Applied Hydrothermal Carbonization

Carbonização Hidrotermal Aplicada

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ABSTRACT

The technology of hydrothermal carbonization (HTC) is a thermal chemical conversion process of organic waste into products in a reactor at low and medium temperatures and pressures, with catalysts, using residual raw materials of diversified origin, such as domestic, industrial, or agricultural. The products from the process have several energies (renewable sources) and environmental applications, such as carbon sink, soil conditioners and nanostructured materials. Implications inherent to the process, such as the type of residual biomass, the carbon phases produced (products), and adaptation of the small-scale system, have been researched in the activities. Experiences show that a laboratory-scale system transforms wet biomass from industrial waste, such as septic tank sludge, into products with application potential. The septic tank effluent originating from the great region of Goiânia was treated through hydrothermal carbonization, generating products in nanometer scale to which value could be added (potential result), in case of application at an industrial scale.

Keywords: Septic sewage stabilization, Carbon sequestration, Sustainable technology, Nanostructures.

RESUMO

A tecnologia de carbonização hidrotermal (HTC) trata de processo de conversão termoquímica de substâncias residuárias orgânicas em produtos em reator em baixas e médias temperaturas e pressões, com catalisadores, utilizando matérias-primas residuais de origem diversificada, tais como doméstica, indústria ou agrícola. Os produtos do processo apresentam diversas aplicações energéticas (fontes renováveis) e ambientais, tais como sumidouro de carbono, condicionadores de solo e materiais nanoestruturados. Implicações inerentes ao processo, tais como o tipo de biomassa residuária, as fases de carbono produzidas (produtos) e adaptação do sistema de pequena escala, têm sido pesquisadas nas atividades. Experiências mostram que sistema em escala laboratorial transforma biomassa úmida de resíduos industriais, como lodo de fossas sépticas, em produtos com potencial de aplicação. O efluente de fossa séptica originário da grande região de Goiânia foi tratado através da carbonização hidrotermal, gerando produtos na escala nanométrica, aos quais poderiam ser agregados valor (resultado potencial), em caso de aplicação na escala industrial.

Palavras-chave: Estabilização de efluente séptico, Sumidouro de carbono, Tecnologia sustentável, Nanoestruturados.

1 INTRODUCTION

Hydrothermal carbonization technology (HTC) converts organic wastes from different sources into valuable products, such as nanometric carbon, without applying high temperatures. Under HTC conditions, the solubility of amorphous particles is significantly increased, and crystallization can occur concomitantly with redissolution and reprecipitation processes. HTC was introduced by the German chemist Bergius in 1913, who applied the technology at temperatures between 170 and 340°C and pressure up to 20 MPa (200 Bar). He was able to synthesize coal in the laboratory, within a period of 230 hours (BERGIUS, 1928 *apud* SCHMOLKE, 2009). HTC operates at lower temperatures than pyrolysis technology (BRAZIL FRAUNHOFER, 2011). The continuation of the work led to the development of synthetic fuels (NOBELPRIZE, 2010).

The theme was taken up by researchers from the Max Planck Institute, Germany, which published a similar method named "hydrothermal carbonization" for converting biomass into charcoal in a period of some hours, reducing the Bergius reaction time (1913). According to the authors, by conventional methods of biomass processes, such as alcoholic fermentation, biogas generation, and charcoal carbonization, the carbon capture is between 30 and 67%. With HTC, almost entirely biomass carbon content can be converted into solid carbon phases. The system used in HTC tests basically consists of a pressure reactor made of stainless steel and coated with PTFE (*Teflon*) to avoid chemical attack effects by the aqueous solution with acidic pH. The temperature reaches up to 200°C, and the pressure around 2 MPa (20 bar) with a reaction time of less than twelve hours. The process is exothermic and after the reaction is complete, about 90 to 99% of the carbon is available in the form of suspended nanoparticles with sizes between 1 and 20 nm (YU *et al*. (2004).

Hydrothermal carbonization allows the transformation of a wide spectrum of biomass into fixed coal with high energy content, comparable to lignite. The manufacturing process requires low to moderate temperatures and pressures. The resulting product can be applied, depending on the raw material, as fuel or for other purposes (TITIRICI; THOMAS; ANTONIETTI, 2007; REIS, 2011).

Hermann and Hüer (2013) employ the HTC process to produce high quality charcoal from agricultural residues, and sewage sludge from wastewater treatment plants (WWTP). The process converts a mixture of at least two organic materials of composition in a range of 1% up to 99% of each residual biomass component. In HTC, the water content should be up to 95%. The process temperature remains at 180°C or above.

Olshausen, Wittmann and Wolf (2012; 2013) present hydrothermal carbonization applied to the conversion of biomass into energy material and soil conditioners. Residual biomasses are from vegetable or animal origin or also from byproducts, such as wood chips, pruning residues, plants, straw, silage and organic residues from agriculture and forestry. They also come from the food and sanitation industry, as well as peat, sludge from the industry of cellulose, bagasse, and the like. These raw materials are converted by the process mainly into humus, coal, compost, water, and carbon dioxide. The application deals with energy use and the transformation of renewable organic raw materials into soil conditioners.

The hydrothermal carbonization process to treat biomass effluents from pressing olives was applied at a temperature of 220°C for 14 hours to decompose 86 organic components of the effluent (POERSCHMANN; WEINER; BASKYR, 2013).

ZANG *et al.* (2021) offer application of HTC technology for treating synthetic sex hormones in effluents or contaminated water, also described by Morais *et al.* (2018) that showed high efficiency of HTC in removing emerging contaminants from wastewater.

Water samples from the river *Rio Meia Ponte* (city of Goiânia, Goiás) were studied by Portuguez *et al.* (2012), who observed the hormone Ethinylestradiol in concentrations of up to 10^{-6} $g \cdot L^{-1}$. These were probably carried in wastewater (sewage) from contraceptive pills and hormone replacement. Concentrations of 10^{-9} $g \cdot L^{-1}$ already affect the reproductive system of fish and humans and treatment technologies to eliminate synthetic hormones from surface water or effluents would be necessary (FERREIRA, 2008).

Discharges from septic tanks are treated with domestic sewage at the Wastewater Treatment Stations (WWTP´s), and in the sectorial policies of the basic sanitation sector, the continuous improvement of sewage treatment and service rates are predicted (SANEAGO, 2018). Thus, HTC technology has the potential for carbon sequestration. The survey introduces HTC to septic tank sludge.

2 DEVELOPMENTS

2.1 METHODOLOGY

Samples and analysis:

The company for basic sanitation services in Goiás (SANEAGO) supported the research with information and data about the sewage treatment in Goiânia. Sampling was carried out at the Wastewater Treatment Plant - WWTP of SANEAGO in the Goiânia 2 region (*ETE Dr. Hélio Seixo de Brito).*

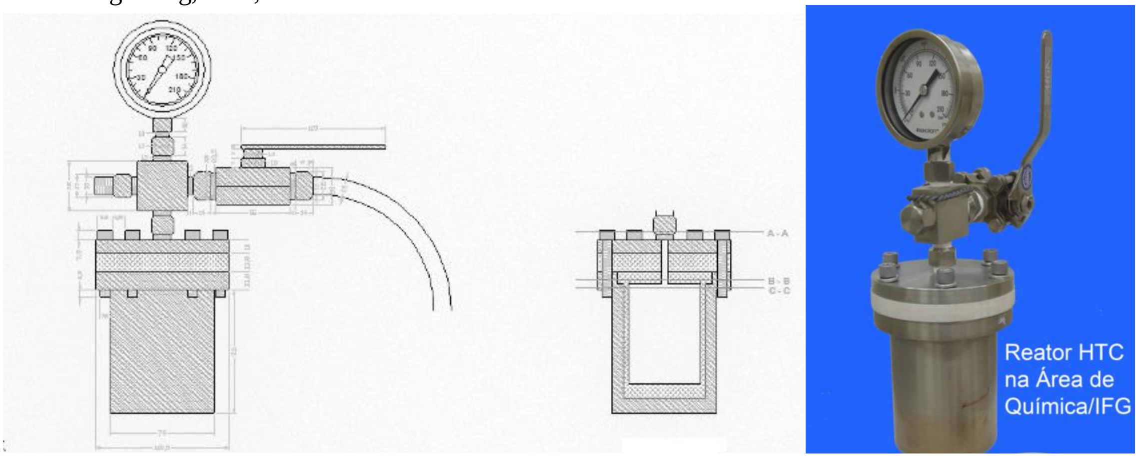
The following parameters of the collected samples were analyzed at the Chemistry laboratories of the Federal Institute of Goiás – IFG (Instituto Federal de Goiás):

1. Dry mass (DM): moisture analysis of mass loss at T=105 °C, equipment MARTE moisture analyzer, model ID 50, São Paulo, S.P., Brazil.
2. Organic matter content: measuring the mass loss by ignition at T=550°C, equipment MARTE furnace, São Paulo, S.P., Brazil.
3. Measurement of the pH with a digital pH meter DIGIMED MARTE, model DM 20, São Paulo, S.P., Brazil.

HTC-Experiments:

The HTC experiments were carried out at IFG's Chemistry laboratory, Campus of Goiânia, GO, Brazil, using an HTC laboratory reactor, which was developed in a partnership with the Environment Campus of the University of Trier in Germany (*Umweltcampus HS- Trier*). The HTC small scale reactor, with a 250 mL volume in 304 stainless steel, holds a resin Polytetrafluoroethylene (PTFE) vessel to avoid chemical attack under pH 3 (adding acidic solutions of sulfuric acid) and supporting inside temperatures of up to 200°C, and pressures of up to 2 MPa (20 bar). The applied reaction time was four hours – see figure 1.

Figure 1: Laboratory scale reactor for Hydrothermal Carbonization HTC developed at the IFG (*Instituto Federal de Goiás).* Technical Drawing: Zang, J.W., 2008.



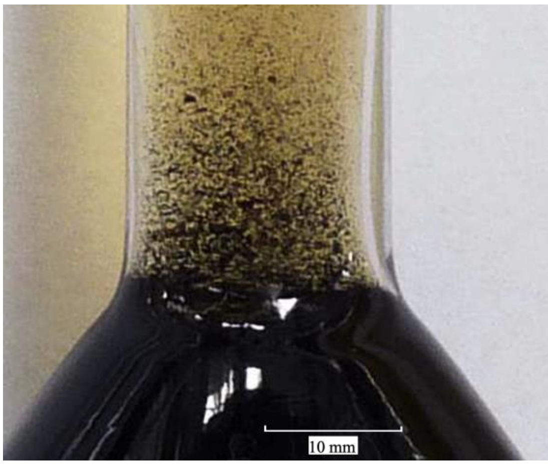
For characterizing the HTC products, the Scanning Electron Microscopy (SEM) analysis method was applied, Philips Brand, Model CM200, Norway.

2.2 RESULTS AND DISCUSSION

The sewage samples show a dry matter (DM) content of 5 to 7% by mass, the organic matter contents were between 20 and 78% of the DM, and the initial pH values of the raw material were 6.0 to 6.8, which was lowered by sulfuric acid to pH 3, before starting the process.

After about four hours of treatment, the sewage was converted into a dark colored suspension (brown) of visible agglomerates of fine particles (Figure 2).

Figure 2: Image of the suspension of solid particles, product of HTC treatment (Macro photography, NIKON Coolpix 990).



The following images, figure 3 (a) and (b), illustrate the appearance and morphology of the sewage sample before and after HTC application.

Figure 3 (a): Images of sewage sample before HTC treatment, SEM image (SEI, 10 KeV).

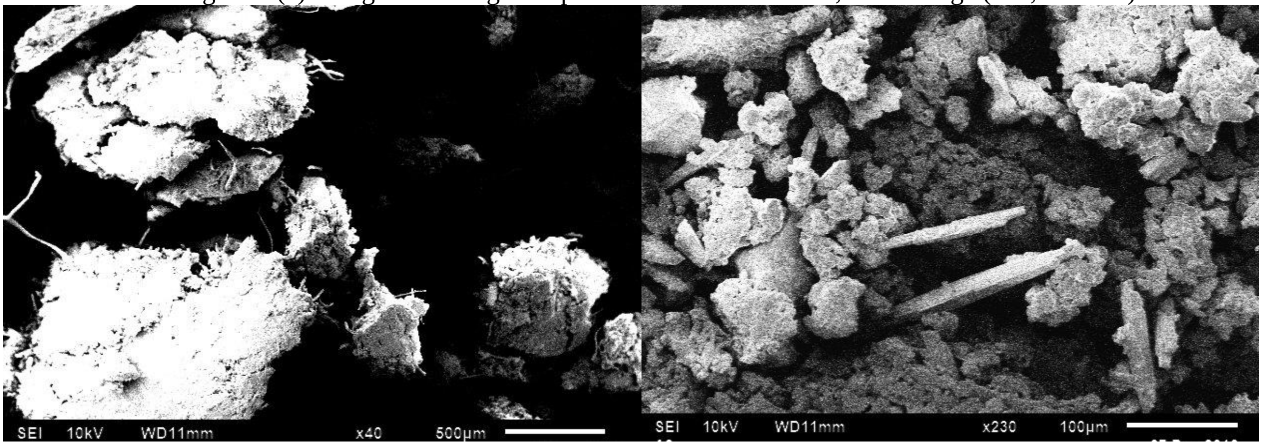
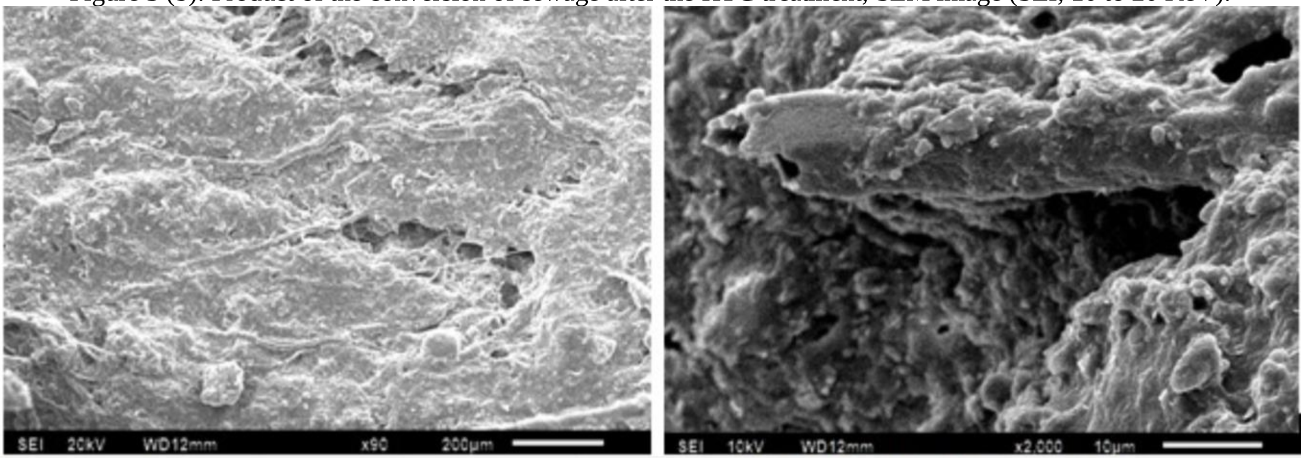


Figure 3 (b): Product of the conversion of sewage after the HTC treatment, SEM image (SEI, 10 to 20 KeV).



The images taken by electron microscopy (SEM) in the images of (a) and (b) indicate morphologies of the raw material (sewage) and the HTC products, respectively. The images of figure 3 (b) show carbonaceous materials in nanometer range (conversion by HTC process). Note the two to eight times higher magnification factor presented in the images of figure 3 (b) when compared to 3 (a).

YU *et al.* (2004) using a similar HTC method in an aqueous solution of up to 80% of water, acidic pH, temperature up to 200°C, pressure of up to 2 MPa (20 bar) and twelve hours of reaction time, converted between 90 to 99% of the carbon content into a mixture of nanoparticles of 1 to 20 nm.

The effects inherent to the process conditions might lead to changes in the morphology, size, and chemical constitution of the products (ZHENG *et al.*, 2001 *apud* Mourão *et al.*, 2009).

According to Titirici; Thomas; Antonietti (2007), metallic ions accelerate the HTC process and generate nanostructures and transitional products such as glucose, furfural compounds, methane, and hydrogen.

Advantages of the process, and the relatively easy separation of the products by means of filtration, can be mentioned.

Other means of separation, centrifugation and distillation should be discussed and tested depending on the needs of the process and the amount and types of energy available, involving wherever possible, the use of renewable energies such as solar energy, or even the use of the generated carbonous products for the process of carbonization (HTC process in pilot or industrial process scales).

Pilot industrial applications of HTC have already been carried out, for example, by a German company in China for the treatment and dehydration of Sludge from Sewage Treatment Plants (TERRANOVA ENERGY, 2021).

Applications of the product as a carbon dioxide (CO_2) sequestrant, and as a soil conditioner, might enhance water retention capacity and cation exchange capacity, and could lead to improved soil quality and plant growth in carbon sink environments (MENEZES *et al.*, 2015).

In nature, this process is found in the form of dark soils named in the literature as "*terra preta*". A possible application is to degraded soil by excessive agricultural production activities (PEARCE, 2005 *apud* TITIRICI; THOMAS; ANTONIETTI, 2007).

3 CONCLUSIONS

The experiments in laboratory scale show that the HTC process has the potential to convert sewage residues into nanometric carbonaceous materials expected to be less harmful to the environment due to the reduction or elimination of toxicity and microbial pollution and with a potential use e.g., as soil conditioners, solid fuels, and liquid P-fertilizers etc.

The process was carried out at temperatures up to 200°C and average pressures of about 1.8 to 2 MPa at acidic pH-range. The concentration of the biomass and water solution influences the reactions and the products: intrinsic effects to the process conditions and changes in the morphology and chemical constitution of the products.

It could be suggested to investigate the combustion value and the possible limitations for product applications due to intermediate co-products, such as liquids and gases such as glucose, furfural compounds, methane, and hydrogen.

Possible applications of the HTC process might be e.g., an easier liquid-solid separation of the HTC products compared to the raw materials, by means of filtration, centrifugation, or distillation. According to the application scale, the use of renewable energies, such as solar energy, might be suggested as a thermal source for drying the products or for direct applications of renewable energy sources in the pilot or industrial process scales.

The HTC process shows itself as carbon dioxide (CO_2) sequestering technology (carbon sink).

Possible applications of HTC products on degraded soils might be sought, following the guidance of regulatory institutions.

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