CHEMICAL ENGINEERING TRANSACTIONS

VOL. 65, 2018

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eliseo Ranzi, Mario Costa

ISBN 978-88-95608- 62-4; **ISSN** 2283-9216

Hydrothermal Carbonization of Biomass: Design of a Bench-Scale Reactor for Evaluating the Heat of Reaction

Fabio Merzari, Michela Lucian, Maurizio Volpe, Gianni Andreottola, Luca Fiori*

University of Trento, Dept. of Civil, Environmental and Mechanical Engineering, via Mesiano 77 - 38123 Trento, Italy
luca.fiori@unitn.it

HydroThermal Carbonization (HTC) is a thermochemical process capable of converting wet biomass into a carbon-enriched solid, commonly referred to as hydrochar. Hydrochar finds application as bio-fuel, soil improver and for the production of carbon-advanced materials. In recent years, interest in HTC technology has grown significantly, in terms of both scientific research and industrial development. The HTC process consists of several reactions occurring both in series and in parallel: hydrolysis, dehydration, decarboxylation, condensation, aromatization, and others. Some reactions are known to be exothermic, while others are endothermic. Knowing the enthalpy of the "whole" HTC reaction would be beneficial in terms of both process design and energy calculations, in particular to evaluate the process heat duty. Unfortunately, such kind of information is barely available in the literature: some data have been obtained at the "micro-scale" using differential scanning calorimetry (DSC), with the limits of using a few milligrams of (usually heterogeneous) biomass per trial, while punctual data at larger scale are actually missing. In order to fill this gap, we designed and constructed in-house a 2 L batch reactor equipped with four thermocouples - placed at different heights inside the reactor - and capable to withstand pressures up to 140 bar and temperatures up to 300 °C. The reactor, controlled in temperature, is heated by four electrical resistances (1 kW each) and thermally insulated. An electric power meter allows monitoring and recording the electrical consumption during HTC trials.

Thermal trials were performed with the bench-scale reactor fed with only water to provide a baseline for calculations. HTC trials were then performed using biomasses, namely organic fraction of municipal solid waste and agave pulp. At the different HTC operating conditions investigated (residence time: 3 h; reactor filling degree: 67 %; temperatures: 180, 220, and 250 °C; dry biomass to water ratio: 0.10 and 0.15), our data testify that the "whole" HTC reaction is exothermic, and the heat released by the reaction increases with temperature. The design of such a reactor and the data obtained so far encourage an in-depth analysis of the enthalpy of the HTC reaction for different biomasses and at various operating conditions.

1. Introduction

In recent years, HTC has attracted considerable attention as a promising process for treating several kinds of organic wastes. HTC occurs in liquid water at temperatures of 160-280 °C and residence times up to 8 h. It is particularly suitable for organic substrates with high moisture content and is interesting for several reasons: it makes wastes hydrophobic, enhancing their drying and storage properties, and increases their energy density, allowing their subsequent upgrading to fuels. Despite the substantial amount of research studies on HTC available in the literature, only few of them addressed the evaluation of the heat released (or consumed) by the chemical reactions occurring during HTC or, similarly, the heat of the "whole" HTC reaction. Although the energy efficiency is largely influenced by the thermal requirements needed to pre-heat the biomass and by the heat recovery system of the plant (Lucian & Fiori 2017), also the heat of reaction could have a significant impact.

Some researchers calculated the heat of reaction from the heats of formation of reactants and products, but reported results with a defined uncertainty (Sunner et al., 1961; Yan et al., 2010).

Funke and Ziegler (2011) measured the heat of reaction performing HTC tests in a DSC apparatus using three substrates (glucose, cellulose and wood) at a temperature of 240 °C for 4-6 h. Their results show that HTC was exothermic in all the analyzed cases, and the measured heat of reaction was equal to -1.06, -1.07 and -

0.76 MJ/kg for glucose, cellulose and wood, respectively. Notably, such values were characterized by a high standard deviation, in the range 14 – 32 %. The limit of the approach by Funke and Ziegler (2011) is the apparatus used which required very small amount of sample (few milligram) for the tests.

The aim of this paper is to evaluate the heat of the HTC reaction using a bench-scale reactor, properly designed and constructed in-house for the purpose. The heat of reaction was determined performing HTC trials on two kinds of biomasses: agave pulp and organic fraction of municipal solid waste.

2. Materials and methods

2.1 Experimental apparatus

A HTC experimental system was designed at the Department of Civil, Environmental and Mechanical Engineering of the University of Trento (Italy) and constructed in-house at the mechanical workshop of the University of Trento according to the European standard UNI EN 13445-3:2014 concerning unfired pressure vessels. The system is composed of two main parts, namely the HTC reactor and the gas measuring system: the left part of Figure 1 shows the piping and instrumentation diagram (P&ID) of the whole system. The HTC reactor consists of a stainless steel AISI 316 batch vessel of 2 L internal volume. The right part of Figure 1 shows 2D and 3D technical drawings of the HTC reactor, while Figure 2 shows a picture of the apparatus. The reactor was designed to withstand temperatures up to 300 °C and pressures up to 140 bar. A gasket (which can be either copper or Teflon) allows sealing between the reactor body and the top flange. The top flange of the reactor is connected to two pipes (2 mm internal diameter), which allow air purging through the needle valves V1 and V2 by flowing nitrogen gas. Since the HTC process is usually carried out between 180 °C and 250 °C, a cold trap was added to the left pipe to protect the pressure transmitter (PT) and the two pressure gauges (PI) from high temperature and avoid any clogging. A rupture disk is positioned in the same pipe, upstream one PI, in order to protect the HTC reactor from pressures greater than the design one and for safety reasons.

The temperature inside the reactor is measured by four thermocouples (T1, T2, T3, T4) that pass through the reactor top flange and are positioned at different heights within the reactor. The temperature transmitters (TT) and the pressure transmitter (PT) send data to a software realized in-house in LabView software environment. The software allows the control of the reactor temperature (TIC) and the monitoring of the four temperatures and the pressure (TIR and PIR).

The reactor is heated by four electrical resistances (1 kW each) inserted into two aluminium shells. Such shells allow an efficient heat transfer on the entire external cylindrical walls of the reactor. The aluminium shells have externally a layer of insulating material to limit thermal dissipation.

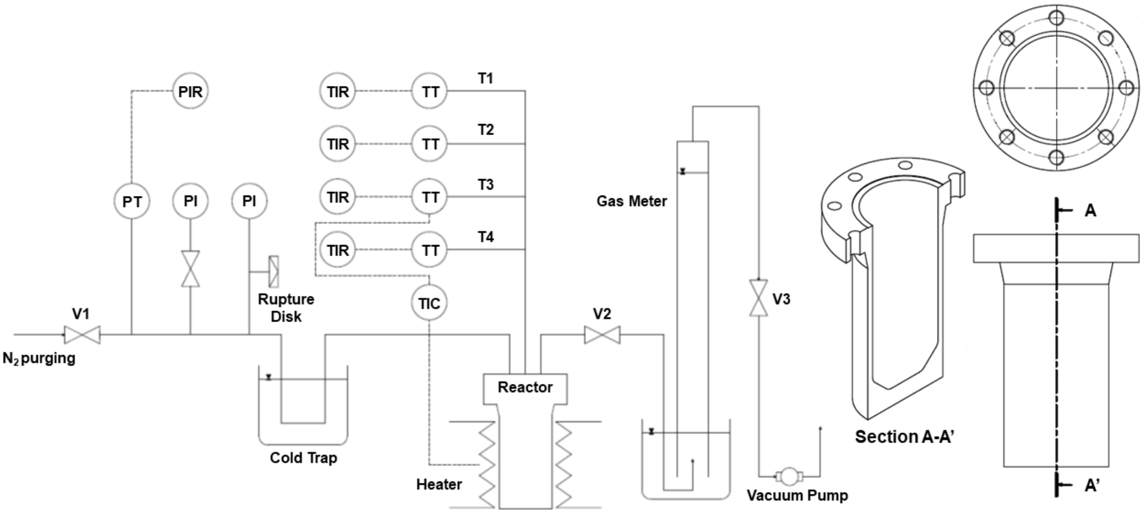

Figure 1: P&ID of the experimental apparatus and technical drawings of the HTC reactor.

Figure 2: HTC reactor.

The shells are equipped with mechanical hinges: during the test (heating phase and constant temperature phase) the shells are tightened on the reactor; once the test is over, the shells are opened to allow the reactor to cool down. Figure 2 shows the reactor with the shells in open position. An electric power meter allows monitoring and recording the electrical consumption during HTC trials: though this measure, data concerning the heat of reaction could be inferred.

When the HTC run is finished, the reactor is cooled down by placing a massive metal disk (at -24 °C) on its bottom and by flowing compressed air on its external walls. When the reactor reaches room temperature, the produced gas is flowed to the gas volume measuring system by opening valve V2. The gas volume measuring system consists of a PVC graduated cylinder with the lower part submerged into water (see P&ID in Figure 1). Before the measurement, a vacuum pump raises the water meniscus up to the zero of the graduated scale. When the produced gas enters into the graduated cylinder, it displaces a certain water volume allowing calculating its own volume.

2.2 Experimental campaign and procedure

The experimental trials presented in this work were aimed at obtaining information on the heat of the HTC reaction. Experimental runs were conducted at three temperatures, namely 180, 220 and 250 °C. Residence time and reactor filling degree were maintained constant at 3 h and 67 %, respectively.

Two different biomasses were tested, namely agave pulp (AP) and organic fraction of municipal solid waste (OFMSW). The dry biomass to water ratio (b/w) was let equal to 0.10 for AP and 0.15 for OFMSW. Tests at each experimental condition were performed at least in duplicate. Raw biomass and deionized water were accurately inserted into the HTC reactor in order to achieve the chosen b/w and reactor filling degree. The reactor was then sealed and nitrogen gas was fluxed for about 3 min through the system to purge it from air. After purging, V1 and V2 valves were closed, and the heating phase started: around 30-35 min were necessary to reach the desired temperature set point. Residence time was started to be counted when the reactor temperature (read from thermocouple T3) reached the set point value. When the 3 h residence time was elapsed, the control system automatically stopped the power supply. The reactor shells were then manually opened, and the reactor cooled down. The quenching phase lasted about 25-30 min, depending on the HTC process temperature. The volume of the gas produced was then measured. The reactor was opened (*i.e.* the reactor body was disconnected from the reactor top flange) and its content was filtered through a dry cellulose filter, and both hydrochar and HTC liquor were collected. Hydrochar, the relevant cellulose filter, and the reactor body were placed inside an oven at 105 °C for at least 8 h. After drying and weighing, the hydrochar yield (solid yield, SY) was computed as the ratio between the mass of hydrochar produced and the initial mass of the feedstock ($g_{hydrochar}/g_{feedstock}$, both on dry basis). The hydrochars were characterized in terms of ultimate and proximate analyses, and higher heating value (HHV).

Gas yield (GY, $g_{gas}/g_{feedstock}$, both on dry basis) was computed by means of the ideal gas law, assuming atmospheric pressure, ambient temperature and only CO_2 as the gaseous product (Basso et al., 2016). The liquid yield (LY, $g_{liquid}/g_{feedstock}$), due species dissolved in the HTC liquor owing to feedstock decomposition, was calculated by difference (LY = 1 − SY − GY).

In order to assess the heat of reaction of the whole HTC process, some experimental runs with deionized water were performed at the same experimental conditions used for the biomasses: 180, 220 and 250 °C, 3 h of residence time and 67 % of reactor filling degree. The electrical power consumptions of these tests were used as the baseline to compute the actual heats of the HTC reaction at the different operating conditions investigated.

2.3 Calculation

The electric power meter allows monitoring and recording the electrical consumption during HTC trials. The heat of reaction was computed separating the constant temperature phase from the transient phase occurring during the initial heating up of the apparatus. Concerning the constant temperature phase, the net energy consumption (E_{net}) was calculated as the final energy consumption of the HTC process after 3 h of residence time (E_f) minus the energy consumption of the transient phase (E_i) as reported in Eq(1).

$$E_{net} = E_f - E_i \tag{1}$$

After the thermal trials, E_{net} for biomasses and water were available (E_{net} for water is due to thermal losses), so Eq(2) allows computing the energy duty (energy produced or consumed) of the HTC process occurring at constant temperature.

$$E_{duty\ (T=constant)} = E_{net,biomass} - E_{net,water} \tag{2}$$

Dividing the energy duty by the initial amount of dry feedstock ($M_{\text{dry feedstock}}$), it is possible to compute the heat of reaction concerning the constant temperature phase, Eq(3).

$$Heat\ of\ reaction_{T=constant} = \frac{E_{duty\ (T=constant)}}{M_{dry\ feedstock}} \tag{3}$$

Concerning the heating up phase, Eq(4) provides the theoretical sensible heat required to heat the biomass/water mixture or, eventually, the water for the tests performed with only deionized water. In Eq(4), c_p is the specific heat, m is the mass charged into the reactor, T_{HTC} is the HTC set point temperature and $T_{ambient}$ is the temperature of the system before power is applied to heat it.

At first, tests with only deionized water were performed. By comparing, for such tests, the energy consumption of the transient phase (E_i) with the value from Eq(4), it was possible to infer the energy losses occurring during the heating up phase. Reasonably, such values of energy losses were considered to apply also for the tests where biomass/water mixtures were used. For such HTC tests, E_i was experimentally measured, Eq(4) was used to calculate the sensible heat, thermal losses known, it was possible to calculate the energy duty $E_{duty\text{-}transient}$ concerning the heating-up phase. Notably, when applying Eq(4) to biomass/water mixtures, the amounts of water and biomass (actually, dry biomass) were calculated considering the experimental values of dry biomass to water ratio; whatever the biomass used (OFMSW or AP), its c_p was assumed equal to 1.26 kJ/(kg K), which is a first approximation reference value for dry organic matter.

$$Theoretical\ sensible\ heat = c_p * m * (T_{HTC} - T_{ambient}) \tag{4}$$

It was thus possible to compute the heat of reaction concerning the transient temperature phase, Eq(5).

$$Heat\ of\ reaction_{transient} = \frac{E_{duty-transient}}{M_{dry\ feedstock}} \tag{5}$$

The total heat of reaction is the sum of the two contributes as reported in Eq(6).

$$Heat\ of\ reaction_{total} = Heat\ of\ reaction_{T=constant} + Heat\ of\ reaction_{transient} \tag{6}$$

3. Results and discussion

Table 1 shows the yields of hydrochar, liquid and gas for each operative conditions for both AP and OFMSW.

As expected from literature, the hydrochar yield decreases with the increase of temperature, while gas yield has an opposite trend (Basso et al., 2015; Fiori et al., 2014; Volpe and Fiori, 2017; Volpe et al., 2018). Concerning agave pulp, solid yield decreases from 54.2 % at 180 °C down to 34.8 % at 250 °C. Liquid and gas yield were not computed for OFSMW, and the hydrochar yield for OFMSW was similar to the hydrochar yield obtained for AP at the same temperature. For AP, gas yield increases from 5.5 % at 180 °C up to 20.4 % at 250 °C.

Table 1: Hydrochar, liquid and gas yields for the tests performed.

Sample	Solid Yield (%$_{d.b.}$)	Liquid Yield (%)	Gas Yield (%$_{d.b.}$)
AP 180 °C	54.2	37.3	5.5
AP 220 °C	50.9	32.3	16.8
AP 250 °C	34.8	44.8	20.4
OFMSW 220 °C	54.8	-	-

Table 2 shows the higher heating values (HHVs) and the ultimate and proximate analyses of raw dry biomasses and hydrochars, and the heats of the HTC reaction. It is possible to observe that the carbon content, the fixed carbon (FC), the HHV, and the heat of reaction increase with HTC temperature, and conversely the oxygen content, the volatile matter (VM) and the ash content decrease. Hydrogen and nitrogen seem quite independent on HTC temperature. Carbon content, for the agave pulp, increased from 48.27 % for the raw feedstock, up to 53.75 % for the hydrochar obtained at 250 °C, while for the OFMSW increased from 51.98 % for the raw substrate to 66.66 % for the hydrochar obtained at 220 °C. HHV for the agave pulp increased from 16.58 MJ/kg$_{d.b.}$ for the raw feedstock, up to 24.56 MJ/kg$_{d.b.}$ for the hydrochar obtained at 250 °C. For the OFMSW, HHV increased from 22.00 MJ/kg$_{d.b.}$ for the raw substrate to 29.90 MJ/kg$_{d.b.}$ for the hydrochar obtained at 220 °C.

In Figure 3, the energy consumption of the HTC trials performed at 220 °C, 3 h and 67 % of filling degree is reported. It is possible to observe that the water has the highest energy consumption (highest curve in Figure 3), while OFMSW has the lowest energy consumption (lowest curve in Figure 3): the HTC reaction makes the energy consumption to decrease, i.e. the “whole” HTC reaction is exothermic. Quantitative data of the heat of reaction are reported in Table 2. Heat of reactions are negative, i.e. the HTC reaction is exothermic in all the cases investigated.

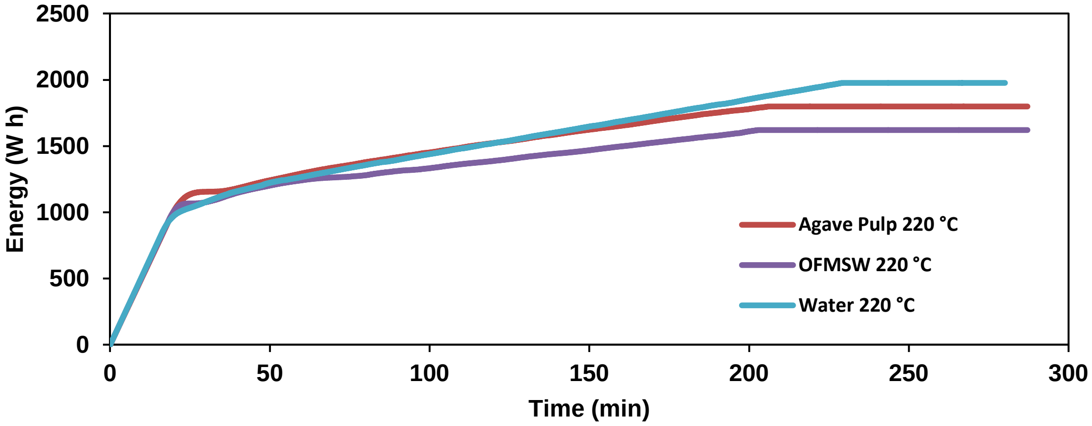

Figure 3: Energy consumption measured at 220 °C and 3 h with agave pulp, OFMSW and water.

Table 2: Heats of reaction, and ultimate and proximate analyses, higher heating values of raw dry biomasses and hydrochars.

Sample	C (%$_{d.b.}$)	H (%$_{d.b.}$)	N (%$_{d.b.}$)	O (%$_{d.b.}$)	Ash (%$_{d.b.}$)	VM (%$_{d.b.}$)	FC (%$_{d.b.}$)	HHV (MJ/kg$_{d.b.}$)	Heat of reaction (MJ/kg$_{d.b.}$)
Raw AP	48.27	6.12	1.47	42.05	2.08	77.90	20.02	16.58	-
AP 180 °C	48.73	6.16	1.63	40.40	3.28	73.92	22.80	19.51	-1.0
AP 220 °C	50.38	6.26	1.44	39.21	2.76	71.07	26.17	21.51	-3.1
APulp 250 °C	53.75	6.21	1.49	36.87	1.52	64.07	34.41	24.56	-3.9
Raw OFMSW	51.98	6.71	3.58	32.33	5.40	80.70	13.90	22.00	-
OFMSW 220 °C	66.66	7.05	3.65	16.8	5.84	69.50	24.70	29.90	-7.3

For the agave pulp, the heat of reaction increases from -1.0 MJ/kg$_{d.b.}$ computed from the experimental run at 180 °C, up to -3.9 MJ/kg$_{d.b.}$ computed from the run at 250 °C. The heat of reaction is maximal for the HTC of OFMSW: -7.3 MJ/kg$_{d.b.}$.

The exothermal character of the HTC reaction here found is in agreement with what reported by Funke et al. (2010). Interestingly, the data here presented testify that the heat released by the HTC reaction increases with temperature.

It is not possible to make straightforward comparisons with data from literature, given their scarcity. Given this premise, it is worth reporting the results by Funke and Ziegler (2011) who obtained heat reaction data using differential scanning calorimetry for cellulose, glucose and wood. The authors performed tests at 240 °C and 4-6 h obtaining values between -0.76 and -1.07 $MJ/kg_{d.b.}$, using a few milligrams of feedstock per trial. Our data confirm the exothermal character of the HTC reaction previously detected by Funke and Ziegler (2011).

4. Conclusions

HTC experimental trials were performed in a bench-scale reactor using two biomasses, namely organic fraction of municipal solid waste and agave pulp at different HTC operating conditions (residence time: 3 h; reactor filling degree: 67 %; temperatures: 180, 220, and 250 °C; dry biomass to water ratio: 0.10 and 0.15). The data reported in this work testify that HTC is an exothermic process, and the heat released by the reaction increases with temperature: from -1.0 $MJ/kg_{d.b.}$ at 180 °C, to -3.9 $MJ/kg_{d.b.}$ at 250 °C for agave pulp, while for the OFMSW the heat of reaction at 220 °C was as high as -7.3 $MJ/kg_{d.b.}$ The data obtained encourage an in-depth analysis of the heat of reaction of the HTC process for other biomasses and operative conditions, such as residence time, temperature, and biomass load.

Acknowledgments

The authors acknowledge Atzwanger s.p.a. for financial support.

References

Basso D., Weiss-Hortala E., Patuzzi F., Castello D., Baratieri M., Fiori L., 2015, Hydrothermal carbonization of off-specification compost: A byproduct of the organic municipal solid waste treatment, Bioresource Technology, 182, 217–224.

Basso D., Patuzzi F., Castello D., Baratieri M., Rada E.C., Weiss-Hortala E., Fiori L., 2016, Agro-industrial waste to solid biofuel through hydrothermal carbonization, Waste Management, 47, 114–121.

Fiori L., Basso D., Castello D., Baratieri M., 2014, Hydrothermal carbonization of biomass: Design of a batch reactor and preliminary experimental results, Chemical Engineering Transaction, 37, 55–60.

Funke A., Ziegler F., 2011. Heat of reaction measurements for hydrothermal carbonization of biomass, Bioresource Technology, 102, 7595–7598.

Funke A., Ziegler F., Berlin T.U., 2010, Hydrothermal carbonization of biomass : A summary and discussion of chemical mechanisms for process engineering, Biofuels, Bioproducts and Biorefining, 4, 160–177.

Lucian M., Fiori L., 2017, Hydrothermal Carbonization of Waste Biomass : Process Design, Modeling, Energy Efficiency and Cost Analysis, Energies, 10, 211.

Sunner S., Wadsö I., 1961. Measurements on heat effects accompanying the wet carbonization of peat in the temperature range 20 to 220 °C. Acta polytechnica Scandinavica, Vol. 297, Royal Swedish Acad. of Engineering Sciences.

UNI EN 13445-3:2014 Unfired pressure vessels.

Volpe M., Fiori L., 2017, From olive waste to solid biofuel through hydrothermal carbonisation: The role of temperature and solid load on secondary char formation and hydrochar energy properties, Journal of Analytical and Applied Pyrolysis, 124, 63–72.

Volpe M., Goldfarb J.L., Fiori L., 2018, Hydrothermal carbonization of Opuntia ficus-indica cladodes: Role of process parameters on hydrochar properties, Bioresource Technology, 247, 310-318.

Yan W., Hastings J.T., Acharjee T.C., Coronella C.J., Vásquez V.R., 2010, Mass and energy balance of wet torrefaction of lignocellulosic biomass, Energy Fuels, 24, 4738-4742.