighted as the dominant process parameter.
- The relatively low temperature of 180 ºC 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.
- While the formation of volatile products V$_1$ remains relatively temperature-independent, an increase in reaction severity leads to elevated production of volatiles V$_2$.
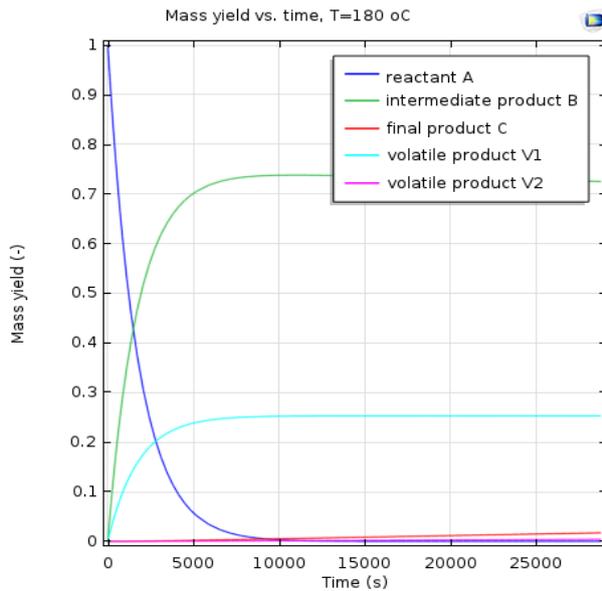
Figure 3. Mass yield versus time of the hydrothermal carbonization of grape marc according to D. Basso et al. [8] for temperature 180 ºC and residence times up to 8 hours.
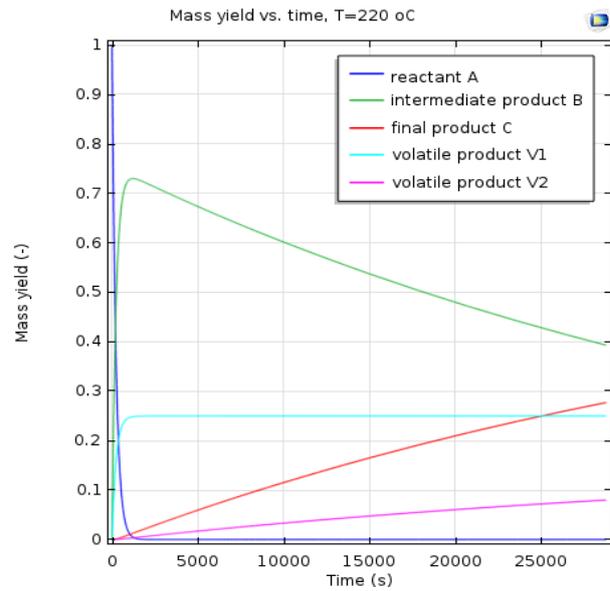
Figure 4. Mass yield versus time of the hydrothermal carbonization of grape marc according to D. Basso et al. [8] for temperature 220 ºC and residence times up to 8 hours.
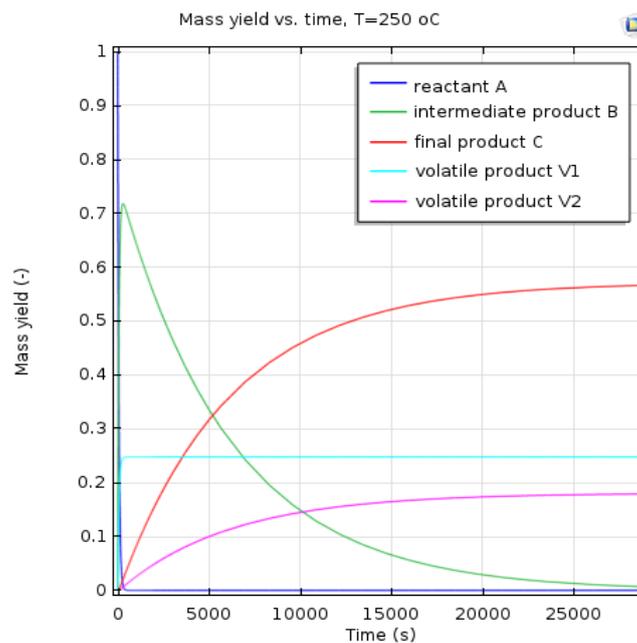

Figure 5. Mass yield versus time of the hydrothermal carbonization of grape marc according to D. Basso et al. [8] for temperature 250 ºC and residence times up to 8 hours.

3.2 Hydrothermal carbonization of soft rush

The solution of the system of equations (7)-(10) leads to distribution of carbon content yield versus time for temperatures of 180, 200, 220 and 240 ºC and residence times up to 50 hours. From Figures 6-9 the following observations can be made:

- Similar to the case of grape marc, temperature is evidently the governing parameter. The formation of hydrochar occurs faster as reaction temperature increases.
- The degradation of the solid substrate requires higher activation energy that that of byproduct and hydrochar formation.

- The concentration of dissolved intermediates affects the final quantities of hydrochar in a critical manner. Elevated temperatures and increased amounts of available intermediate products lead to increased hydrochar formation. This was expressed by a higher reaction order.
- The yield of (gaseous and dissolved byproducts) increases as reaction severity grows.
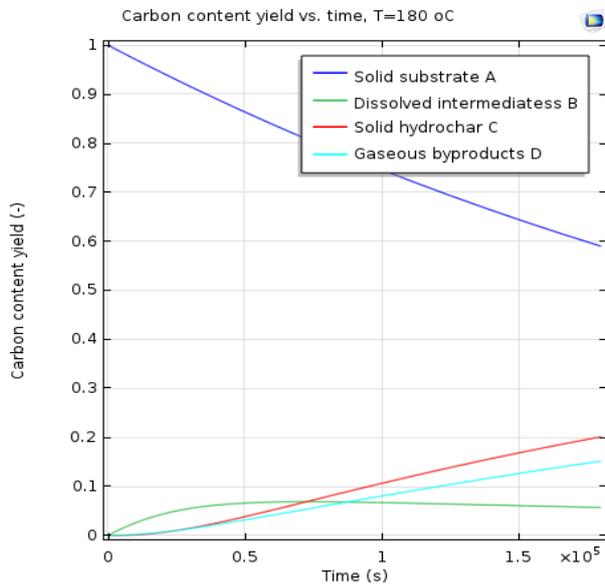

Figure 6. Carbon content yield versus time of the hydrothermal carbonization of soft rush according to M. Jatzwauk and A. Schumpe [11] for temperature 180 ºC and residence times up to 50 hours.

Figure 7. Carbon content yield versus time of the hydrothermal carbonization of soft rush according to M. Jatzwauk and A. Schumpe [11] for temperature 200 ºC and residence times up to 50 hours.
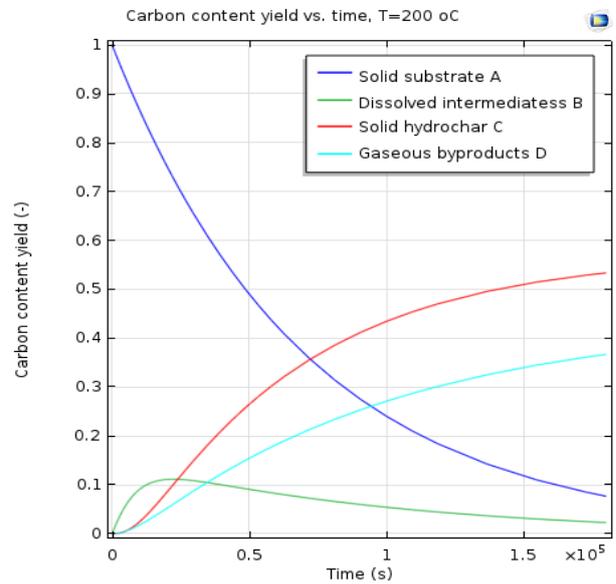

Figure 8. Carbon content yield versus time of the hydrothermal carbonization of soft rush according to M. Jatzwauk and A. Schumpe [11] for temperature 220 ºC and residence times up to 50 hours.
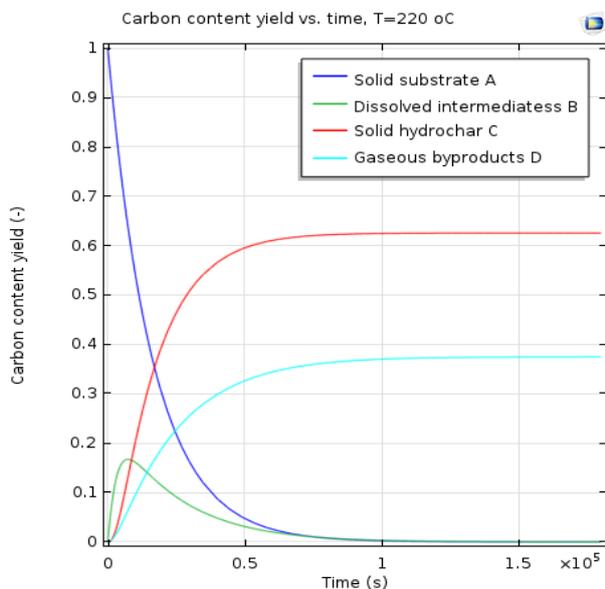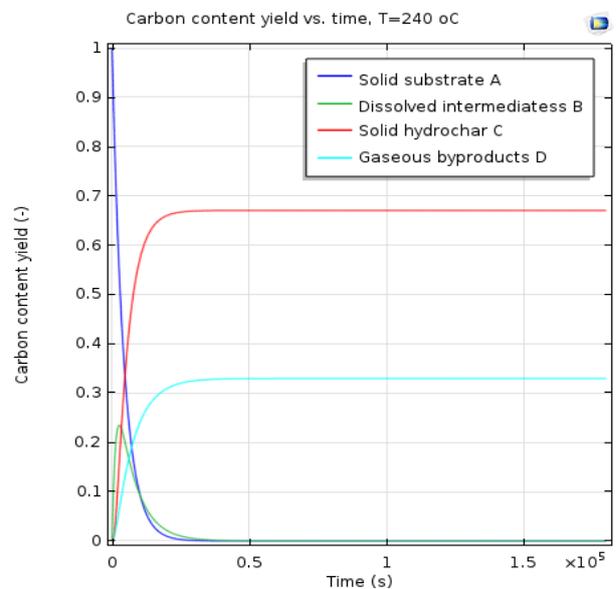

Figure 9. Carbon content yield versus time of the hydrothermal carbonization of soft rush according to M. Jatzwauk and A. Schumpe [11] for temperature 240 ºC and residence times up to 50 hours.

4. Conclusion

The practical application of hydrothermal carbonization, despite its simple principle, its capacity to exploit waste streams and the appealing properties of hydrochar, encounters several drawbacks:

➢ Exhausting experimentation is required in order for an accurate reaction kinetics model to be achieved. This would allow to optimize the reaction conditions towards a more energy-efficient process.

➢ The separation and handling of the byproducts is an additional design burden [12].

➢ The ability to handle large quantities of water is required by large installations since high water-to-biomass ratios facilitate the hydrolysis of the initial feedstock [6, 7].

➢ The final product, even though it has reduced moisture content, needs a drying process because it leaves the reactor in a state of slurry [2, 5].

➢ Elevated temperatures correspond to high pressure inside the reactor, a fact that increases the complexity of a potential installation [13].

Despite the aforementioned disadvantages, hydrothermal carbonization is a highly promising conversion method and several ideas have been proposed in order to increase its efficiency:

➢ The use of additives has been suggested to have a beneficial impact on both the properties of the hydrochar and the process conditions (lower required temperature and pressure). However, its verification needs further study [14].

➢ The process water has been found to contain specific nutrients and its used as a potential fertilizer is being speculated [15].

➢ The energy consumption can be reduced by recirculating the waste streams and preheating the submerged feedstock [16].

➢ The possibility of combining the hydrothermal carbonization with other processes is being examined. A common example is the anaerobic digestion of the process water which is being promoted as a way to further increase the overall energy recovery [17].

➢ Due to their structure, hydrochars can also be used for carbon sequestration (CSS, carbon capture and storage), adsorption and soil amendment purposes [3, 6, 19, 20].

Appendix

C	carbon content yield [-]	n	reaction order [-]
E_a	activation energy [kJ/mol]	R	universal gas constant [8.314 J/mol·K]
k_0	pre-exponential factor [appropriate units]	t	time [s]
k	rate constant [appropriate units]	T	reaction temperature [K]
m	mass yield [-]		

References

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

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

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

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

[5] E. 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.

[6] 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

[7] 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.

[8] D. Basso et al. Modeling the reaction kinetics during hydrothermal carbonization of waste biomass. 22nd European Biomass Conference & Exhibition, Stockholm, Sweden.

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

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

[11] M. Jatzwauk, A. Schumpe. Kinetics of hydrothermal carbonization (HTC) of soft rush. Biomass and Bioenergy 75 (2015) 94-100.

[12] 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.

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

[14] M. A. Rather et al. Hydrothermal carbonization of macrophyte Potamogeton lucens for solid biofuel production. Eng. Sci. Tech., Int. J. (2016). DOI: 10.1016/j.jetsch.2016.08.015.

[15] Y. Fawaz et al. Characterization of biocoal from hydrothermal carbonization of pine needles and palm leaves. Journal of Multidisciplinary Engineering Science and Technology (JMEST), Vol. 2 Issue 11, November, 2015.

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

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

[18] E. Danso-Boateng et al. Kinetics of faecal biomass hydrothermal carbonization for hydrochar production. Applied Energy 11 (2013) 351-357.

[19] K. Nakason et al. Characteristics of hydrochar and liquid fraction from hydrothermal carbonization of cassave rhizone. Journal of the Energy Institute (2017). DOI:10.1016/j.joei.2017.01.002.

[20] N. D. Berge et al. Hydrothermal carbonization of municipal waste streams. Environ. Sci. Technol. 2011, 45, 5696-5703. DOI:10.1021/es2004528.

Panagiotis Kladisios received his MS degree in 2015 in Mechanical Engineering from the National Technical University of Athens. Currently, he is pursuing a Phd degree in heat transfer in the same university. His interests include, among others, solar systems, HVAC and phase change materials. He is the co-author of 2 articles.
E-mail address: pkladisios@hotmail.gr

Athina Stegou-Sagia Achaia, Greece. Mechanical Engineer. m. Nikolaos Sagias, 1 daughter. Education: Dipl. Mechanical Engineer, National Technical University of Athens, Greece, 1979; PhD, Thermodynamics, Properties and Phase Change of Refrigerant Mixtures, 1986. Appointments: Ministry of Public Works, 1980-81; Researcher, 1981-88, Lecturer, 1988-92, Assistant Professor, 1992-97, Associate Professor, 1997-2006, Professor 2006-today, National Technical University of Athens; Fellow, European Community; Experienced Researcher, Queen Mary and Westfield College, University of London, England, 1993-94. Publications: Numerous papers to international journals and international conferences; Books in Heat and Mass Transfer-Unit Operations. Memberships: Greek Technical Chamber, 1979-; Executive Council, Greek Association of Computational Mechanics, Athens, 1994-96, 1998-2000; National Technical University of Athens, The Senate, 2003-04. Address: 9 Iroon Polytechniou Str. Zografou, 15780 Athens, Greece.
E-mail address: asagia@central.ntua.gr