CHEMICAL ENGINEERING TRANSACTIONS
VOL. 86, 2021
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš

ISBN 978-88-95608-84-6; **ISSN** 2283-9216
DOI: 10.3303/CET2186155

Improving Hydrothermal Carbonization (HTC) Processes by Hydrochar Gasification

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Hydrochar is produced by means of hydrothermal carbonization at relatively low temperatures (180-260°C) in sub-critical water. While, in many respects similar to biochar, its physical and chemical properties differ significantly (Basu, 2018). Of particular interest for this work are the higher energy density and lower ash content, that make hydrochar a possible feedstock for gasification plants with energy generation purposes. A gasification step is used instead of direct combustion to convert solid fuels in energy to achieve cleaner combustion and higher efficiency (Wang and Stiegel, 2016). In this work a 400 kg/h hydrochar gasification plant was modelled to identify optimal conditions and energetic yield of hydrochar obtained from municipal sewage. The fixed bed, updraft, gasification reactor was modeled in detail using a multi-scale, multiphase methodology already widely tested on biomass (Corbetta et al., 2015; Ranzi et al., 2014). The gas solid kinetic model was coupled with a detailed gas-phase kinetic scheme with over 200 species, including reaction intermediates, and 2000 reactions for reliable product yield prediction. Using Visual Basic Application as an interface, the predictions from the detailed simulation package were delivered to a commercial simulation package to model the energy generation section of the plant. Aspen HYSYS V10 was used for this purpose for the simplicity of integration and its widespread use in similar industrial plants. The gasification was carried out with air, air enriched in oxygen to 28%, air enriched in oxygen to 35% and pure oxygen with different amounts of steam to control the temperature in the chamber and at different values of equivalence ratio. The gasification performance was evaluated in terms of lower heating value of the generated fuel gas while the H_2S formation was accounted for only in a superficial manner using rules of thumb derived from previous experimental experience.

1. Introduction

Hydrothermal carbonization, from now on shortened to HTC, is a relatively new thermal pre-treatment process for biomass. In this process biomass is treated in subcritical water at relatively low temperatures of 180-260°C with a residence time that can vary from less than 10 min up to 12 hours depending on the feedstock (Kambo and Dutta, 2015). The technology serves a similar purpose to other already established industrial processes, namely, slow pyrolysis, dry-torrefaction and, to some extent, gasification. The operating conditions of these processes are briefly summarized in Table 1. While gasification generates a solid residue, this product does not have properties comparable to biochar. This is because the purpose of gasification is the production of a valuable gaseous stream, while the solid is just a side product with low added value or a waste. The main competing technology of HTC is slow pyrolysis which is the most common production route for biochar used for carbon sequestration, soil amelioration, bioenergy production, and wastewater pollution remediation. Char produced by means of HTC, which from now onward will be referred to as hydrochar, while being obtained in similar thermal conditions to biochar, enjoys significantly different physio-chemical properties and its novelty has left it with no established industrial application yet. In this work the feasibility of hydrochar as a feed for energy generation purposes is investigated in a simulated environment using a kinetic package developed by Ranzi et al., 2014 and validated on biomass and coal gasification applications. Among the kinetic models developed starting from the Ranzi model the one tuned by Bassani et al., 2018 for coal gasification was chosen. This choice is motivated by the fact that conventional biomass models work with three main pseudo-

Paper Received: 29 October 2020; Revised: 12 March 2021; Accepted: 18 April 2021
Please cite this article as: Prifti K., Basso D., Pavanetto R., Manenti F., 2021, Improving Hydrothermal Carbonization (htc) Processes by Hydrochar Gasification, Chemical Engineering Transactions, 86, 925-930 DOI:10.3303/CET2186155

components to represent the biomass, cellulose, hemicellulose, and lignin. HTC however has already undergone a thermal treatment step and the residual is somehow more chemically akin to coal than biomass and for this reason while waiting for experimental data the coal based kinetic modelling approach was chosen.

Table 1: Comparison between main process variables of the most common thermal pre-treatment processes of biomass

Process	Operating Temperature [°C]	Residence time	Heating rate	Product yield [%]		
				Solid	Liquid	Gas
Slow pyrolysis	300-650	5min-12h	10-30 °C/min	25-35	20-30	25-35
HTC	180-260	5min-12h	5-10 °C/min	45-70	5-25	2-5
Dry torrefaction	200-300	30min-4h	10-15 °C/min	60-80	-	20-40
Gasification	600-900	10-20s	50-100 °C/s	<10	<5	>85

2. Methods

To model the kinetics of the system without requiring detailed chemical analysis of the hydrochar and a custom-made kinetic study a more general approach based on the elemental analysis was used (Ranzi et al., 2014). This model assumes that the behaviour of compounds with a similar elemental analysis in gasification is similar, so by using a linear combination of a set of pseudo-components with known devolatilization kinetics, it's possible to estimate the composition of the produced syngas of virtually any compound which can be described by a linear combination of the available pseudo-components (Ranzi et al., 2016). Based on the results obtained from elemental analysis of hydrochar obtained from urban sewage, it was possible to describe this specific hydrochar as a mix of two different grades of coal with ash. Ash, while not being a reactant does have significant catalytic effects on biomass gasification which are included in the kinetic package. In gas-solid reacting systems transport phenomena play a crucial role in the determination of the final product distribution. By coupling the kinetic model with mass and heat transfer phenomena in the particle and on its surface, it is possible to account for:

- Temperature gradients along the radial profile of the hydrochar particle
- Concentration gradients along the radial profile of the hydrochar particle

This can help identifying intraparticle hotspots and optimal hydrochar diameter to achieve conversion of all the reactive biomass. For this purpose, the model includes a discrete separation in finite isotherm volumes in the radial coordinate of the particle. The choice of the number of volumes depends on the size of the particle; very big particles (d > 1 cm) might require 2 or more discrete volumes, dusts (d < 1 mm) can be considered isotherm and described by a single volume. Gas phase kinetics do not suffer from transport phenomena limitations and during plant operations turbulence further helps the mixing of the gas phase. In this condition considering each discrete reactor volume as perfectly mixed is a valid hypothesis. While transport phenomena play no significant role in determining the final product distribution of the gas, the amount of primary and secondary reactions between gas components is extremely high and complex to model. Over the years several models have been developed and implemented for many different applications in combustion and gasification engineering (Ranzi et al., 2016), the one used in thiswork includes about 200 species and 2000 reactions and was developed by Manenti et al., 2013 .
The models cited above are eventually combined with NIST's thermodynamic engine in a dedicated package named GasDS which is responsible for the detailed modelling of the gasification unit.

The operative conditions of the unit change, but some parameters were kept fixed in each simulation:

- reactor geometries show in Figure 1
- reactor operating pressure set at 1.4 bar
- geometry of the hydrochar particle
- composition of the hydrochar particle
- number of discrete volume elements used for the reactor and the particle (2 for the reactor 1 for the particle which has dimensions < 1 mm)
- hydrochar feed flow rate to the gasification chamber set at 7 kg/h
- inlet temperature of the gas streams entering the gasification unit set at 250 °C
- hydrochar humidity set at 15% on dry basis

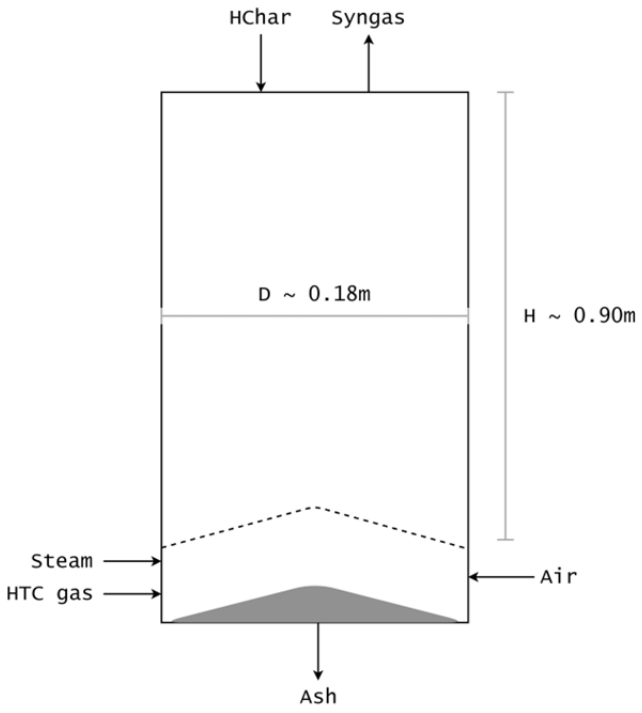


Figure 1: Gasification chamber schematics

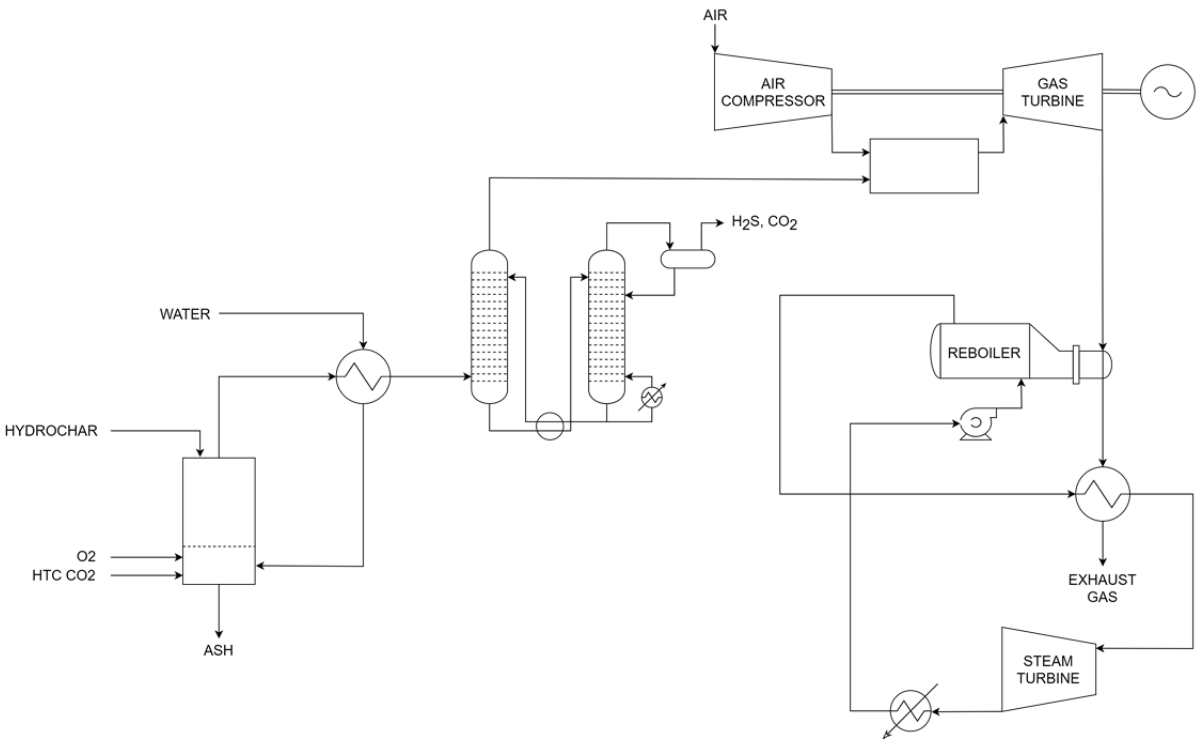


Figure 2: Integrated gasification combined cycle layout

The unit feed is characterized by; the solid hydrochar dropped from the top of the reactor, the oxidant stream (air enriched with oxygen to different degrees), steam to control the temperature and HTC gas. This last stream is the gaseous residue from the hydrothermal carbonization treatment and is mainly composed of CO_2 (>99%) with traces of odoriferous compounds which will be degraded at high temperatures during gasification. The layout of the plant implemented in Aspen HYSYS V10 is reported in Figure 2.

Four sections can be identified; The gasification unit, the CO_2 and H_2S ammine washing, the gas turbine section and the steam turbine section. The steam turbine cycle is a separated module and can be easily detached and exchanged with any kind of thermal utility. A brief estimate of the economics and Aspen HYSYS modelling of the plant will be discussed in detail in later work.

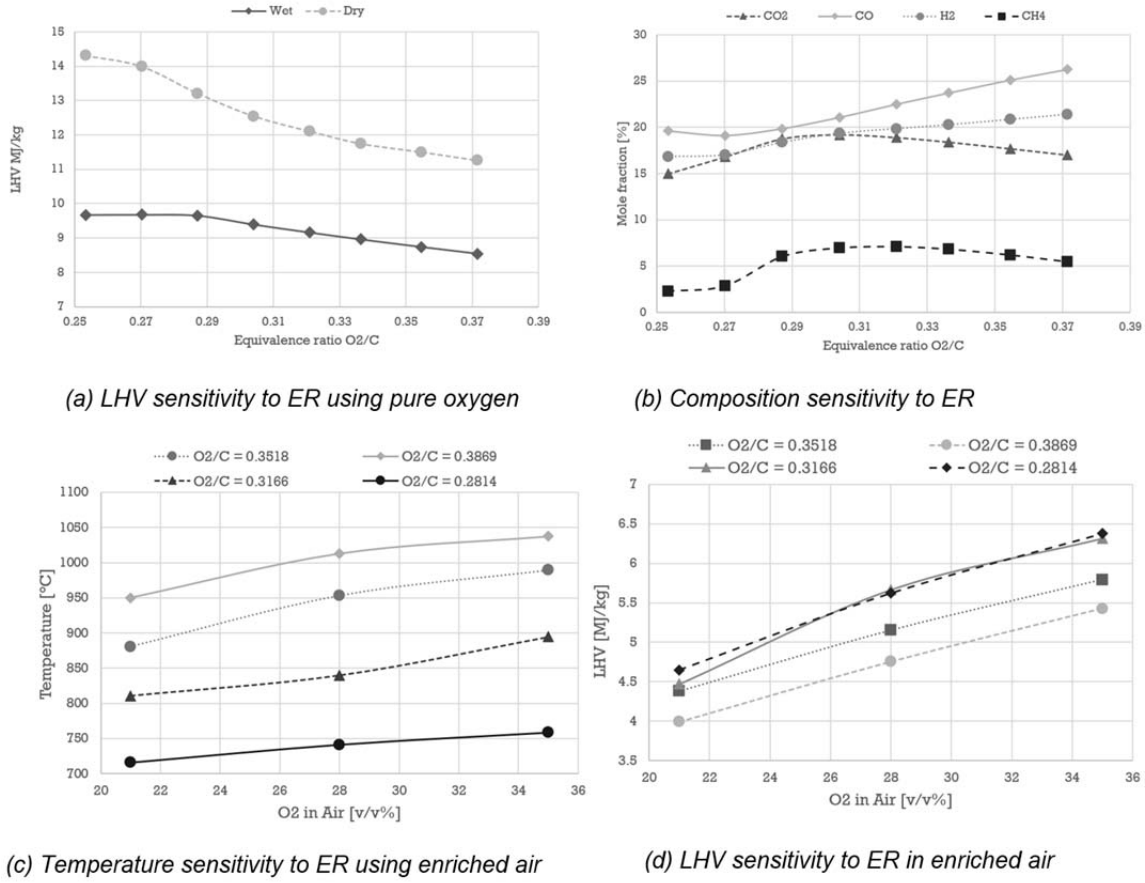
The gas turbine cycle was operated at 15 bar, with the combustor being simulated as a Gibbs reactor reaching the outlet temperature of 1281 °C fed to the gas turbine. The steam cycle was operated with supersaturated steam at 590 °C at 10 bar, with steam being generated using the gas turbine exhaust effluent at 790 °C. The ammine washing was simulated using the 'stream cut' tool to transition thermodynamic package, since MEA is not supported by the Peng-Robinson equation of state. The absorption tower was operated at 15 bar while the regeneration column was simulated at 1.5 bar, the reboiler temperature of the regeneration column was 109.7 °C while the condenser temperature was 69.2 °C. The output of this simulation was linked with the power generating section using another stream cut tool to revert to the Peng Robinson thermodynamics. The external routine solving the gasification chamber was linked to HYSYS using the VBA Excel libraries provided with every installation of Aspen HYSYS.

3. Results

The key parameters that were investigated during the sensitivity analysis include:

- The effect of the equivalence ratio on the Lower Heating Value of the fuel gas
- The effect of the equivalence ration on the composition of the fuel gas
- The effect of enriching air with oxygen on the maximum temperature
- The effect of enriching air with oxygen on Lower Heating Value

The effects of each of these variations was evaluated on the configuration reported in the Methods section and is reported in Figure 3.



(a) LHV sensitivity to ER using pure oxygen

(b) Composition sensitivity to ER

(c) Temperature sensitivity to ER using enriched air

(d) LHV sensitivity to ER in enriched air

Figure 3: Sensitivity analysis results

From the sensitivity analysis the crucial role of the ER in determining the LHV of the fuel gas is evident, but another key player is the degree of enrichment in oxygen. Even a 15% enrichment in O_2 brings more than 40% performance improvement in terms of LHV, which translates also in reduced volume of the downstream units. This consideration alone makes a valid argument for the installation of membranes or selective absorption units to rise the oxygen content in Air and reduce the content of inert gas in the system. If energy generation is not a priority, hydrogen production through water gas shift could be a feasible option. In this scenario a high ER might be a favorable parameter. This is the case because as the ER rises so does the temperature, pushing the equilibrium of the system away from methane to carbon monoxide and hydrogen. High temperatures have also the advantage of removing tar from the system since complete thermal degradation of tars is achieved above 1000 °C. Heat, is another product of the gasification chamber. The fuel gas is used at temperatures close to ambient, so a certain amount of cooling duty is required to bring it down to conditions suitable for ammine washing (in the range of 50 °C). Integrating part of this cooling duty with the HTC process, which is energetically demanding, might be the most successful configuration for the final plant. Finally, a single condition was chosen to run a plant wide simulation of the energy generation. The plant would run with a feed stock of 400 kg/h of hydrochar with almost 50% ash content, at 15bar in a reactor with a 3meter diameter and 5meters of height. A high ER of 0.34 was chosen to avoid tar formation despite a net loss in LHV. All the other conditions are analogous to the ones described in the Methods paragraph. The black box results of the gasification are reported in Table 2 and were sent to the gas turbine.

Table 2: Input output results of the gasification section of the plant

Component	Flow rate [kg/h] IN	Flow rate [kg/h] OUT
Hydrochar	400	197.7
Oxygen	112	0
Nitrogen	370	370
Water	50	83.4
Carbon dioxide	12	167.2
Hydrogen	0	6.2
Carbon monoxide	0	100
Methane	0	18.8

In the simple gas turbine configuration 326.9 kW of power were generated by the turbine, while compression costs amounted to 130.2 kW, resulting in a net electricity production of 195.7 kW. The addition of a steam turbine adds negligible pumping costs and 77.8 kW of electrical power generated by the steam turbine for a total of 273.5 kW of power generated. The addition of a steam turbine for this small production scale plant is probably difficult to justify economically. If the steam cycle is not used a stream of 1559 kg/h of 60% N_2, 31% H_2O, 8% CO_2 and 1% O_2 at 720 °C can be used to generate high pressure steam or used for either the ammine washing regeneration or the HTC thermal requirements

4. Conclusions

A detailed model of a gasification chamber for hydrochar was modelled and used to evaluate the preliminary performance of an integrated gasification power plant. The performance of the gasification chamber is in line with the typical values obtained for biomass in terms of LHV, however the different plant layout that comes from the hydrothermal carbonization section could point the design of the power plant section toward a more unconventional path. Since the HTC process requires a significant amount of thermal duty the implementation of a steam cycle is unlikely to be economically profitable with respect to an energetic integration of the gas turbine effluent with the HTC plant.

Another fact that emerged is that the power produced is unlikely to justify the investment of a conventional turbine for this plant size. The steam turbine can be excluded already as a feasible option considering the marginal profits it brings to the economy of the plant and its costs being superior to the gas turbine.

The evolution of this work will move towards a preliminary economic feasibility study of the power generation section to evaluate whether this is the best application for the fuel gas produced or if a synthetic route to hydrogen might be more appealing.

Acknowledgments

HBI Group for providing the necessary data and technical support on the HTC section plant

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