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RENAN BARROSO SOARES

TOWARD AN EFFECTIVE USE OF MICROALGAE BIOMASS FROM UASB REACTORS: FROM HARVESTING TO SMALL GASIFICATION

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The thesis presented to the Graduate Program in Environmental Engineering of the Federal University of Espírito Santo, as part of the requirements to obtain the title of Doctor of Science in Environmental Engineering.

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Dedication

I dedicate this work to my wife Priscila for patience and understanding on this long journey.

I also dedicate to my parents Uilians and Luciana, for the construction of worth without which nothing would be possible.

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I thank God and life who endowed me with health and tenacity.

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“Work and trust”.

Jerônimo Monteiro

Abstract

Sanitary sewage, traditionally seen as a source of expenses and problems, has come to be seen as an opportunity and source of funds. This is because of the three major current demands of modern society, two can be extracted directly from sewage (water and energy), and one (food) can benefit from the recovery of nutrients to agriculture. Therefore, Wastewater Treatment Plants (WWTP) which go beyond the treatment itself and reuse by-products to improve their energy and economic performance is being increasingly studied. This thesis discussed the reuse of microalgae biomass produced in WWTP as a source of energy. Based on the data from the literature survey, a conceptual scenario for the use of microalgae biomass for microgeneration in WWTP was built. Thermochemical gasification was the chosen conversion process since it is one of the most promising for the microgeneration of electricity. The results showed a production potential of 0.167 kWh/m^3 of treated sewage, and investments financially returned after five years. After this theoretical approach, an experimental investigation was carried out using the microalgae produced in a WWTP pilot, constructed within the area of Companhia Espírito Santense de Saneamento (CESAN), with resources from Financiadora de Estudos e Projetos (FINEP), and in partnership with the company Fluir Engenharia Ambiental. The microalgae were cultivated in two high-rate algal ponds (HRAP), fed with the effluent obtained after wastewater treatment in the UASB reactor (Up-flow Anaerobic Sludge Blanket). The biomass was then harvested in a coagulation-flocculation system, dried, characterized in terms of its calorific value, ultimate, proximate, ash, thermogravimetric, and differential thermal analysis. The effects of seven commercial coagulants on the thermochemical conversion of microalgae were evaluated and the results revealed that coagulants could affect the energy recovery. Some coagulants showed catalytic effects and were beneficial to the gasification process, while others impaired the energy recovery of biomass. Lastly, experimental microalgae gasification was evaluated in a pilot-scale downdraft gasifier. Unlike other studies reported in the literature, which simulate microalgae gasification in laboratory equipment, the gasifier used in this study is a commercial technology, already widespread in the market and present in over 40 countries. Another important difference of this work in relation to the published ones concerns the microalgae type. While the literature generally reports the gasification of pure microalgae species (monoculture), obtained in a controlled manner and free of chemical coagulants used in the harvest stage, this study presents the gasification of biomass composed of different species of microalgae, bacteria and other organisms present in the HRAP, besides chemical coagulants. The effects of air-fuel equivalence ratio (ER) on the produced gas composition, higher heating value (HHV), cold gas efficiency (CGE), and production rate were presented. An increasing and then decreasing trend with ER with a peak was seen, indicating that there is an optimum ER of 0.23 for the best performance of the process. The cold gas efficiency, syngas composition, HHV, and production rate were 87%, 11.86% H_2, 19.45% CO, 8.5% CH_4, 9.82% CO_2, 6.23 MJ/Nm^3, and 2.79 Nm^3/kg biomass dry, respectively. The tests demonstrated the possibility to use wastewater microalgae as fuel in downdraft gasifier. The energy recovery could help drive the WWTP to a more economical and sustainable process.

Keywords: Wastewater; microalgae; biomass; harvesting; gasification; downdraft gasifier; pilot-scale; equivalence ratio; energy; microgeneration; coagulant; catalytic effect; thermochemical behavior; high-rate-ponds.

Resumo

O esgoto sanitário, tradicionalmente visto como fonte de despesas e problemas, passou a ser visto como uma oportunidade e fonte de recursos. Isso porque das três maiores demandas da sociedade, duas podem ser extraídas diretamente do esgoto (água e energia) e uma (alimento) pode se beneficiar da recuperação de nutrientes para a agricultura. Por isso, Estações de Tratamento de Esgoto (ETE), que vão além do tratamento em si e reutilizam subprodutos para melhorar seu desempenho energético e econômico, estão sendo cada vez mais estudadas. Esta tese discutiu a reutilização da biomassa de microalgas produzida na ETE como fonte de energia. Com base na literatura, foi construído um cenário conceitual para o uso de microalgas para produção de eletricidade dentro da ETE. O processo termoquímico de gaseificação foi escolhido, já que é um dos mais promissores para a microgeração. Os resultados mostraram um potencial de produção de 0,167 kWh / m^3 de esgoto tratado e retorno dos investimentos em cinco anos. Após essa abordagem teórica, foi realizada uma investigação experimental utilizando microalgas produzidas em uma ETE piloto, construída dentro da Companhia Espírito Santense de Saneamento (CESAN), com recursos da Financiadora de Estudos e Projetos (FINEP), e em parceria com a empresa Fluir Engenharia Ambiental. As microalgas foram cultivadas em duas lagoas de alta taxa (LAT), alimentadas com o efluente do reator UASB (*Up-flow Anaerobic Sludge Blanket*). A biomassa foi colhida em um sistema de coagulação-floculação, seca, caracterizada em termos de seu valor calorífico, análise elementar, imediata, cinzas, termogravimétrica e fluxo térmico. Os efeitos de sete coagulantes comerciais sobre a conversão termoquímica de microalgas foram avaliados e os resultados revelaram que os coagulantes podem afetar a recuperação de energia. Alguns coagulantes apresentaram efeitos catalíticos e foram benéficos ao processo de gaseificação, enquanto outros prejudicaram a recuperação de energia da biomassa. Por fim, a gaseificação experimental de microalgas foi avaliada em um gaseificador *downdraft* em escala piloto. Diferentemente de outros estudos relatados na literatura, que simulam a gaseificação de microalgas em equipamentos de laboratório, o gaseificador utilizado neste estudo é uma tecnologia comercial, já difundida no mercado e presente em mais de 40 países. Outra diferença importante deste trabalho diz respeito ao tipo de microalgas. Enquanto a literatura geralmente relata a gaseificação de espécies de microalgas puras (monocultivo), obtidas de maneira controlada e livre de coagulantes químico, este estudo apresenta a gaseificação de biomassa composta por diferentes espécies de microalgas, bactérias e outros organismos presentes na LAT, além do coagulante. Os efeitos da razão de equivalência ar-combustível (ER) na composição do gás produzido, poder calorífico (PC), eficiência do gás frio (EGF) e taxa de produção do gás foram avaliados. Uma tendência crescente e decrescente com a variação do ER foi observada, com um pico, indicando um ER ideal de 0,23 para um melhor desempenho do processo. A eficiência do gás frio, a composição de gás, o PC e a taxa de produção foram 87%, 11,86% H_2, 19,45% CO, 8,5% CH_4, 9,82% CO_2, 6,23 MJ / Nm^3 e 2,79 Nm^3 / kg de biomassa seca, respectivamente. Os testes demonstraram a possibilidade de usar microalgas de águas residuais como combustível. A recuperação de energia pode ajudar a conduzir a ETE a um processo mais econômico e sustentável.

Palavras-chaves: Esgoto; microalga; biomassa; colheita; gaseificação; gaseificador *downdraft*; escala piloto; razão de equivalência; energia; micro geração; coagulante; efeito catalítico; comportamento termoquímico; lagoas de alta taxa.

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Chapter 1

Introduction

1.1 Motivation

Basic sanitation prevents human contact with waste, being important for the public health, the environment, and the economy of the country [1]. Even so, according to the National Sanitation Information System (SNIS) [2], the sewage treatment rate in Brazil is only 46.3%. The economic conditions of the population limit the full transfer of the cost of services to the tariff, especially in the poorest cities, making the necessary investments for the sector unfeasible [3]. Sanitation problems can be overcome if the technology adopted presents an attractive economic return. For this, one of the trends is energy recovery from wastewaters [4]. Build Wastewater Treatment Plant (WWTP) more energy-efficient can improve project profitability and attract investment to the sector [5].

One possibility of energy recovery in WWTP involves biogas produced in anaerobic treatment systems [6]. For the state of Espírito Santo alone, it is estimated potential production of 18.5 MW of energy if 60% of the generated sewage will be treated by anaerobic systems [7]. Among the anaerobic treatment systems, UASB reactors (Up-flow Anaerobic Sludge Blanket) are the technology that has experienced the greatest acceptance in the last 20 years. However, to meet the most stringent environmental standards, these processes require an additional treatment step to reduce the remaining organic matter and nutrients [8]. High-rate algal ponds (HRAP) can be used as a complementary treatment of UASB reactors, and it is an interesting alternative from technical, economic and environmental points of view [9]. Such treatment ponds have gained extra motivation in recent years since their large production of microalgae is no longer seen as a problem, but as a raw material for biofuels [10].

Within WWTP, the use of microalgae to produce energy is an alternative that can increase efficiency and reduce process costs [11,12]. On the other hand, when left unused, this amount of energy is not only lost but can also add costs to conventional sludge disposal systems. In this context, WWTP composed by the association of UASB reactors and HRAP represents an interesting alternative for the development of a more economical WWTP. Azeredo [13] evaluated this new integrated WWTP model and demonstrated an energy surplus performance. In addition, the author reported operational simplicity, satisfactory performance at the tertiary level of sewage treatment, and the possibility of phosphorus recovery and sequestration of CO_2.

Among the various processes to convert biomass into energy, the gasification process presents important advantages, such as higher efficiency, lower CO_2 emissions, rapid conversion, and hydrogen production. It is worth mentioning that hydrogen is appointed as the substitute fuel for gasoline and diesel in the future [14]. In addition, the gasification process can overcome typical problems observed in incineration processes such as the need for additional fuel, and emissions of sulfur and nitrogen oxide, heavy metals, ashes, chlorinated dibenzofurans and dioxins [15]. The conversion of biomass to fuel gas still allows the generation of electricity in systems more efficient than steam boilers, such as turbines and gas engines [16]. This is relevant since most of the energy consumed in WWTP is electrical [17].

Thus motivated, this work discusses the energy recovery from microalgae produced in WWTP through the thermochemical gasification process. Studies involving wastewater microalgae gasification are scarce in the literature, such as the works of Zhu et al. [18], Sharara and Sadaka [19] and Zhu et al. [20]. The most gasification studies have been carried out for pure species of microalgae (monoculture) obtained commercially instead of microalgae grown in wastewater. Moreover, the gasifying agent used in these works was not air, the most economical and traditional gasifying agent. To the best of our knowledge, it is the first work involving the wastewater microalgae gasification using a commercial downdraft gasifier and air as the gasifying agent, which gives the work a unprecedentedness.

1.2 Thesis outline

This thesis is written in "Integrated Article Format". The following chapters are based on three articles already published, which will be presented in full versions.

Chapter 2 presents a review article on a conceptual scenario for the use of microalgae biomass for microgeneration in WWTP and the scale in which it is possible. A systematic mapping of literature work was done and a scenario was constructed. All process steps, from microalgae cultivation to energy production, were discussed in this chapter. The reasons that led to the choice of gasification as the energy conversion route for the produced biomass over other processes such as fermentation, digestion and lipid extraction are also described in this chapter. Finally, a cost estimate was made and the suggested WWTP model was displayed in a flowchart. This chapter was published on October 03rd, 2019 in the *Journal of Environmental Management*. https://doi.org/10.1016/j.jenvman.2019.109639.

Chapter 3 shows a published article on the thermochemical conversion of wastewater microalgae and the effects of coagulants used in the harvest process. This chapter analyzed the influence of seven commercial coagulants on the characterization of microalgae biomass. The main thermochemical characteristics of microalgae biomass evaluated were higher heating value (HHV), proximate, ultimate, ash, thermogravimetric and differential thermal analysis. This chapter described all the methodology of biomass production and characterization. This chapter was published on March 02nd, 2020 in the *Algal Research*. https://doi.org/10.1016/j.algal.2020.101864.

Chapter 4 introduces the article submitted with the results obtained from the experimental investigation of wastewater microalgae in a pilot-scale downdraft biomass gasifier. The whole experimental gasification apparatus is described, and the effects of equivalence ratio (ER) on the produced gas composition, HHV, cold gas efficiency (CGE), and production rate were illustrated. This chapter was published on August 14th, 2020 in the *Algal Research.* https://doi.org/10.1016/j.algal.2020.102049.

Finally, Chapter 5 brings the general conclusions of the thesis and suggestions for future works.

1.3 Research objectives

The main objective of this thesis was to evaluate the gasification of microalgae grown in wastewater using a commercial downdraft biomass gasifier. The effect of the ER, the most important parameter on the gas calorific value, was evaluated on the performance of the process in order to find the best experimental condition. It is expected that this experimental investigation contributes to the development of more efficient WWTP.

The specific objectives of this research are:

- ✓ To describe the state of the art of microalgae production, its potential to generate electricity in WWTP and the scale in which it is possible (Chapter 2).
- ✓ To evaluate the effects of coagulants used in the harvest process on the thermochemical conversion of microalgae (Chapter 3).
- ✓ To study the experimental investigation on wastewater microalgae gasification in a pilot-scale downdraft biomass gasifier (Chapter 4).

References

[1] F.N. de S. (Brasil), Manual de saneamento, Funasa, 2006.

[2] SNIS, Diagnósticos dos serviços de água e esgoto 2018, (2020).

[3] S.T. Cassini, Digestão de Resíduos Sólidos Orgânicos e Aproveitamento do Biogás, ABES, RiMa, Rio de Janeiro, 2003.

[4] S. TRIPATHI, Sanitation and Energy, NEW DELHI, INDIA, 2016.

[5] E. Metcalf, M. Eddy, Wastewater engineering: treatment and Resource recovery, Mic Graw-Hill, USA. (2014) 1530–1533.

[6] A.C. Van Haandel, G. Lettinga, Anaerobic sewage treatment: a practical guide for regions with a hot climate., John Wiley & Sons, 1994.

[7] ASPE, Atlas de bioenergia do Espírito Santo, Vitória, 2013.

[8] B. Silveira, C. Cabral, C. Suidedos, C. Platzer, G. Silva, Guia Tecnica De Aproveitamento De Biogás Em Estatacoes De Tratamento De Esgoto, 2015.

[9] M. Von Sperling, C.A. De Lemos Chernicharo, Biological Wastewater Treatment in Warm Climate Regions, IWA Publ. (2005) 1–856. doi:10.5860/CHOICE.45-2633.

[10] C. Wan, M.A. Alam, X.Q. Zhao, X.Y. Zhang, S.L. Guo, S.H. Ho, J.S. Chang, F.W. Bai, Current progress and future prospect of microalgal biomass harvest using various flocculation technologies, Bioresour. Technol. 184 (2015) 251–257. doi:10.1016/j.biortech.2014.11.081.

[11] S. Longo, B.M. d'Antoni, M. Bongards, A. Chaparro, A. Cronrath, F. Fatone, J.M. Lema, M. Mauricio-Iglesias, A. Soares, A. Hospido, Monitoring and diagnosis of

energy consumption in wastewater treatment plants. A state of the art and proposals for improvement, Appl. Energy. 179 (2016) 1251–1268. doi:10.1016/j.apenergy.2016.07.043.

[12] M. Wakeel, B. Chen, T. Hayat, A. Alsaedi, B. Ahmad, Energy consumption for water use cycles in different countries: A review, Appl. Energy. 178 (2016) 868–885. doi:10.1016/j.apenergy.2016.06.114.

[13] L. Azeredo, Potencial energético da co-digestão da biomassa de microalgas no tratamento de esgoto sanitário em reatores UASB., Universidade Federal do Espírito Santo, 2016.

[14] N. Nipattummakul, I.I. Ahmed, S. Kerdsuwan, A.K. Gupta, Hydrogen and syngas production from sewage sludge via steam gasification, Int. J. Hydrogen Energy. 35 (2010) 11738–11745. doi:10.1016/j.ijhydene.2010.08.032.

[15] P. Manara, A. Zabaniotou, Towards sewage sludge based biofuels via thermochemical conversion - A review, Renew. Sustain. Energy Rev. 16 (2012) 2566–2582. doi:10.1016/j.rser.2012.01.074.

[16] E.E.S. Lora, M.A.R. do Nascimento, Geraçao Termelétrica-Planejamento, Projeto e Operaçao, Volume II, (2004).

[17] H. Wang, Y. Yang, A.A. Keller, X. Li, S. Feng, Y. nan Dong, F. Li, Comparative analysis of energy intensity and carbon emissions in wastewater treatment in USA, Germany, China and South Africa, Appl. Energy. 184 (2016) 873–881. doi:10.1016/j.apenergy.2016.07.061.

[18] Y. Zhu, P. Piotrowska, P.J. Van Eyk, D. Boström, C.W. Kwong, D. Wang, A.J. Cole, R. De Nys, F.G. Gentili, P.J. Ashman, Cogasification of Australian brown coal with algae in a fluidized bed reactor, Energy and Fuels. 29 (2015). doi:10.1021/ef502422t.

[19] M.A. Sharara, S.S. Sadaka, Gasification of phycoremediation algal biomass, BioResources. 10 (2015). doi:10.15376/biores.10.2.2609-2625.

[20] Y. Zhu, P. Piotrowska, P.J. Van Eyk, D. Boström, X. Wu, C. Boman, M. Broström, J. Zhang, C.W. Kwong, D. Wang, A.J. Cole, R. De Nys, F.G. Gentili, P.J. Ashman, Fluidized Bed Co-gasification of Algae and Wood Pellets: Gas Yields and Bed Agglomeration Analysis, Energy and Fuels. 30 (2016) 1800–1809. doi:10.1021/acs.energyfuels.5b02291.

Chapter 2

State of the art and microgeneration

A version of this chapter has been published:

Soares, R.B., Martins, M.F., Ricardo Franci Gonçalves, 2019. A conceptual scenario for the use of microalgae biomass for microgeneration in wastewater treatment plants. ***Journal of Environmental Management*** **(Elsevier - Impact Factor: 5.647)** 252, 109639. https://doi.org/10.1016/j.jenvman.2019.109639.

A conceptual scenario for the use of microalgae biomass for microgeneration in wastewater treatment plants

Abstract

Microalgae are a potential source of biomass for the production of energy, which is why the amount of research on this topic has increased in recent years. This work describes the state of the art of microalgae production from wastewater treatment plants (WWTP), its potential to generate electricity and the scale in which it is possible. The methodology used was a systematic review of the gasification of microalgae from 49 articles selected. Based on the review, a conceptual scenario for microgeneration in WWTP using as feedstock microalgae for thermal gasification was developed. The most consistent assumptions for a real scale microgeneration are microalgae production in open ponds using domestic sewage as a nutritional medium; the use of the flocculation process in process of harvesting; microalgae to energy through thermal gasification process using a downdraft gasifier. Considering a WWTP with a 3,000 m^3/d flux capacity, 860 kg / d of dry microalgae biomass might be produced. For which, gasification has a production potential of 0.167 kWh / m^3 of treated sewage, but the energy balance is compromised by the drying process. However, when the biogas produced in anaerobic treatment enter in the model, it is possible to add a surplus of electricity of 0.14 kWh / m^3 of treated sewage. Finally, a cost estimate is made for the acquisition of drying and gasification-electricity generation systems. For this scenario, the results suggest that the investments may be financially returned after five years, with additional potential for further optimization.

Graphical abstract

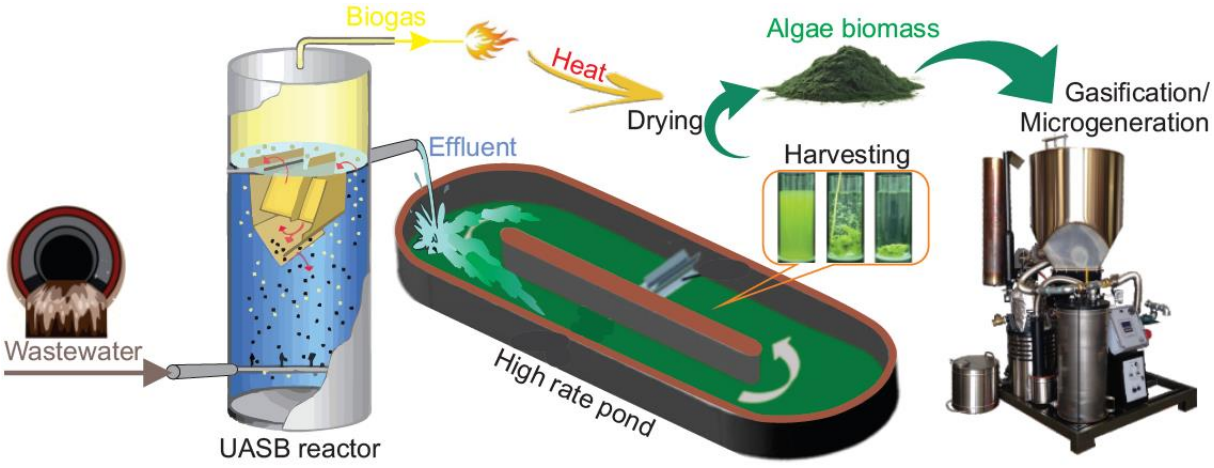

Fig. 2.1. Graphical abstract chapter 2.

Keywords: Wastewater; microalgae production; HRAP; gasification; microgeneration.

Highlights

- Microalgae production from wastewater treatment plants.
- Wastewater as a nutritional medium is a tendency and requires more studies.
- A conceptual scenario for microgeneration is developed.
- The microalgae drying process makes microgeneration unfeasible.
- Hybrid scenario: energy input from biogas makes the process economically viable.

2.1 Introduction

The great biodiversity of microalgae offers numerous applications, including biofuel production for power generation. Microalgae can produce energy-rich substances such as lipids for biodiesel production, calorific gases (hydrogen, methane, carbon monoxide) by water photolysis, biological or thermochemical gasification. Production processes involve major constraints, however, for instance, in minimizing energy consumption for sustainability or in maximizing fuel production.

Microalgae is biomass, since it absorbs the solar radiant energy and CO_2 from the atmosphere to growth [1], and maybe a biosolid as a by-product of the wastewater treatment process [2]. According to Patel et al. [3], these types of biomasses can partially meet the need for liquid and gaseous fuels for integration with existing power generation infrastructure.

Another advantage is that microalgae are the most promising alternative for biofuel production, particularly because it does not compete with food production [1,4]. Manara and Zabaniotou [5] suggest the combination of microalgae production and sewage treatment for biofuel production as the most plausible scenario for the commercial application of microalgae cultivation in the short term. The coexistence of aerobic bacteria and microalgae - which are indigenous to the type of wastewater - presents a synergy that favors biomass growth. While bacteria use oxygen produced by microalgae, microalgae use carbon dioxide produced by the bacteria, increasing the microalgae-bacteria biomass productivity [6].

There are thus two potential scenarios in the above context. One is to grow microalgae using water and nutrients as culture media; the other is to recover microalgae from the high rate open ponds in a wastewater treatment plant (WWTP). In the latter scenario, the biomass is composed of bacteria and different indigenous microalgae strains; for example in a case from southeastern Brazil, such strains are *Chlorococcum sp.*, *Chlorella sp.*,

Scenedesmus sp. and *Tetradesmus sp*. [6]. In both scenarios, harvesting and drying are necessary sub-processes in order to make biomass production feasible.

The use of microalgae to produce energy is an alternative that increases efficiency and reduces WWTP costs. Around 7% of the total energy produced in the world is consumed in WWTPs [7,8]. Moreover, most of the consumed energy is electrical, due to the use of pumps, valves, compressors and other equipment [9]. This energy represents 5 to 30% of the operation costs [10] and is globally the greatest proportion of WWTP costs [10–12].

Microgeneration is often discussed in the context of energy costs reduction. It generally refers to the size and configuration of small to medium energy systems, which make use of renewable energy sources, and can operate independently of grid-supplied power [13]. The type of biomass sources can be incorporated into microgeneration by means of a thermochemical conversion process such as gasification [14]. It offers some important advantages, such as higher energy efficiency; lower CO_2 emission; the rapid conversion of all biomass fractions (lipid, protein, and carbohydrate); and hydrogen production, a calorific gas seen by some researchers as a good future substitute for gasoline and diesel [15].

The objective of this review is to consider the discussion of WWTP based on microalgae recovery, energy demand, and microgeneration, in order to develop a scenario involving the potential production of microalgae biomasses from high rate open ponds to generate electricity. The state of the art in microalgae cultivation, harvesting, drying, and gasification are discussed, and the scale of heat/power generation and economic feasibility are estimated. The review is concluded by presenting a conceptual model and exploring the research gaps and opportunities for microgeneration in WWTP.

The paper is organized as follows. Section 2.2 presents an overview of microalgae, from their characteristics to the advantages of gasification as conversion technology. The gasification process is explained in Section 2.3, as well as the factors leading to the downdraft gasifier as a promising commercial technology for microgeneration. Using the arguments built in this section, a literature review methodology is presented in Section 2.4, to map the publications on microalgae biomass gasification. Extensive data regarding microalgae/gasification is compiled. The compiled data serves to map opportunities for the use of microalgae resource in conversion technologies. A conceptual scenario of using microalgae biomass for microgeneration in a surplus energy system is developed in Section 2.5, based on the data from the literature survey. Economic viability is discussed. Finally, knowledge gaps are highlighted in Section 2.6 in order to guide new studies, and optimization trends to enable the process. A flowchart presents the proposed final process, an optimized hybrid system incorporating gasification into the sewage treatment process.

2.2 Microalgae

In general, microalgae are unicellular organisms that use sunlight, water, and atmospheric CO_2 to grow. Their structure does not involve roots, a stem, and leaves as in plants. Their

general composition is lipid (9.5 to 42%), carbohydrate (17 to 57%) and protein (20 to 50%), in proportions that vary according to the species and growth conditions. Around 100,000 species have been identified, however, only 35,000 have been characterized [16,17]. Currently, only a few species are produced on a scale of hundreds of thousands of tons, such as *Chlorella*, and about ten additional species are commercially explored on a smaller scale. Although there has been commercial production of microalgae for many decades, current production is mainly focused on products of high commercial value, such as nutritional supplements and natural pigments [18]. The use of microalgae for the production of biofuel has only begun to attract interest in recent years, with the need for new sources of clean energy [17,19].

The production of microalgal biomass has several advantages compared to the traditional biomass of terrestrial cultures. Growth rates can be up to 100 times greater than those of terrestrial plants, doubling their biomass in less than a day [1,20]. This means less demand for land and the sustainable use of land. The cultivation of microalgae also does not compete with food production, which promotes more sustainable energy development [1,20]. Other advantages include the potential to grow microalgae in infertile areas, such as deserts and coastal regions, in saline waters, and brackish, and wastewater. Cultivation allows the incorporation of CO_2 generated in industrial processes, adding an extra benefit [16,17,21]. As a result, microalgae has become consolidated as an essential matrix for third-generation biofuels, opening a new dimension in the renewable energy industry. More than 150 companies worldwide, including large oil companies, are interested in producing biofuel from microalgae [22].

2.2.1 Media cultivation

According to Chen et al. [23], there are four main types of microalgae cultivation: phototrophic, heterotrophic, mixotrophic and photoheterotrophic. Phototrophic cultivation refers to processes where the microalgae use light as the energy source and CO_2 as the carbon source. In the heterotrophic cultivation, microalgae can grow not only under phototrophic conditions, but also in the absence of light, using organic carbon as the energy source. When the microalgae can use organic and inorganic carbon and it is able to live in both phototrophic and heterotrophic conditions, mixotrophic cultivation is under control. Photoheterotrophic involves the microalgae using inorganic and organic carbon, plus a light source. Heterotrophic conditions are most easily contaminated and the cost of an organic carbon source is another challenge for commercial production, due to the extra cost of the input [23]. Microalgae are thus normally cultivated under phototrophic conditions, using photosynthesis to capture light energy and fixing inorganic carbon in the form of CO_2 [24].

The growth and composition characteristics of microalgae under phototrophic conditions depend on cultivation variables such as carbon/nutrient sources and amount, irradiance intensity, temperature level, and pH values. Other operating variables are shear stress, inoculum conditions, and the type of reactor [1,25].

Microalgae can assimilate up to 150,000 ppmv CO_2, and as air contains only 360 ppmv, extra CO_2 is supplied to growth media either from external sources such as power plants or in the form of soluble carbonates such as Na_2CO_3 and $NaHCO_3$. Other inorganic nutrients required for microalgae include nitrogen and phosphorus [26].

The solar radiant energy captured by microalgae is used in the Calvin cycle to produce carbohydrates by utilizing CO_2 and H_2O molecules. A minimum of eight light photons are required to generate one mole of base carbohydrate (CH_2O) [26].

Solar energy is equally important to temperature control. Optimal growth takes place between 15 and 30 °C associated with pH, between 7.0 and 8.0 [1]. Simple changes in the environment might decrease microalgae productivity, and increase undesired competitive or predatory organisms [27]. Other factors such as the shear stress, inoculum conditions, type of reactor, and operating modes are thus important to maintain a homogeneous media cultivation and to minimize undesired organisms.

2.2.1.1 Wastewater as a cultivation medium

One of the main reasons to combine WWTP and microalgae cultivation is the high costs of the input. In traditional algal farms, it is common to use nutrients from chemical fertilizers and water from distribution systems. This decreases the system viability [6]. Indeed, microalgae usually require more nutrients for their metabolism than terrestrial plants. Nutrients such as phosphorus need to be added in large amounts to improve cultivation since a significant quantity is captured in the formation of complexes with ions [28,29]. For these reasons, the use of traditional nutrients is not considered sustainable, and a reduction in their use is imperative [30].

Some authors estimate that nutrients will become scarce in the future if agriculture does not change. Phosphorus deposits will be limited and the high nitrogen consumption will cause environmental pollution, such as an increase of NO_2 in the atmosphere and acidification of the environment [30]. Several authors have performed a Life Cycle Assessment (LCA) in processes involving microalgae and pointed out the use of nutrients in the crop as an important contributor to their environmental impact [31,32]. The valorization of sewage and by-products as a nutritional source has been considered as a possible alternative in order to reduce these impacts and make the process more sustainable [33–35]. If transporting nutrients and water is not necessary, a significant amount of money can be saved [36].

Microalgae grown in sewage has been reported as having high productivity [5]. Production in wastewater can be increased with the addition of CO_2 to increase the carbon and nitrogen ratio. The typical wastewater C:N ratio is to 7:1, which is low when compared to the microalgae ratio of 15:1 (C:N) [37]. Microalgae cultivation in wastewater can offer benefits beyond saving water and nutrients, such as nutrient removal from the effluent, the adsorption of heavy metals, generation of oxygen to bacteria and disinfection of the tank [4]. The effluent from anaerobic treatment, for example, have characteristics

that are promising for cultivation, such as low turbidity, which allows the passage of light, organic load and nitrogen predominantly in the ammonium form, best assimilated by microalgae [6].

2.2.2 Microalgae production

2.2.2.1 Systems

Microalgae production can be carried out in closed and opened systems (which have contact with the atmospheric air) [38].

Open systems are usually commercialized at a large scale since they are simpler and cheaper to construct and operate, however, they have low biomass productivity, higher sensibility to biological contaminants and, consequently, limited microalgae species cultivation [39]. Open systems require highly selective environments to avoid contamination from other microalgae species and protozoa. Monoculture cultivation is possible through the maintenance of extreme conditions, although few strains are suitable [26]. pH control can have plays an important role in the maintenance of a high standard in monoculture for certain species, such as *Spirulina* [1] since this species can grow under extreme alkalinity conditions where other organisms cannot live [26].

In commercial terms, high rate algal ponds (HRAP) are the most commonly used open system for microalgae production [18,40] and are designed to maximize production in shallow reservoirs [2]. In order to do so, depths between 0.15 and 0.45 m, typically 0.30 m, are adopted to guarantee light penetration [1], and a paddlewheel is used to improve circulation during the process.

Closed systems have been developed to overcome the aforementioned difficulties. Transparent systems known as photobioreactors (PBR), designed to optimize the growth of photosynthetic organisms, have been improved according to the economic and operational conditions of each project. For example, tubular photobioreactors are usually made of glass or transparent plastic, with a diameter of less than 0.1 m to allow light penetration even in high microalgae concentrations [29].

In comparison to HRAP, PBR allows the production of pure microalgae species [29], however, when the sewage is used as a cultivation medium, the production of pure species is difficult due to the presence of indigenous microalgae in the wastewater, which could grow [6]. Photobioreactors allow higher production than open systems due to the higher operational control (temperature control, low contamination levels, and high CO_2 trapping) [18,29,38], however the use of PBR on a large scale is limited due to the difficulty in exchanging O_2 and CO_2, and the high operation and installation costs that lead to a decrease in their economic viability [24]. Closed PBR is also not well developed for microalgae cultivation using sewage, and requires more study to achieve commercial production [38]. This is not true of HRAP, whose application in WWTP is nowadays relatively common in countries with hot climates [2]. The advantages and disadvantages

of each type of system are discussed by Adeniyi et al. [41] and this natural process presents low Capital Expenditures (CAPEX) and Operating Expenses (OPEX) in a large scale scenario. A comparison of the two systems is presented in Table 2.1, adapted from Rösch and Posten [42].

Table 2.1. Comparison between High Rate Algal Ponds and Photobioreactor.

Parameter	HRAP	PBR
Land footprint	High	Low
Energy requirement	Low	High
Temperature control	No needed	Required
Reactor cleaning	No needed	Required
Risk of contamination	High	Low
Product quality	Variable	Reproducible
Microbiology safety	No	Yes
Biomass productivity	Low	High
Capital and operational cost	Low	High

2.2.2.2 Productivity

According to Farag and Price [43], microalgae growth in batch cultures involves five different phases: the Lag Phase - initial period of slow growth; Exponential Phase - rapid growth and often cell division; Declining Relative Growth Phase - when a growth requirement for cell division is limiting; Stationary Phase - cell division slows due to the lack of resources necessary for growth; Death/Lysis Phase - cells begin to die due to lack of resources. Initially, the indigenous strain in wastewater is grown in batch mode but once the culture reaches the stationary phase, fresh wastewater is supplied continuously, resulting in a steady-state condition, and the beginning of harvest and productivity.

Different values of microalgae productivity in municipal wastewater cultivation are reported by Park et al. [44], with values between 12.7 and 35 g / m^2 / d for cultivation in many countries of the world. Posadas et al. [45] also present productivity within this range, with values of 17 g / m^2 / d for the cultivation in the summer and lower in the winter. Table 2.2 presents microalgae productivity using wastewater and open ponds. The productivity of pure species with other conditional parameters can be found in the review paper by Enamala et al. [46].

Table 2.2. Microalgal productivity in open ponds using wastewater.

Species	Areal productivity (g / m^2 / d)	Ref.
Actinastrum sp.	35	[44]
Micractinium sp.	33	[44]
Pediastrum sp.	25	[44]
Unknown	18.4	[44]
Chlorella sp. Ankistrodesmus sp.	18	[44]
Scenedesmus sp.	17	[45]
Coelostrum sp.	15.3	[44]
Unknown	12.7	[44]

2.2.3 Harvesting methods

The main difficulty in the harvesting stage is the large amount of water associated with the microalgae crop. It is precisely in the microalgal biomass recovery stage that the highest energy demand of the entire production system is concentrated [47]. This is one reason that microalgae cultivation for biofuel production is not yet economically viable. The high cost of harvesting, estimated at 30% of the total cost of biomass production [46,48], may reach 60% of the total biofuel production cost [49].

Developing a cost-effective harvesting method is the industry's biggest challenge. To become competitive, operating costs must be significantly reduced. Finding an alternative that allows the processing of large volumes of microalgae suspensions with minimal cost is essential in order to scale-up the process [18].

The large amount of water results in suspensions that may range from 0.1 to 5 g of total suspended solids (TSS) / L, and are often less than 1 g TSS / L in the effluents from open ponds. Normally, the production of large-scale algal biomass does not exceed 0.5 g / L, which means processing a huge volume of suspension to obtain a significant amount of biomass [47,50,51].

Other microalgae properties that make the harvesting process difficult are density - similar to water; particle size (between 2 and 50 μm); and the electrical surface charge, which is negative (between -7.5 and -40 mV) making the suspension dispersed and electrostatically stable, which prevents the self-aggregation of particles [47,49,50]. This surface charge arises predominantly from the presence of carboxyl groups (-COOH) on the cell surface. At pH values above 4.5, these groups dissociate and become negatively charged [18].

Currently developed technologies for microalgae separation are based on filtration, centrifugation, flotation, and flocculation, or some combination of those methods [52].

The centrifugation process is the fastest and most reliable process, and is indicated to harvest microalgae from pure cultures to recover high-value products such as natural pigments [47], however this method is the most energy intensive and is economically

unfeasible at large scales for biofuels [18,49]. The filtration process is cheaper and presents low efficiency to obtain microalgae in large quantities.

The flotation process using microbubbles is notably more unstable and inefficient for microalgae harvesting [47].

A variety of physical, chemical and biological strategies have been developed to harvest microalgae via flocculation processes. These options can be applied upstream of other processes, aiming to concentrate the biomass and reduce the costs of the following stages [47]. The flocculation process allows concentration of the diluted solutions of 0.5 g / L up to 100 times, forming a liquid and viscous sludge with 50 g TSS / L [18]. The TSS concentration achieved after harvesting is between 2 and 7% of the microalgae in sludge [17]. A downstream dewatering process, such as centrifugation, is required to obtain a cake with 25% of dry material. The energy demand, in this case, is acceptable since the agglutinated microalgae particles are bigger and the volume processed is smaller [18].

For example, more than 95% of the energy required in microalgae centrifugation can be saved if there is a pre-concentration stage with specific coagulants. Due to the potential to treat high inflows, the cost of the process is also cost-effective, and many types of flocculants have been applied [47]. Flocculation usually allows dewatering processes to produce cakes with a total solid concentration with 10 to 30% [51].

Since flocculation allows the fast treatment of large volumes [48], and based on its operational costs, efficiency and technological possibilities, it is currently the most economical and efficient method to harvest of microalgae [47,50,53].

Most microalgae flocculation studies have involved a single species under particular conditions, however flocculation depends on the surface properties of cells and these properties differ between species and vary within the same species depending on culture conditions [18]. Ideal coagulant concentrations may therefore vary significantly from design to design. Values such as 200 mg / L ferric chloride are reported to harvest *Chlorella sp*. [54] and 5 mg / L cationic polymer to harvest *Chlorella vulgaris* [48]. Jar test assays will determine the optimal dosage of coagulant.

Despite its advantages, chemical flocculation incorporates chemical compounds into the biomass. Changes in harvested biomass staining and in the culture medium, have already been pointed out [50]. Aluminum salts can cause cell damage, while iron salts affect the quality of pigments, especially chlorophyll. Aluminum chlorides can inhibit transesterification reactions and impair biodiesel production with biomass [47]. Aluminum sulfate and ferric chloride can also negatively affect anaerobic digestion and biogas production [53]. It is worth noting that the physicochemical characteristics of the biomass harvested, in addition to being dependent on the microalgae species present, are also affected by the culture medium and the harvesting process [22]. The harvesting process should thus be chosen to integrate the downstream treatment stages and biomass conversion, and not only in an isolated form.

Table 2.3 presents dry biomass concentrations obtained in the major microalgae harvest processes described by Shah et al. [55]. Each process received a score for their efficiency

and economy according to Al Hattab et al. [56]. Eight criteria were used for evaluation: (a) dewatering efficiency (b) cost (c) toxicity (d) suitability for industrial-scale (e) time (f) species specificity (g) reusability of media and (h) maintenance. Each criterion was assigned a score between 7 and 15 based on its degree of importance. Higher values were given to the criteria that were deemed most important for the development of an efficient and economic largescale dewatering method for microalgae. Coagulation with organic chemical compounds and centrifugation were the only processes with a total score over 80, suggesting that the methods could be a good combination in order to obtain a more efficient and cost-effective harvesting solution.

Table 2.3. Comparison of microalgae harvesting techniques.

Harvesting Techniques	**Dry solids output concentration (%)**[55]	**Process**	**Score** [56]
Sedimentation	0,5-3	Sedimentation	61
Flotation	7	Dispersed air flotation	77
		Dissolved air flotation	70
Chemical coagulation	3-8	Inorganic coagulation	65
		Organic coagulation	80
Centrifugation	10-22	Disc stack centrifugation	87
		Decanter centrifugation	80
Filtration	2-27	Pressure filtration	74
		Vacuum filtration	75

2.2.4 Drying

The last stage in algal biomass production is drying the wet paste obtained in the harvest process. In general, the moisture is reduced to a 12-15 wt.% content in which the biomass can be stored [57]. The drying stage is normally carried out to extend the life use of the material and needs to be done quickly after harvest, so that the biomass does not spoil [58].

There are many drying systems, which differ in cost and energy demand. The selection of method will depend on the operation and scale of the biomass [57]. For instance, solar drying is the cheapest method of microalgae drying, however it requires a long time and large areas. In this case, part of the energy content of the biomass and some specific compounds can be lost [59].

More efficient and expensive methods to dry microalgae have been studied, such as drum drying, spray drying, fluidized bed drying, freeze-drying and refraction window dehydration technology [59]. Freeze-drying, or lyophilization, has been largely used to dry microalgae in labs, however, the method is very expensive for use at a large scale. Spray drying is the method chosen for products that have high value [58], and rotary kilns

are currently commonly used to dry sludge and biosolids [60], and, as pointed by Bennion et al. [61], to dry microalgae.

2.2.5 Conversion technologies *vs*. fraction converted

Microalgae can be converted into products using a mechanical process for oil extraction, biochemical processes for biogas and alcohol production, and thermochemical processes producing oil, gas, and heat. The selection of the right conversion technology is a key step in ensuring a viable and environmentally sustainable production process [16].

2.2.5.1 Mechanical extraction

There has been a recent resurgence of interest in microalgae as an oil producer for biofuel applications. The extraction of oil is conditioned by the lipid content of the microalgae and not all species have satisfactory amounts, with as low as 2% in *M. aeruginosa* species [62]. Lipids content in microalgae may vary from 1 – 85% of the dry weight, and factors such as nutrient availability have been shown to affect lipid content in many microalgae. When nitrogen deprivation is imposed, for example, photosynthesis continues more slowly, and the flow of fixed carbon is diverted from protein to either lipid or carbohydrate synthesis. Lipid accumulation can be initiated in microalgae by imposing nutrient deficiency like N, P, and K but also reduces growth rates [63]. In general, species with higher lipid content have a slower growth rate [62]. High nutrient (N and P) wastewater crops, such as sanitary sewage, can also inhibit lipid accumulation [64]. The cost of microalgae biodiesel production in the conventional process is still very high, around U$8 per gallon, double the of soy biodiesel [4]. Chisti [29] suggests that, just like a petroleum refinery, a biorefinery could be used to take advantage of each component of microalgae, not just lipids, as a way to cut costs.

2.2.5.2 Biochemical processes

Another route to the recovery of energy from microalgae is reached by biochemical processes, however, they require a long reaction time and involve less conversion than thermal processes [65], so the industry generally does not choose these processes [1].

The production of bioethanol by fermentation involves long processing stages, as they depend on the enzymatic and cellular activities that make up the biochemical processes. The need for pre-treatment in the feedstock also increases the cost of production and only one final product is obtained [1]. The carbohydrate content of alcohol production is also relatively low in microalgae [4].

The degradation of microalgae is incomplete, and involves low biogas production, for anaerobic digestion at 35 ºC. Improvement is only found at a higher temperature, where

the cell wall is broken, exposing its intracellular content to the bacteria. Another difficulty is that the C/N ratio of this biomass is low and does not favor anaerobic digestion [65]. The process provides only partial degradation of the biomass and the use of partially degraded microalgae as a substrate is not viable because it interferes in the metabolism of organisms, and should be avoided owing to its potential to generate sulfides [66].

2.2.5.3 Thermochemical processes

Thermochemical conversion is the most direct path to transforming biomass into different forms of energy [67]. The process involves the thermal decomposition of the organic compounds present in the biomass to produce biofuels [1]. The main advantages are the conversion of whole biomass regardless of the type of macromolecule present [68], high efficiency and low conversion time [69]. This type of conversion can be done by pyrolysis, liquefaction, and gasification, and is applied more commonly than biochemical conversion [1].

The major challenge of pyrolysis is the need to purify the oil produced and the salt content involved in liquefaction is problematic [36]. These techniques are also immature and require considerable development before large-scale application. In contrast, biomass gasification is a well-developed technology and has been applied for decades [65].

Gasification seems to be the most advantageous process. The production of fuel gas makes the subsequent stage of energy generation more direct, simple and compact. Gasifiers coupled with internal combustion engines and generators are already commercialized with high conversion efficiencies [70].

Other processes require intermediate stages, increasing system complexity to an undesirable level, such as with alcohol, biodiesel and steam production, which demand distillation columns, transesterification reactors, and boilers, respectively. Anaerobic digestion does not involve an intermediate conversion process since microorganisms convert biomass directly into biogas, however, only the biodegradable organic fraction of biomass is converted into biogas, and the non-biodegradable organic fraction would need to be removed periodically and sent to final disposition, implying in extra costs.

Gikas [71] compared anaerobic digestion and gasification processes, such as energy recovery systems with sewage sludge produced in a pilot WWTP, with a 380 m^3/d flux capacity. To reduce energy demand in the WWTP, the author developed a different WWTP model, substituting the aerobic process, high in energy consumption, with microwaving and filtration. According to the flowchart developed, the sludge obtained was dewatered in an auger press until 55% humidity. A rotary kiln then reduced the humidity of the solids to 20%, in order to condition the feed to the gasification process. The gas produced fed an internal combustion engine, generating electricity. In the anaerobic digestion system, the dewatered sludge generated biogas in an anaerobic reactor, with 60% of converted organic fraction. When the author compared both systems,

gasification had a more favorable energy balance, even considering the drying energy requirement.

Table 2.4 compares the differences between the main routes of biomass to energy conversion discussed in the text.

Table 2.4. Comparison between the main routes of biomass to energy conversion.

Process	Conversion Time	Conversion Fraction	Biomass Requirements	Final Product	Technology
Extraction	Fast	Partial	High lipid	Oil	Mature
Fermentation	Slow	Partial	High carbohydrate	Alcohol	Mature
Anaerobic digestion	Slow	Partial	High biodegradable	Biogas	Mature
Liquefaction	Medium	Partial	Low salt	Oil	Immature
Pyrolysis	Medium	Total	-	Oil/Gas/Char	Immature
Gasification	Fast	Total	Low moisture	Gas	Mature

2.3 Thermal gasification process

Gasification is a partial oxidation thermochemical process in which carbonaceous substances are converted to gas in the presence of a gasifying agent - usually air - oxygen, water steam, carbon dioxide or mixtures thereof [72]. The flow of the gasifying agent is controlled and partial oxidation takes place [73]. The objective of the process is to produce a highly efficient clean gas synthesis (syngas) [5]. Syngas production can vary from 1 to 3 m^3 / kg of dry biomass [74]. Syngas consists mainly of CO and H_2, mixed with other components, such as CH_4 and CO_2. It may include some light hydrocarbons, such as ethane and propane, and also, heavy hydrocarbons such as tar, condensable between 250-300 °C. Small particles of solid coal waste, alkali metal species, ash and other gases, such as H_2S, HCl, NH_3, H_2O, and N_2, may be present in small quantities. The presence of these gases depends on the characteristics of the biomass, the gasifying agent, the process conditions and the type of gasifier [72,74–76].

The gasifier is the main component of a gasification plant and the biomass and gasifying agent reactants are mixed therein so that the reactions can occur. In some cases, catalysts, additives and inert materials are also fed into the process to improve their performance. The manner in which the reactants come into contact in the gasifier affects the performance of the process and forms the basis for classifying the gasifiers [75].

Two typical gasifier configurations with a fixed bed are updraft and downdraft [72]. In the first, the solids move down relative to the gasifying agent, and the syngas produced move upwards. In the second configuration, both the solid and the syngas are moved downwards [74]. In this reactor, the pyrolytic gases pass through the oxidation zone at high temperatures as the syngas is removed from the bottom of the equipment, and

therefore almost all tar is converted to gas and the syngas is much cleaner than that generated in updraft gasification [76].

The updraft reactor is the oldest model and involves more simplicity and lower costs [75]. This equipment can gasify most of the biomass, however, the syngas produced in these systems contains high quantities of tar, between 10 and 20 wt.%, and therefore, these gasifiers are not suitable when one desires to use syngas in the internal combustion engines [76]. On the other hand, in downdraft gasifiers, tar production can be inferior to 1 wt.% [74,77], making this process preferable to electricity generation in engines and turbines [76].

Fluidized bed gasifiers and other gasifiers variations are also reported in the literature. Gikas [71] shows a horizontally disposed rotary cylindrical gasifier developed by Greene Waste to Energy S.L. (Spain), which allows each stage of the process of gasification to be controlled, increasing the performance of the equipment. In each internal area of the equipment, stirrers homogenize the flux during the process and a thermal jacket covers the equipment controlling all thermal exchanges.

Recent publications involving the gasification process have been addressed in literature review studies. Ruiz et al. [72] reviewed the main factors to be considered in the gasification process, and pointed out the barriers to the generation of electricity. Asadullah [76] reviewed the barriers of each stage of the gasification process, from the collection of biomass to the generation of electricity, and noted syngas cleaning as an important step. Heidenreich and Foscolo [73] provided a detailed review of new concepts of gasification, such as the UNIQUE gasifier, which integrates gasification with syngas cleaning in a single reactor. Abdoulmoumine et al. [78] presented a review of the methods of purification of syngas, discussing the removal of the main contaminants. Molino et al. [74] detailed the gasification technologies, assessing advantages and disadvantages and the potential for use of syngas. Ahmad et al. [75] highlighted the characteristics and performance of different types of gasifiers over different operating parameters, and discussed the economic evaluation of the gasification process. Despite the difficulties pointed out and the challenges still to be overcome, the potential advantages of the biomass gasification process continue to motivate research.

2.4 Microalgae gasification: a systematic review

We used the method developed by Ensslin et al. [79], known as the Proknow-C method, Knowledge Development Process - Constructivist to map the research on microalgae gasification. It is a systematic approach used to organize the information collected in the literature and includes the construction of knowledge in three main stages: preparation of a bibliographic portfolio, bibliometric analysis, and systematic analysis. Articles are selected from defined databases using keywords, then filtered based on specific criteria, such as alignment with the topic of interest and scientific relevance. Finally, redundant and unavailable papers are eliminated [80]. After the establishment of the bibliographic

portfolio, a systematic analysis is conducted in order to elucidate points of interest and gaps to be filled in current research.

The keywords adopted in this review were "microalgae" and "gasification". The SCOPUS database was chosen because it is the largest database [81] of abstracts and citations of literature reviewed, including scientific journals, books and conference work. According to Ferenhof et al. [81], the SCOPUS database had 15,000 indexed newspapers, almost 265 million websites and 18 million patents and other documents in 2014. The database is thus able to provide a comprehensive view of the outcome of the worldwide survey.

169 documents were found in the SCOPUS database on September 2018, the first of which was published in 1991 [82], however the topic has only gained more relevance in the literature in the last decade, and notably in the last five years. The number of documents was reduced to 121 when only journal articles with an impact factor greater than 1.0 were selected. The titles and summaries of these papers were read in order to select only the studies involving the experimental thermal gasification of microalgae. Macroalgae, residual microalgae after extraction of compounds, such as lipids, and non-experimental studies were not considered. Forty-two articles were thus selected and, after careful reading, seven additional references, not included in the SCOPUS but fitting with the criteria of paper selection. were added to the bibliographic portfolio, which was finally composed of 49 documents [28,30,62,64,65,68,83–125].

2.4.1 Species gasified

Despite the variety of known microalgae species (thousands), only 19 different species of microalgae (and *Spirulina cyanobacterium*) have been studied for gasification (Fig. 2.2). Considering the variety of existing and known species, this number is very low and clearly illustrates current ignorance on the subject. It is believed to be related to the ease of culturing and the rate of growth of certain strains.

Among the 19 species of microalgae and cyanobacteria reported, there is a predominance of the *Chlorella Vulgaris* and *Spirulina* commercialized species, used in 50% of the experimental gasification studies. In fact, most of the authors (72%) acquired the microalgae in powder or paste form, and the biomass harvesting process was not clear. Because these species are mostly used in the food industry, it is believed that the harvesting processes employed were not based on the incorporation of products for coagulation-flocculation, to keep the biomass free of chemical contaminants. In today's commercial microalgae systems, despite being expensive and energy-intensive, centrifuges and filters are the most commonly used equipment [126]. In order to obtain bulk products of lower value, such as biofuels, however, the investment and operating costs of these processes compromise the economic viability of the projects [127]. At large scales, the most efficient method of microalgae separation is coagulation-flocculation-sedimentation [53]. Even so, no author evaluated the biomass obtained by coagulation-flocculation and the effect of the chemicals mixed with the biomass on the gasification process. The few authors who reported on microalgae culture and harvesting themselves

adopted incompatible techniques in the context of a large-scale industrial process, such as the scaling of the decanted bed at the bottom of the pond, centrifugation, vacuum and membrane filtration and electro flocculation (Table 2.5). The combination of the coagulation and centrifugation processes, described in Table 2.3 as the highest score, is not reported.

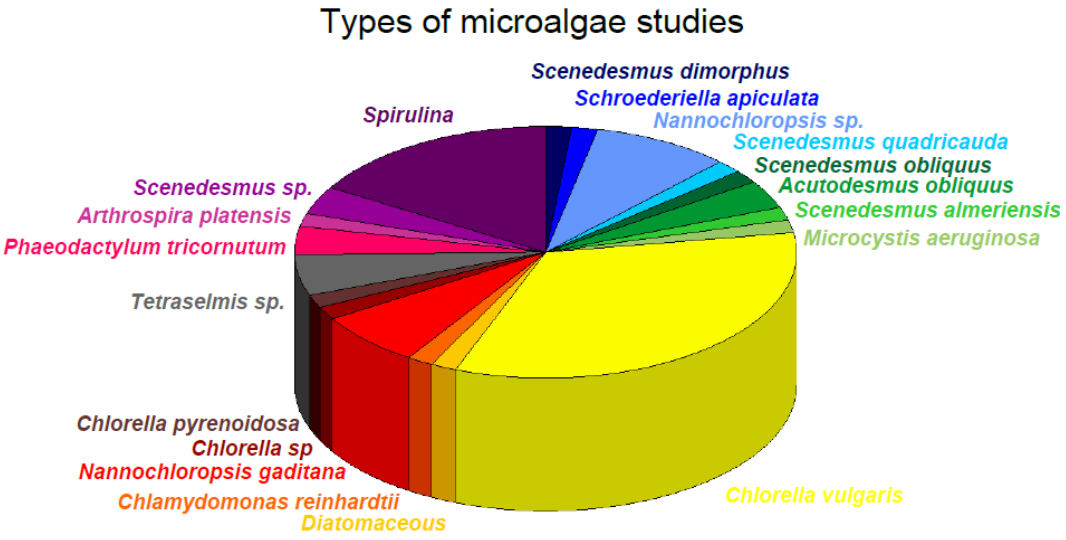

Fig. 2.2. Types of microalgae and cyanobacteria studied in gasification.

Table 2.5. Methods of harvesting microalgae reported.

Microalgae	Harvest Methods	Ref.
Scenedesmus sp. cultivated in sewage	Spontaneous decanting	[65]
Scenedesmus sp. cultivated in sewage	Spontaneous decanting	[4]
Chlorella vulgaris	Vacuum Filtration	[128]
Algae biomass cultivated in sewage	Scraping the bottom of the pond	[64]
Chlorella vulgaris	Centrifugation	[22]
Chlorella vulgaris	Centrifugation	[22]
Tetraselmis sp.	Electro flocculation and centrifugation	[129]
Tetraselmis sp., Schroederiella apiculata and Scenedesmus dimorphus	Centrifugation	[119]
Microcystis aeruginosa	Filtration with membrane	[64]
Chlorella sp.	Centrifugation	[118]

Only three marine species were reported, *Nannochloropsis gaditana*, *Nannochloropsis sp.* and *Tetraselmis sp.*, which together contributed only 21% of the total papers. One

explanation for this may be the higher salt and ash content of marine microalgae, which may hinder the gasification process or require additional pretreatment steps such as washing to remove excess salt. Marine microalgae also typically exhibit lower conversion than freshwater species in some gasification process, although the comparison is made difficult by the different process conditions [106].

The gasification of microalgae grown in wastewater was studied by a few researchers, such as Zhu et al. [65,130]. In these two publications, they used *Scenedesmus sp*. obtained in stabilization ponds fed with industrial and municipal sewage. Sharara and Sadaka [64] recovered a microalgae biomass comprised of native and *Diatomaceous* species in a stabilization pond applied to sewage treatment. The treatment systems were not detailed in terms of configuration and performance, or the characterization of the sewage introduced into the ponds.

To the best of our knowledge, there is an important gap in terms of research in this area. Most gasification studies refer to pure microalgae species, even with sewage cultivation being suggested as the most promising way to convert microalgae into biofuels. The cultivation of pure species in photobioreactors using water and fertilizers does not appear to be the most viable path for biofuel production, for the reasons discussed in Section 2.2. This paper considers biomass as a mixture of microalgae, bacteria, and chemical coagulants, and the gasification process for this type of biomass is still little reported in the literature.

2.4.2 Characteristics of biomass

Different types of microalgae have different compositions (Table 1 in Appendix A), which are normally reported in terms of their proximate analysis, elemental analysis, macromolecules, and higher heating value (HHV).

Proximate analysis can be defined as a technique to measure the chemical properties of a compound based on four particular elements: moisture content, fixed carbon, volatile matter and ash content [131]. These characteristics affect the syngas yield and quality [106]. The analysis of ash and its components were predominant in the discussion of the experimental results, as used to justify the kinetic performance, the conversion and the composition of the syngas. This is because the different chemical elements present in the ash can affect the process in various ways, such as acting as a catalyst, catalyst promoter, catalyst support or sorbents in the gas cleanup. Abdoulmoumine et al. [78] compiled these effects into a Periodic Table, indicating the effect caused by different chemical elements in the process. The average ash content was 14.3%, while the fractions of volatile material and fixed carbons were 66.5% and 14.7%, respectively. Disregarding seawater species, the average ash content is reduced to less than 12%. The species of saline microalgae *Tetraselmis sp*. presented the highest ash content, with 64.4%.

An elemental analysis defines the mean chemical elements present in biomass, which are carbon, hydrogen, oxygen, nitrogen, and sulfur. The higher proportion of oxygen and

hydrogen, compared with carbon, reduces the energy value of a fuel, due to the lower energy contained in carbon-oxygen and carbon-hydrogen bonds, than in carbon-carbon bonds [132]. The presence of oxygen in the biomass reduces its calorific value [77,133], and the presence of sulfur and nitrogen can lead to process contaminants such as HCN, NH_3, CS_2, and H_2S [78]. Of the 34 articles that reported microalgae sulfur content, only six reported a higher percentage than 1% [94,117,119,129,134,135]. The low sulfur content of the algal biomass is an advantage since the thermochemical conversion of biomass can release sulfur in the form of H_2S, a corrosive gas for equipment. According to Molino [74], the maximum sulfur levels in the syngas allowed for use in internal combustion engines and turbine are 20 ppmv. This means that the use of such equipment in electricity generation systems could be limited to high H_2S content. Table 2.6 shows typical engine and turbine requirements for the major syngas contaminants. The elemental analysis results in 46% carbon, 7% hydrogen, 30% oxygen, 8% nitrogen and 1% sulfur. The species of saline microalgae *Tetraselmis sp*. presented the highest sulfur content reported, 6.9%.

Table 2.6. Syngas contaminant limits in equipment.

Equipment	Tar (mg/m^3)	Sulfur (ppmv)	Nitrogen (ppmv)	Alkali (ppmv)	Halides (ppmv)	Particulate (mg/m^3)	Ref.
Turbine	-	< 20	< 50	< 0,02	< 1	-	[78]
Turbine	< 10	< 20	-	< 0,025-0,1	-	< 2,4	[74]
Engine	< 100	< 20	-	< 0,025-0,1	-	< 50	[74]

The composition of the microalgal biomass in terms of macromolecules, as reported by Onwudili et al. [106], means that carbohydrates form H_2 more easily than lipids and proteins. The latter are responsible for inhibiting some reactions of hydrogen formation. Few studies have quantified the levels of protein, carbohydrate and lipid in the biomass to be gasified. Without stratified chemical species present in the biomass studied, the average values of the protein, carbohydrate and lipid levels of microalgae were 46%, 19%, and 19%, respectively. Shumbulo Shuba and Klife [4] compiled information about carbohydrate, protein and lipid microalgae composition in different species and found a wide variation.

Table 1 in Appendix A also presents the HHV content for different microalgae. The mean HHV established was 18.93 MJ / kg. This characterization corroborates the interest of converting microalgae to energy, considering the energy content and high carbon content. Table 2.7 shows a comparison with the calorific value of other fuels, demonstrating the significant amount of energy from microalgae biomass, and its superiority to wood.

Table 2.7. Energy comparison between different fuels.

Fuel	MJ/Kg	Ref.
Gas-oil	45.5	[5]
Natural Gas (NTP)	38.1	[74]
House coal	27 - 31	[74]
Microalgae	18.93	Table 1. in Appendix A (average)
Plastics, wood, paper, rags, garbage	17.6 - 20	[5]
Wood	12 - 19	[74]
Dry sewage sludge	12 - 20	[5]
Black liquor	12.5 - 15.5	[5]

2.4.3 Gasifiers for microalgae gasification

Of the 49 papers evaluated, 29% are simulations of gasification in a thermogravimetric analyzer (TGA). These studies were not considered as gasification experimental tests since the conditions of this equipment do not reflect a realistic scenario of the process. Only 16 papers were found for conventional gasification, less than one-third of the total, [64,65,88,92,94,101,105,107,110,112,113,115,117,119,121,122]. Of those, only six used fixed bed gasifiers, a very low number, considering the greater simplicity, and operational and economic advantages of this equipment [105,110,112,117,119,136]. This may be related to the lower syngas quality obtained in these reactors when compared to other technologies, however it is possible to adjust operational parameters to reduce the contaminants in the product.

A small predominance of studies used fluidized bed gasifiers. Manara and Zabaniotou [5] pointed out that the fluidized bed gasifiers allow a better mass and energy exchange, as well as a homogeneous heat transfer at a higher velocity, facilitating the reaction and reducing the residence time of the load [76]. The process has the advantage of allowing consistent temperatures, kept well below the problematic levels that could lead to the synthesis or accumulation of ash, however these reactors are more operationally sensitive to the type of biomass [72]. The high ash content of some microalgae may limit the use of this technology, due to problems such as defluidization and bed agglomeration, as observed in [137].

According to Alghurabie et al. [137], there are several operational difficulties when gasifying a marine species of microalgae with high ash content, due to the high salt content in these species of microalgae. Freshwater species may also have high ash content in their composition, depending on the culture medium and harvesting processes. This was demonstrated by Zhu et al. [65], for example, during the gasification of the species *Scenedesmus sp*. The authors associated the high ash content after gasification with the cultivation of the species in industrial and municipal wastewater and the harvesting conditions. The high silicon content observed could be related to contamination from sand and other minerals during the cultivation and harvesting processes in the ponds. Elliot et

al. [125] reported a high ash content in the microalgae gasification residue and associated it with mud contamination during the harvest stage.

Hydrothermal processes correspond to 55% of the studied processes in the publications analyzed. The high interest in hydrothermal processes is due to the use of humid biomass, without the need for drying. Conventional gasification requires low moisture biomass, which consumes a lot of energy and reduces efficiency to uneconomic levels [134]. Hydrothermal gasifiers, which adopt fluids under supercritical conditions of pressure and temperature, therefore have a higher thermal efficiency than conventional gasifiers. The process with water also produces less tar [3], which is considered a critical point of biomass gasification [74].

Hydrothermal gasification occurs under pressure and the formation of hydrogen or methane can be prioritized depending on the temperature and the catalyst used. At moderate temperatures (below 500 °C), catalysts are required in order to increase the conversion. Ruthenium is singled out as the most active and selective catalyst for generating methane, however the deactivation of ruthenium by sulfur has been pointed out as a problem, and attempts at regeneration [22] and reuse [138] have been unsuccessful. Hydrothermal gasification is also still under development [16] and is considered a very expensive process for implantation and operation [83]. For this reason, Elliot et al. [125] believed that more research is needed before scaling the technology to a commercial demonstration level. One of the challenges is the presence of salt in these reactors, which can cause corrosion and clogging [36]. The water itself is corrosive under supercritical conditions and high levels of nickel have been observed in the residual liquid of the process, indicating corrosion of the reactor wall [83].

Due to the severe conditions of the process, metals can also be washed from the catalyst. The incorporation of heavy metals and organic compounds makes it difficult to manage large volumes of residual liquid. Attempts to re-use this liquid as a nutritional medium in the cultivation of microalgae have encountered many difficulties. Haiduc et al. [134] found that a nickel concentration of 28 ppm completely inhibited the growth of the microalgae species studied. According to Bagnoud-Velásquez et al. [135], aluminum may form relatively inert complexes, which interfere with cell metabolism. Phosphorus becomes unavailable for enzymatic transport when complexed with aluminum, so that the growth rates of microalgae are inhibited. Patzelt et al. [30] identified at least 28 toxic organic compounds that could cause inhibition in the growth of microalgae, requiring dilution of 1 to 355 to allow the cultivation. Onwudili et al. [106] indicated an even greater dilution, from 1 to 400, due to the presence of phenol. The amount of water for dilution would exceed the capacity of the culture medium of an integrated gasification process and would not be a satisfactory option [30]. A treatment step would thus be necessary to reduce the harmful compounds to tolerable levels.

Elsayed et al. [139] used activated carbon and ultra-violet radiation treatment systems to remove most of the pollutants from the liquid, but they observed a delayed growth of microalgae. Patzelt et al. [30] used the same treatment processes and noted that desirable compounds are also removed, especially nitrogen in the ultraviolet treatment by ammonia volatilization. A 79.6% decrease in nitrogen content and an important limitation of

phosphorus in the feed liquid of the process were observed. Minowa and Sawayama [28] observed a growth of only one-eighth of that expected, for cultivation in recovered and treated solutions of the gasification process, assigning the problem to the lack of nutrients in the diet. The authors suggested the integration of preliminary stages of salt separation, common in hydrothermal processes, with the culture stage, aiming to reuse the salts and supply these nutrients, however such integration would mean even greater plant complexity and higher costs.

Catalysts commonly used to increase the conversion of these processes also increase the complexity of these systems, since compounds present in the biomass rapidly deactivate the catalyst, especially sulfur [22]. The process is also not fully developed, due to the extreme pressure and temperature conditions required [119]. The critical point of the water is 374 ºC and 22 MPa [140].

In contrast, the common gasification of biomass has been well developed and applied for decades. Nevertheless, the technological bottleneck represented by the need to reduce the moisture content of the biomass previously fed in the process remains. The microalgae drying method, based on the circulation and reuse of heat, could considerably reduce energy consumption [121]. In this sense, several drying technologies have been developed [141].

The equipment used in the experiments was practically all on a laboratory scale. Only the experiments of Yang et al. [92] were performed on a larger pilot scale, adopting a bubbling fluidized bed gasifier of 30 kW. Other models of gasifiers, including the more traditional ones, such as the fixed bed downdraft and updraft, have not yet been experimented with on a pilot scale. These reactors have simpler operations and designs, which makes them the preferred and most feasible option for small power generation units [73,76].

Tables 2 and 3 (in Appendix A) compile the information found for hydrothermal and conventional gasification, respectively. The tables include operational parameters, equipment dimensions and some results in order to introduce a summary view of the literature. The gaps in the tables are due to non-available information. In general, it may be noted that the carbon conversion of the process is greater in conventional gasification than in hydrothermal gasification, and tar levels are often not reported.

2.5 Results and discussion

A microgeneration scenario in a WWTP is built in this section, considering the premises that are more similar to a real scale scenario, as described in the text.

Premises:

- Microalgae production in HRAP using domestic sewage as a nutritional medium;
- Use of the flocculation process in the biomass harvesting process;

- Production of mixed biomass composed of different species of microalgae, bacteria and chemical coagulant;
- Use of rotary kilns to dry the biomass to reach the maximum limit of moisture allowed in the gasifier;
- Conversion of biomass to energy through a thermal gasification process using a conventional downdraft gasifier.

Scale:

- The construction of ponds to wastewater treatment is more common in less urbanized places with more area available and smaller demographic density [2]. In Brazil, 70% of cities have less than 20,000 inhabitants [142], therefore, it was estimated the design of a WWTP for 20,000 people;
- Using a per capita sewage flow rate of 150 L / day, as suggested by Sperling [2], it is equivalent to a sewage flow of 3,000 m^3 / day.

Figure 2.3 presents the WWTP model with microgeneration proposed in this study with high rate algae pond cultivation, using the Upflow Anaerobic Sludge Blanket (UASB) effluent.

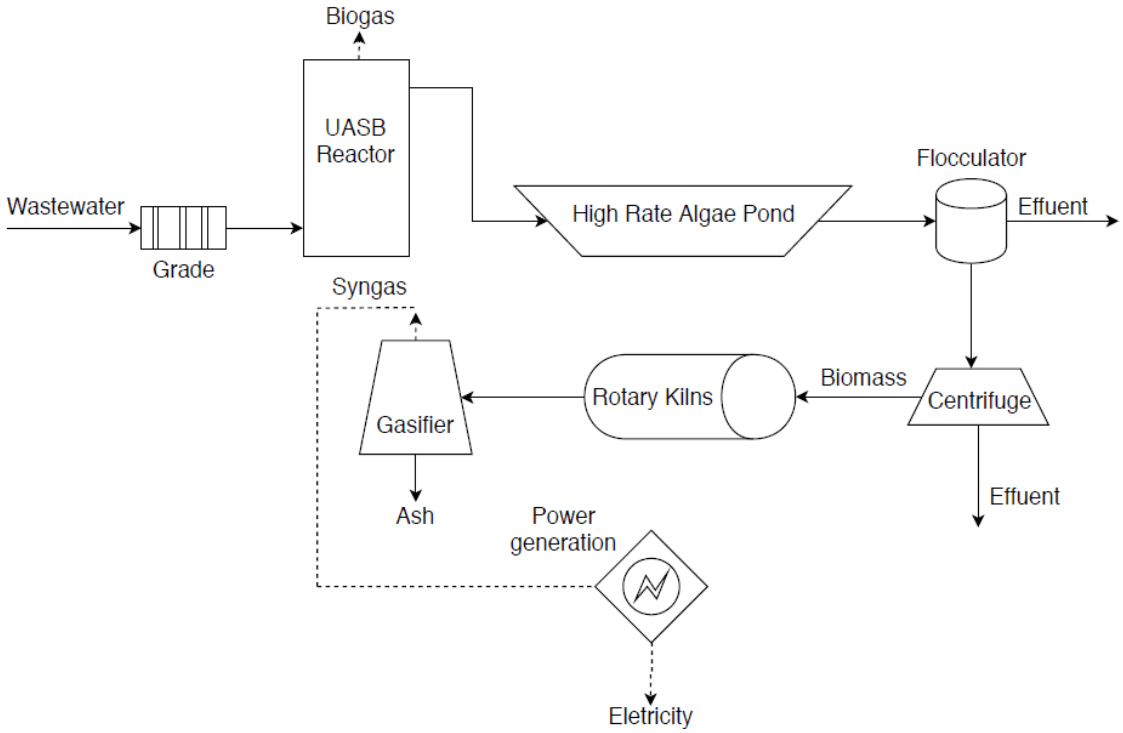

Fig. 2.3. WWTP model with microgeneration.

The UASB reactor is commonly applied in Brazil and the association of both treatment systems results in better effluent quality when compared to a single system. Since the anaerobic process does not remove nutrients to any great extent, there is no harm to the

microalgae production [2]. On the contrary, the effluent nitrogen is predominantly in the ammonium form, which facilitates microalgae assimilation and low turbidity facilitates light penetration in the medium [6]. Another advantage of this association is that the anaerobic reactor does not need a supply of energy for its function, as it also produces biogas, an important additional source of energy, due to the high energy demand in the biomass algae drying process.

2.5.1 Modeling the conceptual scenario

2.5.1.1 Microalgae production estimation

The microalgae-bacteria biomass production in high rate algal ponds can be estimated, according to Park et al. [44], from the maximum photosynthetic conversion rate of sunlight (Equation 2.1).

$$Pba = I_o \,.\, n_{máx} \,/\, H \tag{2.1}$$

Where:

Pba = Production of microalgae-bacteria biomass (g / m².d);

I_0 = Average solar radiation (MJ / m².d);

$\eta_{máx}$ = Maximum photosynthetic conversion efficiency of sunlight (%);

H = Energy value of the biomass as heat, calorific value (kJ / g).

The maximum conversion efficiency of light through photosynthetic processes adopted was 2.4%, according to Park et al. [44]. The smallest annual solar radiation index for Brazil is 16 MJ / m^2.d, according to the Solarimetric Atlas of Brazil [143], and the highest energy value of microalgae indicated in this work, is 23.2 MJ/kg. Both values were adopted in order to obtain more conservative biomass productivity. The calculated biomass production is thus 16.55 g / m^2.d. This value is in accordance with the values reported by Posadas et al. [45] and Park et al. [44] present in Table 2.2.

The superficial pond area, needed to define the total biomass produced in a day, can be calculated according to Mascarenhas et al. [144] (Equation 2.2).

$$A = Q \,.\, HRT \,/\, HL \tag{2.2}$$

Where:

A = surface area of the pond (m^2);

Q = tributary flow (L / d);

HRT - hydraulic retention time (d);

HL = height of water depth (m).

A depth of 0.3 m and a hydraulic holding time of four days, as used by Park et al. [37], were considered. The surface area of the pond required is four hectares, which means an approximate production of 860 kg / d of dry microalgae-bacteria biomass.

2.5.1.2 Power generation evaluation

The energy productivity of a gasifier is a function of the biomass physical-chemical characteristics, such as elemental composition, ash content, calorific value and density. In general, productivity around 1 kWh / kg of dry biomass is assumed, which is similar to wood [145].

Downdraft fixed bed gasifiers are more viable for small scale applications because of the easier fabrication, operation and smaller tar content in the syngas produced, which simplifies a gasifier internal combustion engine system. These gasifiers are not the most suitable for the gasification of high ash biomass, since the process may become slower and more problematic, requiring the adjustment and installation of additional equipment [76], however it is not a concern for microalgae gasification since the ash content is generally low, as shown in Table 1 in Appendix A, although there are some exceptions. The carbon conversion of these conventional processes was also greater than that of other processes, as reported in Tables 2 and 3 in Appendix A. Hydrothermal gasification still needs to overcome several challenges, in any case, as described in Section 2.4.3. Downdraft fixed bed gasifiers integrated with the electricity generation system with biomass have also already been commercialized. Typically, these gasifiers have capacities that vary from 10 kW until 1 MW and are viable only to biomass with humidity content under 30%. Increased contents can compromise the efficiency of the process [146].

Many commercial gasifier manufacturers can be found on the internet. Manufacturer websites reveal different models with different capacities. A manufacturer in India, for example, commercializes gasifiers with a feeding capacity between 240 and 4800 kg / d. It is thus not the gasifier that will limit the implementation of a microgeneration design, using the microalgae obtained in WWTP with capacity under 20,000 inhabitants. In the United States, another manufacturer, specializing in compact gasifiers systems to microgeneration from the biomass, commercializes a unity with nominal operation capacity of 528 kg / d of biomass and production of 440 kWh and another bigger unity,

with nominal operation capacity of 3600 kg / d of biomass and production of 3000 kWh, and both can operate at most 30% humidity. This more compact gasifier of 528 kg / d of biomass and production of 440 kWh, which is therefore more compatible with the proposed WWTP microgeneration scenario, was chosen in this study.

According to the manufacturer's information, the energy productivity of the system is 0.83 kWh / kg of dried biomass. This value matches the productivity reported in the literature, around 1 kWh / kg [145], and is a little under the efficiency reported by Gikas [71] with an optimized gasifier, that had 0.88 kWh / kg dried biomass. The electricity production of 0.83 kWh / kg of dried biomass provided by the manufacturer was maintained, since the value is more conservative than the others reported in the literature.

For a 20,000 inhabitant WWTP, producing 860 kg / d of dried microalgae, as estimated in this scenario, or the equivalent of 1228 kg / d of microalgae with 30% humidity, it would be possible to install two gasifiers of 528 kg / d operating simultaneously, to enable eventual maintenance stops. Using the manufacturer's specifications for a daily feed of 82% of the nominal capacity, 864 kg of humid biomass (604.8 kg dry biomass) would be gasified daily in both gasifiers, producing 502 kWh of electricity, which is equivalent to 0.167 kWh / m^3 of treated sewage, in the proposed scenario in this work (treatment of 3,000 m^3 / d of sewage).

The daily remainder of humid biomass produced and not gasified, 364 Kg / d (29% of the total produced), can contribute to increasing the generation of the system if it operates above 82% nominal capacity, however this portion was not considered, in order to maintain the manufacturer's recommendations and to compensate for the possible losses in the harvest and biomass drying processes. The estimated value is 22% of losses in the harvest, which is coherent with Park et al. [44].

In general, conventional wastewater treatment requires between 0.3 and 0.6 kWh / m^3 [12,147], which means the energy produced of 0.167 kWh / m^3 represents between 28 and 56% of the energy consumption. For WWTP operating with less energy-intensive processes, like ponds, which are the focus of this work, the energy produced could meet the demands of the plant, since the energy consumption of these systems varies between 0.079 until 0.28 kWh / m^3 [9]. This confirms the Gikas surplus potential [71], in the combination of less energy-intensive WWTP models with electricity generation systems from the produced biosolids.

2.5.1.3 Energy balance of the conceptual scenario

According to MetCalf and Eddy [60], the methane production calculated in UASB reactors, at a temperature of 25 ^oC is 0.38 L / g COD. Since municipal sewage is around 600 mg / L COD [2], the total estimated production potential is 228 L CH_4 / m^3 of treated sewage. Even after disregarding a typical loss of 25% of methane due to the effluent of UASB [148], the volume of recovered biogas of 171 L CH_4 / m^3 is significant and represents 1.69 kWh / m^3 of treated sewage, given the calorific power of methane of 35.9

MJ / Nm^3 [148]. By converting this chemical energy into electricity, through an internal combustion engine with 33% efficiency [149], 0.56 kWh / m^3 of electricity can be generated from biogas, more than that produced with biomass gasification.

Table 2.8 presents the energy balance of the proposed system, with the energy consumption for each stage of the process. The energy involved in the flocculation refers to the mixture of chemical products in the affluent and is estimated as 1.5 kWh / ton of biomass, according to the literature [150]. This represents 0.00043 kWh / m^3 in the proposed scenario of this work. The energy required in the ponds is for the paddlewheel and was estimated according to Collet et al. [151], who reported consumption of 0.2 kWh / kg of microalgae, which is equivalent to 0.057 kWh / m^3 in the proposed scenario. Energy apportions of 0.63 kWh / kg of water removed were required by microalgae drying, according to the literature [71]. Considering 75% humidity content for the biomass after the dewatering process in the centrifuge [18,51] (close to the value reported in Table 2.3), the energy required in the drying that can reduce the humidity to 30% (maximum allowed in gasifier) is therefore equivalent to 0.46 kWh / m^3 of treated wastewater. It is worth noting that the initial humidity of 75% is much higher than the 55% described by Gikas [71], in their process of dewatering with less conventional equipment than the centrifuge. If the same consideration is made as that by Gikas [71], the energy needed would be equivalent to 0.14 kWh / m^3 of treated wastewater. This shows that any improvement in the dewatering system will significantly affect the energy balance.

Table 2.8. Electric energy requirements and production for the proposed wastewater treatment process.

Process	**Electric energy kWh / m^3 (raw wastewater)**	**Ref.**
Influent pumping	-0.039	[7]
Degritting	-0.0066	[7]
UASB Reactor	Negligible	[2]
HRAP	-0.057	[151]
Floculation	-0.00043	[150]
Excess sludge pumping	-0.0045	[7]
Centrifuge thickening	-0.016	[7]
Total without drying	-0.123	-
Drying	-0.46	[71]
Total with drying	-0.583	-
Energy from syngas	+0.167	-
Energy from biogas	+0.56	-
Final balance	+0.14	-

According to Table 2.8, if the energy demand for the biomass drying is not considered, the energy produced in the gasification will be surplus to the WWTP demand, however

when the energy needed for the drying process is considered, the syngas gain does not compensate for the drying process needed to gasification. This explains the preoccupation in the literature with the drying stage and the search for new dryer models, that use solar energy. Alternative dewatering systems, with greater efficiency in water removal, are also important, however the energy balance is satisfied even with the current systems of dewatering and drying if the energy of the biogas produced in the UASB is recovered. The WWTP becomes surplus in energy, with in excess of 0.14 kWh / m^3 of treated wastewater.

The value of 0.14 kWh / m^3 of treated wastewater can still be optimized. Some of the biogas, for example, could be used to generate the heat needed in the drying stage, avoiding the loss in thermal generation, due to the limited efficiency of the combustion engine. Only a proportion of the excess of the biogas would thus be converted into electricity. Another possibility for improving the performance of the system is in the recovery of the heat contained in the flue gas and in the syngas. CO_2 recovery of the combustion gases in the pond can also be used to maximize microalgae production. The literature indicates a potential to produce up to 30% more if CO_2 was introduced in the system to increase carbon support [44].

2.5.1.4 Cost estimation

Only the costs involved with the implementation of the gasification and power generation system at WWTP, which is the purpose of this paper, were considered. All revenues from fees for sewage treatment, as well as the costs of this process, were disregarded. It is noteworthy that it is only the UASB reactor, without the association of a complementary treatment such as high rate ponds, that is not able to remove nutrients from the sewage, where the treatment is limited to the secondary level [2]. The values obtained in reais were converted to US dollars at the price of R$4.00/$1.00.

The price of energy was based on the tariff policy of the Brazilian state utility, which applies the lowest values, among the largest utilities in the country, $0.08440238 / kWh [152]. With the surplus of 0.14 kWh / m^3 calculated, the energy revenue equals $0.01181633 / m^3 of treated wastewater or $35.45 / d. Another $30 / d could be saved, considering that 864 kg of carbonated wet biomass would no longer go to the landfill since the costs for the final disposal of this waste are estimated at $34.75 / ton [152]. Total direct and indirect revenue is thus $65.45 / day or $23,888.88 / year.

The cost of each gasification-power generation units is $33,500. The cost of the rotary kiln drying system is $60,000 for a drying capacity of 2.4 tons / d. The values were provided by the equipment manufacturers themselves. The final cost of purchasing new equipment would thus be $127,000. This would require just over five years for a return on investment.

Although this simple cost estimation does not account for extra costs for employee training, equipment maintenance, depreciation, and so on, it is notable that WWTP

construction projects usually have a 20-year lifespan. The process also has the potential for further optimization, as noted previously. Savings can be achieved at the largest scale. Environmental factors may also add interest to the project, since the proposed system acts on tertiary sewage treatment with self-sufficient renewable energy, alleviating the demand for fossil fuels. Finally, where energy and landfill costs for the final disposal of biosolids are more expensive, the system may prove even more advantageous.

2.6 Trends and knowledge gaps

No review article was found that exclusively addressed the gasification of microalgae. Chen et al. [153] and Raheem et al. [16] reviewed thermochemical microalgae conversion processes and included gasification more generally, including six and eight gasification studies, respectively. Biller and Ross [154] and Patel et al. [3] reviewed the hydrothermal technologies applied for algal biomass and addressed supercritical gasification, including, respectively, six and five supercritical gasification studies.

The compilation of information supplied by this work through the systematic review indicates trends and knowledge gaps that are important for guiding new research, and assisting in technological development.

As noted in this work, there is still much that needs to be studied to turn microalgae gasification into a commercial reality. Most publications use baseline considerations that would not easily be applied in a large-scale scenario such as biofuel production. It is necessary to cultivate microalgae in systems demanding less input, with less energy demand and the utilization of nutrients from waste sources. This means producing biomass composed of different species of microalgae and bacteria in open ponds rather than cultivating pure species in photobioreactors. It is also necessary to direct the harvesting processes to the use of coagulants-flocculants, which are more economical for large-scale production, giving up centrifuges and other processes that are more energy-intensive when used alone. The incorporation of these chemical flocculating and coagulant compounds into the biomass and its effects on the process need to be better understood and optimized. Many metals are beneficial to the process by acting catalytically in the reaction [78], and their introduction at the harvest stage could be advantageous. Thermodynamic studies of heat recovery and biomass drying are also necessary in order to make feasible the use of downdraft gasifiers where technology is consolidated, and so that the costs of implementation and operation are more compatible for smaller scales, where one imagines the gasification of microalgae biomass. Pilot-scale experimental studies are required, since the bench-scale may not note the operational difficulties that are verified on a real scale. The reuse of CO_2 from the flue gases in the ponds could also be adapted to maximize the productivity of microalgae. A flowchart of the model is shown in Figure 2.4 as a summary of all these recommendations for the perceived most feasible scenario.

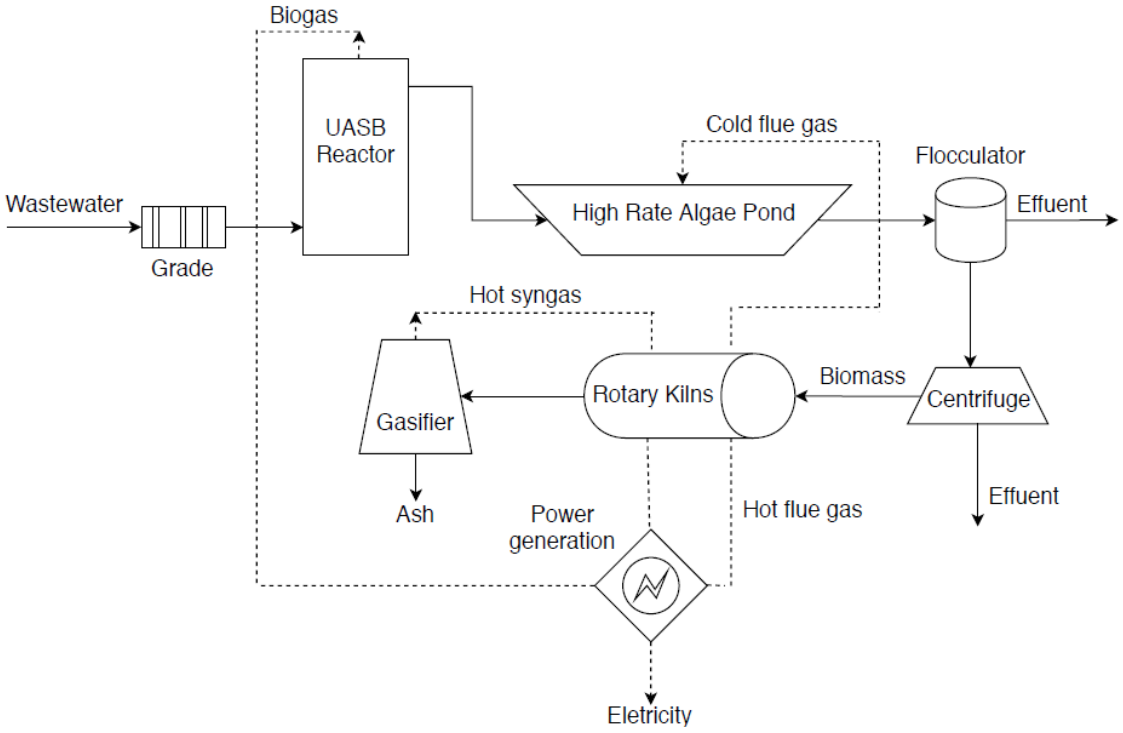

Fig. 2.4. Flowchart for the suggested biomass gasification process.

2.7 Conclusion

This work carried out an extensive systematic review including 49 articles and mapped the experimental gasification of microalgae. The results showed that most studies have been carried out for pure species of microalgae (monoculture) obtained commercially. Systems that are more compatible with the biofuel scenario still need to be studied, such as the gasification of microalgae biomass collected by coagulation-flocculation processes, and sewage recovery as a nutritional medium. Pilot-scale studies are also required. The number of studies involving hydrothermal gasification was useful, however, the use of more conventional gasifiers, such as the downdraft fixed bed, is still under-researched. A conceptual scenario for the use of microalgae biomass for microgeneration in wastewater treatment plants was constructed using the most consistent assumptions for a real scale. This involved the cultivation of several species of microalgae and bacteria together in HRAP, harvesting via coagulation-flocculation, and generation of electricity in the downdraft gasifier system and the internal combustion engine. These choices were based on a review of the literature presented. The result of the evaluation suggests the generation of 0.167 kWh / m^3 of treated sewage, enough to supply the entire energy demand of a WWTP with processes that are less intense in energy, such as anaerobic treatment, although the high energy required for the drying of microalgae makes the energy balance of the system deficient. Options to overcome this challenge include the reuse of heat from flue gas and syngas and the integration of anaerobic sewage treatment processes, with the generation and energetic use of biogas. It is noteworthy that it is only the anaerobic treatment, without the association of a complementary treatment such as high rate ponds

and microalgae production, that is not able to remove nutrients from the sewage, where the treatment is limited to the secondary level. When biogas produced in anaerobic treatment was considered, WWTP created a surplus of electricity of 0.14 kWh / m^3 of treated sewage. A cost estimate was made for the acquisition of drying and gasification-electricity generation systems. The results suggest that investment may be financially returned after five years, with additional potential for further optimization.

References

[1] Singh B, Bauddh K, Bux F. Algae and environmental sustainability. vol. 7. Springer; 2015. doi:10.1007/978-81-322-2641-3.

[2] Sperling M Von, Lemos Chernicharo CA De. Biological Wastewater Treatment in Warm Climate Regions. IWA Publ 2005:1–856. doi:10.5860/CHOICE.45-2633.

[3] Patel B, Guo M, Izadpanah A, Shah N, Hellgardt K. A review on hydrothermal pre-treatment technologies and environmental profiles of algal biomass processing. Bioresour Technol 2016;199. doi:10.1016/j.biortech.2015.09.064.

[4] Shumbulo E, Ki D. Microalgae to biofuels : ‘ Promising ’ alternative and renewable energy , review 2018;81:743–55. doi:10.1016/j.rser.2017.08.042.

[5] Manara P, Zabaniotou A. Towards sewage sludge based biofuels via thermochemical conversion - A review. Renew Sustain Energy Rev 2012;16:2566–82. doi:10.1016/j.rser.2012.01.074.

[6] Pereira MV, Dassoler AF, Antunes PW, Gonçalves RF, Cassini ST, Vinicius M, et al. Indigenous microalgae biomass cultivation in continuous reactor with anaerobic effluent : effect of dilution rate on productivity , nutrient removal and bioindicators. Environ Technol 2018;0:1–13. doi:10.1080/09593330.2018.1549105.

[7] Longo S, d’Antoni BM, Bongards M, Chaparro A, Cronrath A, Fatone F, et al. Monitoring and diagnosis of energy consumption in wastewater treatment plants. A state of the art and proposals for improvement. Appl Energy 2016;179:1251–68. doi:10.1016/j.apenergy.2016.07.043.

[8] Wakeel M, Chen B, Hayat T, Alsaedi A, Ahmad B. Energy consumption for water use cycles in different countries: A review. Appl Energy 2016;178:868–85. doi:10.1016/j.apenergy.2016.06.114.

[9] Wang H, Yang Y, Keller AA, Li X, Feng S, Dong Y nan, et al. Comparative analysis of energy intensity and carbon emissions in wastewater treatment in USA, Germany, China and South Africa. Appl Energy 2016;184:873–81. doi:10.1016/j.apenergy.2016.07.061.

[10] Chae KJ, Kang J. Estimating the energy independence of a municipal wastewater treatment plant incorporating green energy resources. Energy Convers Manag 2013;75:664–72. doi:10.1016/j.enconman.2013.08.028.

[11] Vieira AS, Ghisi E. Water-energy nexus in low-income houses in Brazil: the influence of integrated on-site water and sewage management strategies on the energy consumption of water and sewerage services. J Clean Prod 2016;133:145–62. doi:10.1016/j.jclepro.2016.05.104.

[12] Shen Y, Linville JL, Urgun-demirtas M, Mintz MM, Snyder SW. An overview of biogas production and utilization at full-scale wastewater treatment plants (WWTPs) in the United States : Challenges and opportunities towards energy-neutral WWTPs. Renew Sustain Energy Rev 2015;50:346–62. doi:10.1016/j.rser.2015.04.129.

[13] Antonelli M, Martorano L. A study on the rotary steam engine for distributed generation in small size power plants. Appl Energy 2012;97:642–7. doi:10.1016/j.apenergy.2011.11.054.

[14] Chen W-H, Lin B-J, Huang M-Y, Chang J-S. Thermochemical conversion of microalgal biomass into biofuels: A review. Bioresour Technol 2014;184:314–27. doi:10.1016/j.biortech.2014.11.050.

[15] Nipattummakul N, Ahmed II, Kerdsuwan S, Gupta AK. Hydrogen and syngas production from sewage sludge via steam gasification. Int J Hydrogen Energy 2010;35:11738–45. doi:10.1016/j.ijhydene.2010.08.032.

[16] Raheem A, Wan Azlina WAKG, Taufiq Yap YH, Danquah MK, Harun R. Thermochemical conversion of microalgal biomass for biofuel production. Renew Sustain Energy Rev 2015;49:990–9. doi:10.1016/j.rser.2015.04.186.

[17] Jankowska E, Sahu AK, Oleskowicz-Popiel P. Biogas from microalgae: Review on microalgae's cultivation, harvesting and pretreatment for anaerobic digestion. Renew Sustain Energy Rev 2017;75:692–709. doi:10.1016/j.rser.2016.11.045.

[18] Vandamme D, Foubert I, Muylaert K. Flocculation as a low-cost method for harvesting microalgae for bulk biomass production. Trends Biotechnol 2013;31:233–9. doi:10.1016/j.tibtech.2012.12.005.

[19] Abdur S, Aldin S, Ali M, Mozahar M. Biological CO 2 fi xation with production of microalgae in wastewater – A review. Renew Sustain Energy Rev 2017;76:379–90. doi:10.1016/j.rser.2017.02.038.

[20] Lam MK, Lee KT. Cultivation of Chlorella vulgaris in a pilot-scale sequential-baffled column photobioreactor for biomass and biodiesel production. Energy Convers Manag 2014;88. doi:10.1016/j.enconman.2014.08.063.

[21] Moody JW, McGinty CM, Quinn JC. Global evaluation of biofuel potential from microalgae. Proc Natl Acad Sci U S A 2014;111. doi:10.1073/pnas.1321652111.

[22] Peng G, Vogel F, Refardt D, Ludwig C. Catalytic Supercritical Water Gasification: Continuous Methanization of Chlorella vulgaris. Ind Eng Chem Res 2017;56. doi:10.1021/acs.iecr.7b00042.

[23] Chen C, Yeh K, Aisyah R, Lee D, Chang J. Bioresource Technology Cultivation , photobioreactor design and harvesting of microalgae for biodiesel production : A

critical review. Bioresour Technol 2011;102:71–81. doi:10.1016/j.biortech.2010.06.159.

[24] Siqueira FG. Microalgae biorefineries : The Brazilian scenario in perspective. N Biotechnol 2017. doi:10.1016/j.nbt.2016.04.007.

[25] Martínez RG. Microalgae harvesting in wastewater treatment plants : application of natural techniques for an efficient flocculation. Universitat Politècnica de Catalunya, 2016.

[26] Brennan L, Owende P. Biofuels from microalgae — A review of technologies for production , processing , and extractions of biofuels and co-products 2010;14:557–77. doi:10.1016/j.rser.2009.10.009.

[27] Bartley ML, Boeing WJ, Dungan BN, Holguin FO, Schaub T. pH effects on growth and lipid accumulation of the biofuel microalgae Nannochloropsis salina and invading organisms 2014:1431–7. doi:10.1007/s10811-013-0177-2.

[28] Minowa T, Sawayama S. A novel microalgal system for energy production with nitrogen cycling. Fuel 1999;78:1213–5. doi:10.1016/S0016-2361(99)00047-2.

[29] Chisti Y. Biodiesel from microalgae 2007;25:294–306. doi:10.1016/j.biotechadv.2007.02.001.

[30] Patzelt DJ, Hindersin S, Elsayed S, Boukis N, Kerner M, Hanelt D. Hydrothermal gasification of Acutodesmus obliquus for renewable energy production and nutrient recycling of microalgal mass cultures. J Appl Phycol 2015;27:2239–50. doi:10.1007/s10811-014-0496-y.

[31] Pérez-López P, González-García S, Allewaert C, Verween A, Murray P, Feijoo G, et al. Environmental evaluation of eicosapentaenoic acid production by Phaeodactylum tricornutum. Sci Total Environ 2014;466–467:991–1002. doi:10.1016/j.scitotenv.2013.07.105.

[32] Pérez-López P, González-García S, Ulloa RG, Sineiro J, Feijoo G, Moreira MT. Life cycle assessment of the production of bioactive compounds from Tetraselmis suecica at pilot scale. J Clean Prod 2014;64. doi:10.1016/j.jclepro.2013.07.028.

[33] Medeiros DL, Sales EA, Kiperstok A. Energy production from microalgae biomass: Carbon footprint and energy balance. J Clean Prod 2015;96. doi:10.1016/j.jclepro.2014.07.038.

[34] Maranduba HL, Robra S, Nascimento IA, da Cruz RS, Rodrigues LB, de Almeida Neto JA. Reducing the life cycle GHG emissions of microalgal biodiesel through integration with ethanol production system. Bioresour Technol 2015;194:21–7. doi:10.1016/j.biortech.2015.06.113.

[35] De Benedetti B, Barbera AC, Freni P, Tecchio P. Wastewater valorization adopting the microalgae accelerated growth. Desalin Water Treat 2015;53:1001–11. doi:10.1080/19443994.2013.848412.

[36] Duman G, Uddin MA, Yanik J. Hydrogen production from algal biomass via steam

gasification. Bioresour Technol 2014;166. doi:10.1016/j.biortech.2014.04.096.

[37] Park JBK, Craggs RJ. Wastewater treatment and algal production in high rate algal ponds with carbon dioxide addition 2010;5:633–40. doi:10.2166/wst.2010.951.

[38] Ting H, Haifeng L, Shanshan M, Zhang Y, Zhidan L, Na D. Progress in microalgae cultivation photobioreactors and applications in wastewater treatment : A review 2017;10. doi:10.3965/j.ijabe.20171001.2705.

[39] Eboibi BE, Lewis DM, Ashman PJ, Chinnasamy S. Effect of operating conditions on yield and quality of biocrude during hydrothermal liquefaction of halophytic microalga Tetraselmis sp. Bioresour Technol 2014;170. doi:10.1016/j.biortech.2014.07.083.

[40] Razzak SA, Hossain MM, Lucky RA, Bassi AS, De Lasa H. Integrated CO<inf>2</inf>capture, wastewater treatment and biofuel production by microalgae culturing - A review. Renew Sustain Energy Rev 2013;27:622–53. doi:10.1016/j.rser.2013.05.063.

[41] Adeniyi OM, Azimov U, Burluka A. Algae biofuel : Current status and future applications. Renew Sustain Energy Rev 2018;90:316–35. doi:10.1016/j.rser.2018.03.067.

[42] Rösch C, Posten C. SCHWERPUNKT Challenges and Perspectives of Microalgae Production Focus. Tech – Theor Und Prax 2012;21:5–16.

[43] Farag I, Price K. Resources Conservation in Microalgae Biodiesel Production. Int J Eng Tech Res 2013;1:49–56.

[44] Park JBK, Craggs RJ, Shilton AN. Bioresource Technology Wastewater treatment high rate algal ponds for biofuel production. Bioresour Technol 2011;102:35–42. doi:10.1016/j.biortech.2010.06.158.

[45] Posadas E, Morales M, Gomez C, Acién FG, Muñoz R. Influence of pH and CO2 source on the performance of microalgae-based secondary domestic wastewater treatment in outdoors pilot raceways. Chem Eng J 2014. doi:10.1016/j.cej.2014.12.059.

[46] Kumar M, Enamala S, Chavali M, Donepudi J. Production of biofuels from microalgae - A review on cultivation , harvesting , lipid extraction , and numerous applications of microalgae. Renew Sustain Energy Rev 2018;94:49–68. doi:10.1016/j.rser.2018.05.012.

[47] Wan C, Alam MA, Zhao XQ, Zhang XY, Guo SL, Ho SH, et al. Current progress and future prospect of microalgal biomass harvest using various flocculation technologies. Bioresour Technol 2015;184:251–7. doi:10.1016/j.biortech.2014.11.081.

[48] Gerchman Y, Vasker B, Tavasi M, Mishael Y, Kinel-Tahan Y, Yehoshua Y. Effective harvesting of microalgae: Comparison of different polymeric flocculants. Bioresour Technol 2017;228:141–6. doi:10.1016/j.biortech.2016.12.040.

[49] Castrillo M, Lucas-Salas LM, Rodr??guez-Gil C, Mart??nez D. High pH-induced flocculation-sedimentation and effect of supernatant reuse on growth rate and lipid productivity of Scenedesmus obliquus and Chlorella vulgaris. Bioresour Technol 2013;128:324–9. doi:10.1016/j.biortech.2012.10.114.

[50] Ummalyma SB, Gnansounou E, Sukumaran RK, Sindhu R, Pandey A, Sahoo D. Bioflocculation: An alternative strategy for harvesting of microalgae – An overview. Bioresour Technol 2017;242:227–35. doi:10.1016/j.biortech.2017.02.097.

[51] Das P, Thaher MI, Abdul Hakim MAQM, Al-Jabri HMSJ, Alghasal GSHS. Microalgae harvesting by pH adjusted coagulation-flocculation, recycling of the coagulant and the growth media. Bioresour Technol 2016;216:824–9. doi:10.1016/j.biortech.2016.06.014.

[52] Guldhe A, Singh B, Rawat I, Ramluckan K, Bux F. Efficacy of drying and cell disruption techniques on lipid recovery from microalgae for biodiesel production. Fuel 2014;128:46–52. doi:10.1016/j.fuel.2014.02.059.

[53] Anthony RJ, Ellis JT, Sathish A, Rahman A, Miller CD, Sims RC. Effect of coagulant/flocculants on bioproducts from microalgae. Bioresour Technol 2013;149:65–70. doi:10.1016/j.biortech.2013.09.028.

[54] Seo YH, Sung M, Kim B, Oh YK, Kim DY, Han JI. Ferric chloride based downstream process for microalgae based biodiesel production. Bioresour Technol 2015;181:143–7. doi:10.1016/j.biortech.2015.01.004.

[55] Shah JH, Deokar A, Patel K, Panchal K, Mehta A V. A Comprehensive Overview on Various Method of Harvesting Microalgae According to Indian Perspective. Int. Conf. Multidiscip. Res. Pract., vol. I, 2014, p. 313–7.

[56] Al M, Ghaly A, Hammoud A. Microalgae Harvesting Methods for Industrial Production of Biodiesel : Critical Review and Comparative Analysis Fundamentals of Renewable Energy and Applications 2015;5. doi:10.4172/20904541.1000154.

[57] Shelef G, Sukenik A, Green M. Microalgae Harvesting and Processing : A Literature Review. Colorado: 1984.

[58] Grima EM, Acie FG, Medina AR, Chisti Y. Recovery of microalgal biomass and metabolites : process options and economics. Biotechnol Adv 2003;20:491–515. doi:10.1016/S0734-9750(02)00050-2.

[59] Microalgae B, Horsman M, Wu N, Lan CQ, Dubois-calero N. ARTICLES : BIOCATALYSTS AND BIOREACTOR DESIGN 2008:815–20. doi:10.1021/bp.070371k.

[60] Metcalf E, Eddy M. Wastewater engineering: treatment and Resource recovery. Mic Graw-Hill, USA 2014:1530–3.

[61] Bennion EP, Ginosar DM, Moses J, Agblevor F, Quinn JC. Lifecycle assessment of microalgae to biofuel: Comparison of thermochemical processing pathways. Appl Energy 2015;154. doi:10.1016/j.apenergy.2014.12.009.

[62] Kwon EE, Yi H, Kwon H-H. Energy recovery from microalgal biomass via enhanced thermo-chemical process. Biomass and Bioenergy 2014;63:46–53. doi:10.1016/j.biombioe.2014.01.039.

[63] Photobioreactor L, Padovani G, Rodolfi L, Zittelli GC, Biondi N, Bonini G, et al. Microalgae for Oil : Strain Selection , Induction of Lipid Synthesis and Outdoor Mass Cultivation in a 2009;102:100–12. doi:10.1002/bit.22033.

[64] Sharara MA, Sadaka SS. Gasification of phycoremediation algal biomass. BioResources 2015;10:2609–25. doi:10.15376/biores.10.2.2609-2625.

[65] Zhu Y, Piotrowska P, Van Eyk PJ, Boström D, Wu X, Boman C, et al. Fluidized Bed Co-gasification of Algae and Wood Pellets: Gas Yields and Bed Agglomeration Analysis. Energy and Fuels 2016;30:1800–9. doi:10.1021/acs.energyfuels.5b02291.

[66] Stucki S, Vogel F, Ludwig C, Haiduc AG, Brandenberger M. Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. Energy Environ Sci 2009;2. doi:10.1039/b819874h.

[67] López-González D, Fernandez-Lopez M, Valverde JL, Sanchez-Silva L. Comparison of the steam gasification performance of three species of microalgae by thermogravimetric-mass spectrometric analysis. Fuel 2014;134:1–10. doi:10.1016/j.fuel.2014.05.051.

[68] Hognon C, Dupont C, Grateau M, Delrue F. Comparison of steam gasification reactivity of algal and lignocellulosic biomass: Influence of inorganic elements. Bioresour Technol 2014;164:347–53. doi:10.1016/j.biortech.2014.04.111.

[69] Raheem A, Sivasangar S, Wan Azlina WAKG, Taufiq Yap YH, Danquah MK, Harun R. Thermogravimetric study of Chlorella vulgaris for syngas production. Algal Res 2015;12. doi:10.1016/j.algal.2015.08.003.

[70] Lora EES, Nascimento MAR do. Geração Termelétrica: Planejamento, Projeto e Operação (Volume 2). Rio Janeiro, Ed Interciência n.d.;2.

[71] Gikas P. Towards energy positive wastewater treatment plants. J Environ Manage 2017;203:621–9. doi:10.1016/j.jenvman.2016.05.061.

[72] Ruiz JA, Juárez MC, Morales MP, Muñoz P, Mendívil MA. Biomass gasification for electricity generation: Review of current technology barriers. Renew Sustain Energy Rev 2013;18:174–83. doi:10.1016/j.rser.2012.10.021.

[73] Heidenreich S, Foscolo PU. New concepts in biomass gasification. Prog Energy Combust Sci 2015;46:72–95. doi:10.1016/j.pecs.2014.06.002.

[74] Molino A, Chianese S, Musmarra D. Biomass gasification technology: The state of the art overview. J Energy Chem 2016;25:10–25. doi:10.1016/j.jechem.2015.11.005.

[75] Ahmad AA, Zawawi NA, Kasim FH, Inayat A, Khasri A. Assessing the gasification performance of biomass: A review on biomass gasification process

conditions, optimization and economic evaluation. Renew Sustain Energy Rev 2016;53:1333–47. doi:10.1016/j.rser.2015.09.030.

[76] Asadullah M. Barriers of commercial power generation using biomass gasification gas: A review. Renew Sustain Energy Rev 2014;29:201–15. doi:10.1016/j.rser.2013.08.074.

[77] Bittencourt FLF, Lourenço AB, Dalvi EA, Martins MF. Thermodynamic assessment of human feces gasification: an experimental-based approach. SN Appl Sci 2019;1:1077. doi:10.1007/s42452-019-1104-1.

[78] Abdoulmoumine N, Adhikari S, Kulkarni A, Chattanathan S. A review on biomass gasification syngas cleanup. Appl Energy 2015;155:294–307. doi:10.1016/j.apenergy.2015.05.095.

[79] Afonso MHF, Souza JV de, Ensslin SR, Ensslin L. Como Construir Conhecimento Sobre O Tema De Pesquisa? Aplicação Do Processo Proknow-C Na Busca De Literatura Sobre Avaliação Do Desenvolvimento Sustentável. Rev Gestão Soc e Ambient 2012;5:47–62. doi:10.5773/rgsa.v5i2.424.

[80] Viegas C V., Bond AJ, Vaz CR, Borchardt M, Pereira GM, Selig PM, et al. Critical attributes of Sustainability in Higher Education: A categorisation from literature review. J Clean Prod 2016;126:260–76. doi:10.1016/j.jclepro.2016.02.106.

[81] Ferenhof HA, Vignochi L, Selig PM, Lezana ÁGR, Campos LMS. Environmental management systems in small and medium-sized enterprises: An analysis and systematic review. J Clean Prod 2014;74:44–53. doi:10.1016/j.jclepro.2014.03.027.

[82] Bull SR. The U.S. department of energy biofuels research program. Energy Sources 1991;13. doi:10.1080/00908319108909000.

[83] Ekpo U, Ross AB, Camargo-Valero MA, Williams PT. A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate. Bioresour Technol 2016;200. doi:10.1016/j.biortech.2015.11.018.

[84] Guan Q, Wei C, Savage PE. Hydrothermal gasification of Nannochloropsis sp. with Ru/C. Energy and Fuels 2012;26. doi:10.1021/ef3007992.

[85] Fermoso J, Corbet T, Ferrara F, Pettinau A, Maggio E, Sanna A. Synergistic effects during the co-pyrolysis and co-gasification of high volatile bituminous coal with microalgae. Energy Convers Manag 2018;164:399–409. doi:10.1016/j.enconman.2018.03.023.

[86] Duan P-G, Li S-C, Jiao J-L, Wang F, Xu Y-P. Supercritical water gasification of microalgae over a two-component catalyst mixture. Sci Total Environ 2018;630:243–53. doi:10.1016/j.scitotenv.2018.02.226.

[87] Miller A, Hendry D, Wilkinson N, Venkitasamy C, Jacoby W. Exploration of the gasification of Spirulina algae in supercritical water. Bioresour Technol 2012;119:41–7. doi:10.1016/j.biortech.2012.05.005.

[88] Raheem A, Sivasangar S, Wan Azlina WAKG, Taufiq Yap YH, Danquah MK, Harun R. Thermogravimetric study of Chlorella vulgaris for syngas production. Algal Res 2015;12:52–9. doi:10.1016/j.algal.2015.08.003.

[89] Tiong L, Komiyama M, Uemura Y, Nguyen TT. Catalytic supercritical water gasification of microalgae: Comparison of Chlorella vulgaris and Scenedesmus quadricauda. J Supercrit Fluids 2016;107. doi:10.1016/j.supflu.2015.10.009.

[90] Guan Q, Savage PE, Wei C. Gasification of alga Nannochloropsis sp. in supercritical water. J Supercrit Fluids 2012;61:139–45. doi:10.1016/j.supflu.2011.09.007.

[91] Elsayed S, Boukis N, Patzelt D, Hindersin S, Kerner M, Sauer J. Gasification of Microalgae Using Supercritical Water and the Potential of Effluent Recycling. Chem Eng Technol 2016;39. doi:10.1002/ceat.201500146.

[92] Yang K-C, Wu K-T, Hsieh M-H, Hsu H-T, Chen C-S, Chen H-W. Co-gasification of woody biomass and microalgae in a fluidized bed. J Taiwan Inst Chem Eng 2013;44. doi:10.1016/j.jtice.2013.06.026.

[93] Sanchez-Silva L, López-González D, Garcia-Minguillan AM, Valverde JL. Pyrolysis, combustion and gasification characteristics of Nannochloropsis gaditana microalgae. Bioresour Technol 2013;130. doi:10.1016/j.biortech.2012.12.002.

[94] Raheem A, Wan Azlina WAKG, Taufiq Yap YH, Danquah MK, Harun R. Optimization of the microalgae Chlorella vulgaris for syngas production using central composite design. RSC Adv 2015;5. doi:10.1039/c5ra10503j.

[95] Caputo G, Dispenza M, Rubio P, Scargiali F, Marotta G, Brucato A. Supercritical water gasification of microalgae and their constituents in a continuous reactor. J Supercrit Fluids 2016;118:163–70. doi:10.1016/j.supflu.2016.08.007.

[96] López-González D, Fernandez-Lopez M, Valverde JL, Sanchez-Silva L. Comparison of the steam gasification performance of three species of microalgae by thermogravimetric-mass spectrometric analysis. Fuel 2014;134. doi:10.1016/j.fuel.2014.05.051.

[97] Soreanu G, Tomaszewicz M, Fernandez-Lopez M, Valverde JL, Zuwała J, Sanchez-Silva L. CO2gasification process performance for energetic valorization of microalgae. Energy 2017;119:37–43. doi:10.1016/j.energy.2016.12.046.

[98] Razzak SA, Ali SAM, Hossain MM, Mouanda AN. Biological CO2 fixation using Chlorella vulgaris and its thermal characteristics through thermogravimetric analysis. Bioprocess Biosyst Eng 2016;39:1651–8. doi:10.1007/s00449-016-1640-7.

[99] Qadi NMN, Hidayat A, Takahashi F, Yoshikawa K. Co-gasification kinetics of coal char and algae char under CO<inf>2</inf> atmosphere. Biofuels 2017;8. doi:10.1080/17597269.2016.1224292.

[100] Brown TM, Duan P, Savage PE. Hydrothermal liquefaction and gasification of

Nannochloropsis sp. Energy and Fuels 2010;24:3639–46. doi:10.1021/ef100203u.

[101] Hu Z, Ma X, Jiang E. The effect of microwave pretreatment on chemical looping gasification of microalgae for syngas production. Energy Convers Manag 2017;143:513–21. doi:10.1016/j.enconman.2017.04.023.

[102] Hu Z, Jiang E, Ma X. Microwave pretreatment on microalgae: Effect on thermo-gravimetric analysis and kinetic characteristics in chemical looping gasification. Energy Convers Manag 2018;160:375–83. doi:10.1016/j.enconman.2018.01.057.

[103] Bach Q-V, Chen W-H, Sheen H-K, Chang J-S. Gasification kinetics of raw and wet-torrefied microalgae Chlorella vulgaris ESP-31 in carbon dioxide. Bioresour Technol 2017. doi:10.1016/j.biortech.2017.03.153.

[104] Figueira CE, Moreira PF, Giudici R. Thermogravimetric analysis of the gasification of microalgae Chlorella vulgaris. Bioresour Technol 2015;198:717–24. doi:10.1016/j.biortech.2015.09.059.

[105] Qadi NMN, Zaini IN, Takahashi F, Yoshikawa K. CO<inf>2</inf> Cogasification of Coal and Algae in a Downdraft Fixed-Bed Gasifier: Effect of CO<inf>2</inf> Partial Pressure and Blending Ratio. Energy and Fuels 2017;31. doi:10.1021/acs.energyfuels.6b03148.

[106] Onwudili JA, Lea-Langton AR, Ross AB, Williams PT. Catalytic hydrothermal gasification of algae for hydrogen production: Composition of reaction products and potential for nutrient recycling. Bioresour Technol 2013;127. doi:10.1016/j.biortech.2012.10.020.

[107] Palumbo AW, Sorli JC, Weimer AW. High temperature thermochemical processing of biomass and methane for high conversion and selectivity to H<inf>2</inf>-enriched syngas. Appl Energy 2015;157. doi:10.1016/j.apenergy.2015.07.072.

[108] Peng G, Ludwig C, Vogel F. Catalytic supercritical water gasification: Interaction of sulfur with ZnO and the ruthenium catalyst. Appl Catal B Environ 2017;202:262–8. doi:10.1016/j.apcatb.2016.09.011.

[109] Stucki S, Vogel F, Ludwig C, Haiduc AG, Brandenberger M. Catalytic gasification of algae in supercritical water for biofuel production and carbon capture. Energy Environ Sci 2009;2:535–41. doi:10.1039/b819874h.

[110] Liu G, Liao Y, Wu Y, Ma X. Synthesis gas production from microalgae gasi fi cation in the presence of Fe 2 O 3 oxygen carrier and CaO additive. Appl Energy 2018;212:955–65. doi:10.1016/j.apenergy.2017.12.110.

[111] Chakinala AG, Brilman DWF, Van Swaaij WPM, Kersten SRA. Catalytic and non-catalytic supercritical water gasification of microalgae and glycerol. Ind Eng Chem Res 2010;49:1113–22. doi:10.1021/ie9008293.

[112] Liu G, Liao Y, Wu Y, Ma X. Application of calcium ferrites as oxygen carriers for microalgae chemical looping gasi fi cation. Energy Convers Manag 2018;160:262–72. doi:10.1016/j.enconman.2018.01.041.

[113] Alghurabie IK, Hasan BO, Jackson B, Kosminski A, Ashman PJ. Fluidized bed gasification of Kingston coal and marine microalgae in a spouted bed reactor. Chem Eng Res Des 2013;91. doi:10.1016/j.cherd.2013.04.024.

[114] Bagnoud-Velásquez M, Brandenberger M, Vogel F, Ludwig C. Continuous catalytic hydrothermal gasification of algal biomass and case study on toxicity of aluminum as a step toward effluents recycling. Catal Today 2014;223:35–43. doi:10.1016/j.cattod.2013.12.001.

[115] Liu G, Liao Y, Wu Y, Ma X, Chen L. Characteristics of microalgae gasification through chemical looping in the presence of steam. Int J Hydrogen Energy 2017;42. doi:10.1016/j.ijhydene.2017.07.173.

[116] Lane DJ, Ashman PJ, Zevenhoven M, Hupa M, Eyk PJ Van, Nys R De, et al. Combustion Behaviour of Algal Biomass – Carbon Release , Nitrogen Release and Char Reactivity. Energy & Fuels 2013;28:41–51.

[117] Hu Z, Jiang E, Ma X. The effect of oxygen carrier content and temperature on chemical looping gasification of microalgae for syngas production. J Energy Inst 2018. doi:10.1016/j.joei.2018.05.001.

[118] Kirtania K, Joshua J, Kassim MA, Bhattacharya S. Comparison of CO2 and steam gasification reactivity of algal and woody biomass chars. Fuel Process Technol 2014;117:44–52. doi:10.1016/j.fuproc.2013.02.006.

[119] Lane DJ, Van Eyk PJ, Ashman PJ, Kwong CW, De Nys R, Roberts DA, et al. Release of Cl, S, P, K, and Na during thermal conversion of algal biomass. Energy and Fuels 2015;29. doi:10.1021/acs.energyfuels.5b00279.

[120] Peng G, Vogel F, Refardt D, Ludwig C. Catalytic Supercritical Water Gasification: Continuous Methanization of Chlorella vulgaris. Ind Eng Chem Res 2017;56:6256–65. doi:10.1021/acs.iecr.7b00042.

[121] Zhu Y, Piotrowska P, Van Eyk PJ, Boström D, Kwong CW, Wang D, et al. Cogasification of Australian brown coal with algae in a fluidized bed reactor. Energy and Fuels 2015;29. doi:10.1021/ef502422t.

[122] Hirano A, Hon-Nami K, Kunito S, Hada M, Ogushi Y. Temperature effect on continuous gasification of microalgal biomass: Theoretical yield of methanol production and its energy balance. Catal Today 1998;45:399–404. doi:10.1016/S0920-5861(98)00275-2.

[123] Möbius A, Boukis N, Hindersin S, Kerner M. Cultivation and hydrothermal gasification of microalgae scenedesmus obliquus-first experimental results. Chemie-Ingenieur-Technik 2015;87. doi:10.1002/cite.201500002.

[124] Haiduc AG, Brandenberger M, Suquet S, Vogel F, Bernier-Latmani R, Ludwig C. SunCHem: An integrated process for the hydrothermal production of methane from microalgae and CO<inf>2</inf>mitigation. J Appl Phycol 2009;21:529–41. doi:10.1007/s10811-009-9403-3.

[125] Elliott DC, Hart TR, Neuenschwander GG, Rotness LJ, Olarte M V., Zacher AH.

Chemical processing in high-pressure aqueous environments. 9. Process development for catalytic gasification of algae feedstocks. Ind Eng Chem Res 2012;51:10768–77. doi:10.1021/ie300933w.

[126] Lananan F, Mohd Yunos FH, Mohd Nasir N, Abu Bakar NS, Lam SS, Jusoh A. Optimization of biomass harvesting of microalgae, Chlorella sp. utilizing auto-flocculating microalgae, Ankistrodesmus sp. as bio-flocculant. Int Biodeterior Biodegrad 2016;113:391–6. doi:10.1016/j.ibiod.2016.04.022.

[127] Ummalyma SB, Mathew AK, Pandey A, Sukumaran RK. Harvesting of microalgal biomass: Efficient method for flocculation through pH modulation. Bioresour Technol 2016;213:216–21. doi:10.1016/j.biortech.2016.03.114.

[128] Razzak SA, Hossain MM, Lucky RA, Bassi AS, De Lasa H. Integrated CO<inf>2</inf> capture, wastewater treatment and biofuel production by microalgae culturing - A review. Renew Sustain Energy Rev 2013;27. doi:10.1016/j.rser.2013.05.063.

[129] Lane DJ, Ashman PJ, Zevenhoven M, Hupa M, Van Eyk PJ, De Nys R, et al. Combustion behavior of algal biomass: Carbon release, nitrogen release, and char reactivity. Energy and Fuels 2014;28:41–51. doi:10.1021/ef4014983.

[130] Zhu Y, Piotrowska P, Van Eyk PJ, Boström D, Kwong CW, Wang D, et al. Cogasification of Australian brown coal with algae in a fluidized bed reactor. Energy and Fuels 2015;29:1686–700. doi:10.1021/ef502422t.

[131] Dayana S, Sharuddin A, Abnisa F, Mohd W, Wan A. A review on pyrolysis of plastic wastes. Energy Convers Manag 2016;115:308–26. doi:10.1016/j.enconman.2016.02.037.

[132] Mckendry P. Energy production from biomass (part 1): overview of biomass 2002;83:37–46.

[133] Demirba A. Calculation of higher heating values of biomass fuels. Fuel 1997;76:431–4.

[134] Haiduc AG, Brandenberger M, Suquet S, Vogel F, Bernier-Latmani R, Ludwig C. SunCHem: An integrated process for the hydrothermal production of methane from microalgae and CO<inf>2</inf> mitigation. J Appl Phycol 2009;21. doi:10.1007/s10811-009-9403-3.

[135] Bagnoud-Velásquez M, Brandenberger M, Vogel F, Ludwig C. Continuous catalytic hydrothermal gasification of algal biomass and case study on toxicity of aluminum as a step toward effluents recycling. Catal Today 2014;223. doi:10.1016/j.cattod.2013.12.001.

[136] Liu G, Liao Y, Wu Y, Ma X, Chen L. Characteristics of microalgae gasification through chemical looping in the presence of steam. Int J Hydrogen Energy 2017;42:22730–42. doi:10.1016/j.ijhydene.2017.07.173.

[137] Alghurabie IK, Hasan BO, Jackson B, Kosminski A, Ashman PJ. Fluidized bed gasification of Kingston coal and marine microalgae in a spouted bed reactor.

Chem Eng Res Des 2013;91:1614–24. doi:10.1016/j.cherd.2013.04.024.

[138] Guan Q, Wei C, Savage PE. Hydrothermal gasification of Nannochloropsis sp. with Ru/C. Energy and Fuels 2012;26:4575–82. doi:10.1021/ef3007992.

[139] Elsayed S, Boukis N, Patzelt D, Hindersin S, Kerner M, Sauer J. Gasification of Microalgae Using Supercritical Water and the Potential of Effluent Recycling. Chem Eng Technol 2016;39:335–42. doi:10.1002/ceat.201500146.

[140] Caputo G, Rubio Blazquez P, Dispenza M, Scargiali F, Marotta G, Brucato A. Supercritical water gasification of microalgae and their constituents. 22nd Int. Congr. Chem. Process Eng. CHISA 2016 19th Conf. Process Integr. Model. Optim. Energy Sav. Pollut. Reduction, PRES 2016, vol. 1, 2016, p. 685–6.

[141] Qadi NMN, Zaini IN, Takahashi F, Yoshikawa K. CO<inf>2</inf>Cogasification of Coal and Algae in a Downdraft Fixed-Bed Gasifier: Effect of CO<inf>2</inf>Partial Pressure and Blending Ratio. Energy and Fuels 2017;31:2927–33. doi:10.1021/acs.energyfuels.6b03148.

[142] Monteiro JHP. Manual de gerenciamento integrado de resíduos sólidos 2001.

[143] Chigueru T. Atlas Solarimétrico do Brasil: Banco de dados solarimetricos. Univ Da UFPE 2000.

[144] Mascarenhas LCA, von Sperling M, Chernicharo CA de L. Avaliação do desempenho de lagoas de polimento rasa, em série, para o pós-tratamento de efluentes de reator UASB. Eng Sanitária e Ambient 2004;9.

[145] Caproni VG, Fermi VE, Cesari V, Kensington S, Mach VE. An energy-biochar chain involving biomass gasification and rice cultivation in Northern Italy 2013:192–201. doi:10.1111/gcbb.12028.

[146] Susastriawan AAP, Saptoadi H. Small-scale downdraft gasi fi ers for biomass gasi fi cation : A review 2017;76:989–1003. doi:10.1016/j.rser.2017.03.112.

[147] Soares RB, Memelli MS, Roque RP, Gonçalves RF. Comparative Analysis of the Energy Consumption of Different Wastewater Treatment Plants 2017;3:79–86. doi:10.11648/j.ijaaa.20170306.11.

[148] Lobato LCS, Chernicharo CAL, Souza CL. Estimates of methane loss and energy recovery potential in anaerobic reactors treating domestic wastewater 2012:2745–53. doi:10.2166/wst.2012.514.

[149] Felipe I, Barros RM, Lucio G, Filho T. Electricity generation from biogas of anaerobic wastewater treatment plants in Brazil : an assessment of feasibility and potential. J Clean Prod 2016;126:504–14. doi:10.1016/j.jclepro.2016.03.072.

[150] Vandamme D. Flocculation based harvesting processes for microalgae biomass production. Faculty of Bioscience Engineering, 2013.

[151] Collet P, Hélias Arnaud A, Lardon L, Ras M, Goy R-A, Steyer J-P. Life-cycle assessment of microalgae culture coupled to biogas production. Bioresour Technol 2011;102. doi:10.1016/j.biortech.2010.06.154.

[152] Rosenfeldt S. VIABILIDADE TÉCNICO-ECONÔMICA DE PRODUÇÃO DE ENERGIA ELÉTRICA EM ETEs A PARTIR DO BIOGÁS. vol. 1ª Edição. 2016.

[153] Chen WH, Lin BJ, Huang MY, Chang JS. Thermochemical conversion of microalgal biomass into biofuels: A review. Bioresour Technol 2014;184:314–27. doi:10.1016/j.biortech.2014.11.050.

[154] Biller P, Ross AB. Hydrothermal processing of algal biomass for the production of biofuels and chemicals. Biofuels 2012;3:603–23. doi:10.4155/bfs.12.42.

[155] Hu Z, Ma X, Jiang E. The effect of microwave pretreatment on chemical looping gasification of microalgae for syngas production. Energy Convers Manag 2017;143. doi:10.1016/j.enconman.2017.04.023.

[156] Chakinala AG, Brilman DWF, Van Swaaij WPM, Kersten SRA. Catalytic and non-catalytic supercritical water gasification of microalgae and glycerol. Ind Eng Chem Res 2010;49. doi:10.1021/ie9008293.

[157] Tiong L, Komiyama M, Uemura Y, Nguyen TT. Catalytic supercritical water gasification of microalgae: Comparison of Chlorella vulgaris and Scenedesmus quadricauda. J Supercrit Fluids 2016;107:408–13. doi:10.1016/j.supflu.2015.10.009.

[158] Liu G, Liao Y, Wu Y, Ma X. Synthesis gas production from microalgae gasification in the presence of Fe<inf>2</inf>O<inf>3</inf>oxygen carrier and CaO additive. Appl Energy 2018;212:955–65. doi:10.1016/j.apenergy.2017.12.110.

[159] Liu G, Liao Y, Wu Y, Ma X. Application of calcium ferrites as oxygen carriers for microalgae chemical looping gasification. Energy Convers Manag 2018;160:262–72. doi:10.1016/j.enconman.2018.01.041.

[160] Peng G, Ludwig C, Vogel F. Catalytic supercritical water gasification: Interaction of sulfur with ZnO and the ruthenium catalyst. Appl Catal B Environ 2017;202:262–8. doi:10.1016/j.apcatb.2016.09.011.

[161] Qadi NMN, Hidayat A, Takahashi F, Yoshikawa K. Co-gasification kinetics of coal char and algae char under CO2 atmosphere. Biofuels 2017;8:281–9. doi:10.1080/17597269.2016.1224292.

[162] Sanchez-Silva L, López-González D, Garcia-Minguillan AM, Valverde JL. Pyrolysis, combustion and gasification characteristics of Nannochloropsis gaditana microalgae. Bioresour Technol 2013;130:321–31. doi:10.1016/j.biortech.2012.12.002.

[163] Caputo G, Dispenza M, Rubio P, Scargiali F, Marotta G, Brucato A. Supercritical water gasification of microalgae and their constituents in a continuous reactor. J Supercrit Fluids 2016;118. doi:10.1016/j.supflu.2016.08.007.

[164] Aziz M. Integrated hydrogen production and power generation from microalgae. Int J Hydrogen Energy 2016;41:104–12. doi:10.1016/j.ijhydene.2015.10.115.

[165] Guan Q, Wei C, Savage PE. Kinetic model for supercritical water gasification of algae. Phys Chem Chem Phys 2012;14. doi:10.1039/c2cp23792j.

Chapter 3

Microalgae production and characterization

A version of this chapter has been published:

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Thermochemical Conversion of Wastewater Microalgae: The Effects of Coagulants Used in the Harvest Process

Abstract

Microalgae are a promising alternative energy source for the future due to their high growth rate, cultivation potential in a wastewater environment, and its higher heating value (HHV). However, until nowadays, only the properties for pure species of microalgae that disregard the presence of coagulants used at the harvesting stage are known. In this study, the effects of these coagulants on the thermochemical conversion of wastewater microalgae were evaluated. The results showed a catalytic effect of coagulants. Tannin-based polymer reduced devolatilization temperature peaked at 308 to 274 ºC. Although the maximum devolatilization rate occurred in microalgae without coagulants, 4.57 %/min at 308 ºC, polyquaternium polymer accelerated the total biomass degradation. At a temperature of 892 ºC, 14.1% of microalgae remained to be degraded, while in the presence of this polymer, it was only 7.5%. This coagulant presented the best results, such as low cost, high efficiency, a small reduction in HHV, and improvement in the thermochemical behavior of microalgae biomass. The aliphatic amines polymer was the only coagulant that showed chlorine in the ash analysis, preventing its release as acid gases. Therefore, it was suggested as the better coagulant along with the polyquaternium polymer. For inorganic coagulants, the large amount added prevented an in-depth catalytic assessment, and the results portray the effect of coagulant mass incorporated into microalgae more than the catalytic effect. Iron and aluminum coagulants reduced significantly microalgae HHV from 21.58 MJ/kg to 12.91–14.45 MJ/kg.

Graphical Abstract

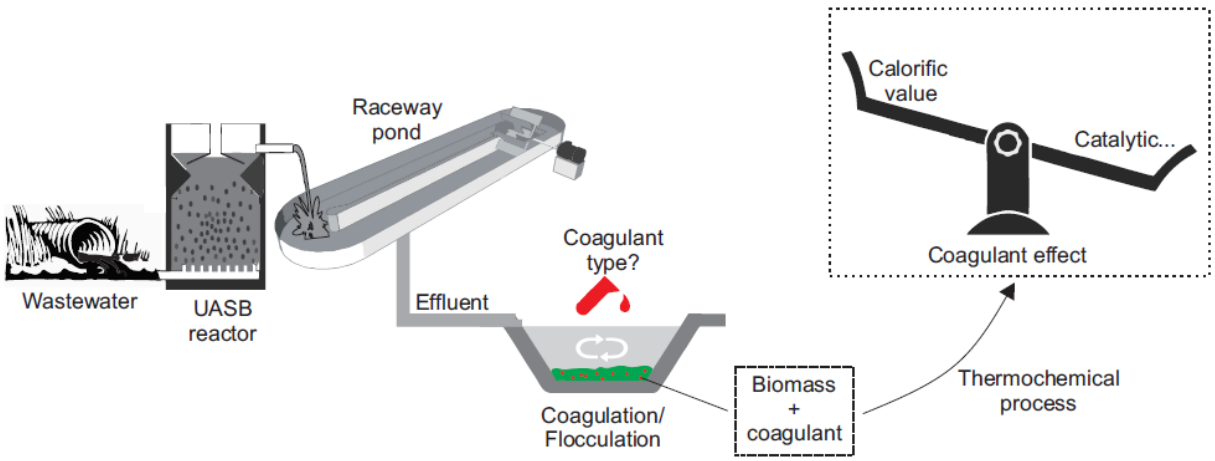

Fig. 3.1. Graphical abstract chapter 3.

Keywords: Microalgae; coagulant; catalytic effect; thermochemical behavior.

Highlights

- Coagulants can significantly alter the characteristics of microalgae biomass.
- Thermal degradation behavior showed differences.
- Catalytic effects of coagulants were observed.
- Aliphatic amines polymer prevented chlorine release as acid gases.
- The use of coagulants can be applied to benefit subsequent processes.

3.1 Introduction

Research on microalgae-based wastewater treatment has increased in recent years. Despite the original idea of using microalgae for wastewater treatment to remove the excess nutrients of the secondary effluent, it is now being considered more as a resource for energy [1,2]. This is because, unlike other biomass, microalgae can double in size in less than a day [3,4]. Moreover, the use of microalgae to produce energy in a wastewater treatment plant (WWTP) is an alternative that can increase efficiency and reduce process costs [5,6]. Almost all WWTPs require a large amount of energy input, mostly as electricity, implying a high cost and carbon emissions [7].

Currently, energy production from microalgae is not economically viable due to the high cost of harvesting [8,9]. Normally, the production of large-scale microalgae biomass does not exceed 0.5 g/L, which means processing a huge volume of suspension to obtain a significant amount of biomass [10]. An in-depth makes it imperative to use a cheap technology for the harvesting process; for this reason, flocculation is indicated as the most economical method since it allows the quick treatment of large volumes [9–12].

On the other hand, the coagulants incorporated in biomass in the harvesting process might affect subsequent processes. For instance, the yield in biofuel production from flocculated microalgae using ferric sulfate and centrifuged microalgae is different [13]. There is also a change in the yield of bioproducts produced from microalgae harvested using aluminum sulfate and cationic starch [12]. Aluminum chlorides may inhibit transesterification reactions and negatively affect biodiesel production [10]. Aluminum sulfate and ferric chloride can affect anaerobic digestion and, consequently, biogas generation [12]. Inorganic fractions in the biomass increase the ash content and reduce the calorific value, but they can also act positively on thermochemical conversion, acting as a catalyst, catalyst promoter, catalyst support, or as sorbents in the product cleanup [14,15]. Therefore the effect of chemical elements present in microalgae cannot be overlooked since it had a direct impact on the subsequent process [16].

Nevertheless, typically, the microalgae's characterization is described as a pure species (monoculture) and coagulant-free, usually purchased from food supplement stores or grown under controlled conditions in the laboratory. It does not reflect the characteristics

of microalgae produced in WWTPs, which involves biomass composed by different microalgae species and bacteria under coagulants presence [2].

Besides coagulants, the use of wastewater effluent as a culture medium also causes changes in microalgae composition. Differences in chemical characteristics of food-grade commercial microalgae or microalgae grown under controlled conditions in the laboratory and microalgae produced using wastewater effluent are mentioned in the literature [15,17].

Thus, the objective of this paper is to evaluate the effects of coagulants used in the harvest process on the thermochemical conversion of microalgae produced using wastewater effluent in a WWTP. The evaluation was carried out in terms of its calorific value and ultimate and proximate characteristics. The thermochemical behavior was studied by thermogravimetric analysis and differential thermal analysis. Finally, the chemical elements presented in the residue post-conversion were analyzed to check the released or trapped elements.

3.2 Materials and Methods

3.2.1 The wastewater treatment plant

The experimental WWTP is composed of a UASB reactor (up-flow anaerobic sludge blanket) measuring 1.0 m in diameter, 4.8 m usable height, 3.8 m^3 usable volume, and 0.14 L/s average flow rate. A grating system, preliminary to UASB reactor, was used to remove coarse solids from raw wastewater produced in the City of Vila Velha, located in the State of Espírito Santo, Brazil. After treatment in the UASB reactor, effluent fed two high-rate ponds (HRAP), both measuring 13.7 m^3 useful total volume, with two 10 m long channels, 2.4 m wide with a 22.8 m^2 superficial area. The system has been operating for more than two years in continuous mode.

3.2.2 Jar Test simulations

The effluent from HRAP was collected, and then Jar Test simulations were performed to quantify the best coagulant dosage to apply in the harvesting process. The Jar Test simulations were run in triplicate with the ponds' natural pH conditions and according to parameters, stirred at 105 rpm for 2 min (mixing), 30 rpm for 10 min (flocculation), and 30 min (decanting), according to CETESB (1987) in "*Técnica de Abastecimento e Tratamento de Água – Volume 2 – Tratamento de Água*". To each jar was added 2.0 L of effluent, and the supernatant samplings were collected at 1.0 L from the bottom, after decanting time. Six jars were used in each test. A digital pH meter measured the pH, and separation efficiency was estimated based on optical density at 750 nm, comparing initial and final values as reported by Das et al. [18] (Equation 3.1).

$$\text{Harvesting efficiency} = 100 \times (ODi - ODf) / ODi \quad (3.1)$$

Where:

ODi — initial optical density;

ODf — final optical density.

To represent a realistic scenario, the material used as coagulants were obtained commercially instead of high-purity laboratory reagents use. Ferric chloride, ferrous aluminum sulfate, aluminum polychloride, aliphatic amines polymer, and polyquaternium polymer were tested. These coagulants were chosen to cover both traditional inorganic coagulants and new alternative polymers. Hydrated lime was also tested since many species can be harvested with efficiency greater than 95% by pH increase [10]. Moreover, it is a low-cost material, and the presence of calcium in biomass can bring benefits to thermochemical processes since this material absorbs undesirable contaminant gases in the process [19]. Coagulant costs were obtained directly from suppliers and the values in reais were converted to US dollars at the price of R$4.00/$1.00. Thus, it was possible to estimate the harvest cost by multiplying the amount of coagulant required by its unit cost.

3.2.3 Microalgae biomass harvesting and preparation

The biomass produced was harvested in three different ways. In the first, 200 L of effluent from HRAP was transferred to a plastic drum, and the better coagulant dosage found in the Jar Test was applied. A mechanical stirrer was coupled onto the plastic drum and continuously stirred for 30 min, then 24 h for decanting. A valve coupled to the cylinder was used to drain water. The biomass, at the bottom of the plastic drum, was densified in a fabric.

The second way consists of a vacuum filtration with a Büchner flask and Büchner funnel in order to evaluate the microalgae biomass without the coagulant. The biomass that adhered to filter paper was gently removed with a spatula and transferred to a crucible for drying.

Finally, microalgae biomass produced in the WWTP separation system was also collected. This system operates continuously with the addition of a tannin-based polymer at 50 mg/L of effluent and represents the third way used to harvest microalgae in this work. This coagulant dosage was previously defined, according to Cassini et al. [20].

Fig. 3.2 presents the experimental unit and summarizes the whole process of obtaining biomass applied in this study. After harvesting, the microalgae biomass was dried and sanitized at 105 °C for at least 12 h. Then, each sample was milled in a Ring Mill to get

a fine powder. Lastly, samples were stored in closed Eppendorf tubes and submitted to the characterization tests.

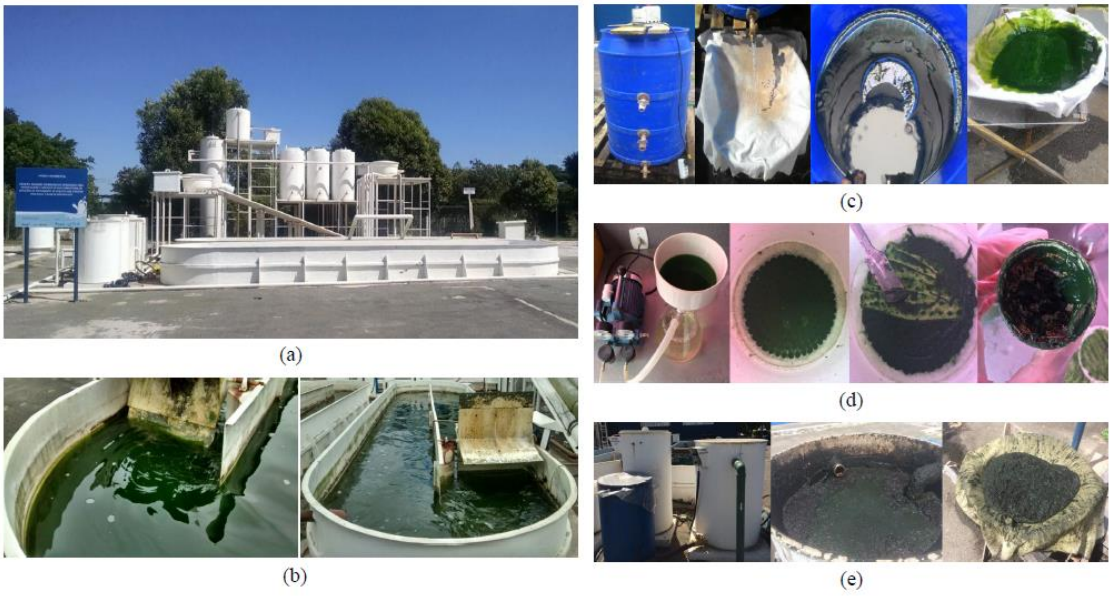

Fig. 3.2. Experimental unit: (a) Pilot wastewater treatment plant; (b) High-rate ponds; (c) First microalgae harvesting method; (d) Second microalgae harvesting method; (e) Third microalgae harvesting method.

3.2.4 Thermochemical methods

The Higher Heating Value (HHV) was performed in triplicate by a calorimeter (C2000 IKA-Werke) using 0.5 g of the sample. The calorimetric pump was sealed and, automatically, injected pure oxygen at a pressure of 30 bar. The post-combustion residue, composed of ashes, was collected and analyzed by an X-ray fluorescence spectrometer (EDX720 SHIMADZU). The EDX720 includes a Rhodium (Rh) X-ray tube and Si(Li) detector operating at 15-50 kV and 1,000 mA. The ultimate analysis was performed in triplicate using an Elemental Composition Analyzer (ECA) model 2400, series II, PerkinElmer. The proximate analysis was performed in a Thermogravimetric Analyzer TGA701 LECO. The moisture analysis and volatile solids were performed at 105 °C and 950 °C, respectively, using an inert nitrogen atmosphere in both cases. Ash analysis was performed at 750 °C using an oxygen oxidizing atmosphere, as recommended by ASTM D5142. The thermogravimetric analyses were performed by TA INSTRUMENTS Q600, with a 50 mg sample capacity and a 1,500 °C maximum heating temperature. The tests were performed in a crucible and alumina rod, with a heating rate of 10 °C/min to the temperature of 900 °C, with a nitrogen flow of 50 mL/min and an approximately 25 mg sample.

Thermogravimetric analysis (TGA) is a technique in which the weight loss of a sample is continuously measured under a controlled temperature. The Differential thermogravimetric (DTG) curve can be further obtained by differentiating the TGA curve. The Differential thermal analysis (DTA) evaluates the heat flux and provides an adequate description of the physicochemical changes in solid fuel that undergo endothermic and exothermic events. These techniques have received immense attention in understanding solid fuel degradation to release energy and has been used to figure out the thermal behavior of microalgae in different processes such as combustion, pyrolysis, and gasification [17,21].

3.2.5 Statistical analyses

The data presented in the manuscript were from three replicates. Statistical analyses were performed by Microsoft Excel software. Experimental results present the mean ± standard deviation.

3.3 Results and discussion

3.3.1 Coagulants evaluation in the harvest process

Fig. 3.3 shows efficiency achieved at the harvesting process for different coagulants. As can be seen, ferric chloride and hydrated lime only exhibit efficiency above 80% when used at concentrations above 100 mg/L. Therefore, they were the only chemicals tested at dosages above 100 mg/L. Hydrated lime and polyquaternium polymer display a peak in their efficiency, with an express decline to higher concentrations. Aliphatic amine polymer presents a practically constant efficiency at higher dosages.

Based on Fig. 3.3, the recommended coagulant dosage was set by balancing quantity and efficiency. The best dosage refers to the value obtained when the efficiency increase does not vary by more than 8%, even if the dosage is increased. Table 3.1 shows the coagulant dosage used in the harvesting process, separation efficiency, pH effluent, and cost estimation. The tannin-based coagulant cost, used in the continuous WWTP separation system, is also described in Table 3.1.

The natural pH of the pond ranged from 8.1 to 9.1. This slightly alkaline pH was already expected due to the CO_2 consumption in the medium [22]. After the addition of the coagulants, all coagulants reduced the pH of the supernatant except the polyquaternium polymer, which kept it constant, and the hydrated lime, which increased it. The average pH of the supernatant varied between 6.2 and 11.4, reaching its minimum and maximum when ferric chloride and hydrated lime were used, respectively. It was noticed that hydrated lime would require pH correction of supernatant before disposal. Brazilian resolution specifies a pH range between 5 and 9 for effluent disposal [23].

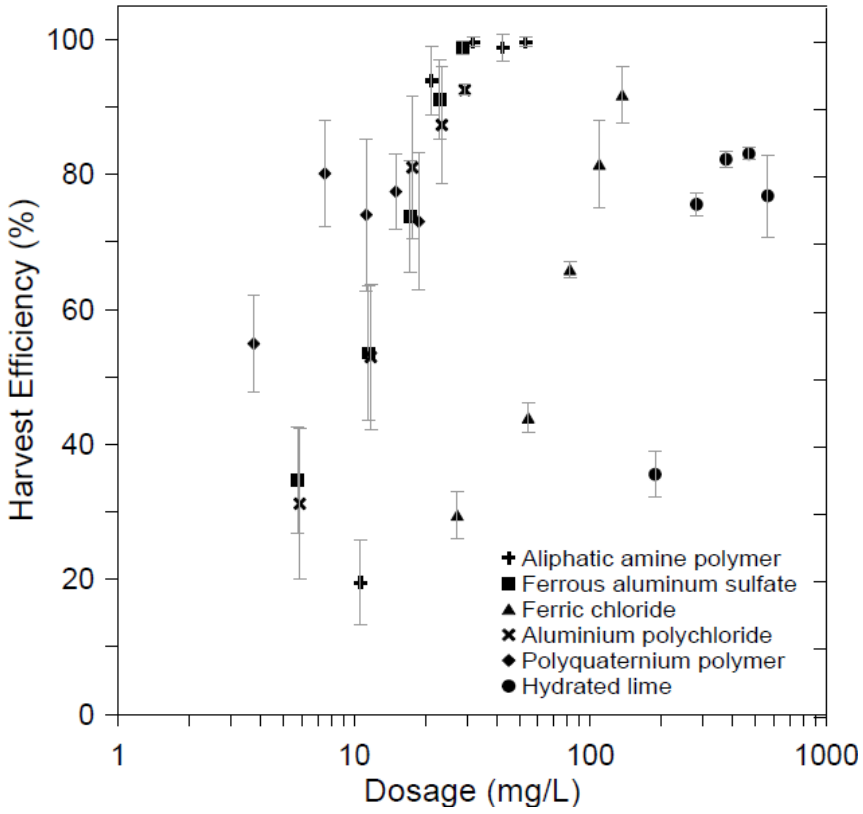

Fig. 3.3. Efficiency achieved at the harvesting process for different coagulants. Data are shown as mean (n = 3) ± standard deviation.

Table 3.1. Coagulants evaluation in the harvest process. Data are shown as mean (n = 3) ± standard deviation.

Coagulants	**Average pH pond**	**Used dosage mg/L**	**Average harvest Efficiency %**	**Average pH supernatant**	**Ref.**	**Harvest cost U$/1,000m^3**
Aliphatic amines polymer	8.5 ± 0.2	21.25	93.9 ± 5.0	7.8 ± 0.2	-	140
Ferrous aluminum sulfate	8.3 ± 0.3	22.96	91.1 ± 5.8	6.9 ± 0.4	-	50
Aluminum polychloride	8.7 ± 0.4	23.5	87.4 ± 8.6	7.2 ± 0.1	-	187
Ferric chloride	8.7 ± 0.4	136.5	91.8 ± 4.2	6.2 ± 0.1	-	270
Polyquaternium polymer	9.1 ± 0.4	7.5	80.1 ± 7.8	9.1 ± 0.4	-	55
Hydrated lime	8.1 ± 0.5	282	75.6 ± 1.8	11.4 ± 0.4	-	42
Tannin-based Polymer	8.0	50	90.0	Not available	[20]	215

The coagulant cost to processing 1,000 m^3 under the conditions studied varied widely, from U$42 for hydrated lime up to U$270 for ferric chloride. More expensive coagulants did not necessarily result in a higher final cost due to dosages varying significantly. Ferrous aluminum sulfate and polyquaternium polymer presented a low harvesting cost

for 91% and 80% efficiency, respectively. The most efficient coagulant in the harvesting process was aliphatic amines polymer, and its cost was intermediate between the most expensive and the cheapest. Despite its high cost, tannin-based coagulant has been used in the WWTP separation system because it is an organic coagulant and microalgae anaerobic digestion has been studied by other researchers in the pilot WWTP.

3.3.2 Microalgae biomass characterization

3.3.2.1 Qualitative analysis

Fig. 3.4 presents aspects of microalgae biomass obtained after the drying and mill process, as well as ashes collected after HHV measurement. In both biomass and ash, all samples had a different color and aspect, which shows a significant influence of coagulants on microalgae.

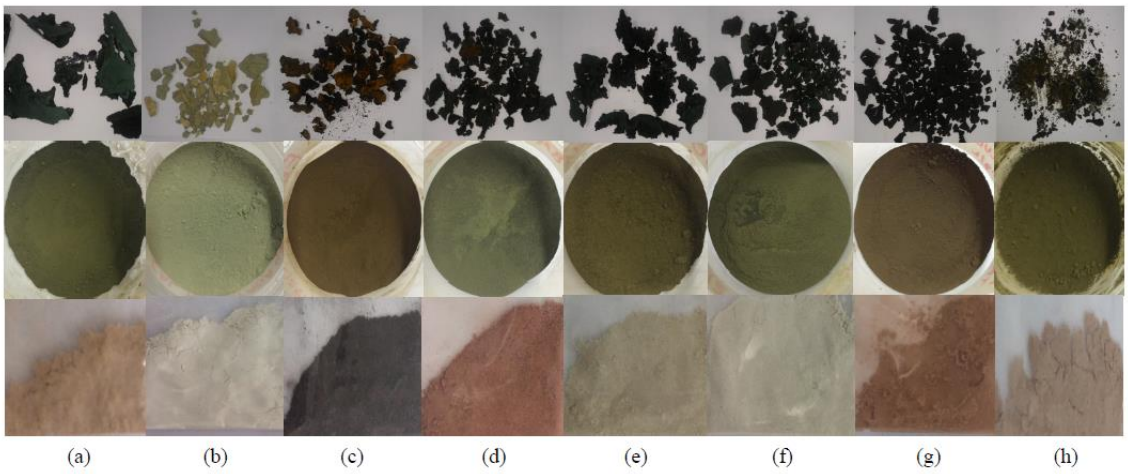

Fig. 3.4. Aspects of microalgae biomass and ash obtained: (a) Polyquaternium polymer; (b) Hydrated lime; (c) Ferric chloride; (d) Ferrous aluminum sulfate; (e) Aliphatic amines polymer; (f) Aluminum polychloride; (g) Tannin-based polymer; (h) No coagulant.

Polyquaternium polymer gave biomass a less fragmented aspect as if a kind of "glue" that bound the material (Fig.3.4a). It was also noted in biomass with aliphatic amines polymer, although less pronounced (Fig.3.4e).

Biomass produced with hydrated lime (Fig.3.4b) and ferric chloride (Fig.3.4c) presented whitish and reddish coloration, respectively, as a result of the substantial amount of these materials used, whereas biomass produced with polymer presented greenish tone, similar to one obtained without coagulant presence (Fig.3.4h) as a consequence of lower dosage used. Biomass produced with aluminum-based coagulants (Fig.3.4d and f) presented a

matte silver-gray color, typical of this metal, while biomass produced from tannin-based polymers showed a brownish coloration similar to the tannin (Fig.3.4g).

Regarding the ashes aspects, different colors were observed, such as white, black, red, and light pink and orange. The different coloration observed can be related to the ease of electronic transition for metals with incomplete d-orbitals, such as iron in biomass produced with ferric chloride and ferrous aluminum sulfate. In contrast, the presence of s- and p-block metals of the periodic table, such as calcium and aluminum, gave whitish and light tones to sludge [24]. This can explain the more pronounced color in Fig. 3.4 (c and d) and the less pronounced color in Fig. 3.4 (b and f). The aspects of soft grey (sand color) ash described by Hossain et al. [25] for Stigonematales sp. mixed microalgae collected from rainwater drains were not observed in any sample. This is further evidence that the type of microalgae, cultivation, and harvest alter the biomass produced.

3.3.2.2 Quantitative analysis

Table 3.2 shows the HHV of all microalgae biomass evaluated, as well as other sources of energy and pure microalgae species, for comparison purposes. According to Show et al. [26] and Pereira et al. [27], the most commonly found microalgae in wastewater are Chlorella and Scenedesmus; therefore, these species were added to Table 3.2.

As can be seen in Table 3.2, the microalgae biomass without the coagulants presence presented the highest HHV, 21.58 MJ/kg—close to that reported in the literature. This HHV value is similar to that of Eucalyptus globulus and Pinus pinaster wood, ratifying its energy potential.

A small amount of the polyquaternium polymer did not practically change the HHV of biomass (decrease 1.8%). However, all other coagulants significantly reduced the HHV of microalgae. The second-lowest HHV reduction was observed using tannin-based polymer (decrease 13.7%). Despite the high dosage used, the organic content of this polymer may have contributed to this result as the coagulant is also burned. The lowest HHV was 3.37 MJ/kg (decrease 84%) for biomass produced with hydrated lime use, which makes it unfeasible for energy recovery. A substantial amount of hydrated lime, used to elevate pH and to separate microalgae, caused an excess of inorganic fraction in biomass that justifies this low HHV. However, hydrated lime was the cheapest material, and this type of harvesting could be applied when the process requires only the microalgae removal from effluent and energy recovery is not desired. The hydrated lime could be recycled in this hypothetical process.

Table 3.2. Biomass characterization. Data are shown as mean (n = 3) ± standard deviation.

Biomass	HHV (MJ/kg)	Ash	Volatile	Fixed Carbon	Moisture	C	H	N	O	Ref.
No coagulant	21.58 ± 0.07	7.50	71.80	14.89	5.81	43.66 ± 0.20	6.52 ± 0.22	9.27 ± 0.03	33.06	-
Polyquaternium polymer	21.19 ± 0.09	8.31	69.80	13.62	8.27	43.83 ± 0.12	6.63 ± 0.19	7.35 ± 0.01	33.86	-
Tannin-based polymer	18.61 ± 1.15	10.60	59.32	24.71	5.36	47.74 ± 0.88	5.90 ± 0.14	6.28 ± 0.10	29.49	-
Aliphatic amines polymer	16.18 ± 0.15	19.00	60.76	10.59	9.64	34.61 ± 0.01	5.76 ± 0.04	5.41 ± 0.10	35.23	-
Aluminum polychloride	12.19 ± 0.19	27.08	55.06	7.86	10.00	25.46 ± 0.13	5.60 ± 0.03	3.92 ± 0.01	37.95	-
Ferrous aluminum sulfate	12.91 ± 0.13	28.38	55.99	6.25	9.39	28.63 ± 0.09	5.53 ± 0.09	4.34 ± 0.01	30.33	-
Ferric chloride	14.45 ± 0.03	31.08	62.25	2.78	3.89	31.05 ± 0.03	5.17 ± 0.06	5.08 ± 0.05	27.63	-
Hydrated lime	3.37 ± 0.07	48.78	47.47	0.00	3.80	16.01 ± 0.12	1.93 ± 0.01	1.18 ± 0.01	32.11	-
Bituminous coal	23.18	21.29	28.13	44.22	6.36	56.77	3.79	0.61	1.08	[29]
Wood *Eucalyptus globulus*	17.6	0.5	86.3	13.3	-	46.2	5.8	0.2	47.2	[30]
Wood *Pinus pinaster*	20.1	0.2	85.8	14.1	-	48.4	6.0	0.1	45.3	[30]
Paper	17.57	6.0	-	-	-	43.4	5.8	0.3	44.3	[31]
Paper	-	5.85	-	-	36.80	27.40	3.76	0.16	25.60	[32]
Plastic	-	6.59	-	-	4.2	63.57	12.00	0.90	9.02	[32]
Used-plastic-waste Refuse-Derived Fuels	23.73	25.17	62.99	7.70	-	41.88	6.50	0.78	24.59	[33]
High density polyethylene	43.10	0	99.70	0.30	-	85.71	14.29	0	0	[34]
Scenedesmus quadricauda	-	4.8	-	-	-	47.71	7.17	5.78	28.3	[35]
Scenedesmus sp.	15.40	37.8	54.3	7.9	7	36.2	4.7	4.2	19.3	[36]
Chlorella sp.	-	13.3	56.75	24.45	5.5	43.92	6.10	7.39	29.29	[37]
Chlorella vulgaris	21.10	9.8	82.7	4.5	3.4	46.8	6.9	9.7	26.3	[38]
Chlorella vulgaris	18.69	8.72	78.98	12.3	-	45.49	6.61	10.28	28.69	[39]

Other coagulants reduced HHV but not enough to avoid energy recovery since those values are in the same range as Eucalyptus globulus and Pinus pinaster wood. Moreover, the HHV could be increased by removing ash through an acid wash, even if this means additional costs. After acid-washing, Liu et al. [28] reported a decrease of ash content of *Scenedesmus* from 44.66 to 14.45%, increasing HHV from 9.51 MJ/kg to 24.23 MJ/kg. The higher the ash was, the lower the HHV [15].

Ferric chloride produced microalgae biomass with intermediate HHV (14.45 MJ/kg) as compared to others. However, the high cost of harvesting discourages its application. Biomass produced with aluminum polychloride presented the second-lowest HHV and the third-largest cost, which means an unfavorable final balance for its use. The biomasses produced with the aliphatic amines polymer and ferrous aluminum sulfate presented intermediate values, both for HHV and for costs, and could be better evaluated, together with the polyquaternium polymer, which had the best result in terms of HHV. Further study for these coagulants is recommended, with Jar Test simulations under different pH conditions and economic scenarios. It may be favorable to invest in alkalizing and/or acidifying chemical agents and additional steps to adjust the pond effluent pH before the harvesting process, to decrease the amount of coagulant, cost, and HHV impact, since coagulants have different efficiency according to the pH of the medium.

Table 3.2 also presents the results obtained for proximate and ultimate analysis. In addition to HHV, fixed carbon and volatile material contribute to better energy utilization, while higher ash and moisture content can be problematic for the energy conversion processes. Low nitrogen and oxygen and high carbon and hydrogen content are also desired. As can be seen in Table 3.2, for microalgae without a coagulant, the results are close to those reported in the literature.

Only microalgae biomass without coagulant and biomass obtained with polymers provided biomass with ash content below 20%. The increase in the ash content is associated with the presence of metal ions in the harvested biomass [13]. The results show that coagulants significantly alter the microalgae ash content, which could compromise subsequent energy recovery processes. Ash may cause operational problems [15], and the use of biomass with high ash content is not feasible unless another lower ash biomass is mixed to give an acceptable ash level [40].

In general, the volatiles fractions present in Table 3.2 were high. The highest value of 71.80% was determined for microalgae biomass without coagulants. The results are following the literature since microalgae generally have a volatile content much higher than solid fossil fuels like coal and peat [15]. These values were reduced as the ash content increased. An interesting result was the third-highest volatile content (62.25%) being for microalgae with ferric chloride despite its high ash content (31.08%). It may be associated with chlorine impregnated in biomass, released at high temperatures. It is important to mention that the presence of chlorinated compounds in gases may damage equipment [41].

As well as volatile content, the fixed carbon content was also reduced as the ash content increased. This is clearly observed in the microalgae with hydrated lime. However, unlike

what is thought, the microalgae free of coagulant did not have the highest fixed carbon. It presented the second highest fixed carbon content (14.89%). The first highest fixed carbon content (24.71%) and carbon content (47.74%) were produced with the organic tannin-based polymer. The results suggest that organic coagulants may increase the fixed carbon and carbon content in biomass.

In the context of moisture, all biomass presented a percentage less than or equal to 10%. For biomass produced with aluminum-based coagulants, higher values were found, probably because of the hygroscopic properties of these coagulants [24]. The ultimate analysis exhibited in Table 3.2 brings a high percentage of carbon and hydrogen in biomass, which is good for energy recovery. Hydrocarbons represent just over half of microalgae biomass without coagulant, with polyquaternium polymer, and tannin-based polymer. However, the percentage of carbon decreases significantly in biomass when the other coagulants are applied due to the increase in the ash content. Another point to be highlighted is that the nitrogen content in microalgae biomass is much higher than other fuels described in Table 3.2.

3.3.3 Ash content evaluation

Table 3.3 displays the results obtained for ash composition. The microalgae biomass produced without coagulants presented the highest number of chemical elements, 19 in total. The high amount of trace elements incorporated in biomass is in agreement with the literature. According to Hossain et al. [25], microalgae are grown in wastewater that typically contains more abundant inorganic components than fresh and marine water, as well as the species cultivated in the laboratory under controlled conditions.

Despite the high number of elements present in biomass, the mass fraction of elements calcium, potassium, and phosphorus corresponded to almost 74% of ash weight. This shows that ashes could be valuable for obtaining fertilizers. Ash and inorganic elements normally are beneficial in agriculture [28].

The biomass obtained with the polyquaternium polymer, due to the low applied concentration, showed a similar ash composition of microalgae without a coagulant, except chlorine content was not detected. This may indicate the synergistic effect between coagulant and biomass, which may modify chemical bonds between the elements, affecting their physicochemical properties. As mentioned by Manara and Zabaniotou [41], it is important to verify the mobility of chemical elements such as sulfur, nitrogen, and chlorine when biomass is used in thermochemical processes. These elements are expected to appear as HCl, H_2S, and NH_3 or be trapped in heavy metals. Considering that chlorine release into gases can damage equipment, the presence of the polyquaternium polymer has been adverse to energy conversion processes. Regarding sulfur, the higher content found in the ashes suggests that this coagulant partially inhibited its release, although the small percentage difference requires caution for this type of analysis.

Table 3.3. Ash composition in microalgae.

	No coagulant	Polyquaternium polymer	Aliphatic amines polymer	Tannin-based polymer	Ferrous aluminum sulfate	Aluminum polychloride	Ferric chloride	Hydrated lime
Al	-	-	-	-	40.25	49.81	-	-
Ca	28.02	29.07	32.29	16.30	8.78	12.71	1.69	95.86
K	25.22	23.33	17.88	13.01	4.81	7.58	2.44	0.20
P	20.74	21.41	19.01	17.89	19.12	19.92	6.68	-
Cl	9.02	-	14.56	-	-	-	-	-
Fe	7.35	11.14	7.46	17.04	19.96	3.60	87.46	0.53
Si	5.54	9.21	4.72	29.08	3.58	4.52	-	2.26
Ti	1.26	1.84	0.97	2.08	0.39	0.32	-	-
S	0.93	2.22	1.52	3.08	2.45	1.01	1.58	0.52
Zn	0.21	0.24	0.23	0.59	0.31	0.17	-	0.02
Mn	0.46	1.06	0.74	0.38	0.13	0.18	0.12	0.09
Zr	0.72	0.02	0.01	0.02	-	-	-	-
Sr	0.19	0.29	0.31	0.08	0.08	0.08	0.02	0.38
Cr	0.13	-	-	0.08	0.09	0.05	-	-
Cu	0.09	0.08	0.09	0.21	0.03	0.02	0.01	0.02
Br	0.04	0.02	0.05	-	-	-	-	-
Rb	0.03	0.03	0.03	0.03	-	0.01	-	-
Ag	0.01	0.03	0.02	-	-	0.02	-	-
Ni	0.02	0.02	-	0.08	-	-	-	-
V	0.01	-	0.01	0.04	0.03	-	-	-
Mo	-	-	-	0.01	-	-	-	-
Sc	-	-	-	-	-	-	-	0.12
Co	-	-	-	-	-	-	-	0.01
Pd	-	-	-	-	-	0.01	-	-
Ba	-	-	0.10	-	-	-	-	-

The aliphatic amines polymer, also used in low amounts, presented values similar to microalgae biomass without coagulants; however, the significant loss of potassium in the ashes is highlighted. In addition, as opposed to the previous polymer, it raised the concentration of chlorine in the ashes. Indeed, it was the only coagulant that increased the fraction of chlorine in the ashes. All others presented zero chlorine content, indicating total chlorine volatilization at high temperatures. This result suggests that certain types of coagulants can be used to enhance the process properties, favoring or disfavoring specific characteristics. The chlorine found in ash can be a major discovery as the release of acid gases is a major challenge in energy conversion processes. This shows that harvesting steps need to be carefully evaluated in order to obtain a more cost-effective scenario, not only for the harvesting step itself but for the whole energy conversion process.

The tannin-based polymers exhibited a marked distinction for biomass without coagulants. The iron and silicon contents increased significantly. Unlike the other samples studied, this sample was harvested in the continuous WWTP separation system, so, although this polymer is an organic compound, the high silicon content may be indicative of dust and sand particles incorporated during the harvesting stage. This incorporation of dirt into the harvesting system has been described in the literature [15]. Potassium, calcium, and phosphorus levels were sharply reduced in ash content while sulfur increased.

As expected, all inorganic coagulants evaluated had a prevalence of metals in the ashes, including aluminum, iron, and calcium, for ferrous aluminum sulfate, aluminum chloride, ferric chloride, and hydrated lime. As these elements increased, phosphorus and potassium fractions were reduced, decreasing the potential for use of ashes as fertilizer.

Beyond the potential of ash reuse in agriculture, the presence of inorganic chemical elements in the biomass can affect the energy conversion process in various ways [14]. Alkaline metals, such as potassium, for example, play a catalytic role in the gasification process, increasing conversion [42]. The use of catalysts decreases the pyrolysis temperature and increases the conversion of microalgae to gaseous products [43]. It can also be used to reduce the formation of unwanted compounds, such as tar in gasification, by catalyzing its breakdown or preventing its formation [42]. Other studies have proved the influence of catalysts on hydrogen enrichment in syngas [14]. Alkaline earth metals are also catalysts but less so than alkaline metals [44]. Several works are reported in the literature and describe the catalytic effects of chemical presents in biomass [16,36,43–46].

Different from alkaline and alkaline earth metal, silicon and phosphorus are inhibitory because they form inactive alkaline silicates and phosphates [44]. What is more, when silicon reacts with alkali metals, it turns the ash into a mobile, sticky liquid that blocks the pipes in equipment [25]. As a result, the total influence of metals will depend on the balance between the elements present. It is worth mentioning that the presence of silicon in microalgae is lower than terrestrial biomass [44].

Metals such as iron and aluminum are typically present in commercial coagulants and also act positively in the gasification process [47]. Moreover, since compounds present in the biomass rapidly deactivate the catalyst, especially sulfur [48], the incorporation of the catalyst continuously into the harvesting process can be very advantageous. Beyond ensuring continuous catalyst supply it avoids an additional step in the process of mixing the catalyst into

microalgae homogenously. This further reinforces the importance of trying to combine the ideal coagulant in the harvesting process for gains in subsequent processes.

3.3.4 Thermogravimetric analysis

The literature usually reports the process of thermal decomposition of microalgae in three stages. In the first stage, moisture and very light volatiles are lost at temperatures below 200 ºC. The second stage typically occurs between 200 and 600 ºC when most of the organic compounds are decomposed, so this is the main stage. In the third stage, weight loss can be observed due to the decomposition of carbonaceous residues at a very slow rate above 600 ºC [13,17,47,49–51].

In terms of enthalpy changes, the thermal profiles described a large endothermic transition corresponding to dehydration in the first stage, a slight exothermic event in the second stage, representing the decarboxylation, and a non-noticeable exothermic peak in the third stage [17].

Despite this general behavior in the thermal degradation of microalgae, one DTG peak or more can be related to different microalgae species [52]. Even for the same microalgae, the DTG profiles can be different if microalgae were cultivated under different conditions [52] or harvested at different times [49]. Multi-peaks recorded in the DTG curve during the second stage might be attributed to the variation in the degradation of different cellular macromolecules such as lipids, proteins, and carbohydrates [13]. At around 300–320 °C, the peak is referred to as the decomposition of proteins and carbohydrates, while the peak around 410–440 °C corresponds to the decomposition of lipids [17]. It justifies peaks accompanied by a shoulder or by smaller peaks [21].

Fig. 3.5 shows the thermal properties of microalgae biomass using TGA/DTG/DTA. Distinct thermal profiles were exhibited, although all were similar to the profile reported in the literature previously described in this section.

The thermal degradation behavior of microalgae without coagulant can be seen in Fig. 3.5(a), and the profile of the curves are similar to those reported by Ansari et al. [17]. The first stage of dehydration was observed at temperatures below 135 ºC, with a weight loss of approximately 7% related to the removal of moisture and very light volatiles contained in the microalgal cells. The second stage occurred between 155 and 535 ºC and corresponded to a devolatilization process that proceeded with a high rate. More than 50% of mass loss can be attributed to this in this zone. Both the moisture and volatiles fractions lost are in good agreement with the proximate analysis presented in Table 3.2 as well as the temperature range and loss percentage reported in the literature [51,53]. The shoulder observed between 400–450 ºC can be attributed to the decomposition of lipids [17,21]. As mentioned by Marcilla et al. [51], a shoulder or smaller peaks can be associated to the decomposition of different kinds of triglycerides and other hexane-soluble compounds.

DTA profiles also agree with the literature [17] and suggest a slight exothermic reaction in the second stage. Though pyrolysis is generally noted for presenting endothermic reactions, since devolatilization consumes energy, the exothermic reaction can be explained by the oxygen released from volatile compounds that turn the atmosphere oxidative [54].

After 535 ºC, the degradation occurred at a slow and constant rate that did not present an abrupt difference in the derivative to present a peak. This slow rate represents the third stage and follows the same behavior described in the literature [13,17,49–51].

The TGA curve shows a percentage of remaining mass (21.7%) above the ash content reported in Table 2 (7.5%). However, the TGA curve was still not stable at 890 ºC, indicating that the degradation of carbonaceous substances retained in the solid residues continued. The same was observed by Raheem et al. [55], who investigated the thermal degradation behavior of *Chlorella vulgaris* and described a slightly lower weight loss rate at 628 °C to 1,000 °C. It is possible to observe in the authors' work an unstabilized TGA curve, even at 1,000 °C, which presented a residual mass value of approximately 18%. Sanchez-Silva et al. [53] also reported higher thermal stability in microalgae, as they decomposed in a broader temperature range. According to the authors, the residue does not remain constant until temperatures above 900 ºC. Fong et al. [43] studied the thermal degradation behavior for *Chlorella vulgaris* at rates of 10, 20, 30, 50, and 100 °C/min under nitrogen. At the rate of 10 °C/min (the same used in this work), it was observed that the TGA curve was not yet constant even after 800 ºC, just like in this work.

The thermal degradation behavior of microalgae with polymeric coagulants can be seen in Fig. 3.5(b), Fig. 3.5(c), and Fig. 3.5(d). The microalgae degradation in the presence of the polyquaternium polymer showed more similar behavior to the microalgae without coagulants due to the low dosage used, although no curve was the same. All polymers reduced peak size in the second stage of degradation, but the tannin-based polymer presented the lowest peak size and the most different thermal profile among the evaluated polymers. This may be related to the different harvesting methods applied, which added silicon and other impurities to the biomass.

Fig. 3.5(b) shows the thermal degradation of microalgae with a tannin-based polymer. The first stage of dehydration was observed at temperatures below 150 ºC, with a weight loss of approximately 14% related to the removal of moisture and very light volatiles contained in the microalgal cells. This is double that found for the microalgae free of coagulants and represents more very light composts since the moisture of both is similar. Another difference was a higher shoulder distinguished near the top of the main peak in the second stage. This shoulder can also be observed in Fig. 3.5(c) and shows the thermal degradation of microalgae with the aliphatic amines polymer.

Microalgae with the polyquaternium polymer do not present a shoulder or peaks significantly different from those observed for the microalgae without coagulant, as seen in Fig. 3.5(d). However, an interesting point observed for this coagulant is that the residual mass at 890 ºC is smaller, around 15%, while the other microalgae with polymers were above 20%, similar to microalgae without coagulants. This may suggest that the polyquaternium polymer had a synergistic effect in anticipating total material degradation. Disregarding the ash fraction of the microalgae without and with the polyquaternium polymer—7.50 and 8.31%, respectively—14.1% of solid remained to be degraded, while in the presence of the polymer, only 7.5% remained, at a temperature of 892 ºC.

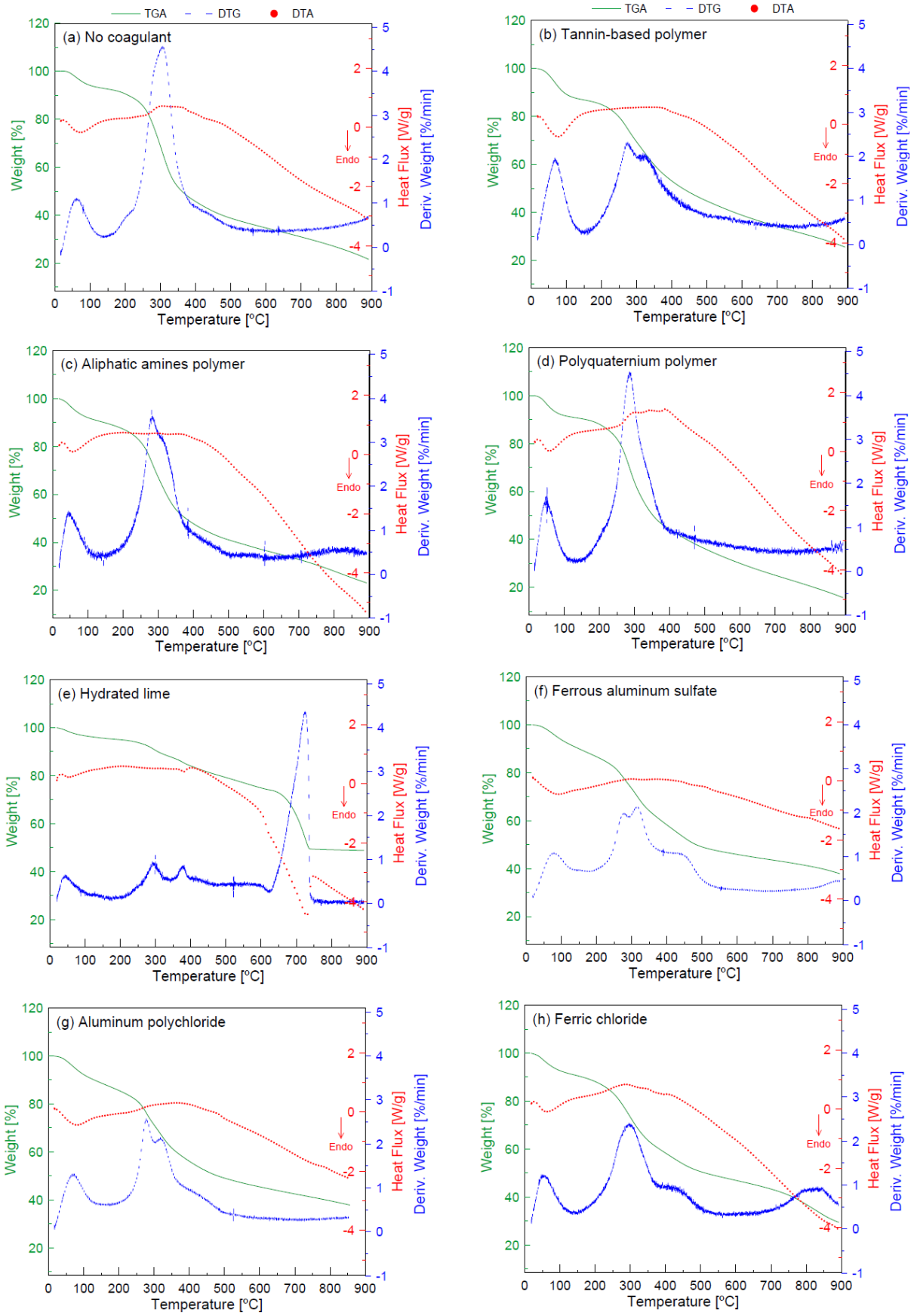

Fig. 3.5. Thermal analysis of microalgae biomass using TGA/DTG/DTA.

Considering the DTA profile, biomass with the polyquaternium polymer showed a more significant exothermic peak compared to biomass without coagulant, as is noted in Fig. 4(d). The maximum heat flow was 1.44 W/g, which is twice the value measured for the biomass without coagulant. For the other polymers, this increase in the exothermic effect in the second stage of degradation is not as pronounced in the DTA curves.

Fig. 3.5(e) presents the thermal degradation of microalgae with hydrated lime. As a consequence of a large amount of lime in the biomass, this graphic was the most different from the others. The first peak observed below 110 ºC can be attributed to moisture loss. The two small peaks between 275 and 450 ºC may be related to the small fractions of organic matter and inorganic transformation. Unlike all the other samples and literature, the largest mass loss was verified in the third stage, between 625 and 765 ºC. This large peak in higher temperatures reflects a large amount of inorganic material in the sample and may be justified by the degradation of hydrated lime and carbonates that could have been formed by the presence of CO_2 in the medium [24]. Calcium hydroxide and calcium carbonate decompose at 580 and 825 °C, respectively [56].

Fig. 3.5(f), Fig. 3.5(g) and Fig. 3.5(h) presents the thermal degradation of microalgae with ferrous aluminum sulfate, aluminum polychloride, and ferric chloride, respectively. A greater number of peaks and shoulders can be observed in these figures, compared to microalgae with polymers and without coagulants. This thermal behavior can be attributed to the inorganic compounds present in biomass. For example, iron and aluminum chlorides degrade below 300 ºC, while iron and aluminum sulfates degrade at 480 and 770 ºC, respectively [56]. The last peak observed in Fig. 4(h) around 800 ºC can also be attributed to inorganic content. López-González et al. [16] found peaks around 1,000 ºC for *Scenedesmus almeriensis*, *Nannochloropsis gaditana*, and *Chlorella vulgaris* and explained its occurrence by two facts: the devolatilization of char and the decomposition of mineral matter.

Considering the DTA profile, the presence of inorganic coagulants suggests a decrease in the energy released in the second stage of degradation compared to the biomass free of coagulant, except for ferric chloride, where it is possible to notice a slightly exothermic region for the second stage in its DTA curve. For other inorganic coagulants, the exothermic effect in the second stage of degradation is not as pronounced in the DTA curves. Biomass with ferrous aluminum sulfate showed a maximum heat flow of only 0.12 W/g—six times smaller than the value measured for the biomass without coagulant.

All DTG curves are plotted overlapping each other in Fig. 3.6 to allow a global view of the thermal profile and to compare the effect of each coagulant on biomass. As mentioned by Yang et al. [47], the peak of the DTG curve represents the activation of the thermochemical reaction, the height of the peak identifies the capability to release volatile matter from a reaction during the slow pyrolysis process, and the temperature of the peak indicates the reaction temperature. Thus, the thermal degradation shown in Fig 3.6 reveals that all samples decomposed differently and in multiple stages and, therefore, would behave differently during a thermal process.

The experimental curve indicates that the thermal degradation process starts at around 130 °C and continues to around 540 °C. After this temperature, no peak was observed in the DTG curve, except those attributed to inorganic compound degradation in microalgae with hydrated lime and ferric chloride. The absence of peaks after 500 ºC is in agreement with the literature

[57,58]. Wang et al. [59] showed that most compounds decomposed below 500 ºC for microalgae.

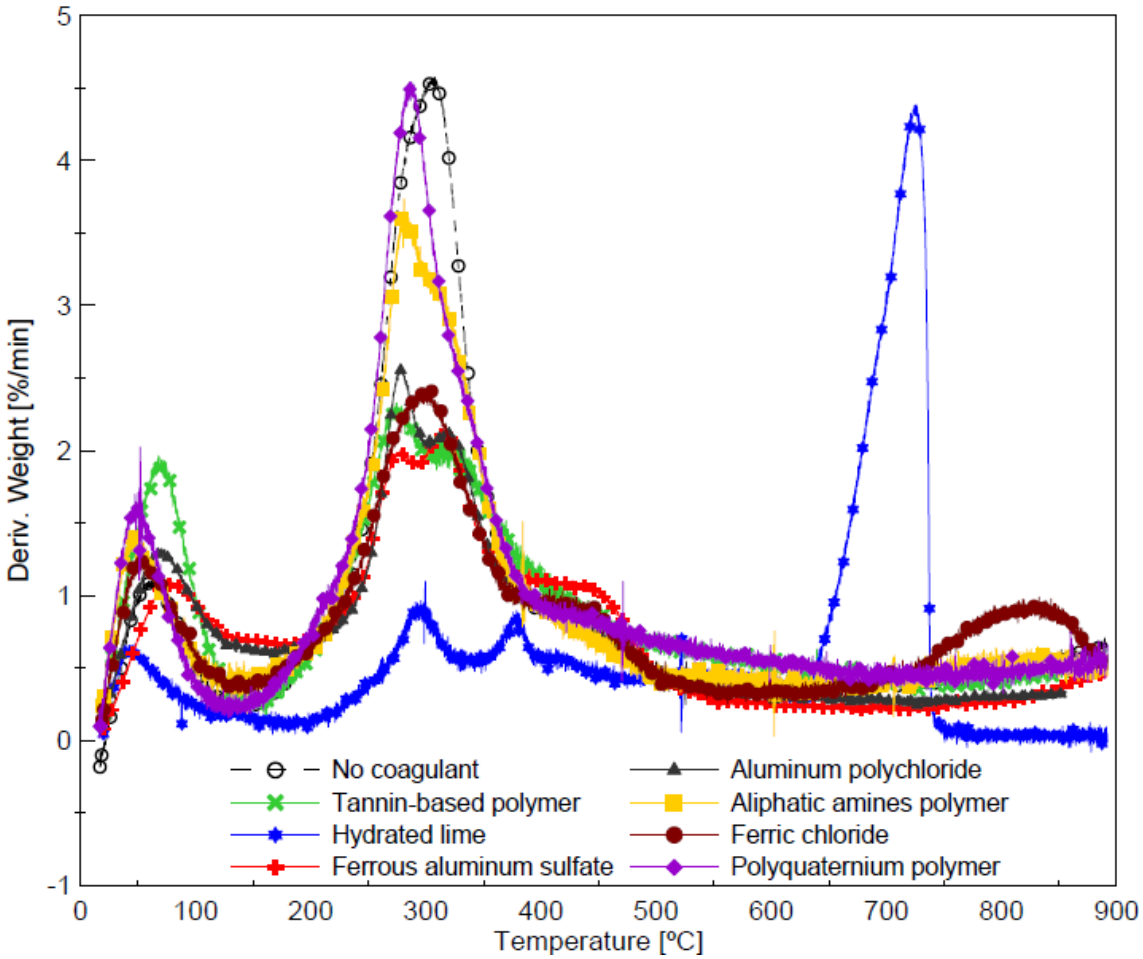

Fig. 3.6. DTG characteristics of microalgae at different coagulants.

The peaks observed in the first step of degradation (below 200 ºC) were more significative with tannin-based polymer coagulants; 9.69% of mass loss already disregarded the percentage of humidity. This value was double or triple those observed for the other samples studied.

Comparing the peak's height in the second stage, the maximum degradation occurred in microalgae free of coagulants, 4.57 %/min at 308 ºC. It is practically the same temperature reported by Liu et al. [52] for the thermal degradation of microalgae. In the presence of coagulants, the maximum degradation rate ranged from 2.14 %/min (ferrous aluminum sulfate) to 4.54 %/min (polyquaternium polymer). The maximum degradation in microalgae free of additional chemical compounds is in accordance with Fong et al. [43]. The authors added the catalyst HZSM-5 zeolite, limestone, and an HZSM-5/limestone mixture in *Chlorella vulgaris* and showed a lower peak.

The results displayed in Fig. 3.6 suggest the catalytic effect of coagulants. Except for microalgae biomass with ferrous aluminum sulfate, which increased the peak temperature from 308 to 316 ºC in the devolatilization stage, all the other coagulants reduced it, with the lowest

temperature being 274 ºC, measured in presence of the tannin-based polymer. The catalytic effect is more evident in microalgae biomass with the polyquaternium polymer. Even when the low dosage was used, this coagulant not only reduced the devolatilization temperature to 278 °C but also had the smallest mass degraded at the final experiment temperature. For inorganic coagulants, the large amount added prevented a deep catalytic assessment, and the results more portray the effect of coagulant mass incorporated into microalgae.

3.4 Conclusion

By comparing different commercial coagulants, this study showed how coagulants used in the harvesting process could modify the properties of microalgae biomass and, thus, influence the energy recovery process. All coagulants reduced the HHV, from 1.8% to 84%, but mainly inorganic coagulants as a result of the high ash incorporated. These inorganic coagulants must be well evaluated before applying in the harvesting process if energy recovery from microalgae is desired. The coagulant used also affects the thermochemical profile, and the catalytic effect was better observed in polymers due to the low dosage used. The maximum degradation of 4.57 %/min occurred in microalgae free of coagulants, at 308 ºC, but the polyquaternium polymer accelerated total biomass degradation. Moreover, this polymer appears to increase heat release in the second stage of decomposition. In general, this coagulant presented the best results, such as low cost, high efficiency, a small reduction in HHV, and improvement in the thermochemical behavior of microalgae biomass. On the other hand, the aliphatic amines polymer was the only coagulant that showed chlorine in the ash analysis, indicating a possible trapping effect. This can be a major discovery, as the release of acid gases is a major challenge in energy conversion processes. Therefore, aliphatic amines polymer also is suggested as the better coagulant along with the polyquaternium polymer.

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References

[1] K. Li, Q. Liu, F. Fang, R. Luo, Q. Lu, W. Zhou, S. Huo, P. Cheng, J. Liu, M. Addy, P. Chen, D. Chen, R. Ruan, Microalgae-based wastewater treatment for nutrients recovery: A review, Bioresour. Technol. 291 (2019) 121934. doi:10.1016/j.biortech.2019.121934.

[2] R.B. Soares, M.F. Martins, Ricardo Franci Gonçalves, A conceptual scenario for the use

of microalgae biomass for microgeneration in wastewater treatment plants, J. Environ. Manage. 252 (2019) 109639. doi:10.1016/j.jenvman.2019.109639.

[3] B. Singh, K. Bauddh, F. Bux, Algae and environmental sustainability, Springer, 2015. doi:10.1007/978-81-322-2641-3.

[4] M.K. Lam, K.T. Lee, Cultivation of Chlorella vulgaris in a pilot-scale sequential-baffled column photobioreactor for biomass and biodiesel production, Energy Convers. Manag. 88 (2014). doi:10.1016/j.enconman.2014.08.063.

[5] S. Longo, B.M. d'Antoni, M. Bongards, A. Chaparro, A. Cronrath, F. Fatone, J.M. Lema, M. Mauricio-Iglesias, A. Soares, A. Hospido, Monitoring and diagnosis of energy consumption in wastewater treatment plants. A state of the art and proposals for improvement, Appl. Energy. 179 (2016) 1251–1268. doi:10.1016/j.apenergy.2016.07.043.

[6] M. Wakeel, B. Chen, T. Hayat, A. Alsaedi, B. Ahmad, Energy consumption for water use cycles in different countries: A review, Appl. Energy. 178 (2016) 868–885. doi:10.1016/j.apenergy.2016.06.114.

[7] H. Wang, Y. Yang, A.A. Keller, X. Li, S. Feng, Y. nan Dong, F. Li, Comparative analysis of energy intensity and carbon emissions in wastewater treatment in USA, Germany, China and South Africa, Appl. Energy. 184 (2016) 873–881. doi:10.1016/j.apenergy.2016.07.061.

[8] M. Kumar, S. Enamala, M. Chavali, J. Donepudi, Production of biofuels from microalgae - A review on cultivation , harvesting , lipid extraction , and numerous applications of microalgae, Renew. Sustain. Energy Rev. 94 (2018) 49–68. doi:10.1016/j.rser.2018.05.012.

[9] Y. Gerchman, B. Vasker, M. Tavasi, Y. Mishael, Y. Kinel-Tahan, Y. Yehoshua, Effective harvesting of microalgae: Comparison of different polymeric flocculants, Bioresour. Technol. 228 (2017) 141–146. doi:10.1016/j.biortech.2016.12.040.

[10] C. Wan, M.A. Alam, X.Q. Zhao, X.Y. Zhang, S.L. Guo, S.H. Ho, J.S. Chang, F.W. Bai, Current progress and future prospect of microalgal biomass harvest using various flocculation technologies, Bioresour. Technol. 184 (2015) 251–257. doi:10.1016/j.biortech.2014.11.081.

[11] S.B. Ummalyma, E. Gnansounou, R.K. Sukumaran, R. Sindhu, A. Pandey, D. Sahoo, Bioflocculation: An alternative strategy for harvesting of microalgae – An overview, Bioresour. Technol. 242 (2017) 227–235. doi:10.1016/j.biortech.2017.02.097.

[12] R.J. Anthony, J.T. Ellis, A. Sathish, A. Rahman, C.D. Miller, R.C. Sims, Effect of coagulant/flocculants on bioproducts from microalgae, Bioresour. Technol. 149 (2013) 65–70. doi:10.1016/j.biortech.2013.09.028.

[13] S. Wang, M. Yerkebulan, A.E. Abomohra, S. El-khodary, Q. Wang, Bioresource Technology Microalgae harvest influences the energy recovery : A case study on chemical flocculation of Scenedesmus obliquus for biodiesel and crude bio-oil production, Bioresour. Technol. 286 (2019) 121371. doi:10.1016/j.biortech.2019.121371.

[14] N. Abdoulmoumine, S. Adhikari, A. Kulkarni, S. Chattanathan, A review on biomass

gasification syngas cleanup, Appl. Energy. 155 (2015) 294–307. doi:10.1016/j.apenergy.2015.05.095.

[15] F. Sotoudehniakarani, A. Alayat, A.G. Mcdonald, Journal of Analytical and Applied Pyrolysis Characterization and comparison of pyrolysis products from fast pyrolysis of commercial Chlorella vulgaris and cultivated microalgae, J. Anal. Appl. Pyrolysis. 139 (2019) 258–273. doi:10.1016/j.jaap.2019.02.014.

[16] D. López-González, M. Fernandez-Lopez, J.L. Valverde, L. Sanchez-Silva, Pyrolysis of three different types of microalgae : Kinetic and evolved gas analysis pez-Gonz a, Energy. 73 (2014) 33–43. doi:10.1016/j.energy.2014.05.008.

[17] F.A. Ansari, B. Ravindran, S.K. Gupta, M. Nasr, I. Rawat, F. Bux, Techno-economic estimation of wastewater phycoremediation and environmental bene fi ts using Scenedesmus obliquus microalgae, J. Environ. Manage. 240 (2019) 293–302. doi:10.1016/j.jenvman.2019.03.123.

[18] P. Das, M.I. Thaher, M.A.Q.M. Abdul Hakim, H.M.S.J. Al-Jabri, G.S.H.S. Alghasal, Microalgae harvesting by pH adjusted coagulation-flocculation, recycling of the coagulant and the growth media, Bioresour. Technol. 216 (2016) 824–829. doi:10.1016/j.biortech.2016.06.014.

[19] D. López-González, M. Fernandez-Lopez, J.L. Valverde, L. Sanchez-Silva, Comparison of the steam gasification performance of three species of microalgae by thermogravimetric-mass spectrometric analysis, Fuel. 134 (2014). doi:10.1016/j.fuel.2014.05.051.

[20] S.T. Cassini, S.A. Francisco, P.W.P. Antunes, R.N. Oss, R. Keller, Harvesting Microalgal Biomass grown in Anaerobic Sewage Treatment Effluent by the Coagulation-Flocculation Method: Effect of pH , Brazilian Arch. Biol. Technol. . 60 (2017).

[21] Q. Bach, W. Chen, Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review, Bioresour. Technol. 246 (2017) 88–100. doi:10.1016/j.biortech.2017.06.087.

[22] B. Zhao, Y. Su, Process effect of microalgal-carbon dioxide fixation and biomass production: a review, Renew. Sustain. Energy Rev. 31 (2014) 121–132.

[23] C.N. do M.A. CONAMA, Resolução No 430, Diário Of. Da União. 92 (2011) 89. doi:10.1073/pnas.0703993104.

[24] J.D. Lee, H.E. Toma, K. Araki, R.C. Rocha, Química inorgânica não tão concisa, Edgard Blucher, 1999.

[25] N. Hossain, J. Zaini, T.M.I. Mahlia, A.K. Azad, Elemental , morphological and thermal analysis of mixed microalgae species from drain water, Renew. Energy. 131 (2019) 617–624. doi:10.1016/j.renene.2018.07.082.

[26] P.L. Show, M.S.Y. Tang, D. Nagarajan, T.C. Ling, C.-W. Ooi, J.-S. Chang, A holistic approach to managing microalgae for biofuel applications, Int. J. Mol. Sci. 18 (2017). doi:10.3390/ijms18010215.

[27] M.V. Pereira, A.F. Dassoler, P.W. Antunes, R.F. Gonçalves, S.T. Cassini, M. Vinicius,

A.F. Dassoler, P.W. Antunes, Indigenous microalgae biomass cultivation in continuous reactor with anaerobic effluent : effect of dilution rate on productivity , nutrient removal and bioindicators, Environ. Technol. 0 (2018) 1–13. doi:10.1080/09593330.2018.1549105.

[28] H. Liu, Y. Chen, H. Yang, F.G. Gentili, U. Söderlind, X. Wang, W. Zhang, H. Chen, Hydrothermal carbonization of natural microalgae containing a high ash content, Fuel. 249 (2019) 441–448. doi:10.1016/j.fuel.2019.03.004.

[29] X. Lin, Y. Wu, C. Wu, L. Yao, X. Wu, L. Chen, K. Cen, Evolution of volatile cloud in pulverized coal combustion with high-speed digital inline holographic visualization, Fuel. 241 (2019) 199–206. doi:https://doi.org/10.1016/j.fuel.2018.10.133.

[30] C. Telmo, J. Lousada, N. Moreira, Proximate analysis, backwards stepwise regression between gross calorific value, ultimate and chemical analysis of wood, Bioresour. Technol. 101 (2010) 3808–3815. doi:https://doi.org/10.1016/j.biortech.2010.01.021.

[31] T.B. Reed, A. Das, Handbook of Biomass Downdraft Gasifier Engine Systems, (1988).

[32] M. Shahabuddin, B.B. Krishna, T. Bhaskar, G. Perkins, Advances in the thermo-chemical production of hydrogen from biomass and residual wastes: Summary of recent techno-economic analyses, Bioresour. Technol. 299 (2020) 122557. doi:https://doi.org/10.1016/j.biortech.2019.122557.

[33] C. Kungkajit, G. Prateepchaikul, T. Kaosol, Influence of Plastic Waste for Refuse-Derived Fuel on Downdraft Gasification, Energy Procedia. 79 (2015) 528–535. doi:https://doi.org/10.1016/j.egypro.2015.11.529.

[34] S. Zhang, S. Zhu, H. Zhang, X. Liu, Y. Xiong, High quality H2-rich syngas production from pyrolysis-gasification of biomass and plastic wastes by Ni–Fe@Nanofibers/Porous carbon catalyst, Int. J. Hydrogen Energy. 44 (2019) 26193–26203. doi:https://doi.org/10.1016/j.ijhydene.2019.08.105.

[35] L. Tiong, M. Komiyama, Y. Uemura, T.T. Nguyen, Catalytic supercritical water gasification of microalgae: Comparison of Chlorella vulgaris and Scenedesmus quadricauda, J. Supercrit. Fluids. 107 (2016) 408–413. doi:10.1016/j.supflu.2015.10.009.

[36] Y. Zhu, P. Piotrowska, P.J. Van Eyk, D. Boström, X. Wu, C. Boman, M. Broström, J. Zhang, C.W. Kwong, D. Wang, A.J. Cole, R. De Nys, F.G. Gentili, P.J. Ashman, Fluidized Bed Co-gasification of Algae and Wood Pellets: Gas Yields and Bed Agglomeration Analysis, Energy and Fuels. 30 (2016) 1800–1809. doi:10.1021/acs.energyfuels.5b02291.

[37] K. Kirtania, J. Joshua, M.A. Kassim, S. Bhattacharya, Comparison of CO2 and steam gasification reactivity of algal and woody biomass chars, Fuel Process. Technol. 117 (2014) 44–52. doi:10.1016/j.fuproc.2013.02.006.

[38] U. Ekpo, A.B. Ross, M.A. Camargo-Valero, P.T. Williams, A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate, Bioresour. Technol. 200 (2016). doi:10.1016/j.biortech.2015.11.018.

[39] G. Liu, Y. Liao, Y. Wu, X. Ma, Synthesis gas production from microalgae gasi fi cation

in the presence of Fe 2 O 3 oxygen carrier and CaO additive, Appl. Energy. 212 (2018) 955–965. doi:10.1016/j.apenergy.2017.12.110.

[40] J. Lee, D. Sohn, K. Lee, K. Young, Chemosphere Solid fuel production through hydrothermal carbonization of sewage sludge and microalgae Chlorella sp . from wastewater treatment plant, Chemosphere. 230 (2019) 157–163. doi:10.1016/j.chemosphere.2019.05.066.

[41] P. Manara, A. Zabaniotou, Towards sewage sludge based biofuels via thermochemical conversion - A review, Renew. Sustain. Energy Rev. 16 (2012) 2566–2582. doi:10.1016/j.rser.2012.01.074.

[42] N.M.N. Qadi, I.N. Zaini, F. Takahashi, K. Yoshikawa, CO<inf>2</inf> Cogasification of Coal and Algae in a Downdraft Fixed-Bed Gasifier: Effect of CO<inf>2</inf> Partial Pressure and Blending Ratio, Energy and Fuels. 31 (2017). doi:10.1021/acs.energyfuels.6b03148.

[43] M.J.B. Fong, A.C.M. Loy, B.L.F. Chin, M.K. Lam, S. Yusup, Z.A. Jawad, Bioresource Technology Catalytic pyrolysis of Chlorella vulgaris : Kinetic and thermodynamic analysis, Bioresour. Technol. 289 (2019) 121689. doi:10.1016/j.biortech.2019.121689.

[44] C. Hognon, C. Dupont, M. Grateau, F. Delrue, Comparison of steam gasification reactivity of algal and lignocellulosic biomass: Influence of inorganic elements, Bioresour. Technol. 164 (2014) 347–353. doi:10.1016/j.biortech.2014.04.111.

[45] N.M.N. Qadi, A. Hidayat, F. Takahashi, K. Yoshikawa, Co-gasification kinetics of coal char and algae char under CO<inf>2</inf> atmosphere, Biofuels. 8 (2017). doi:10.1080/17597269.2016.1224292.

[46] A.S. Al-Dughaither, H. de Lasa, HZSM-5 Zeolites with Different SiO2/Al2O3 Ratios. Characterization and NH3 Desorption Kinetics, Ind. Eng. Chem. Res. 53 (2014) 15303–15316. doi:10.1021/ie4039532.

[47] C. Yang, C. Wang, R. Li, B. Zhang, Q. Qiu, B. Wang, H. Yang, Y. Ding, Pyrolysis of microalgae : A critical review, 186 (2019) 53–72. doi:10.1016/j.fuproc.2018.12.012.

[48] G. Peng, F. Vogel, D. Refardt, C. Ludwig, Catalytic Supercritical Water Gasification: Continuous Methanization of Chlorella vulgaris, Ind. Eng. Chem. Res. 56 (2017). doi:10.1021/acs.iecr.7b00042.

[49] S. Wang, B. Bernard, A.E. Abomohra, Q. Wang, Z. He, Y. Feng, B. Zhang, C. Hui, Journal of Analytical and Applied Pyrolysis Characterization and pyrolysis behavior of the green microalga Micractinium conductrix grown in lab-scale tubular photobioreactor using Py-GC / MS and TGA / MS, J. Anal. Appl. Pyrolysis. 135 (2018) 340–349. doi:10.1016/j.jaap.2018.08.019.

[50] K. Azizi, M. Keshavarz, H. Abedini, Bioresource Technology Characteristics and kinetics study of simultaneous pyrolysis of microalgae Chlorella vulgaris , wood and polypropylene through TGA, Bioresour. Technol. 243 (2017) 481–491. doi:10.1016/j.biortech.2017.06.155.

[51] A. Marcilla, A. Gómez-Siurana, C. Gomis, E. Chápuli, M.C. Catalá, F.J. Valdés, Characterization of microalgal species through TGA / FTIR analysis : Application to nannochloropsis sp Thermochimica Acta Characterization of microalgal species through

TGA / FTIR analysis : Application to nannochloropsis sp ., (2009). doi:10.1016/j.tca.2008.12.005.

[52] Y.-Q. Liu, L.R.X. Lim, J. Wang, R. Yan, A. Mahakhant, Investigation on Pyrolysis of Microalgae Botryococcus braunii and Hapalosiphon sp., Ind. Eng. Chem. Res. 51 (2012) 10320–10326. doi:10.1021/ie202799e.

[53] L. Sanchez-Silva, D. López-González, J. Villaseñor, P. Sánchez, J.L. Valverde, Thermogravimetric-mass spectrometric analysis of lignocellulosic and marine biomass pyrolysis, Bioresour. Technol. 109 (2012) 163–172. doi:10.1016/j.biortech.2012.01.001.

[54] F. Lopes, F. Bittencourt, A. Barbosa, L. Elias, A. Dalvi, M. Ferreira, Thermodynamic assessment of human feces gasification : an experimental - based approach, SN Appl. Sci. 1 (2019) 1–13. doi:10.1007/s42452-019-1104-1.

[55] A. Raheem, S. Sivasangar, W.A.K.G. Wan Azlina, Y.H. Taufiq Yap, M.K. Danquah, R. Harun, Thermogravimetric study of Chlorella vulgaris for syngas production, Algal Res. 12 (2015). doi:10.1016/j.algal.2015.08.003.

[56] R.H. Perry, D.W. Green, J.O. Maloney, Perry's chemical engineers' handbook, 7th ed, McGraw-Hill New York, New York, 1997.

[57] W. Chen, Y. Chu, J. Liu, J. Chang, Thermal degradation of carbohydrates , proteins and lipids in microalgae analyzed by evolutionary computation, Energy Convers. Manag. 160 (2018) 209–219. doi:10.1016/j.enconman.2018.01.036.

[58] K. Azizi, M. Keshavarz, H. Abedini, Bioresource Technology Simultaneous pyrolysis of microalgae C . vulgaris , wood and polymer : The e ff ect of third component addition, 247 (2018) 66–72. doi:10.1016/j.biortech.2017.09.059.

[59] X. Wang, B. Zhao, X. Yang, Co-pyrolysis of microalgae and sewage sludge : Biocrude assessment and char yield prediction, Energy Convers. Manag. 117 (2016) 326–334. doi:10.1016/j.enconman.2016.03.013.

Chapter 4

Wastewater microalgae gasification

A version of this chapter has been published:

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Experimental investigation of wastewater microalgae in a pilot-scale downdraft gasifier

Abstract

Microalgae are potential feedstock for biofuels due to higher heating value and rapid growth rate. It can be cultivated in sewage, avoiding costs associated with clean water and nutrients, making the possibility of energy generation from wastewater treatment plants appealing. Compact microgeneration systems involving biomass gasifiers are already commercialized for small-scale projects and could be adapted for use with microalgae in wastewater. In this study, an experimental investigation of a commercial downdraft gasifier was conducted using microalgae produced in a wastewater treatment plants. The effects of the air-fuel equivalence ratio on syngas composition, higher heating value, and production rates were evaluated. An increasing and then decreasing trend in equivalence ratio with a peak was observed, indicating that the optimum equivalence ratio for the best performance is 0.23. The cold gas efficiency was 87%, higher heating value was 6.2 MJ/Nm^3, and the production rate was 2.8 Nm^3/kg dry biomass. The syngas composition was 11.9% H_2, 19.5% CO, 8.5% C_xH_y, and 9.8% CO_2. The H_2/CO ratio observed in the syngas was 0.61, which is very close to the 0.60 recommended for synthetic fuel production (Fischer-Tropsch gasoline and diesel).

Graphical Abstract

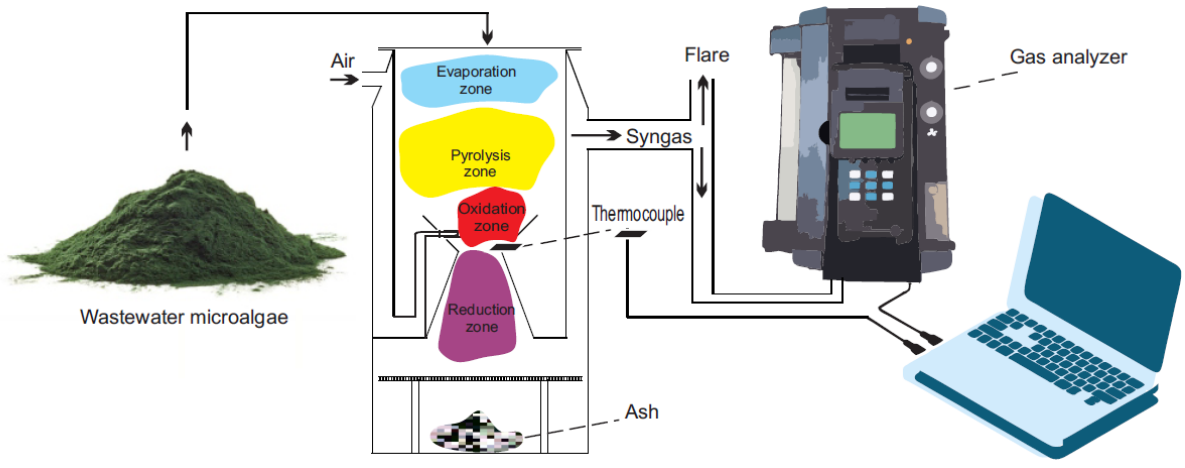


Fig. 4.1. Graphical abstract chapter 4.

Keywords: Gasification; Cold gas efficiency; Equivalence ratio; Wastewater treatment plant.

Highlights

- Wastewater microalgae were gasified in a commercial downdraft gasifier.
- Air was used as the gasifying agency and the best equivalence ratio was 0.23.
- The syngas composition was 11.9% H_2, 19.5% CO, 8.5% CH_4, and 9.8% CO_2.
- The H_2/CO ratio was very close to the recommended for synthetic fuel production.
- The syngas calorific value was 6.2 MJ/Nm^3 and the cold gas efficiency was 87%.

4.1 Introduction

Energy use in the distribution of drinking water and wastewater treatment plants (WWTPs) is estimated to be 7% of the total energy produced globally [1]. High energy consumption increases operating costs [2,3] and greenhouse gas emissions [4–6]. Besides, increasing uncertainties about the future of fossil fuels and the rising global energy demand [7,8] motivates scientists to discover new energy sources, processes, and technologies to make WWTPs more economical and sustainable [5,9]. For instance, the large production of microalgae biomass observed in ponds is no longer seen as a problem but can be viewed as feedstock for energy production because microalgae can double in volume in less than a day [10–12].

Among various technologies that use biomass as fuel to produce energy, gasification is one of the most promising and suitable technologies for small-scale power generation [13,14]. The process involves thermal decomposition of organic compounds in the presence of a gasifying agent (usually air, oxygen, steam or CO_2) to produce a combustible gas, called syngas. The main advantages of gasification are the conversion of the entire biomass, high efficiency, and short conversion time [15–17]. Gasifiers coupled with internal combustion (IC) engines and generators are already commercialized [18]. These types of power plants are becoming increasingly efficient, and they can revolutionize energy production in WWTPs due to their ability to produce energy that can meet local energy demand [14].

Microgeneration of energy in WWTPs using microalgae gasification was evaluated by Soares et al. [19], who developed a conceptual scenario based on an extensive systematic literature review, suggesting that the implementation of a downdraft gasifier has a production potential of 0.167 kWh/m^3 of treated sewage, and the investment may be financially returned. However, the amount of energy required to dry microalgae must be recovered through process optimization and integration.

To date, only six researchers [20–25] have gasified microalgae using fixed bed gasifiers and none were conducted at a large scale, according to the extensive systematic literature review done by Soares et al. [19]. Moreover, the gasifying agents used in these works were not air, the most economical and traditional gasifying agent [17,26]. Despite the fact that air generates syngas with lower calorific values (4–7 MJ/Nm^3) due to its high nitrogen content that makes it insufficient for application on more sophisticated and efficient equipment, such as fuel cell, this syngas is viable for application in internal combustion engines and provides an economical and efficient process for small and medium gasification units [27,28].

There is still a lack of knowledge regarding the best parameters to use for microalgae gasification in downdraft gasifiers using air as the gasifying agent. The air-fuel equivalence ratio (ER), for example, is considered the most important parameter on the calorific value of syngas and must be evaluated to recover as much energy as possible [17,29]. An excessively low ER results in incomplete gasification, while a high ER results in excessive formation of combustion products at the expense of fuel gases [26]. In addition, most gasification studies have been conducted using pure species of microalgae (monoculture) obtained commercially, instead of microalgae grown in the wastewater [19]. As mentioned by Soares et al. [30], microalgae produced with wastewater effluent and harvested by traditional coagulation processes can alter the thermochemical profile of the biomass. The incorporation of metals in biomass, for example, reduces the calorific value, but it can also act positively on thermochemical conversion, acting as a catalyst [31,32].

For these reasons, this study conducted an experimental investigation on wastewater microalgae in a pilot-scale downdraft biomass gasifier. To the best of our knowledge and based on the extensive systematic literature review of Soares et al. [19], this is possibly the first work involving wastewater microalgae gasification using a commercial downdraft gasifier with air as the gasifying agent. The biomass was produced in a pilot WWTP and harvested by coagulation with a tannin-based polymer. Different ERs were tested and the best parameter for energy recovery was observed.

4.2 Experimental details

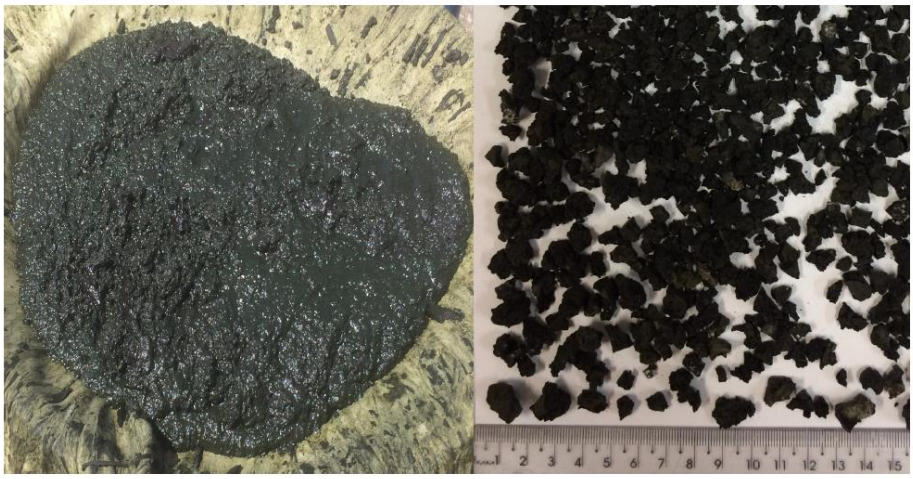
4.2.1 Wastewater microalgae production

The microalgae were produced in two high rate algae ponds (HRAP), both measuring 13.7 m^3 of useful volume, with two 10 m long channels, 2.4 m in width with 22.8 m^2 of superficial area. The HRAP was fed with the effluent obtained after wastewater treatment into an up-flow anaerobic sludge blanket (UASB) reactor, measuring 1.0 m in diameter, 4.8 m usable height, 3.8 m^3 usable volume, and 0.14 L/s average flow rate. A grating system, preliminary to UASB reactor, was used to remove coarse solids from raw domestic wastewater produced in the City of Vila Velha, located in the State of Espírito Santo, southeastern Brazil. Harvesting was done in a continuum coagulation-flocculation system using 50 mg/L of a tannin-based polymer, following the methods as conducted by Cassini et al. [33]. The biomass was densified in a fabric, dried at 60 ºC in an outdoor furnace to eliminate odors, sanitized at 105 °C in an indoor furnace for at least 12 h, and then characterized. Complete removal of moisture was done to avoid degradation of the biomass during the storage period until the gasification experiments were carried out.

The wastewater microalgae biomass produced was composed of different microalgae species and bacteria under coagulants presence rather than a selected pure specie of microalgae (monoculture) [19]. The bacteria and microalgae were indigenous to the type of wastewater. From domestic wastewater produced in southeastern Brazil, different indigenous microalgae strains are reported in the literature, such as *Chlorococcum sp*., *Chlorella sp*., *Scenedesmus sp*., and *Tetradesmus sp*. [34]. As mentioned by Jebali et al. [35], treatment facilities wastewater is

naturally colonized by species such as *Chlorella sp*., *Scenedesmus sp*., or microalgae belonging to the *Bacillariophyta* and *Cyanobacteria* groups.

Fig. 4.2 shows the wastewater microalgae biomass before and after drying. The biomass naturally fragmented during the drying process, resulting in solid pieces of firm consistency and dark color, similar to coal. The dark color could be associated with tannin coagulant. Another observation was an unpleasant odor produced during the drying process that dissipated after an initial period of drying at 60 ºC in an outdoor furnace. Most of the solid pieces (52.5%) were particles between 4.7 and 9.5 mm in size; therefore, this size range was used in the gasification process without additional adjustments. 34.8% of the solid pieces were particles above 9.5 mm in size, 12.7% of the particles were below 4.7 mm, and no significant amount of dust was observed. Only the particles between 4.7 and 9.5 mm in size were gasified.



(a) (b)

Fig. 4.2. Wastewater microalgae biomass aspect before (a) and after (b) drying.

4.2.2 Wastewater microalgae characterization

The main energetic characteristics of the microalgae produced were evaluated. The higher heating value (HHV) was performed using a calorimeter (C2000, IKA-Werke, Germany) and 0.5 g of sample. The post-combustion residue, composed of ashes, was collected and analyzed by an X-ray fluorescence spectrometer (EDX720, SHIMADZU, Japan). The EDX720 includes a Rhodium (Rh) X-ray tube and Si(Li) detector operating at 15-50 kV and 1,000 mA. The proximate analysis was performed using a thermogravimetric analyzer (TGA701, LECO, Germany). The ultimate analysis was performed using an elemental composition analyzer (PE 2400 series II, PerkinElmer, USA). The carbon, hydrogen, and nitrogen content of the sample were determined directly, while oxygen was obtained by difference. The amounts are given in wt.% of the sample on a dry basis. The thermogravimetric analyses (TGA), differential thermogravimetric (DTG), and differential thermal analysis (DTA) were performed by Thermal Analyzer (Q600, TA INSTRUMENTS, USA) with a 50 mg sample capacity and a 1500 °C maximum heating temperature. The tests were performed with a heating rate of 10 °C/min to a temperature of 900 °C, with a nitrogen flow of 50 mL/min, and a 25 mg sample.

Table 4.1 presents the microalgae's characterization and Fig. 4.3 shows the thermal degradation of microalgae. The microalgae's characterization and thermochemical profile were similar to those reported in the literature [36–41], and the high silicon content may be indicative of dust and sand particles incorporated during the harvesting stage [30]. A clear peak in the DTG curve can be observed in Fig. 4.3 for a temperature below 150 °C, with a weight loss of approximately 14% related to the removal of moisture [30]. This stage of dehydration is also observed in the DTA curve, whose endothermal character is proved by the negative heat flux. Furthermore, the two overlapping peaks appearing in the DTG curve for a temperature range from 250 to 450 °C may be attributed to the pyrolysis of the carbohydrates and proteins contained in the microalgae. Around 410–440 °C, the peak is referred to as the decomposition of lipids, while the peak around 300–320 °C corresponds to the decomposition of carbohydrates and proteins [40]. It justifies peaks accompanied by smaller peaks or by a shoulder [42].

Table 4.1. Microalgae's characterization. Data are shown as mean (n = 3) ± Standard deviation.

	Value (wt%)
HHV (MJ/kg)	18.6 ± 0.7
Bulk Density (kg/m^3)	1200 ± 62
Proximate analysis	
Moisture	5.4
Volatile matter	59.3
Fixed carbon	24.7
Ash	10.6
Ultimate analysis	
C	47.7 ± 2.5
H	5.9 ± 0.5
N	6.3 ± 0.3
O	29.5 ± 3.3
Ash analysis	
Si	29.08
P	17.89
Fe	17.04
Ca	16.30
K	13.01
Others	6.68

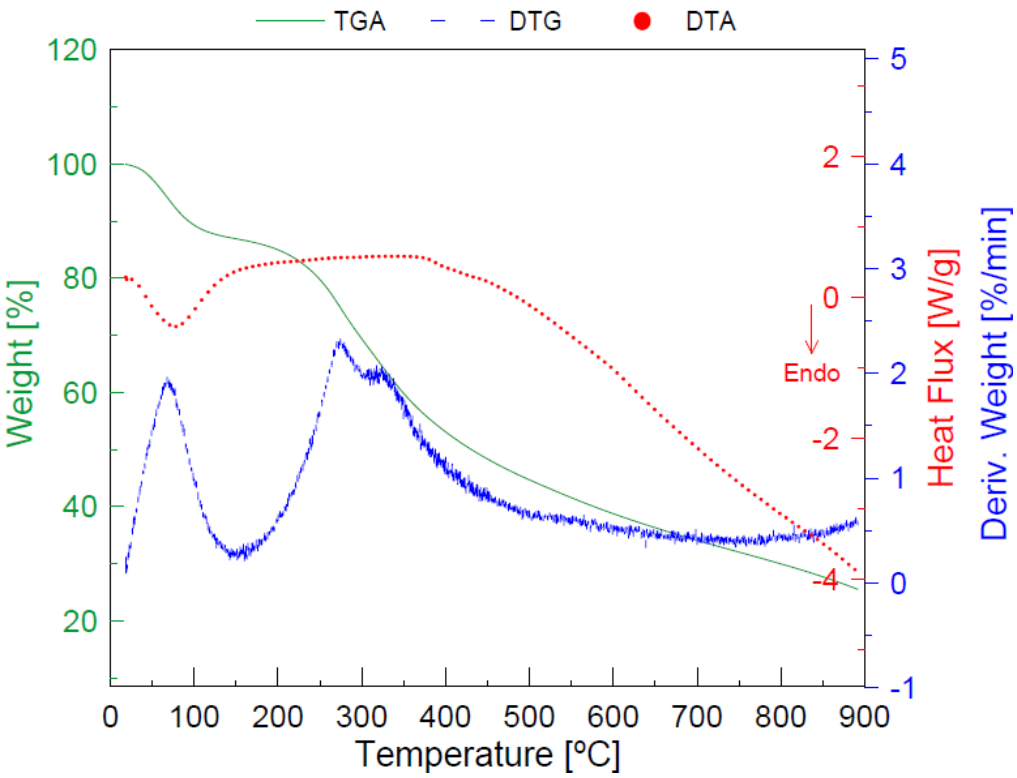


Fig. 4.3. Thermochemical profile of microalgae.

4.2.3 Gasifier

The gasifier used in this research was an All Power Labs Power Pellet GEK 20 kW downdraft biomass gasifier designed and manufactured in California/USA by All Power Labs Inc. [43]. Relevant technical data are presented in Table 4.2. The full description and images of the device can be accessed at the manufacturer's website [43].

Table 4.2. GEK Gasifier technical data.

Parameter	Specifications
Max continuous power output	15 kW @ 50Hz & 18 kW @ 60Hz
Biomass consumption	22 kg per hour at 18 kW
Biomass moisture	up to 30 wt%.
Biomass particle size recommended	1 to 4 cm
Biomass ash content recommended	Less than 5%
GEK gasifier weight	1065 kg
GEK gasifier dimension	1.4 m x 1.4 m x 2.2 m
Feedstock hopper capacity	0.325 m^3
Maximum gas output	60 m^3/h ~20kWe or 380,000 BTU/h

4.2.4 Gasification setup

The gasifying agent used in the process was air. The moisture content of the biomass was adjusted before each run, adding water to 30 wt%, the maximum value in the gasifier's specifications. Gasifying biomass with the maximum moisture allowed in the gasifier means less energy consumption in the drying process during feedstock conditioning. Batch gasification experiments were conducted using different amounts of wet microalgae biomass (500, 750, 1000, and 1500 g) and airflow (0.08, 0.11, and 0.14 m^3/min) to obtain different ERs and to check the ER influence on the process. First, the runs were performed once with distinct ERs (0.14, 0.23, 0.28, and 0.47), and the results were plotted in terms of HHV versus ER to find a performance curve for the process. After defining the performance curve, the runs were repeated in the best ER region to corroborate the results.

Before the gasification experiments, the gasifier was completely emptied and cleaned and filled with biomass. A butane burner was used to start-up the gasifier. The gasifier operated under a small negative pressure for suction and the airflow was measured using an orifice plate. The temperature inside the gasifier was monitored during the operation with two K-type thermocouples, one located at the combustion zone, and another located at the syngas exit at the reactor bottom. Once the reactor was charged and gasification started, the syngas produced was directed to the flare and a part of it was sampled by a silicone hose connected to a gas analyzer (454 M/XL, TESTO, Germany) capable of performing real time measurements. During the experiments, no catalyst elements were used. Due to the robustness of the equipment, the measurement of temperature is limited to the supra cited reactor zones.

The species O_2, CO, and H_2 were analyzed at the syngas exit (at the bottom of the reactor – online measurements) using electrochemical sensors, while CO_2 and C_xH_y were analyzed using non-dispersive infrared sensor technology (NDIR) and heated bead sensors, respectively. C_xH_y represents all hydrocarbons, which are grouped in a single measurement on the equipment. Records of the gasifier temperature and syngas composition were made every second and stored on the computer. The syngas composition and gasification temperatures were obtained as mean values for each run. Due to safety limitations of the gas analyzer, it was not possible to conduct a continuous C_xH_y measurement at concentrations above 4%. In this case, a polyvinylidene fluoride (PVDF) gas bag, with 85.7 L capacity, was used to store the syngas; then, the C_xH_y concentration was estimated after dilution with air.

An overview of the experimental downdraft gasification unit and some chemical reactions that occur inside the gasifier were extracted from the literature [17,28] and compiled in Fig. 4.4. The process was characterized by a downward co-current flow of the air and biomass. The biomass was fed into the top of the gasifier, passed through the drying, pyrolysis, oxidation, and, lastly, the reduction zone, where syngas was removed from the bottom of the reactor [44]. The air entered above the constriction that divided the reduction and combustion zones. The reduction zone occurs below the constriction, where the hot charcoal reacts with the products of combustion and pyrolysis zones to produce syngas [13]. The energy released by the oxidation zone supplied the drying, pyrolysis, and reduction reactions [17].

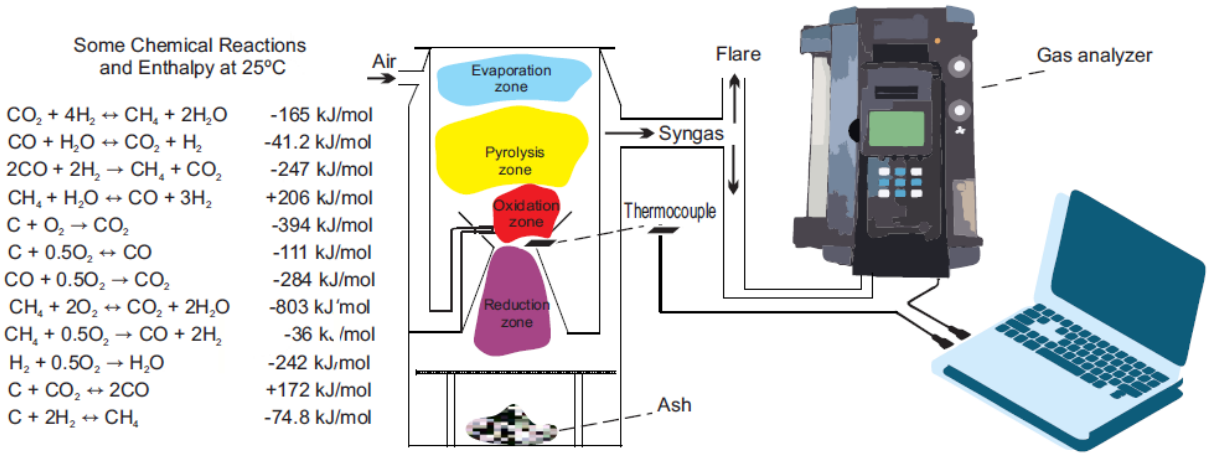


Fig. 4.4. Experimental downdraft gasification unit and main chemical reactions involved.

4.2.5 Process evaluation

The syngas HHV was calculated from the concentration of the combustible components and its combustion enthalpy at 25 ºC (Fig. 4.4). The C_xH_y present in the gas analyzer was considered CH_4 for this calculation since heavy hydrocarbons condense before being analyzed in the gas analyzer. Moreover, light hydrocarbons present in syngas are mainly CH_4 and some C_2–C_3 [45]. According to Ferreira et al. [26], light hydrocarbons can be lumped into methane with good acceptance.

The ER for each run was calculated by equation (4.1), as mentioned in Zainal et al. [46].

$$ER = (F_{air} * T_{run}) / M_{air} , \quad (4.1)$$

where F_{air} = flow rate of air supply, T_{run} = time of run, and M_{air} = mass input of air stoichiometric.

Additionally, the syngas volume produced was calculated by equation 4.2, based on the assumption that the nitrogen in the air input was inert and had the same amount of nitrogen as in the syngas [14,47]. Also, it was assumed that all the nitrogen in the biomass does not leave the process as N_2 in the syngas but as NOx, NH_3, or other compounds. Although this consideration may not be entirely true, it does not represent significant errors. Even if all the nitrogen in the biomass became N_2, the number of moles would be very small and would represent less than 6% of the total N_2 fed in the process.

$$V_{syngas} * xN_2 = V_{Air} * 0.79 , \quad (4.2)$$

where V_{syngas} = syngas volume, xN_2 = nitrogen volume fraction in syngas, and V_{Air} = air volume.

As mentioned by Bittencourt et al. [48], the main performance indicator of the gasifier was computed by the cold gas efficiency (CGE) and calculated by equation (4.3), according to Allesina et al. [14].

$$CGE = (V_{syngas} * HHV_{syngas}) / (M_{bio.dry} * HHV_{bio.dry}) , \quad (4.3)$$

where V_{syngas} = the syngas volume, HHV_{syngas} = the syngas HHV, $M_{bio.dry}$ = the mass of dry wastewater microalgae biomass, and $HHV_{bio.dry}$ = the dry wastewater microalgae biomass HHV.

4.2.6 Statistical analyses

The data presented in this paper came from *n* replicates, and the value of *n* is described along with the Tables 4.1 and 4.3. Experimental results are presented as the mean ± standard deviation. Error bars represent standard deviation.

4.3 Results and discussion

Table 4.3 summarizes the experimental results, as well as other data from the literature for comparison. Even though this study is possibly the first work involving wastewater microalgae gasification using a commercial downdraft gasifier with air as the gasifying agent, it is possible to compare the results obtained in this study with results reported for general biomass gasification in downdraft gasification units, or as reported for wastewater microalgae gasification on a laboratory scale.

The experimental results presented in Table 4.3, mainly those obtained using an ER of 0.23, were compared to values reported in the literature. The ER calculated varied from 0.14 to 0.47, which is close to the range of 0.19 to 0.43 for ideal and theoretical gasification mentioned in the literature [46]. In general, the HHV for syngas produced in a downdraft gasifier is between 4.5 and 5 MJ/Nm^3 [45], and the results obtained for wastewater microalgae gasification in this work are close to these values. When compared to wastewater microalgae gasification reported by Sharara and Sadaka [49], the syngas composition is close; however, they did not compute the CH_4 fraction, so the HHV was different.

Another distinguished value is the low syngas production rate reported by Sharara and Sadaka [49] and associated with high ash content in the microalgae (40%), almost four times the amount reported in this paper. According to Molino et al. [45], typical syngas production varies from 1 to 3 Nm^3/kg dry biomass, and values found in this work were within this range (i.e., 1.4–2.8 Nm^3/kg dry biomass). Only for a very high ER (0.47), was the production of syngas out of the expected range at 3.9 Nm^3/kg dry biomass; however, this syngas showed a lower HHV due to high nitrogen content and thus, exhibited lower efficiency. This result confirms the poor performance (ER >0.43) reported by some researchers [46].

The gasification temperature range was 873 to 949 ºC, which is within the range of 800 to 1100 ºC, typical for large-scale gasification projects described in the literature [17,45], and within the range of 760 to 960 ºC for wastewater microalgae gasification in a laboratory-scale auger reactor [49]. Temperatures below 900 ºC were observed for ER less than 0.23, while temperatures above 900 ºC were observed for ER of 0.23 and above. This behavior follows the literature, since increasing the ER, the gasifier's temperature increases, as there is more oxygen per volume of biomass for conducting the partial combustion reactions [17]. However, it was not possible to observe a linear correlation between ER and temperature in the results obtained. It is noteworthy that the average bed temperature can be decreased when there is a higher amount of reagent fed at room temperature; this may justify the relatively low temperatures

found at the highest ER. The experimental result at a higher temperature (949 ºC) produced the best results: high CO and H_2 content, consequently higher syngas HHV and CGE. As mentioned by Asadullah [44], high-temperature gasification leads to a desired high yield of CO and H_2, while reducing the tar content. The increase in H_2 production is due to the tar thermal cracking reaction and favoring the products of endothermic reactions. Therefore, the endothermic reforming reactions of hydrocarbon were improved with the increasing temperature [29].

The CGE calculated varied from 31.9 to 87.0% due to changes in the syngas composition for different ERs. Usually, the literature reports CGE between 30 and 60% for downdraft gasifiers [27], although higher values have been reported, such those as presented in Table 4.3. In this work, no value below 30% was recorded, but over 60% efficiency was achieved with ERs of 0.23 and 0.24. This may indicate that wastewater microalgae gasification can achieve high efficiency, if the ER is properly adjusted. Higher ER creates more oxidation environment in the gasifier, and thus lower syngas HHV. Whereas, lower ER results in higher syngas HHV; however, the tar yield is considerably higher. The higher syngas HHV and lower tar concentration in the syngas are of prime importance for achieving high efficiency. Therefore, ER optimization is necessary [44].

Also, unlike terrestrial biomass, microalgae lack of lignin, more recalcitrant in terms of thermochemical conversion [53,54]. Moreover, wastewater microalgae can contain metals that could play a catalytic role in the gasification process, thus increasing conversion [30]. The use of catalysts decreases the pyrolysis temperature and the formation of unwanted compounds, such as tar in gasification, by catalyzing its breakdown or preventing its formation, and increases the conversion of microalgae to gaseous products [20,55]. Alkaline metals and alkaline earth metals, for example, play a catalytic role in the gasification process, increasing conversion [16,20]. On the other hand, silicon and phosphorus are inhibitory because they form inactive alkaline silicates and phosphates. As a result, the total influence of metals will depend on the balance between the elements present [16].

Fig. 4.5 shows the CGE and the syngas production rates at different ERs. While CGE presented a maximum point, syngas production increased linearly as the ER rose. A similar trend was obtained in the literature [46]. The efficiency decreased for ERs above 0.24, despite higher syngas volume due to high nitrogen content, consequently lower the HHV.

Fig. 4.6 shows the influence of ER on syngas composition and HHV. The HHV increased with the increase in ER up to a peak value of ER = 0.23 before it started to decrease, principally due to the decrease in CO and increase in CO_2. The highest HHV was observed at ER = 0.23 that can be attributed to the high CO fraction. Zainal et al. [46] also observed a peak in HHV for wood chips gasification using a downdraft gasifier and attributed it to the CO fraction in syngas. The best ER for wood chips gasification reported by Zainal et al. [46] was 0.38, suggesting that the ideal ER for wastewater microalgae gasification is lower than other fuels due to microalgae's characteristics. In addition to the absence of lignin, microalgae generally have a volatile content much higher than fuels, like coal and peat, and could facilitate the gasification process [32]. Another possibility is the presence of catalytic metals in wastewater microalgae [30]. However, it is difficult to generalize as each biomass is unique. The best ER for corn straw and switchgrass gasification, for example, reported by Gai and Dong [51] and Bhoi et al. [52], were 0.32 and 0.22 respectively.

Table 4.3. Experimental gasification results and relevant data from the literature. Data are shown as mean ± Standard deviation.

Nº of Runs	Wet biomass load (g)	V_{Air} (L/min)	ER	Run time (s)	Temperature (ºC)	Syngas composition (%)						HHV_{syngas} (MJ/Nm^3)	$V_{syngas}/M_{bio.dry}$ (Nm^3/kg)	$HHV_{syngas}/M_{bio.dry}$ (MJ/kg)	CGE (%)
						O_2	H_2	CO	C_xH_y	CO_2	N_2				
2	1500	136	0.14	481	889±79	3.4±1.1	8.8±0.9	13.7±0.8	6.2±1.3	10.2±1.6	57.8±1.1	4.5±0.2	1.4±0.0	6.3	31.9±1.1
3	1000	78	0.21	840	873±40	2.9±0.7	9.3±0.8	15.6±2.2	7.0±0.7	9.8±0.5	55.3±2.3	5.0±0.4	2.2±0.1	11.0	56.4±6.5
2	1000	136	0.23	530	949±4	1.8±0.3	11.9±1.2	19.5±0.1	8.5±1.1	9.8±0.8	48.6±3.0	6.2±0.5	2.8±0.2	17.4	87.0±12.4
3	1000	107	0.24	711	901±10	2.0±0.7	10.4±1.5	15.9±2.1	7.6±0.5	10.6±0.5	53.6±3.0	5.4±0.2	2.7±0.2	14.6	71.4±6.9
1	750	136	0.28	500	908	4.5	4.7	8.8	6.5	12.4	63.0	3.6	2.7	9.7	48.9
1	500	136	0.47	558	911	1.0	3.5	7.3	3.0	13.5	71.5	3.2	3.9	14.5	43.5
Ref.	**Biomass type**														
[49]	Wastewater microalgae	-	-		960	-	11.4	16.9	-	11.6	-	3.57	0.80	2.9	-
[50]	Wood	0.42	-		700-1000	-	15.2	22.1	1.7	10.2	50.8	5.80	2.17	12.6	70.9
[46]	Wood chips	0.38	-		1000	1.69	14.05	24.04	2.02	14.66	43.62	5.34	-	-	80
[14]	Cotton crop residues	-	-		830	3.8	17.5	21.1	1.7	8.0	45.2	6.77	2.08	14.1	64.16
[26]	Brewer's spent grain	0.20	-		>700	2.5	16.6	16.9	5.7	15.1	43.2	-	2.06	-	82.5
[51]	Corn straw	0.32	-		800-1150	0.81	13.51	19.81	5.34	11.58	55.67	5.39	2.14	11.5	67.23
[52]	Switchgrass	0.22	-		734±94	-	9.7	18	-	-	-	5.8	-	-	57
[52]	Red cedar	0.24	-		756±241	-	15	18.2	-	-	-	6.0	-	-	75

Notes: V_{Air} = air volume; *ER* = equivalence ratio; HHV_{syngas} = syngas higher heating value; V_{syngas} = syngas volume;

$M_{bio.dry}$ = mass of dry wastewater microalgae biomass; *CGE* = cold gas efficiency.

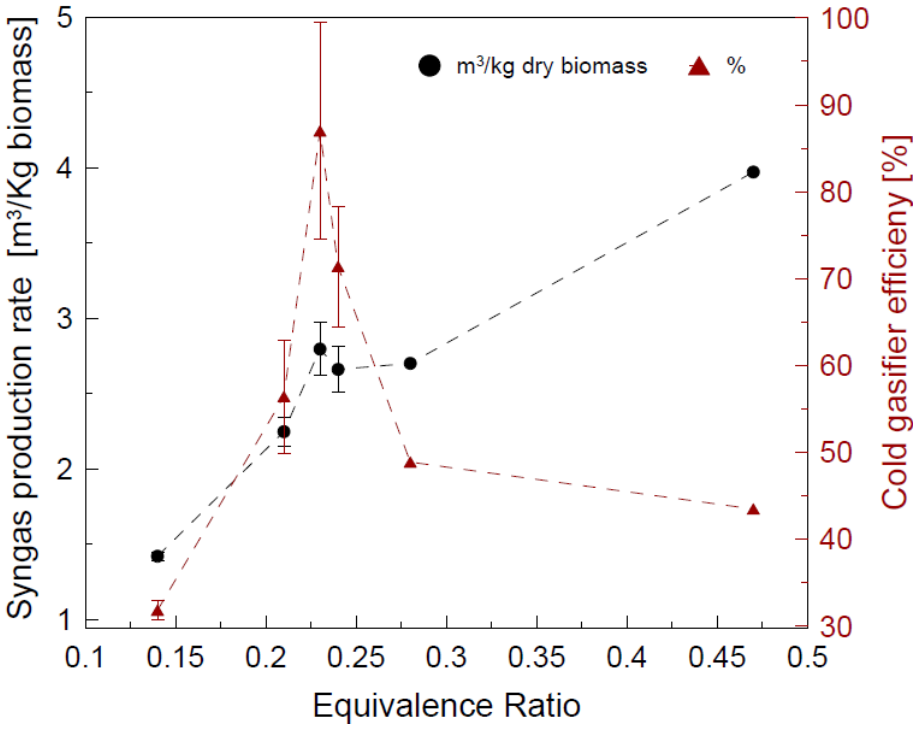


Fig. 4.5. Variation of cold gasifier efficiency and syngas production rate with equivalence ratio. Error bars represent standard deviation.

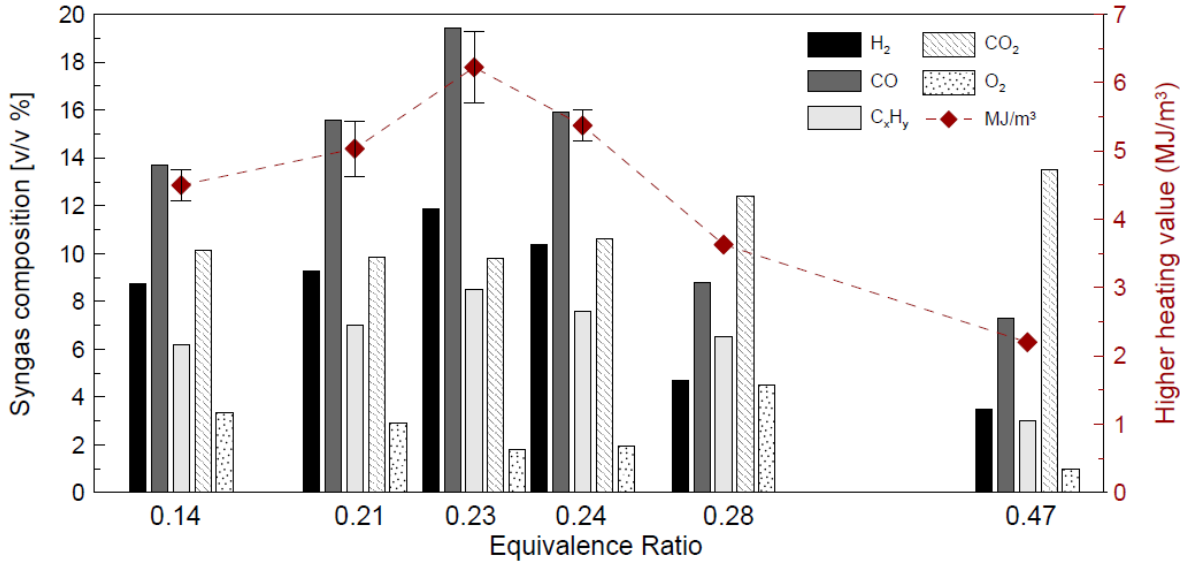


Fig. 4.6. Equivalence ratio influence on syngas composition and calorific value. Error bars represent standard deviation.

The syngas composition, and consequently the HHV, were practically the same in ER of 0.21 and 0.24 due to their positions around the peak of ER. Varying ER from 0.21 to 0.14 caused a gradual reduction of all combustible gases. This reduction was much more drastic when the ER was modified in the opposite direction, from 0.24 to 0.47. The percent CO_2 was almost constant from ER 0.14 to 0.24, rising 20 and 30% for ER 0.28 and 0.47, respectively, and became the

predominant compound in the syngas. It is interesting to note that changing the ER by only 0.02, down or up, caused noticeable changes in the composition. The same phenomenon was observed by Ferreira et al. [26] who gasified brewers´ spent grains in a pilot-scale downdraft reactor and reported a difference of almost 1 MJ/Nm^3 in syngas for a variation in the ER of only 0.03. This confirms the reason that ER should be considered the most important parameter in the calorific value of syngas [17,29].

Regarding the characteristics of the biomass used in this experiment, including particle size, moisture, and ash content created no operational issues during the experiment. Also, the need for processing microalgae biomass into briquettes was not necessary because microalgae biomass was naturally reduced in particle size during the drying step of gasification. Typically, downdraft gasifiers require a particle size less than 51 mm [45], and all wastewater microalgae biomass produced after the drying step was within this range. Although a uniform particle size helps overcome certain operational problems, such as pressure variations throughout the bed and blockage of the gasifier at the feed input [50], the particle size is considered to be of minor influence on syngas composition, when compared to others parameters such as the ER [29].

Even though the moisture (maximum recommended by manufacturer) and ash content (double that recommended by manufacturer) were high, gasification proceeded normally. However, it is important to emphasize that a high ash or moisture content in wastewater microalgae biomass can make the gasification process inviable. Downdraft gasifiers are not the most suitable reactors for the gasification of high ash biomass, since the process may become slower and more problematic, requiring the adjustment and installation of additional equipment [44]. Besides, the use of biomass with high humidity directly in the gasifier will result in great amounts of energy losses in the overall process [29]. Therefore, the harvest process must be well managed to ensure proper drying and avoid excess inorganic coagulants and incorporation of sand and dirt during the production of microalgae [19,30].

Despite our main interest in evaluating the syngas calorific value instead of its application in chemical product synthesis, it is important to note that the H_2/CO ratio in the syngas was 0.61 at ER 0.23, which is very close to the 0.60 recommended by Ciferno and Marano [56] for synthetic fuel production (Fischer-Tropsch gasoline and diesel). For this syngas application, the H_2/CO ratio of 0.61 could reduce the complexity and the cost of the process because additional equipment is not needed to correct the characteristics of the syngas to match the H_2/CO ratio ideal [26].

4.4 Conclusions

Wastewater microalgae gasification using a commercial downdraft gasifier was analyzed as a function of air-fuel ER. At ER of 0.23, the syngas HHV reached an optimum value, indicating the best performance of microalgae gasification at this scale of downdraft gasifier. The CGE, syngas production, and HHV on average were 87%, 2.8 Nm^3/kg biomass dry, and 6.2 MJ/Nm^3, respectively. The syngas composition was 11.9% H_2, 19.5% CO, 8.5% C_xH_y, and 9.8% CO_2. Besides, the H_2/CO ratio in the syngas was 0.61, which is very close to the recommended value for synthetic fuel production, such as Fischer-Tropsch gasoline and diesel (i.e. 0.60).

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References

[1] M. Wakeel, B. Chen, T. Hayat, A. Alsaedi, B. Ahmad, Energy consumption for water use cycles in different countries: A review, Appl. Energy. 178 (2016) 868–885. doi:10.1016/j.apenergy.2016.06.114.

[2] K.J. Chae, J. Kang, Estimating the energy independence of a municipal wastewater treatment plant incorporating green energy resources, Energy Convers. Manag. 75 (2013) 664–672. doi:10.1016/j.enconman.2013.08.028.

[3] A.S. Vieira, E. Ghisi, Water-energy nexus in low-income houses in Brazil: the influence of integrated on-site water and sewage management strategies on the energy consumption of water and sewerage services, J. Clean. Prod. 133 (2016) 145–162. doi:10.1016/j.jclepro.2016.05.104.

[4] H. Wang, Y. Yang, A.A. Keller, X. Li, S. Feng, Y. nan Dong, F. Li, Comparative analysis of energy intensity and carbon emissions in wastewater treatment in USA, Germany, China and South Africa, Appl. Energy. 184 (2016) 873–881. doi:10.1016/j.apenergy.2016.07.061.

[5] P. Singh, A. Kansal, Energy and GHG accounting for wastewater infrastructure, Resour. Conserv. Recycl. (2015). doi:10.1016/j.resconrec.2016.07.014.

[6] Y. Gu, Y.N. Dong, H. Wang, A. Keller, J. Xu, T. Chiramba, F. Li, Quantification of the water , energy and carbon footprints of wastewater treatment plants in China considering a water – energy nexus perspective, Ecol. Indic. 60 (2016) 402–409. doi:10.1016/j.ecolind.2015.07.012.

[7] N. Nipattummakul, I.I. Ahmed, S. Kerdsuwan, A.K. Gupta, Hydrogen and syngas production from sewage sludge via steam gasification, Int. J. Hydrogen Energy. 35 (2010) 11738–11745. doi:10.1016/j.ijhydene.2010.08.032.

[8] D.M. Wall, S. McDonagh, J.D. Murphy, Cascading biomethane energy systems for sustainable green gas production in a circular economy, Bioresour. Technol. 243 (2017). doi:10.1016/j.biortech.2017.07.115.

[9] E. Buonocore, S. Mellino, G. De Angelis, G. Liu, S. Ulgiati, Life cycle assessment indicators of urban wastewater and sewage sludge treatment, Ecol. Indic. (2015). doi:10.1016/j.ecolind.2016.04.047.

[10] B. Singh, K. Bauddh, F. Bux, Algae and environmental sustainability, Springer, 2015. doi:10.1007/978-81-322-2641-3.

[11] M.K. Lam, K.T. Lee, Cultivation of Chlorella vulgaris in a pilot-scale sequential-baffled

column photobioreactor for biomass and biodiesel production, Energy Convers. Manag. 88 (2014). doi:10.1016/j.enconman.2014.08.063.

[12] C. Wan, M.A. Alam, X.Q. Zhao, X.Y. Zhang, S.L. Guo, S.H. Ho, J.S. Chang, F.W. Bai, Current progress and future prospect of microalgal biomass harvest using various flocculation technologies, Bioresour. Technol. 184 (2015) 251–257. doi:10.1016/j.biortech.2014.11.081.

[13] L. V Martínez, J.E. Rubiano, M. Figueredo, F.G. María, Experimental study on the performance of gasi fi cation of corncobs in a downdraft fi xed bed gasi fi er at various conditions, (2019). doi:10.1016/j.renene.2019.10.034.

[14] G. Allesina, S. Pedrazzi, F. Allegretti, N. Morselli, M. Puglia, G. Santunione, P. Tartarini, Gasification of cotton crop residues for combined power and biochar production in Mozambique, Appl. Therm. Eng. 139 (2018) 387–394. doi:10.1016/j.applthermaleng.2018.04.115.

[15] A. Raheem, S. Sivasangar, W.A.K.G. Wan Azlina, Y.H. Taufiq Yap, M.K. Danquah, R. Harun, Thermogravimetric study of Chlorella vulgaris for syngas production, Algal Res. 12 (2015). doi:10.1016/j.algal.2015.08.003.

[16] C. Hognon, C. Dupont, M. Grateau, F. Delrue, Comparison of steam gasification reactivity of algal and lignocellulosic biomass: Influence of inorganic elements, Bioresour. Technol. 164 (2014) 347–353. doi:10.1016/j.biortech.2014.04.111.

[17] J.A. Ruiz, M.C. Juárez, M.P. Morales, P. Muñoz, M.A. Mendívil, Biomass gasification for electricity generation: Review of current technology barriers, Renew. Sustain. Energy Rev. 18 (2013) 174–183. doi:10.1016/j.rser.2012.10.021.

[18] E.E.S. Lora, O.J. Venturini, Geração Termelétrica: Planejamento, Projeto e Operação (Volume 2), 2012.

[19] R.B. Soares, M.F. Martins, Ricardo Franci Gonçalves, A conceptual scenario for the use of microalgae biomass for microgeneration in wastewater treatment plants, J. Environ. Manage. 252 (2019) 109639. doi:10.1016/j.jenvman.2019.109639.

[20] N.M.N. Qadi, I.N. Zaini, F. Takahashi, K. Yoshikawa, CO<inf>2</inf> Cogasification of Coal and Algae in a Downdraft Fixed-Bed Gasifier: Effect of CO<inf>2</inf> Partial Pressure and Blending Ratio, Energy and Fuels. 31 (2017). doi:10.1021/acs.energyfuels.6b03148.

[21] D.J. Lane, P.J. Van Eyk, P.J. Ashman, C.W. Kwong, R. De Nys, D.A. Roberts, A.J. Cole, D.M. Lewis, Release of Cl, S, P, K, and Na during thermal conversion of algal biomass, Energy and Fuels. 29 (2015). doi:10.1021/acs.energyfuels.5b00279.

[22] G. Liu, Y. Liao, Y. Wu, X. Ma, Synthesis gas production from microalgae gasi fi cation in the presence of Fe 2 O 3 oxygen carrier and CaO additive, Appl. Energy. 212 (2018) 955–965. doi:10.1016/j.apenergy.2017.12.110.

[23] G. Liu, Y. Liao, Y. Wu, X. Ma, Application of calcium ferrites as oxygen carriers for microalgae chemical looping gasi fi cation, Energy Convers. Manag. 160 (2018) 262–272. doi:10.1016/j.enconman.2018.01.041.

[24] G. Liu, Y. Liao, Y. Wu, X. Ma, L. Chen, Characteristics of microalgae gasification through chemical looping in the presence of steam, Int. J. Hydrogen Energy. 42 (2017)

22730–22742. doi:10.1016/j.ijhydene.2017.07.173.

[25] Z. Hu, E. Jiang, X. Ma, The effect of oxygen carrier content and temperature on chemical looping gasification of microalgae for syngas production, J. Energy Inst. (2018). doi:10.1016/j.joei.2018.05.001.

[26] S. Ferreira, E. Monteiro, L. Calado, V. Silva, P. Brito, C. Vilarinho, Experimental and Modeling Analysis of Brewers´ Spent Grains Gasification in a Downdraft Reactor, Energies. 12 (2019) 4413.

[27] S. Heidenreich, P.U. Foscolo, New concepts in biomass gasification, Prog. Energy Combust. Sci. 46 (2015) 72–95. doi:10.1016/j.pecs.2014.06.002.

[28] P. Manara, A. Zabaniotou, Towards sewage sludge based biofuels via thermochemical conversion - A review, Renew. Sustain. Energy Rev. 16 (2012) 2566–2582. doi:10.1016/j.rser.2012.01.074.

[29] A.A. Ahmad, N.A. Zawawi, F.H. Kasim, A. Inayat, A. Khasri, Assessing the gasification performance of biomass: A review on biomass gasification process conditions, optimization and economic evaluation, Renew. Sustain. Energy Rev. 53 (2016) 1333–1347. doi:10.1016/j.rser.2015.09.030.

[30] R.B. Soares, M.F. Martins, R.F. Gonçalves, Thermochemical Conversion of Wastewater Microalgae: The Effects of Coagulants Used in the Harvest Process, Algal Res. 47 (2020). doi:https://doi.org/10.1016/j.algal.2020.101864.

[31] N. Abdoulmoumine, S. Adhikari, A. Kulkarni, S. Chattanathan, A review on biomass gasification syngas cleanup, Appl. Energy. 155 (2015) 294–307. doi:10.1016/j.apenergy.2015.05.095.

[32] F. Sotoudehniakarani, A. Alayat, A.G. Mcdonald, Journal of Analytical and Applied Pyrolysis Characterization and comparison of pyrolysis products from fast pyrolysis of commercial Chlorella vulgaris and cultivated microalgae, J. Anal. Appl. Pyrolysis. 139 (2019) 258–273. doi:10.1016/j.jaap.2019.02.014.

[33] S.T. Cassini, S.A. Francisco, P.W.P. Antunes, R.N. Oss, R. Keller, Harvesting Microalgal Biomass grown in Anaerobic Sewage Treatment Effluent by the Coagulation-Flocculation Method: Effect of pH , Brazilian Arch. Biol. Technol. . 60 (2017).

[34] M.V. Pereira, A.F. Dassoler, P.W. Antunes, R.F. Gonçalves, S.T. Cassini, M. Vinicius, A.F. Dassoler, P.W. Antunes, Indigenous microalgae biomass cultivation in continuous reactor with anaerobic effluent : effect of dilution rate on productivity , nutrient removal and bioindicators, Environ. Technol. 0 (2018) 1–13. doi:10.1080/09593330.2018.1549105.

[35] A. Jebali, F.G. Acién, C. Gómez, J.M. Fernández-Sevilla, N. Mhiri, F. Karray, A. Dhouib, E. Molina-Grima, S. Sayadi, Selection of native Tunisian microalgae for simultaneous wastewater treatment and biofuel production, Bioresour. Technol. 198 (2015) 424–430.

[36] S. Wang, B. Bernard, A.E. Abomohra, Q. Wang, Z. He, Y. Feng, B. Zhang, C. Hui, Journal of Analytical and Applied Pyrolysis Characterization and pyrolysis behavior of the green microalga Micractinium conductrix grown in lab-scale tubular photobioreactor using Py-GC / MS and TGA / MS, J. Anal. Appl. Pyrolysis. 135 (2018) 340–349.

doi:10.1016/j.jaap.2018.08.019.

[37] S. Wang, M. Yerkebulan, A.E. Abomohra, S. El-khodary, Q. Wang, Bioresource Technology Microalgae harvest influences the energy recovery : A case study on chemical flocculation of Scenedesmus obliquus for biodiesel and crude bio-oil production, Bioresour. Technol. 286 (2019) 121371. doi:10.1016/j.biortech.2019.121371.

[38] K. Azizi, M. Keshavarz, H. Abedini, Bioresource Technology Characteristics and kinetics study of simultaneous pyrolysis of microalgae Chlorella vulgaris , wood and polypropylene through TGA, Bioresour. Technol. 243 (2017) 481–491. doi:10.1016/j.biortech.2017.06.155.

[39] A. Marcilla, A. Gómez-Siurana, C. Gomis, E. Chápuli, M.C. Catalá, F.J. Valdés, Characterization of microalgal species through TGA / FTIR analysis : Application to nannochloropsis sp Thermochimica Acta Characterization of microalgal species through TGA / FTIR analysis : Application to nannochloropsis sp ., (2009). doi:10.1016/j.tca.2008.12.005.

[40] F.A. Ansari, B. Ravindran, S.K. Gupta, M. Nasr, I. Rawat, F. Bux, Techno-economic estimation of wastewater phycoremediation and environmental bene fi ts using Scenedesmus obliquus microalgae, J. Environ. Manage. 240 (2019) 293–302. doi:10.1016/j.jenvman.2019.03.123.

[41] C. Yang, C. Wang, R. Li, B. Zhang, Q. Qiu, B. Wang, H. Yang, Y. Ding, Pyrolysis of microalgae : A critical review, 186 (2019) 53–72. doi:10.1016/j.fuproc.2018.12.012.

[42] Q. Bach, W. Chen, Pyrolysis characteristics and kinetics of microalgae via thermogravimetric analysis (TGA): A state-of-the-art review, Bioresour. Technol. 246 (2017) 88–100. doi:10.1016/j.biortech.2017.06.087.

[43] APL (2016) Power Pallet 20 kW., (2020). http://wiki.gekgasifier.com/w/page/6123718/FrontPage.

[44] M. Asadullah, Barriers of commercial power generation using biomass gasification gas: A review, Renew. Sustain. Energy Rev. 29 (2014) 201–215. doi:10.1016/j.rser.2013.08.074.

[45] A. Molino, S. Chianese, D. Musmarra, Biomass gasification technology: The state of the art overview, J. Energy Chem. 25 (2016) 10–25. doi:10.1016/j.jechem.2015.11.005.

[46] Z.A. Zainal, A. Rifau, G.A. Quadir, K.N. Seetharamu, Experimental investigation of a downdraft biomass gasifier, Biomass and Bioenergy. 23 (2002) 283–289.

[47] C.Y. Li, Y. Shen, J.Y. Wu, Y.J. Dai, C. Wang, Experimental and modeling investigation of an integrated biomass gasi fi er – engine – generator system for power generation and waste heat recovery, 199 (2019) 1–15. doi:10.1016/j.enconman.2019.112023.

[48] F.L.F. Bittencourt, A.B. Lourenço, E.A. Dalvi, M.F. Martins, Thermodynamic assessment of human feces gasification: an experimental-based approach, SN Appl. Sci. 1 (2019) 1077. doi:10.1007/s42452-019-1104-1.

[49] M.A. Sharara, S.S. Sadaka, Gasification of phycoremediation algal biomass, BioResources. 10 (2015) 2609–2625. doi:10.15376/biores.10.2.2609-2625.

[50] T.B. Reed, A. Das, Handbook of Biomass Downdraft Gasifier Engine Systems, (1988).

[51] C. Gai, Y. Dong, Experimental study on non-woody biomass gasification in a downdraft gasifier, Int. J. Hydrogen Energy. 37 (2012) 4935–4944.

[52] P.R. Bhoi, R.L. Huhnke, A. Kumar, S. Thapa, N. Indrawan, Scale-up of a downdraft gasifier system for commercial scale mobile power generation, Renew. Energy. 118 (2018) 25–33.

[53] A. Raheem, W.A.K.G. Wan Azlina, Y.H. Taufiq Yap, M.K. Danquah, R. Harun, Optimization of the microalgae Chlorella vulgaris for syngas production using central composite design, RSC Adv. 5 (2015). doi:10.1039/c5ra10503j.

[54] Q. Guan, P.E. Savage, C. Wei, Gasification of alga Nannochloropsis sp. in supercritical water, J. Supercrit. Fluids. 61 (2012) 139–145. doi:10.1016/j.supflu.2011.09.007.

[55] M.J.B. Fong, A.C.M. Loy, B.L.F. Chin, M.K. Lam, S. Yusup, Z.A. Jawad, Bioresource Technology Catalytic pyrolysis of Chlorella vulgaris : Kinetic and thermodynamic analysis, Bioresour. Technol. 289 (2019) 121689. doi:10.1016/j.biortech.2019.121689.

[56] J.P. Ciferno, J.J. Marano, Benchmarking biomass gasification technologies for fuels, chemicals and hydrogen production, US Dep. Energy. Natl. Energy Technol. Lab. (2002).

Chapter 5

Conclusions and suggestions

5.1 Conclusions

The goal of this work was to improve our fundamental understanding of energy recovery from microalgae produced in WWTP, through the thermochemical gasification process. The methodology to achieve this goal involved a systematic and extensive literature review, microalgae production in a pilot WWTP, characterization, and gasification in a commercial downdraft biomass gasifier.

Initially, a thorough study in the literature revealed that most studies have been carried out for pure species of microalgae obtained commercially. There are few studies that consider microalgae grown in sewage, although the culture medium influences the characteristics of the microalgae. Likewise, the presence of chemical coagulants in the microalgae and their interference in the process is neglected, even though flocculation is the most suitable harvesting method for the production of microalgae as biofuel. Moreover, the number of studies involving conventional gasifiers, such as the downdraft fixed bed, is still under-researched and pilot-scale studies are required. Other technologies much more complex, such as hydrothermal gasification, has been preferred in order to avoid the drying stage. However, before abandoning traditional gasification systems, already consolidated and commercialized worldwide, it is necessary to evaluate all options for drying and optimizing the process. Options to overcome this challenge include the reuse of heat from flue gas and syngas and the integration of anaerobic sewage treatment processes, with the generation and energetic use of biogas. Using the most consistent assumptions for a real scale, a conceptual scenario for the use of microalgae biomass for microgeneration in WWTP was constructed in this work. A flowchart presented the proposed final process, an optimized hybrid system incorporating gasification into the sewage treatment process. The result suggested the generation of 0.167 kWh/m^3 of treated sewage. A cost estimate was made for the acquisition of drying and gasification-electricity generation systems, and the results showed that investment may be financially returned after five years. All this work of compiling and analyzing information is useful for highlight knowledge gaps to guide new studies, and optimization trends to enable the process.

Afterwards, the sensitivity of thermochemical behavior to coagulant used in the harvesting stage was studied, since it is a central topic to applied processes. The literature usually only describes the microalgae properties free of coagulants and this work showed how seven different commercial coagulants can modify the properties of microalgae biomass and, thus, influence the energy recovery process. All coagulants tested in this work reduced the HHV of microalgae, from 1.8% to 84%, but mainly inorganic coagulants as a result of the high ash incorporated. The coagulant used also affects the thermochemical profile. The maximum degradation of 4.57 %/min occurred in microalgae free of coagulants, at 308 ºC, but the polyquaternium polymer accelerated total biomass degradation. Moreover, this polymer appears to increase heat release in the second stage of decomposition. The aliphatic amines polymer was the only coagulant that showed chlorine in the ash analysis, indicating a possible trapping effect. This can be a major discovery, as the release of acid gases is a major challenge in energy conversion processes. This further reinforces the importance of trying to combine the ideal coagulant in the harvesting process for gains in subsequent processes. The harvesting steps need to be carefully evaluated in order to obtain a more cost-effective scenario, not only for the harvesting step itself but for the whole energy conversion process.

Finally, the experimental investigation on wastewater microalgae and the sensitivity of gasification performance to ER were evaluated. Understanding the interplay between ER and higher efficiency is essential for predicting and optimizing the process. This work represents for the first time a wastewater microalgae gasification using air as the gasifying agency in a commercial downdraft gasifier. The effects of ER on the syngas composition, HHV, and production rate showed an increasing and then decreasing trend with ER with a peak was seen, indicating that there is an optimum ER of 0.23 for the best performance of the process. The CGE, syngas composition, HHV, and production rate were 87%, 11.86% H_2, 19.45% CO, 8.5% CH_4, 9.82% CO_2, 6.23 MJ/Nm^3, and 2.79 Nm^3 /kg biomass dry, respectively. The tests demonstrated the possibility to use wastewater microalgae with 30 wt%. of moisture as biofuel in commercial downdraft gasifiers.

The results presented in this thesis have substantial implications for improving the fundamental understanding of wastewater microalgae gasification. The energy recovery could help drive the WWTP to a more economical and sustainable process and more studies are demanded.

5.2 Recommendations for future work

Although this study has shown promising results for the fundamental understanding of microalgae gasification, several recommendations for further research can be proposed:

Detailed economic analysis for the implementation of the microalgae gasification system in WWTP with UASB and HRAP reactors.

Jar Test studies with different pH conditions, to check the efficiency of coagulants under different pH conditions.

Estimation of costs for the application of alkali or acidic compounds, in case of changing the pH of the ponds.

A thorough evaluation of other coagulants, in order to verify their catalytic effects on the gasification process.

Gasification of the sludge mixture of the UASB reactor with microalgae, in order to incorporate all the sludge produced in the energy recovery process.

Thermodynamic modeling of the gasification process, in order to estimate the reuse of heat from the hot gases produced, for the biomass drying process.

Gasification of the microalgae in a different moisture condition, according to the results presented in the thermodynamic modeling.

Exergy analysis to determine the source, location, and magnitude of inefficiencies related to the gasification process.

Electricity production from the produced syngas.

Appendix A. Data compilation of microalgae from characterization to products of gasification

Table 1 (Appendix A). Compilation of the microalgae characterization.

Microalgae	C	H	O	N	S	Moisture	Volatile	Fixed Carbon	Ash	HHV (MJ/Kg)	Protein	Carbohydrate	Lipid	Ref.
Chlorella vulgaris	49.88	7.546	32.329	9.33	0.915	-	-	-	-	-	-	-	-	[155]
Chlorella vulgaris	48.9	6.8	31.3	6.9	-	-	-	-	6.1	-	-	-	-	[28]
Chlorella vulgaris	53.01	8.67	35.05	3.26	-	0	74.59	16.39	9.02	22.02	-	-	-	[103]
Chlorella vulgaris	45.8	7.9	38.7	7.5	-	-	-	-	7	-	50	15	13	[156]
Chlorella vulgaris	46.8	6.9	26.3	9.7	0.5	3.4	82.7	4.5	9.8	21.1	-	-	-	[83]
Chlorella vulgaris	48.3	7.3	32.9	3	-	3.7	-	-	4.8	-	58.1	12.4	13.5	[104]
Chlorella vulgaris	45.49	6.61	28.69	10.28	0.21	-	78.98	10.23	8.72	18.69 (LHV)	-	-	-	[115]
Chlorella vulgaris	-	-	-	-	-	5.9	-	-	7	23.2	-	-	-	[106]
Chlorella vulgaris	47.13	6.71	23.08	9.88	-	5.4	-	-	7.8	-	64.4	10	12.4	[157]
Chlorella vulgaris	50.39	6.01	22.78	14.77	6.05	6.3	83.5	3.8	5.1	22.5	-	-	-	[94]
Chlorella vulgaris	40.67	5.27	39.7	-	-	6.89	78.4	7.85	6.86	14.94	-	-	-	[128]
Chlorella vulgaris	45.49	6.61	28.69	10.28	0.21	-	78.98	12.3	8.72	18.692	-	-	-	[158]
Chlorella vulgaris	49.99	7.39	27.4	9.48	0.5	-	81.84	12.91	5.25	19.57	-	-	-	[159]
Chlorella vulgaris	53.32	7.14	27.87	10.04	1.63	6.57	51.75	32.1	9.61	-	-	-	-	[117]
Chlorella vulgaris	50	7.1	33.8	5.8	0.53	-	-	-	3.4	-	-	-	-	[160]
Chlorella sp.	43.92	6.1	29.29	7.39	-	5.5	56.75	24.45	13.3	-	-	-	-	[134]
Chlorella pyrenoidosa	51.88	7.51	27.31	8.49	0.62	-	-	19.92	4.62	-	-	-	10.78	[86]

(continued on next page)

Table 1 – (continued)

Microalgae	C	H	O	N	S	Moisture	Volatile	Fixed Carbon	Ash	HHV (MJ/Kg)	Protein	Carbohydrate	Lipid	Ref.
Spirulina platensis	47.8	6.8	30.6	10.6	0.6	-	-	-	7.3	-	-	-	-	[66]
Spirulina platensis	-	-	-	-	-	7.8	-	-	7.6	21.2	-	-	-	[106]
Spirulina platensis	47.83	7.37	25.85	10.87	0.66	11.81	-	-	7.69	19.67	-	-	-	[92]
Spirulina	-	-	-	-	-	-	79.25	7.69	13.06	-	-	-	-	[161]
Spirulina	44.77	6.46	39.69	9.09	0.56	-	77.17	13.33	9.5	16.04	-	-	-	[141]
Spirulina	45.7	6.3	26.7	10.2	0.8	-	-	-	10.3		-	-	-	[125]
Spirulina	41	6.4	32.2	6.1	0.4	6.7	-	-	7.2	16.94	-	-	-	[122]
Arthrospira platensis	48.5	6.59	26.6	9.49	0.54	3.8	-	-	8.8	-	-	-	-	[68]
Nannochloropsis salina	54.2	7.8	27.5	4.2	0.6	-	-	-	6.7	-	-	-	-	[125]
Nannochloropsis sp.	43.3	6	25.1	6.4	0.53	-	-	-		19	52	12	28	[100]
Nannochloropsis sp.	38.3	5.6	35.1	6.1	-	-	66.6	56.1	14.9	15.9	62	9	18	[85]
Nannochloropsis gaditana	47.26	7.03	38.5	6.72	0.49	5.12	75.91	8.29	10.68	-	-	-	-	[162]
Nannochloropsis gaditana	53.47	7.92	31.68	6.93	-	-	-	-	14	21.12	38	12	32	[163]
Phaeodactylum tricornutum	51.93	6.79	22.73	7.28	1.16	-	-	-	10.11	-	-	-	-	[135]
Phaeodactylum tricornutum	57.03	7.46	24.97	8	1.28	-	-	-	12.45	-	-	-	-	[134]
Tetraselmis sp.	42.1	8.7	35.4	6.7	6.9	7.9	41.9	< 1	64.4	15.5	-	-	-	[129]
Tetraselmis sp.	17	3.3	-	2.5	2.1	6.4	35.5	5.90 %	58.6	-	-	-	-	[119]
Chlamydomonas reinhardtii	52.7	7.25	20.4	9.02	0.67	5.1	-	-	10.6	-	-	-	-	[68]
Scenedesmus quadricauda	47.71	7.17	28.3	5.78		6.2	-	-	4.8	-	26.8	42.7	19.5	[100]
Scenedesmus sp.	32.6	4.7	19.3	4.2	0.97	7	54.3	7.9	37.8	15.4	-	-	-	[121]
Acutodesmus obliquus	51.8	7.13	29.23	8.13	0.63	-	-	-	10	23.3	-	-	-	[139]
Schroederiella apiculata with *Scenedesmus dimorphus*	41.3	5.8	-	6.9	1.01	10.8	57.7	19	23.3	-	-	-	-	[119]
Microalgae-bacteria biomass cultivated in sewage	28.26	3.63	23.06	2.83	0.57	13.8	42.2	15.9	41.9	10.55	-	-	-	[64]
Not specified	51.68	7.19	28.9	8.81	0.48	4.5	-	-	2.93	23.07	-	-	-	[107]
Native saline microalgae and *Spirulina*	27.1	3.7	15.2	6	0.9	-	-	-	60.1	-	-	-	-	[125]

Table 2 (Appendix A). Compilation of hydrothermal gasification of microalgae.

Microalgae	Dimension Gasifier (cm)	Inner diameter Gasifier (mm)	Volume Gasifier (mL)	Algae content, mass %	Catalyst	Operating time (min)	Carbon conversion (%)	Temperature (ºC)	Pressure (MPa)	Feeding	Gas composition, volume %	Ref.
Phaeodactylum tricornutum	-	-	-	4.5	2% Ru/C	30	31.3	420	32.3	0.7 kg/h	41.3% CO_2, 12.5% CH_4, 0.1% CO, 26.4% H_2, 11.5% C_2H_6, 8.2% C_3H_8.	[135]
Phaeodactylum tricornutum	15.24	14.3	-	5.1	2% Ru/C	67	74	400	30	30 ml	34.4% CH_4, 2% C_2H_6, 0.7% C_3H_8, 56.7% CO_2, 0.6% CO, 5.5% H_2.	[124]
Nannocloropsis gaditana	40	25	-	3	Na_2CO_3 / K_2CO_3	2.133	86	663	24	2.5 ml/min	52% H_2, 17.9% CH_4, 23% CO_2, 2.4% C_2H_4, 4.7% C_2H_6.	[163]
Chlorella vulgaris	-	-	75	6.25	-	30	-	500	-	1 g	-	[83]
Chlorella vulgaris	-	-	120	12.6	5g, 10g and 15g Ni	-	70.1 @ 15g Ni	350	18	30 g	37.5% CH_4, 10% H_2, 18.8% CO_2, 3.7% others @ 15g Ni	[28]
Chlorella vulgaris	151.5	36	-	3-15	5% Ru/C	-	45 - 50	400	28	1.4 kg/h	-	[22]
Chlorella vulgaris	151.5	36	-	3-15	5% Ru/C	-	45 - 50	400	28	1.4 kg/h	37.1% H_2, 33.1% CO_2, 29.8% CH_4 @ 3% algae.	[160]
Chlorella vulgaris	15	2	0.5	7.3	2% Ru / 4%Ni-21%/Mo / 5%Co-20%Mo / 0,63%Pt-0,68% / Ni / Inconel	2	53 with no catalyst	600	24	0.01 – 12 ml/min	7% H_2, 22% CO, 25% CH_4, 26% CO_2, 20% C_2-C_3 with no catalyst	[156]
Chlorella vulgaris / Scenedesmus quadricauda	15	-	8.5	5	12% Ni/Al / 68.2% Ni / Raney	15	80 - 90	385	26	0.16 g	$CH_4 > CO_2 > H_2 > CO$	[157]

(continued on next page)

Table 2 – (continued)

Microalgae	Dimension Gasifier (cm)	Inner diameter Gasifier (mm)	Volume Gasifier (mL)	Algae content, mass %	Catalyst	Operating time (min)	Carbon conversion (%)	Temperature (ºC)	Pressure (MPa)	Feeding	Gas composition, volume %	Ref.
Chlorella vulgaris / Spirulina platensis	-	-	-	6.25	NaOH / 5% Ni/Al_2O_3	30	74 / 78.4	500	36	1 g	%Molar: 59% H_2, 26.5% CH_4, 14.5% C_2-C_4 @ *Spirulina*; 52.6% H_2, 27% CH_4, 19.7% C_2-C_4 @ *Chlorella*	[106]
Spirulina platensis	-	-	30	20 / 10 / 5 / 2.5	2% Ru/C / 2% Ru/ZrO_2	60 / 360	93 @ 360min	399 / 409	30.8 - 34.5	30 ml	52.4% CH_4, 38% CO_2, 8.2% H_2, 1.2 % C_2H_6, 0.2% C_3H_8, traces of CO	[66]
Spirulina	60	2.03	-	25 / 17.5	-	0.067 / 0.15	36.7 @ 550ºC and 0.15 min	550 / 600	23.4	7.11 g/L s	-	[87]
Spirulina and *native microalgae / diatomaceous / Spirulina / Nanocrolos sp*	182.8	25.4	-	21.6 / 24.4 / 22.2 / 25	Ru/C	360 - 600	90 / 48 / 40 / 59	350	20	1.0 / 1.2 / 1.4 / 1.5 L/min	52.1% CH_4, 42% CO_2, 3.3% H_2, 2.5% C_2H_6 @ *Spirulina*; 49.1% CH_4, 48.3% CO_2, 1.8% H_2 @ *diatomaceous*; 62.5% CH_4, 36.5% CO_2, 0.9% H_2 @ *Spirulina and native microalgae;* 57.2% CH_4, 39.3% CO_2, 2.1% H_2, 0.8% C_2H_6 @ *Nanocrolos sp*	[125]
Acutodesmus obliquus	-	-	-	2.5 / 5	-	480 / 1380 / 2700 / 3000	60 - 65 @ 650ºC, 480min and 5% algae	600 / 625 / 650	28	3.6 / 4.8 g/min	-	[30]
Acutodesmus obliquus	75	18	-	2.5 / 5 / 10 / 15 / 20	K_2CO_3	2.33 - 2.15	96.4 @ 2.5% algae, 82 @ 20% algae	600 / 620 / 650 / 690	28	2.5 g/min	44.7% H_2, 33% CO_2, 19.1% CH_4, 2.9% C_2H_6 @ 2.5% algae	[139]
Nannochloropsis sp.	19.2	18	35	21[164]	-	60	-	200 / 250 / 300 / 350 / 400 / 450 / 500	35	4.27 g	-	[100]

(continued on next page)

Table 2 – (continued)

Microalgae	Dimension Gasifier (cm)	Inner diameter Gasifier (mm)	Volume Gasifier (mL)	Algae content, mass %	Catalyst	Operating time (min)	Carbon conversion (%)	Temperature (ºC)	Pressure (MPa)	Feeding	Gas composition, volume %	Ref.
Nannochloropsis sp	11	10	10	15 / 10 / 4.7 / 1	-	77	60 @ 550ºC and 4.3%	450 / 500 / 550	24	0.24 g	% Molar: 30% H_2, 32% CO_2, 25% CH_4 @ 550ºC and 4.7% algae	[165]
Nannochloropsis sp.	-	-	5	4.3	5% Ru/C	75	45	410	≥ 22	0.12 g	% Molar: 42% CO_2, 38% H_2, 18% CH_4, 2% C_2H_X, traces of CO	[138]

Table 3 (Appendix A). Compilation of conventional gasification on bench scale.

Microalgae	Type Gasifier	Dimension Gasifier (cm)	Inner diameter Gasifier (mm)	Moisture % mass	Gasifying agent	Carbon conversion (%)	Gasifying agent Flow (mL/min)	Agent / fuel ratio	Temperature (ºC)	Particle Size (mm)	Load	Tar	Gas composition, volume %, and observations	Ref.
Microalgae cultived in sewage	Horizontal Tubular	132	60	13.8	Air		20 / 18.1	-	760 / 860 / 960	-	34.7 / 36.1 / 40.9 g/min	16.6 %	16.9% CO, 11.4% H_2 11.6% CO_2 @ 960ºC	[64]
Scenedesmus sp. cultivated in sewage	Fluidized bed	120	77	10	Steam	75.7	-	2.1 air and 0.5 steam	821 ± 23	6	0.87 kg/h	-	Cogasification of 10 wt.% algae with coal increased CO and H_2 and decrease CO_2 yield	[121]
Scenedesmus sp. cultivated in sewage	Fluidized bed	120	77	10	Steam	54.8	4.8	2.8 air and 0.5 steam	881 ± 18	6	0.9 kg/h	-	Cogasification of 10 wt.% algae with wood increased CO and H_2 and decrease CO_2 yield	[65]
Spirulina	Fixed bed Downdraft	51	30	-	CO_2	-	200	-	950 - 1000	100	50	-	-	[141]
Spirulina	Horizontal Tubular	520	30	79	O_2	93 @ 850ºC	0.39	-	850 / 950 / 1000	-	0.25 g/min	-	34.5% H_2, 18% CO, 32.9% CO_2, 10.7% CH_4, 2.1% C_2H_4, 0.2% O_2 @ 850ºC	[122]

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Table 3 – (continued)

Microalgae	Type Gasifier	Dimension Gasifier (cm)	Inner diameter Gasifier (mm)	Moisture % mass	Gasifying agent	Carbon conversion (%)	Gasifying agent Flow (mL/min)	Agent / fuel ratio	Temperature (ºC)	Particle Size (mm)	Load	Tar	Gas composition, volume %, and observations	Ref.
Spirulina platensis	Fluidized bed (30 kW)	190	76 in bed region and 198 in freeboard region	2.21	Air / Steam	-	-	ER: 0.2 / 0.3 / 0.4	700 / 800	6 diameter and 10 length	-	about 5-15g/ Nm^3	32% CO_2, 30% CO, 24% H_2, 9% CH_4 @ 800ºC and ER 0.3	[92]
Tetraselmis sp. / Mix *Schroederiella apiculata* and *Scenedesmus dimorphus*	Fixed bed	140	50	-	CO_2	100	-	-	500 - 1100	0.25	1 - 4 g	-	-	[119]
Tetraselmis sp.	Fluidized bed	120	77	< 20	Steam	-	35	0.5	850	1 - 3.35 / 1 - 2	1.43 kg/h	visual presence	Rapid bed sintering due high salt content	[137]
Chlorella vulgaris	Fixed bed	-	14	-	Fe_2O_3 / Steam	77.19 @ 850ºC	0.0432 g/min steam	0.25 molar Fe_2O_3/ C	700 / 750 / 800 / 850 / 900	< 74	0.379 g	-	Fe increased CO_2, H_2 and CO and reduced CH_4 and C_2H_m	[115]
Chlorella vulgaris	Fluidized bed	39.6	15	6.3	Air	-	-	ER: 0.1 / 0.2 / 0.26 / 0.30 / 0.35	500 / 600 / 700 / 800 / 900	0.1	0.6 g / 1 g / 1.5 g / 2 g / 2.5 g	-	%Molar: 31.4% H_2, 26.86% CO, 28.33% CO_2, 13.33% CH_4 @ 800ºC, ER 0.2 and 2g feeding	[69]

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Table 3 – (continued)

Microalgae	Type Gasifier	Dimension Gasifier (cm)	Inner diameter Gasifier (mm)	Moisture % mass	Gasifying agent	Carbon conversion (%)	Gasifying agent Flow (mL/min)	Agent / fuel ratio	Temperature (ºC)	Particle Size (mm)	Load	Tar	Gas composition, volume %, and observations	Ref.
Chlorella vulgaris	Horizontal Tubular	-	-	5.93	O_2	-	10	-	700 / 800 / 900	-	0.1 g / 0.25 g / 0.3 g / 0.5 g	11.6 18.5 %wt	45.9% H_2, 4.2% CO, 50.1% CO_2, 3.7% CH_4 @ 800ºC and 0.3 g feeding	[94]
Chlorella vulgaris	Horizontal Tubular	-	-	-	Fe_2O_3	85	-	0.5:0.5	800	< 0.2	1 g	<4%	18.12% H_2, 59.23% CO 15.06% CO_2, 7.58% CH_4.	[155]
-	Entrained flow	45.7	89	3 - 5	Steam / CH_4	> 90 %	-	-	1327 / 1377 / 1427 / 1477 / 1527	< 149	5 - 20 mg/s	-	-	[107]

Appendix B. Publications

Chapters in books

1. SOARES, RENAN BARROSO; OSS, RODRIGO NUNES; MARTINS, MÁRCIO FERREIRA; GONÇALVES, RICARDO FRANCI. Microalgas: uma oportunidade para melhorar os indicadores de saneamento no Brasil. In: Gustavo Henrique Cepolini Ferreira. (Org.). Geografia, Políticas e Democracia 3. 1ed.Ponta Grossa/PR: Atena Editora, 2019, v. 3, p. 38-48. DOI: 10.22533/at.ed.208191710.

2. SOARES, R. B.; GONCALVES, R. F. Recuperação de bioprodutos a partir da gaseificação do lodo de esgoto sanitário. In: Alberdan Silva Santos. (Org.). Avanços Científicos e Tecnológicos em Bioprocessos. 1ed.Ponta Grossa/PR: Atena, 2018, v., p. 172-178. DOI 10.22533/at.ed.475180110.

Articles in journals

1. SOARES, RENAN BARROSO; MARTINS, MARCIO FERREIRA; GONÇALVES, RICARDO FRANCI. A conceptual scenario for the use of microalgae biomass for microgeneration in wastewater treatment plants. JOURNAL OF ENVIRONMENTAL MANAGEMENT, v. 252, p. 109639, 2019. https://doi.org/10.1016/j.jenvman.2019.109639.

2. SOARES, RENAN BARROSO; MARTINS, MARCIO FERREIRA; GONÇALVES, RICARDO FRANCI. Thermochemical Conversion of Wastewater Microalgae: The Effects of Coagulants Used in the Harvest Process. ALGAL RESEARCH, v. 47, 2020. https://doi.org/10.1016/j.algal.2020.101864.

3. SOARES, RENAN BARROSO; MARTINS, MARCIO FERREIRA; GONÇALVES, RICARDO FRANCI. Experimental investigation of wastewater microalgae in a pilot-scale downdraft gasifier. ALGAL RESEARCH, v. 51, 2020. https://doi.org/10.1016/j.algal.2020.102049

4. SOARES, R. B.; PETERLI Z; MARTINS, M. F.; GONCALVES, R. F. Avaliação do poder calorífico da biomassa algal obtida por coagulação-floculação. REVISTA DAE, v. 68(223), p. 78-87, 2020. DOI: https://doi.org/10.36659/dae.2020.030

5. SOARES, RENAN BARROSO; ASSIS, TATIANA IZATO; DASSOLER, ALINE; AMARANTE, LEONARDO MONJARDIM. Levantamento bibliométrico e mapeamento da análise de ciclo de vida para microalgas: uma revisão da literatura. BRAZILIAN JOURNAL OF DEVELOPMENT, v. 5, p. 32984-32995, 2019. DOI:10.34117/bjdv5n12-354.

6. BARROSO SOARES, RENAN; GONÇALVES, RICARDO FRANCI. Comparative Analysis of the Energy Consumption of Different Wastewater Treatment Plants. INTERNATIONAL JOURNAL OF ARCHITECTURE, ARTS AND APPLICATIONS, v. 3, p. 79, 2017. DOI: 10.11648/j.ijaaa.20170306.11.

7. SOARES, RENAN BARROSO; GONÇALVES, RICARDO FRANCI. Consumption of Electrical Energy in Water Supply and Wastewater Systems in Brazil. URBAN STUDIES AND PUBLIC ADMINISTRATION, v. 1, p. 51, 2018. https://doi.org/10.22158/uspa.v1n1p51.

8. BARROSO SOARES, RENAN BARROSO SOARES; FRANCI GONGALVES, RICARDO; FERREIRA MARTINS, MÁRCIO. Avaliação bibliométrica para a gaseificação de microalgas. EXTENSIONISMO, INNOVACIÓN Y TRANSFERENCIA TECNOLÓGICA, v. 5, p. 458, 2019. DOI 10.30972.

Articles in congress

1. SOARES, R. B.; GONÇALVES, R. F.; MARTINS, M. F.; SANTOS, J. J. C. S.. Modelagem Termodinâmica do Reaproveitamento de Calor em Gaseificadores visando Secagem de Lodo. In: IX Encontro Científico de Física Aplicada, 2018, São Paulo. Blucher Physics Proceedings. São Paulo: Editora Blucher, 2018. v. 4. p. 36-42.

2. SOARES, R. B.; Assis, T. I; Dassoler, A.; Amarante, L. M.. Levantamento bibliométrico e mapeamento da análise de ciclo de vida para microalgas: uma revisão da literatura. In: XII SESMA e II WORKSHOP de Biorremediação de áreas contaminadas, 2018, Vitória. Anais do XII Seminário Estadual sobre Saneamento e Meio Ambiente e II WORKSHOP de Biorremediação de áreas contaminadas. Vitória: ABES, 2018. p. 87-92.

3. SOARES, R. B.; MARTINS, M. F.; GONCALVES, R. F. Análise do potencial energético de lodos algáceos obtidos por diferentes coagulantes. In: Congresso Internacional SUSTENTABILIDADE URBANA 14ª Jornada Urbenere e 2ª Jornada Cires, 2018, Vila Velha. Congresso Internacional SUSTENTABILIDADE URBANA 14ª Jornada Urbenere e 2ª Jornada Cires, 2018. p. 2339-2348.

4. SOARES, R. B.; GONCALVES, R. F.; MARTINS, M. F. Primer encuentro de la Red Iberoamericana de Investigación, Desarrollo y Transferencia para la Aplicación de Energias Renovables y Cuidado del Ambiente. In: RibERA, 2018, Corrientes. RibERA, 2018, 2018.

5. SOARES, R. B.; MEMELLI, M.; ROQUE, R. P.; GONCALVES, R. F. Análise Comparativa de Consumo Energético de Diferentes Estações de Tratamento de Esgoto. In: EURO ELECTS 2017, 2017, São Leopoldo. ANAIS DO IX ENCONTRO NACIONAL, VII ENCONTRO LATINO-AMERICANO, II ENCONTRO LATINO-AMERICANO E EUROPEU SOBRE EDIFICAÇÕES E COMUNIDADES SUSTENTÁVEIS, 2017.

6. SOARES, R. B.; GONCALVES, R. F. CONSUMO DE ENERGIA ELÉTRICA EM SISTEMAS DE ABASTECIMENTO DE ÁGUA E DE ESGOTAMENTO SANITÁRIO NO BRASIL. In: Congresso ABES FENASAN 2017, 2017, São Paulo. Encontro Técnico Congresso Nacional de Saneamento e Meio Ambiente, 2017.