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LARISSA CASTRO AMPESE

VALORIZATION OF MACAÚBA HUSKS THROUGH THE INTEGRATION OF REACTORS OF SUBCRITICAL WATER HYDROLYSIS AND ANAEROBIC DIGESTION FOR METHANE PRODUCTION

VALORIZAÇÃO DE CASCAS DE MACAÚBA ATRAVÉS DA INTEGRAÇÃO DE REATORES DE HIDRÓLISE EM ÁGUA SUBCRÍTICA E DE DIGESTÃO ANAERÓBIA PARA PRODUÇÃO DE METANO

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Orientadora: Profa. Dra. Tânia Forster Carneiro
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RESUMO

Macaúba é uma palmeira tropical nativa da América do Sul e Central que apresenta alto potencial para a produção de biodiesel. Apesar dos avanços na produção de biocombustíveis, os resíduos e coprodutos da macaúba não são necessariamente recuperados como fontes de energia. Nesse sentido, uma análise bibliométrica para avaliar as potenciais aplicações da macaúba e investigar alternativas para os coprodutos sólidos foi elaborada. O estudo de bibliometria mostrou que entre os anos de 1900 a 2020 374 artigos e revisões foram publicados, sendo o Brasil o maior contribuinte e as instituições brasileiras as mais relevantes. Um grande potencial de diferentes aplicações da macaúba para fins energéticos, farmacêuticos e alimentares, ainda poderiam ser explorados, incluindo uma lacuna de conhecimento sobre a recuperação de seus coprodutos. O objetivo deste estudo é avaliar a valorização da casca da Macaúba proveniente da produção de biodiesel por meio do pré-tratamento com hidrólise com água subcrítica (10 g de alimentação, 200° C de temperatura, vazão de 10 mL min^{-1} e pressão de 14 MPa) seguido de digestão anaeróbia (regime semicontínuo e 35 ° C de temperatura) para produzir de metano. Os resultados do hidrolisado obtido seguido de digestão (PT+AD) mostram geração de 56,9% de metano e produção de biogás de 0,36 mL g^{-1} cascas, e 42,19% de metano e produção de biogás de 0,04 mL g^{-1} cascas para o reator controle (somente digestão anaeróbia), após aproximadamente 40 dias de experimento. A análise energética indica que é possível obter-se 2893,8 J g^{-1} de energia elétrica ou 3617,3 J g^{-1} de energia térmica utilizando-se o pré-tratamento de hidrólise com água subcrítica. Conclui-se que a economia da macaúba brasileira e as políticas públicas de bioenergia e descarbonização poderão criar novas rotas de recuperação de energia para o estabelecimento de Mecanismos de Desenvolvimento Sustentável.

Palavras-chave: *Resíduos lignocelulósicos; Análise Bibliométrica; Bioenergia; Digestão Anaeróbica; Tecnologia Supercrítica; Biogás; Mitigação de GEE.*

ABSTRACT

Macaúba is a native tropical palm native from South and Central America that shows high potential for biodiesel production. Despite the advances in biofuel production, *macaúba's* wastes and coproducts are not necessarily recovered as energy sources. In this regard, a bibliometric analysis was carried out, to evaluate *macaúba's* potential applications and investigate alternative routes to the solid by-products. The bibliometric study showed a total of 374 articles and reviewes were published since 1900 to 2020, aditioanally Brazil is the most productive country, and brazialian institutions are the most relevant. A great potential of multiple energetic, farmacal, and alimentary applications for *macaúba* could be explored, and it includes a lack of knowledge in the field of byproducts recovery. The aim of the study it to evaluate the valorization *macaúba*'s husks from biodiesel production through subcritical water hydrolysis (SWH) pretreatment (10 g of powdered husks for feeding, temperature at 200º C, 10 mL min^{-1} of flow and pressure of 14 MPa), followed by anaerobic digestion (semicontinuous regime at 35ºC) for methane production. The results show the pretreatment of husks with SWH followed by anaerobic digestion generate 56.9% of methane and biogas production production of 0.36 mL g^{-1} husks, and 42.19% of methane and biogas production production of 0.04 mL g^{-1} husks for the control reactor (only treated with anaerobic digestion), after approximately 40 days of experiment. The energetic analysis show it is possible to obtain 2893.8 J g^{-1} of electric energy, or 3617.3 J g^{-1} of thermal energy through the SWH pretreatment. As conclusions it was found the Brazilian *macaúba*'s economy, the bioenergy and decarbonation public policies could create new routes to energy recovery and to stablish Mechanisms of Sustainable Development.

Keywords: *Lignocellulosic Byproducts; Bibliometric Analysis; Bioenergy; Anaerobic Digestion; Supercritical Technology; Biogas; GHG Mitigation.*

Sumário

CAPÍTULO 1- Introdução geral, objetivos e estrutura da dissertação

1.1. Introdução Geral

A macaúba (*Acrocomia aculeata*) é uma planta nativa das Américas do Sul e Central, pertence à família Arecaceae, e ocorre em todas as regiões do Brasil: Norte, Sul, Sudeste, Nordeste e Centro-Oeste (BAZZO, B. R. *et al.*, 2018; DE LIMA *et al.*, 2018). A planta é vigorosa e possui a capacidade de se adaptar a diversos tipos de solo, como os arenosos e argilosos, tendo sua maior ocorrência em áreas de alta incidência solar e em solos férteis (CESAR, A. D. *et al.*, 2015). Os frutos da macaúba dividem-se em 4 partes: casca (ou epicarpo) caracterizada por ser fibrosa e resistente, polpa (ou mesocarpo) com alto teor de óleo e amarelada, uma camada de tecido escuro (endocarpo) e, em seu interior, uma ou mais nozes brancas (endosperma) (EVARISTO, A. B.; GROSSI, J. A. S.; CARNEIRO, A. D. O.*;* *et al.*, 2016). O óleo extraído da polpa de macaúba é rico em ácido oleico, apresenta alta estabilidade oxidativa e operabilidade a baixas temperaturas, enquanto o óleo extraído da(s) noz(es) é rico em ácidos graxos saturados de cadeia curta (BAZZO, B. R. *et al.*, 2018; BELTRÃO, 2007).

Atualmente a obtenção de energia através do consumo de materiais fósseis é uma prática considerada ambientalmente e ecologicamente não sustentável, acarretando a emissão de bilhões de toneladas de dióxido de carbono (CO_2) para a atmosfera anualmente (CHANDRA *et al.*, 2012; WAGNER *et al.*, 2018). Uma fonte de energia alternativa à fóssil é a biomassa, podendo essa ser obtida de plantações (açúcares/amido), materiais celulósicos, resíduos do processamento alimentício, resíduos urbanos, resíduos de origem animal, entre outros (CHANDRA *et al.*, 2012; NUNES *et al.*, 2020). Dentre as supracitadas, a fonte de biomassa renovável mais abundante e passível de conversão energética é a lignocelulósica (ALVIRA *et al.*, 2010; SANCHEZ; CARDONA, 2008; SAWATDEENARUNAT *et al.*, 2015).

Devido ao alto conteúdo de óleo presente nos frutos, a aplicação da macaúba para o setor energético é considerada promissora, podendo ser utilizada, por exemplo, na produção de biodiesel (RENCORET *et al.*, 2018). Tradicionalmente a cadeia produtiva de macaúba é baseada na colheita manual dos frutos localizados no chão, o que pode resultar na obtenção de produtos com óleo de baixa qualidade (CESAR, A. D. *et al.*, 2015; DA MOTTA *et al.*, 2002). No intuito de amenizar esse problema, o Programa Nacional de Produção e Uso do Biodiesel (PNPB) em 2004, inicialmente incentivando a adição de biodiesel ao diesel comercializado no Brasil e, em seguida, estabelecendo proporções obrigatórias de biodiesel no diesel nacional que, atualmente, é de 12% (B12) (ANP, 2020; BRASIL, 2016). De forma complementar também foi implantado o Governo de Minas Gerais, estado responsável pela maior produção de macaúba no Brasil, instituiu a Lei Pró-Macaúba (BRASIL, 2011) de incentivo ao cultivo, à extração, à comercialização, ao consumo e à transformação da macaúba. Adicionalmente, o Governo Federal estabeleceu em 2003 a Comissão Executiva Interministerial do Biodiesel (CEIB) e o Grupo Gestor (GG) como estratégias que visam reduzir a emissão de poluentes e aumentar a produção de combustíveis obtidos de biomassa renovável.

A **Figura 1** apresenta o fruto da macaúba, suas partes e as principais aplicações de cada material. A polpa do fruto, após sua prensagem e extração de óleo, gera uma torta rica em material proteico, que pode ser utilizada na produção de bioetanol (DA SILVA; RODRIGUES, 2014; MELO, 2012). O endocarpo pode ser transformado em carvão, para a obtenção de energia térmica (EVARISTO, A. B.; GROSSI, J. A. S.; CARNEIRO, A. D. O.*; et al.*, 2016; MELO, 2012). Os óleos extraídos do mesocarpo e do endosperma podem ser aplicados à produção de biodiesel, à indústria química e de cosméticos (MELO, 2012). O processamento da macaúba para a produção de biodiesel inclui a geração de coprodutos, tais como as cascas, que correspondem a 22,6% do fruto, e não apresentam composição satisfatória de óleo, portanto não são utilizadas para a obtenção do mesmo (COLOMBO, C. A. *et al.*, 2018; TEIXEIRA *et al.*, 2018).

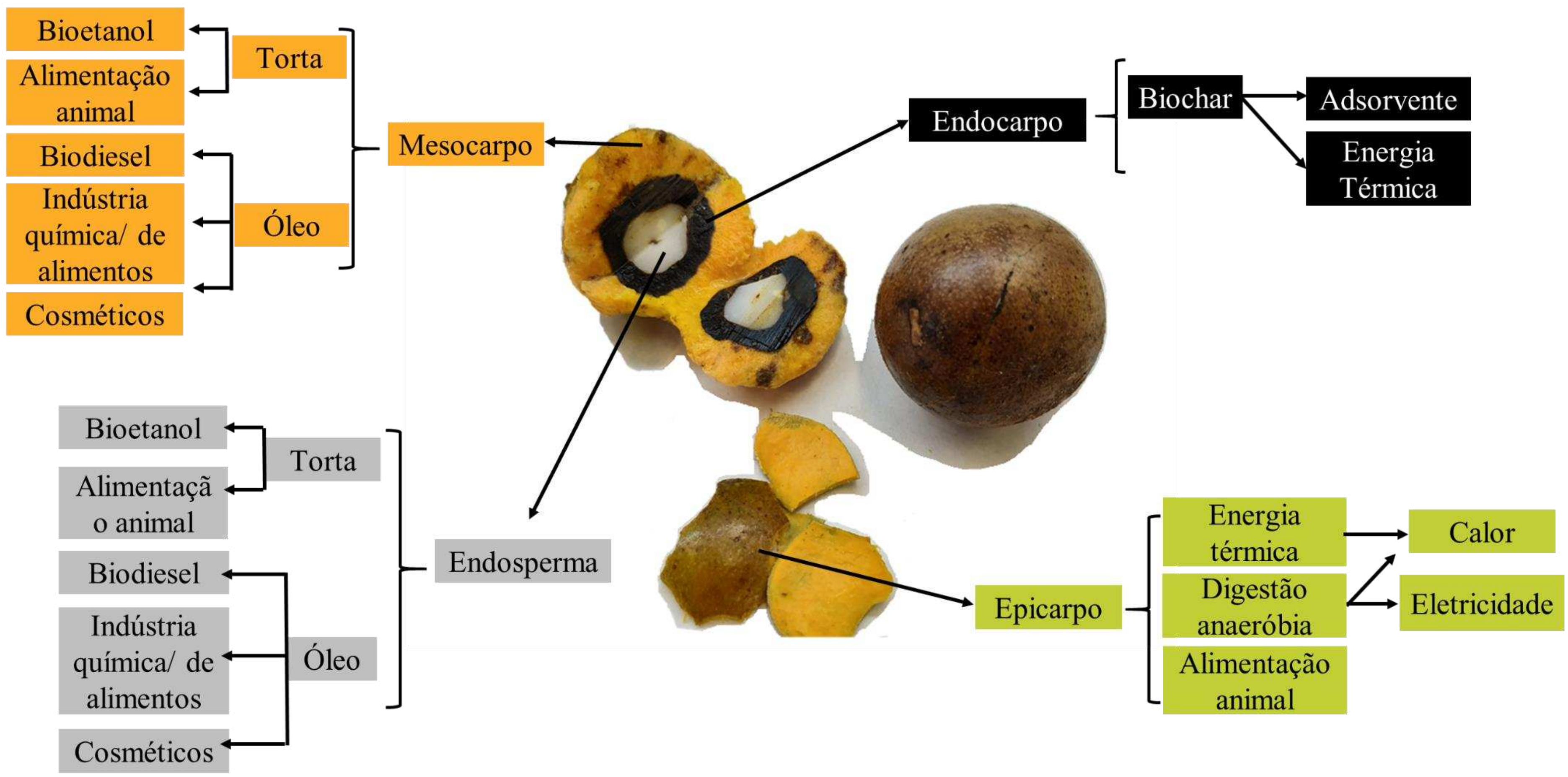

Figura 1. Partes da macaúba e suas principais aplicações.

O dado mais atualizado relativo à produção de macaúba no Brasil, estimado pelo Instituto Brasileiro de Geografia e Estatística, data do ano de 2017 e corresponde a 484 toneladas (IBGE, 2017), gerando aproximadamente 109 tons de cascas. O conteúdo total de lignina presente nas cascas de macaúba é descrito como 35,26%, e sua principal aplicação é o seu uso na obtenção de energia térmica, através da produção de carvão, podendo ainda ser aplicada para digestão anaeróbia e para alimentação animal (TEIXEIRA *et al.*, 2018). Devido à sua composição, as cascas de macaúba consistem em uma fonte de material lignocelulósico, que apresenta grande potencial na obtenção de energia renovável através da tecnologia de digestão anaeróbia (SAWATDEENARUNAT *et al.*, 2015). Nestas condições, microrganismos anaeróbios convertem a biomassa em biogás contendo metano (CH_4), que pode ser aplicado a veículos leves/pesados, em atividades de cozinha, ou à produção de energias elétrica ou térmica, diminuindo os impactos climáticos negativos amplamente associados ao uso de combustíveis fósseis (FERREIRA, S. F.; BULLER, L. S.; BERNI, M.*; et al.*, 2019; SCARLAT *et al.*, 2018; WAGNER *et al.*, 2018).

A digestão anaeróbia para obtenção de metano é atualmente utilizada para resíduos alimentares, resíduos sólidos e outros materiais lignocelulósicos (WAGNER *et al.*, 2018; YANG *et al.*, 2015; ZHANG *et al.*, 2018). Todavia resíduos lignocelulósicos, constituídos majoritariamente de celulose, hemicelulose e lignina, representam um desafio para serem submetidos à digestão anaeróbia, principalmente porque a lignina presente em tal biomassa fornece resistência à degradação química e biológica, prevenindo a destruição celular por parte de fungos, bactérias e enzimas (CHANDRA *et al.*, 2012; WAGNER *et al.*, 2018; ZHENG *et al.*, 2014). Esta resistência à degradação completa torna necessária a utilização de pré-tratamentos visando melhores rendimentos de biogás (WAGNER *et al.*, 2018; ZHENG *et al.*, 2014). Consequentemente diversos estudos tem sido realizados, testando diferentes pré-tratamentos físicos, químicos e biológicos (ZHENG *et al.*, 2014). Nesse contexto, pré-tratamentos executados em condições sub/supercríticas mostraram-se de grande interesse e proporcionaram resultados favoráveis em estudos recentes (ALVIRA *et al.*, 2010; LACHOS-PEREZ; BROWN*;* *et al.*, 2017; MATSAKAS *et al.*, 2015). Quando aplicada a materiais lignocelulósicos, a hidrólise em água subcrítica (entre 100-374 °C mantida líquida através do controle de pressão) permite a conversão do material recalcitrante em açúcares de cadeia curta, que podem ser facilmente consumidos durante a digestão anaeróbia (PRADO *et al.*, 2016).

Numerosos trabalhos envolvendo a macaúba fornecem informações sobre sua caracterização, cultivo e seu potencial energético para a produção de biodiesel. Não foram encontrados estudos relatando o uso da análise bibliométrica para melhor compreensão de pesquisas já desenvolvidas com o fruto. A análise bibliométrica envolve o uso de modelos matemáticos e métodos estatísticos para avaliar o conteúdo de áreas específicas da literatura, baseando-se na estrutura, relação e variação de dados coletados de bancos de dados científicos. Tais estudos permitem estimar avanços do conhecimento em determinados campos e, adicionalmente, identificar áreas de estudo pouco exploradas (JIANG *et al.*, 2019).

O crescente interesse na produção de macaúba decorrente de sua promissora aplicação energética e seu uso na produção de biodiesel podem resultar no aumento da quantidade de coprodutos, dentre eles as cascas, gerados no Brasil, como consequência na elevação da produção de macaúba. Isto deve ocorrer principalmente nos estados de Minas Gerais (MG), Goiás (GO) e São Paulo (SP), classificados como os três maiores produtores nacionais de macaúba (CESAR, A. D. *et al.*, 2015; DA MOTTA *et al.*, 2002). Comumente o destino dado para este coproduto é a produção de carvão, para conversão em energia térmica (TEIXEIRA *et al.*, 2018). Não foram encontrados trabalhos relatando o uso da hidrólise em água subcrítica como pré-tratamento de cascas de macaúba e sua posterior digestão anaeróbia. Além disso, a utilização das cascas para a produção de biogás consiste em uma oportunidade de grande potencial para a valorização de coprodutos da extração de óleo de macaúba, favorecendo a implementação de uma economia circular.

1.2. Objetivos

1.2.1. Objetivo Geral

O objetivo deste trabalho é estudar a valorização de coprodutos orgânicos (biomassa) procedentes da extração de óleo de macaúba, especificamente as cascas, para obtenção de produtos de maior valor agregado e energia, através da integração entre as tecnologias supercrítica e digestão anaeróbia.

1.2.2. Objetivos específicos

- ✓ Fazer análise bibliométrica para mapear os produtos em potencial da macaúba e verificar as possibilidades para o seu processamento.

- ✓ Realizar ensaios nas melhores condições do processo de hidrólise em água subcrítica (temperatura, vazão e pressão) para pré-tratamento de cascas de macaúba;

- ✓ Caracterizar os hidrolisados da etapa de pré-tratamento com água subcrítica material passível de fermentação;

- ✓ Integrar as tecnologias hidrotérmica e digestão anaeróbia através do uso dos hidrolisados, obtidos por tratamento subcrítico, nos reatores anaeróbios, bem como avaliar o processo de digestão anaeróbia;

- ✓ Determinar o rendimento e a composição do biogás gerado durante o processo de digestão anaeróbia.

1.3. Estrutura da Dissertação

O presente documento encontra-se dividido em capítulos. Os artigos que apresentam a revisão bibliográfica e os resultados experimentais correspondem a artigos que estão publicados ou estão sendo revisados em revistas científicas internacionais da Área de Engenharia de Alimentos.

O **Capítulo 1** é constituído da Introdução, onde são fornecidas informações acerca do tema central da dissertação, apresentando brevemente os pontos mais importantes a serem estudados, o objetivo geral e os específicos do trabalho e a estrutura da dissertação. Inicialmente foi apresentada a planta e o fruto de interesse para o estudo. Em seguida foram discutidas fontes energéticas de origem fóssil e a importância de sua substituição por fontes renováveis. Justificou-se o crescente interesse pela macaúba para aplicações energéticas, bem como foram apresentados, de forma suscinta, a destinação dada aos coprodutos gerados na produção de biodiesel de macaúba. Apresentou-se a tecnologia de digestão anaeróbia e algumas de suas aplicações, bem como a dificuldade em sua aplicação para coprodutos lignocelulósicos. Discutiu-se acerca da realização de pré-tratamentos que favoreçam a digestão anaeróbia desses coprodutos, identificando-se a hidrólise em água subcrítica como uma alternativa promissora.

O **Capítulo 2** apresenta um estudo de análise bibliométrica. Foram apresentadas as principais áreas de realização de estudos com macaúba e o crescimento no número de trabalhos publicados com o decorrer dos anos. Foram identificados os autores, países e instituições mais importantes e a maneira que se relacionam. Indicaram-se as principais palavras-chave utilizadas pelos autores e as revistas onde o maior número de publicações ocorre. Descreveram-se as aplicações do óleo extraído da macaúba, e os coprodutos gerados, bem como suas aplicações. A análise bibliométrica visa estudar as pesquisas envolvendo a macaúba e os principais trabalhos desenvolvidos e, adicionalmente, identificar oportunidades e lacunas de conhecimento para a realização de estudos envolvendo a macaúba.

Os resultados experimentais do Capítulo 2 são apresentados na forma de artigo científico com título "MACAÚBA'S WORLD SCENARIO: A BIBLIOMETRIC ANALYSIS" e autores Larissa Castro Ampese, L. Selene Buller, Y. Machaca Monroy, M. Perez Garcia, A. R. Ramos, T. Forster-Carneiro. Este artigo foi publicado no periódico Biomass Conversion and Biorefinery em março de 2021.

O **Capítulo 3** relata o processo de hidrólise em água subcrítica das cascas de macaúba em um reator semi-contínuo na temperatura de 200°C, pressão de 14 MPa, fluxo de água de 10 mL min^{-1} e 40 min de tempo de retenção. O hidrolisado obtido foi submetido à digestão anaeróbia em condições mesofílicas de temperatura (35°C), em regime semi-contínuo, com alimentações realizadas três vezes por semana. Descreve a utilização das cascas trituradas de macaúba submetidas à digestão anaeróbia como controle do processo no qual o pré-tratamento foi utilizado. Foram avaliados o volume e composição do biogás produzido durante a digestão anaeróbia. O reator contendo hidrolisado utilizou 76,36 g de macaúba e produziu 27,3 L de biogás e 15,53 L de metano, enquanto o reator de digestão anaeróbia sem pré-tratamento consumiu 617,47 g de macaúba e gerou 22,6 L de biogás e 9,53 L de metano.

Os resultados experimentais do Capítulo 3 são apresentados na forma de artigo científico com título "VALORIZATION OF MACAÚBA HUSKS FROM BIODIESEL PRODUCTION USING SUBCRITICAL WATER HYDROLYSIS PRETREATMENT

FOLLOWED BY ANAEROBIC DIGESTION" e autores Larissa Castro Ampese, Luz Selene Buller, Jordan Myers, Michael Timko, Gilberto Martins, Tânia Forster-Carneiro. Este artigo foi submetido ao Journal of Environmental Chemical Engineering em fevereiro de 2021.

O Capítulo 4 apresenta as discussões gerais da dissertação.

O Capítulo 5 apresenta as principais conclusões da dissertação bem como os trabalhos futuros.

CAPÍTULO 2 - Cenário mundial da macaúba: uma análise bibliométrica

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MACAÚBA'S WORLD SCENARIO: A BIBLIOMETRIC ANALYSIS

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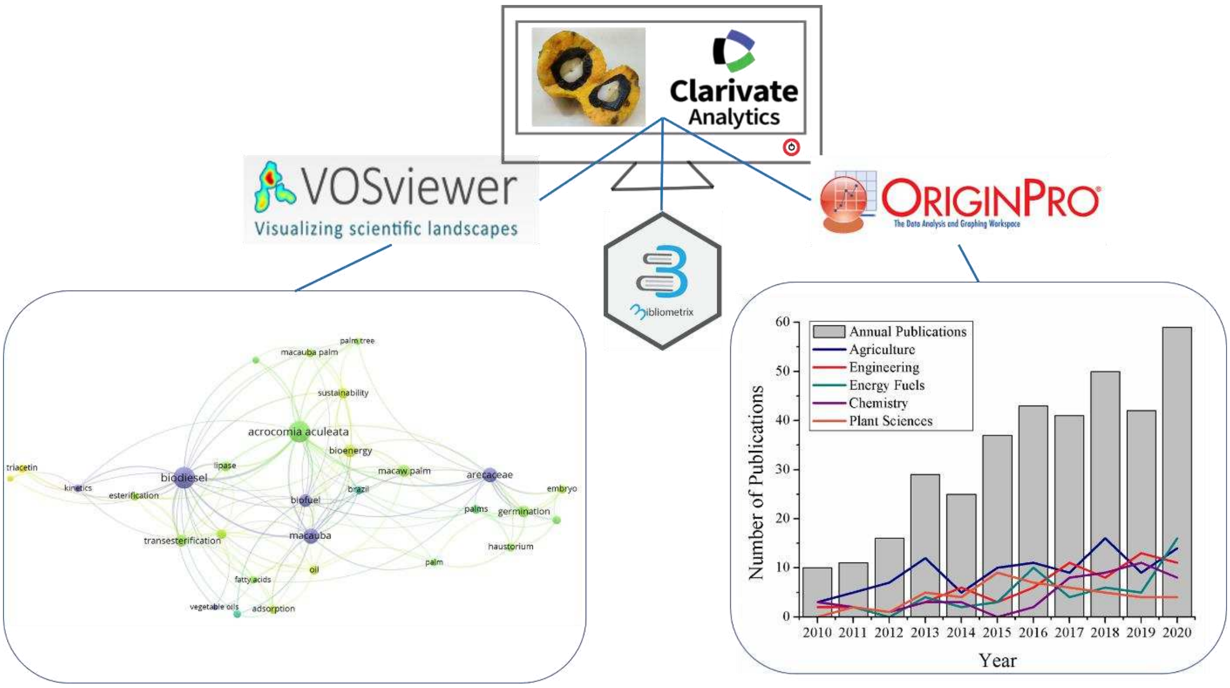
Graphical abstract



ABSTRACT

Macaúba is a tropical palm native in South and Central America, and its fruits present a high-quality oil for biodiesel production. Notwithstanding, *macaúba*'s wastes and by-products are not usually repurposed as energy sources. This study shows a bibliometric analysis to assess *macaúba*'s current applications and to investigate other energy recovery routes for its by-products. All the investigations focused on information about the main research fields related to *macaúba*. The study showed that only 397 articles and reviews were published from 1900 until 2021 and Brazil has the largest number of publications. Although oleic and protein *macaúba*'s by-products are applied as animal feed, some conversion routes related to the lignocellulosic contents, present in non-edible parts, were identified thermal conversion, combustion, gasification, pyrolysis, biochemical conversion, fermentation, esterification, and anaerobic digestion. From the agricultural perspective, plant characterization, germination, embryogenesis, and seed development were also found. From the bibliometric study, the different potential applications of *macaúba* for energy, pharmaceutical, and food purposes were listed to support the identification of a knowledge gap on its by-products revaluation.

Keywords: *By-products, Waste, Bioenergy, Systematic Review, Acrocomia aculeata*

DECLARATIONS

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1. INTRODUCTION

Acrocomia aculeata, "*macaúba*", a member of the Arecaceae family, is native to South and Central America (BAZZO *et al.*, 2018). The plant is highly productive, arborescent, and spiny, producing large bunches of fruits (BAZZO *et al.*, 2018; EVARISTO; GROSSI; CARNEIRO*; et al.*, 2016; MANFIO *et al.*, 2012; SCARIOT *et al.*, 1995). The palm is more vigorous infertile soils, occurring mainly in areas with high solar radiation. It can equally adapt to sandy and clayey soils and presents a low water requirement (CESAR *et al.*, 2015). *Macaúba's* fruits are composed of: tough and fibrous husk (epicarp), yellow and oleic fleshy pulp (mesocarp), and a black tissue (endocarp) containing one or even two white nuts (endosperm) (BELTRÃO, 2007; EVARISTO; GROSSI; CARNEIRO*; et al.*, 2016). *Macaúba* has an interesting chemical composition, starting from the husks' lignin content is 27.52%, while the values for pulp cake, endocarp, and kernel cake are, respectively, 29.25%, 31.67%, and 32.70% (EVARISTO; GROSSI; CARNEIRO*; et al.*, 2016). For the husks, elemental composition, the values of carbon (C), hydrogen (H), and nitrogen (N) are equal to 47.20%, 7.26%, and 0.43%. The content of C, H, and N in the pulp cake are 43.84%, 7.42%, and 0.88%, in the endocarp 48.00%, 6.19%, and 0.56%. Finally, for the kernel cake, the elemental content is 45.00% C, 7.41% H, and 6.35% N (EVARISTO; GROSSI; CARNEIRO*; et al.*, 2016). The fruit kernel fatty acid composition is lauric acid (43.6%), oleic acid (25.5%), myristic acid (8.5%), caprylic acid (6.2%), capric acid and palmitic acid (5.3%), linoleic acid (3.3%) and stearic acid (2.4%). The fatty acid content from the mesocarp is oleic acid (53.4%), palmitic acid (18.7%), linoleic acid (17.7%), palmitoleic acid (4.0%), stearic acid (2.8%) and linolenic acid (1.5%) (CESAR *et al.*, 2015). The oil extracted from the mesocarp is rich in oleic acid. It presents high oxidative stability and operability at low temperatures. At the same time, the oil from the endosperm is rich in short-chain saturated fatty acids, mainly employed for pharmaceutical and cosmetic purposes (BAZZO *et al.*, 2018; BELTRÃO, 2007). Both oils present suitable physicochemical properties for biodiesel production, which results from the high presence of lauric acid that facilitates esterification reactions (CESAR *et al.*, 2015). Additionally, *macaúba* oil extracted from pulp is rich in oleic acid, resulting in biodiesel of good quality containing high monosaturated esters in high concentration (PASA *et al.*, 2020). The by-products, husks and endocarp are mainly destined for combustion (MELO, 2012).

Macaúba's species occurs in almost the whole Brazilian territory. It is spread over all five (5) regions of the country - North, Northeast, Midwest, Southeast and South (DE LIMA *et al.*, 2018). The main producers are located in *Minas Gerais* state, where an expressive economic importance/potential is observed. (CESAR *et al.*, 2015; DA MOTTA *et al.*, 2002). Because of *macaúba's* natural occurrence in Brazil and its oil characteristics, a growing biodiesel industry is flourishing, especially in *Minas Gerais* state (COLOMBO *et al.*, 2018; DE FREITAS GRUPIONI *et al.*, 2020). Cruz et al. (2020) showed data about *macaúba's* biodiesel production and reported it's composition as follows: 64.50% of carbon and 39.23 $MJ.kg^{-1}$ of higher heating value (HHV). Despite the high-quality biodiesel obtained from *macaúba's* oil, it's an incipient industry that still requires further research (CRUZ, GLAUBER *et al.*, 2020).

Macaúba's productive chain is primarily extractive, and the fruits are manually picked up from the ground, resulting in a low-quality final product (CESAR *et al.*, 2015; DA MOTTA *et al.*, 2002). For this reason, several measures were adopted by the Government of Minas Gerais, such as the "*Pro Macaúba's Law*" (BRASIL; HORIZONTE), which encourages the cultivation, extraction, marketing, consumption and processing steps. Brazilian biodiesel can be obtained from several raw materials, like fats and oils from animals, palm (*Elaies* sp.), sunflower (*Heliantusannus*), babassu (*Orbignyaphalerata*), *macaúba* (*Acrocomia aculeata*), *pequi* (*Brasilia caryocar*), soybean (*Glycine max*) and even from sugarcane (*Saccharum officinarum*) (CESAR *et al.*, 2015). According to ANP (National Petroleum Agency) the main raw material for biodiesel production in Brazil is soybean oil, which reached 4,000,116.40 m³ in 2019, 67.80% of the total national production. The most recent data available for the Brazilian soybean biodiesel production, from January to April 2020, corresponds to 1,367,036.54 m³, which is 70.58% of the total production (ANP, 2020). Brazilian soybean biodiesel is predominant. In 2018, the country's exports accounted for 83,605,198 tons of soybeans, opening opportunities for other oil crops with great potential for biodiesel production (FAOSTAT, 2018).

Considering the high productivity of *macaúba* in terms of oil, the flourishing biodiesel industry presents great potential for further expansion. Even considering a conservative scenario with a low density of 400 plants.ha^{-1}.$year^{-1}$, the oil production would be 2.5-ton oil.ha^{-1}.$year^{-1}$, while in an optimal situation, the yield could reach 5 ton.ha^{-1}.$year^{-1}$ (COLOMBO *et al.*, 2018). Additionally, the cultivation of *macaúba* is feasible for small farmers. The cost of commercial crops (US$ 24.64/ton in 2011) was very competitive when compared to other cultures in the same year, like *Jatropha curcas* (jatropha, US$ 47.18/ton), *Ricinus communis L.* (Castor bean, US$ 151.91/ton) and soybean (US$ 79.35/ton) (CESAR *et al.*, 2015). In 2014 the price of *macaúba* oil in state of Minas Gerais was estimated in R$3.70/L of pulp oil and R$4.00/L of nut oil, which correspond to US$ 0.7/L and US$0.76/L (SILVA; DE ANDRADE, 2014). The National Supply Company (Conab), with the federal government, established the minimal price for Brazilian *macaúba* in 2019 as 0.665 R$/kg of fruit or 0.13 US$/kg of fruit (MAPA, 2019). Nowadays, *macaúba* is only cultivated on a small scale combined with other land uses, consequently the data to assess the biomass production costs are highly uncertain (CERVI *et al.*, 2020; PIMENTEL *et al.*, 2009). A recent research was conducted to evaluate the techno-economic potential of biojet fuel production in Brazil for future development, considering multiple feedstocks, including *macaúba* (CERVI *et al.*, 2020). An increase in biomass potential is observed, and biomass production costs will generally decrease toward 2030, assuming average values 4% lower than in 2015. The same study indicates that *macaúba* is able to grow over suitable areas in Cerrado (Savannah). Notwithstanding, if no major on-farm improvements are introduced, the production costs could be higher in the coming years (CERVI *et al.*, 2020). Finally, it is noteworthy to highlight that the oil demand is so high that virtually all of the worldwide bio-oil produced is absorbed by the market, placing *macaúba* and its biodiesel in good prospects (CESAR *et al.*, 2015). In 2020 the oil demand presented a decrease because of the pandemics, with historic turbulence in energy markets (IEA, 2020). In December 2019, the global oil demand presented the strongest annual growth in a year, reaching 900 kb/d (kilo barrel per day) (IEA, 2019). The preliminary forecast to total world oil crop production for 2020/21 is 613.3 million tons (FAOSTAT, 2021). For biodiesel production, there are some advantages of *macaúba* over other crops: (i) high oil productivity (that may reach 5,000 kg of oil per $ha^{-1}.year^{-1}$) in a relatively easy extraction process, (ii) plant adaptation to different soil types, (iii) contribution to degraded areas recovery (from mixing *macaúba's* cultivation with intercrop and agroforestry systems), (iv) high CO_2 absorption capacity (10.00 $Mg.ha^{-1}$), almost 3-fold higher than soybean (3.52 $Mg.ha^{-1}$), while 3-fold lower than palm oil (29.30 $Mg.ha^{-1}$), (v) profitability for farmers and rising market prices (in 2009 the cost of *in natura macaúba* was around USD $25.ton^{-1}$, and in 2011 it increased by 30% to USD 32), (vi) job generation, and (vii) a market in expansion presenting a growth of 20.9% from 2010 to 2015 (BORCIONI; NEGRELLE, 2012; CESAR *et al.*, 2015; COLOMBO *et al.*, 2018; MANFIO *et al.*, 2012; PIMENTEL *et al.*, 2009; VILLANUEVA *et al.*, 2008).

In 2003, the Brazilian government adopted two strategies to reduce pollutants' emissions and to boost the production of fuels from renewable biomass, the Inter-ministerial Executive Committee on Biodiesel (CEIB, from Portuguese) and the Management Group (GG). Further, in 2004, a new state policy, the National Program of Biodiesel Production and Use (PNPB, from Portuguese), encouraged a criterial mixture of biodiesel in diesel. From 2005 to 2007, the B2 blend was commercialized as a mixture of 2% biodiesel and 98% of diesel. Since 2008, biodiesel's fixed additions in the marketed diesel became mandatory, and, more recently, in March 2020, the B12 proportion was regulated (ANP, 2020; BRASIL, 2016).

Another Brazilian Government state policy called "RenovaBio" was established to accomplish the Paris Agreement's national commitments in 2016 (BRASIL, 2017). RenovaBio aims to recognize all kinds of biofuels and their use to assure the country's energy security while contributing to the fuel sector decarbonization. Among these biofuels, special attention is given to ethanol, second-generation ethanol, biodiesel, biogas and biomass (ANP, 2020).

An attractive development strategy for Brazil, an agro producer country, is the rational use of renewable energy from biomass. The use of residual biomass as a source of energy and materials on a sustainable basis is essential to achieve higher energy use rates and maintain or expand the country's energy security. Obtaining new products that favor the development of a ‘circular economy’, recycling, reusing and adding value to materials at the end of their consumption cycles requires advances in the use of existing technologies and innovation. A 'circular economy' minimizes the generation of waste and recovers by-products energy while closing industrial cycles (GENG *et al.*, 2019; STAHEL, 2016).

Despite several research types on *macaúba's* characterization, cultivation and potential biodiesel production were found in the scientific literature, no bibliometric studies were identified. The bibliometric analysis involves mathematical models and statistical methods to assess a particular research field's literature information. It is based on the structure, relationship, and variation law of the collected literature data, and allows setting the knowledge advances in the target field. A peculiar utility of the bibliometric analysis is the prediction of developing hotspots and new or ascending research fields to collect information about knowledge gaps in a specific area (JIANG *et al.*, 2019).

This study presents a bibliometric analysis of *macaúba's* potential applications to investigate further alternatives for fruit processing and recovering energy through by-products. Finally, this study aimed to identify possible knowledge gaps on macaúba's by-products energy recovery to support future research.

2. MATERIALS AND METHODS

2.1. Data Collection

The bibliometric study followed six steps (**Figure 1**): (I) topic definition to describe, in detail, the current state of *macaúba's* research; (II) selection of databases and platforms privileging those that offer the necessary analytical tools for bibliometric calculations; (III) selection of keywords to prepare the literature data collection; (IV) bibliographic search; (V) data exportation; and (VI) data analysis.

Scientific output data were obtained from the core collection of Science Citation Index Expanded (SCI-E) – Clarivate Analytics' ISI – Web of Science© (WoS - https://webofknowledge.com/) to "Topic" (title, abstract, authors' keywords and Keywords Plus) on January, 14th 2021. The type of search applied was "basic search" and the types of documents were filtered to "article" and "review" to obtain reliable and accurate details on the Topic. A total of 397 publications were gathered, using "*macaúba*" or "macauba" or "macaw palm" or "*Acrocomia aculeata*" as the search query, for the period from 1900 to 2021.

Data obtained from all databases of SCI-E– Clarivate Analytics' ISI – WoS© to "Topic" (title, abstract, authors' keywords, and Keywords Plus) on January, 18th 2021 were applied to analyze the patents related to *macaúba* scientific. The type of search applied was "basic search" and the types of documents were filtered to "patent". A total of 14 patents were gathered, using "*macaúba*" or "macauba" or "macaw palm" or "*Acrocomia aculeata*" as the search query, for the period from 1900 to 2021.

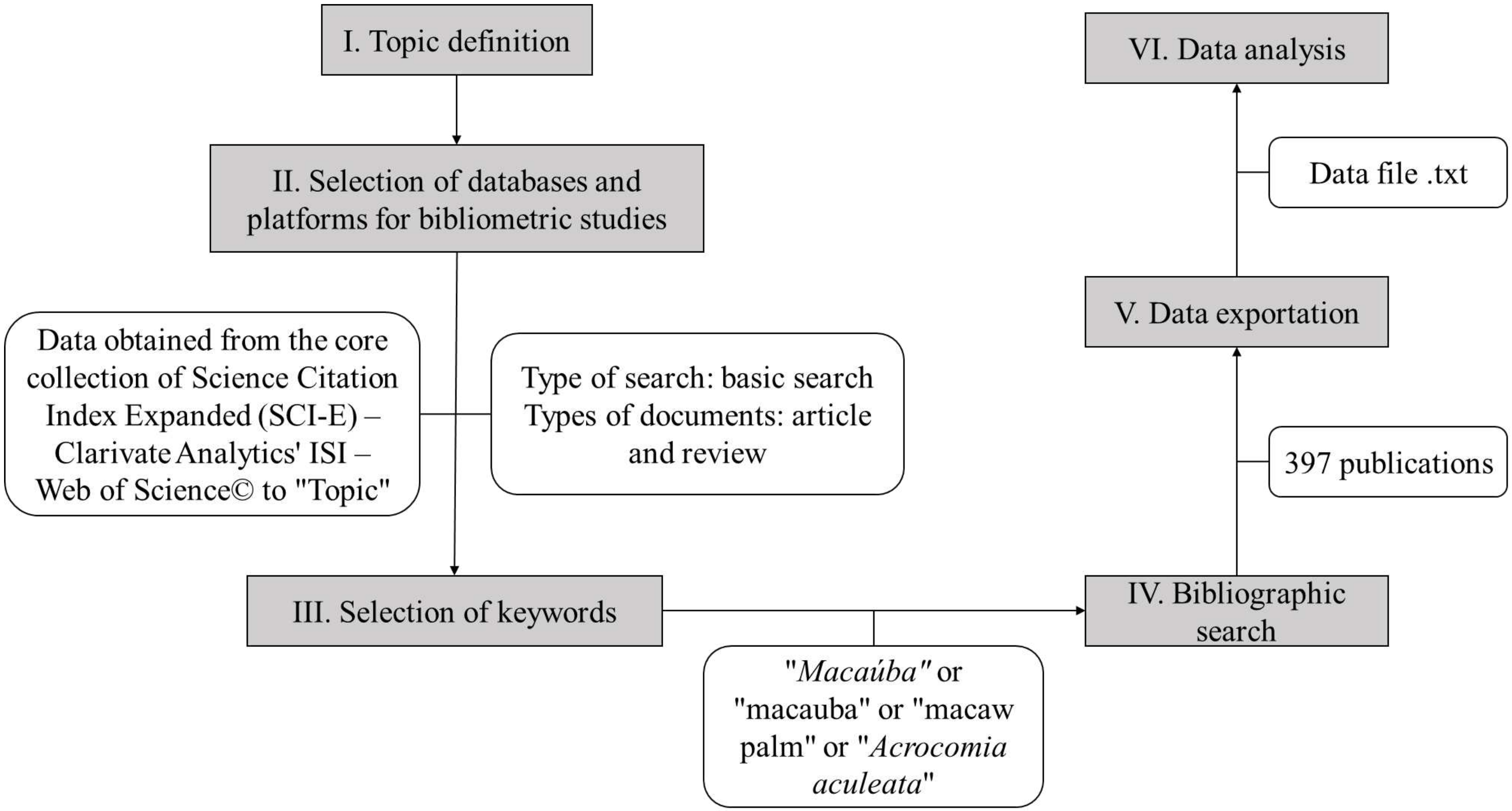


Figure 1. The six steps to produce the bibliometric study.

2.2.Bibliometric Analysis

The "Bibliometrix" package (R language) was used to obtain a three-field plot identifying the countries and how they are related to the most common authors' keywords and sources in *macaúba* field (R CORE TEAM, 2020). Besides, the obtained dataset was applied to VOSviewer software to build clusters containing information related to authors, coauthors and the most common authors' keywords (VOSVIEWER, 2019). Finally, Origin® was applied to analyze the absolute number of publications per year in the last decade and the 5 most frequent research areas. All the data for the bibliometric analysis was extracted from WoS.

The VOSviewer software starts the maps building from a co-occurrence matrix. A similarity matrix is calculated to correct the differences in the total number of item occurrences or co-occurrences in the first step. In the next step, a two-dimensional map is obtained by applying the mapping technique to the similarity matrix, and issues with high similarity are located close to each other. In contrast, items that have low similarity are located far from each other. Finally, the map is translated, rotated and reflected. This way, the same co-occurrence matrix should always yield the same map (VAN ECK; WALTMAN, 2010). For the final maps, the distance between two items reflects the strength of the relation between them (VAN ECK; WALTMAN, 2007). On the images, the thicker the lines that connect the items, the higher is the strength linking them, and generally, the smaller the distance between items, the more related they are (VAN ECK; WALTMAN, 2010).

The VOSviewer software running set was defined as the "full counting" method. This choice makes it possible to account for how many times an author or coauthor, or keyword appeared in the different documents. Publications with more than 15 authors were not included, and the minimum number of documents per author was set to 5. The authors' names were reduced to their initials. From the initial 1387 authors identified in the original search, 30 met the established threshold and, some of them were not connected. In the study of authors' keywords, the initial number was 1076, and 35 completed the limits. Finally, only the 30 words with the highest total link strength were selected.

3. RESULTS AND DISCUSSION

3.1. Bibliometric Analysis

In the past 10 years, 363 documents including "*macaúba*", or "macauba", or "macaw palm", or "*Acrocomia aculeata*" were found, corresponding to 91.44% of all WoS publications. **Figure 2** presents the number of publications from 2010 until January 14th, 2021. The lines represent the number of publications for the top 5 research fields.

The most expressive research field is agriculture (101 publications), followed by engineering (66), energy fuels (52), chemistry (50) and plant sciences (47), anyway, the number of publications per area does not follow a trend. It is possible to notice an increasing number of documents, with the highest level in 2020 (59) and a slight decay in 2019 (42). Yet, in recent years, a growing interest in *macaúba* for cleaner and renewable energy production allows inferring that more studies in plant and seed development and processing follow the same energy research trend, probably to support higher yields for energy purposes.

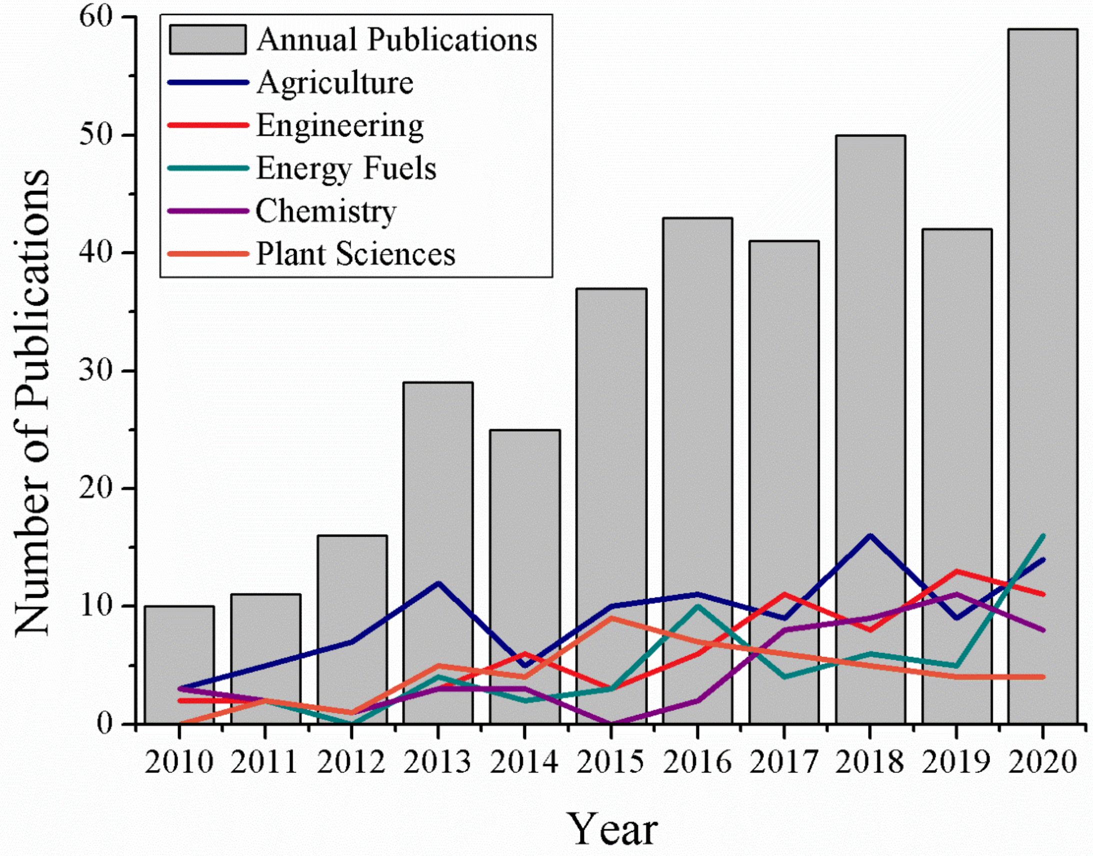


Figure 2. The absolute number of publications (bars) and the number of publications in the most frequent research areas per year of publication for the last 10 years.

Table 1 presents the most discussed issues over the years, also including the main research fields. One document related to *Salto Macaúba's* farm was present only for a coincidence of the term "*macaúba*" (TOSCANO *et al.*, 2010). No other miscommunications like this were noted. From 2010, studies related to energy became evident, especially for biodiesel production (ALVES *et al.*, 2010; NOGUEIRA *et al.*, 2010) and the use of by-products for coal (BOAS *et al.*, 2010). After 2014 a higher number of researches on biofuels are present, which are correlated to the increasing interest in cleaner energy sources and sustainability. Even though the main destination of *macaúba* by-products is for animal feed, research on energy obtention through pyrolysis and coal production from non-edible parts is in evidence. In the same period, it is possible to observe an increase in by-products valorization as biochar for the adsorption of different chemicals. Still, this theme appeared for the first time in 2012 in the adsorption of dyes (VIEIRA *et al.*, 2012). For the year 2020 (**Table 1**) the research area of energy fuels was the most expressive, with 16 accepted publications, corresponding to 27.12% of the total (59 papers). In second place, appeared agriculture with 14 publications (23.73%), followed by engineering with 11 articles (18.64%).

Table 1. Year of publication, main research fields, issues discussed and number of documents.

Year	Research field	Issue	Number of Documents	References
2010	Agriculture (30%), Chemistry (30%)	Microwave activation of enzymatic catalysts; catalysts using Cadmium compounds; liquid-liquid equilibrium for biodiesel production; use of *macaúba's* waste for coal production; use of *macaúba's* oil combined with cassava starch in thermoplastic biofilms; the bacteria characterization in an alcoholic beverage made from *macaúba's* sap; studies on embryogenesis, germination, anatomy, histochemistry of *macaúba's* structures	10	(ALCANTARA-HERNANDEZ *et al.*, 2010; ALVES; DE CARVALHO, 2010; ALVES *et al.*, 2010; BOAS *et al.*, 2010; DA SILVA *et al.*, 2010; MOURA *et al.*, 2010; NOGUEIRA *et al.*, 2010; RIBEIRO *et al.*, 2010; SCHLEMMER; SALES, 2010).
2011 to 2012	Agriculture (30.73%*)	Use of *macaúba's* co-products as animal feed; plant characterization; germination, embryo and seeds development; use of *macaúba* cake as adsorbent for the removal of Methylene Blue and Congo Red;	12	(BORCIONI; NEGRELLE, 2012; CARRERA *et al.*, 2012; DA FONSECA *et al.*, 2012; DE AZEVEDO *et al.*, 2012; MOURA *et al.*, 2010; NETO *et al.*, 2012; RIBEIRO *et al.*, 2010; RIBEIRO; OLIVEIRA; GARCIA, 2012; RIBEIRO; OLIVEIRA; CARVALHO*;* *et al.*, 2012; RIBEIRO *et al.*, 2011; RUFINO *et al.*, 2011; SOARES *et al.*, 2011; VIEIRA *et al.*, 2012).
2013	Agriculture (41,38%)	Production of biodiesel and ethanol from *macaúba*; seedling studies	11	(BANDEIRA *et al.*, 2013; BASSO; DA SILVA*;* *et al.*, 2013; BASSO; MEIRELLES*;* *et al.*, 2013; BERTON *et al.*, 2013; CARVALHO *et al.*, 2013; DONA *et al.*, 2013; GENOVESE-MARCOMINI *et al.*, 2013; GONCALVES *et al.*, 2013; LOPES *et*

				al., 2013; OLIVEIRA, T. G. S. *et al.*, 2013; RIBEIRO *et al.*, 2013).
2014	Engineering (24%)	Production of biodiesel; *macaúba* use as animal feed; germination and seed development	10	(AGUIEIRAS *et al.*, 2014; ALVES *et al.*, 2014; AZEVEDO *et al.*, 2014; BASKIN; BASKIN, 2014; BASSO *et al.*, 2014; IHA *et al.*, 2014; LUIS; SCHERWINSKI-PEREIRA, 2014; NAVARRO-DIAZ *et al.*, 2014; NETO *et al.*, 2014; SILVA, W. C. E. *et al.*, 2014).
2014 to 2018	Agriculture (25.31%*), Engineering (17.78%*)	Seed germination; embryogenesis; plant medical properties; biofuel production; harvest and post-harvest treatments; oil extraction; animal feed; emerging contaminants removal using activated carbon from residual *macaúba* biomass; application of the *macaúba's* endocarp for Ni (II) biosorption optimization; biochar for adsorption of fatty acid methyl esters; plant and genotype characterization	18	(AGOSTINI-COSTA, 2018; ALTINO *et al.*, 2017; ARENA *et al.*, 2018; BARRETO *et al.*, 2016; BICALHO *et al.*, 2015; CARVALHO *et al.*, 2015; CESAR *et al.*, 2015; DA CONCEICAO *et al.*, 2017; DA SILVA *et al.*, 2017; DA SILVA *et al.*, 2018; DAMASCENO *et al.*, 2018; DE SOUZA *et al.*, 2016; DOS SANTOS *et al.*, 2017; EVARISTO; GROSSI; CARNEIRO*; et al.*, 2016; EVARISTO; GROSSI; PIMENTEL*; et al.*, 2016; FERREIRA *et al.*, 2018; MOURA *et al.*, 2018; OLIVEIRA *et al.*, 2014; RODRIGUES *et al.*, 2017; TRENTINI *et al.*, 2017).
2019	Engineering (30.95%)	Methods to improve esterification and transesterification reactions; aviation biofuels production; botanical information of *macaúba*; productivity tests; genetic parameters for plants selection;	21	(AGUIEIRAS *et al.*, 2019; BATISTA *et al.*, 2019; COELHO *et al.*, 2019; CORREA *et al.*, 2019; DA SILVA *et al.*, 2019; DE

		embryogenesis; post-harvest treatments to higher/better oil production; *macaúba's* medicinal purposes; sensory characteristics; antibiotic, cytotoxic and antioxidant activities of the oil extracted from the pulp; oil extraction methods and properties; *macaúba* as animal feed; use of biochar for uranium adsorption from aqueous solutions; influence and role of the different biomass components during pyrolysis		ALMEIDA *et al.*, 2019; FERREIRA, F. N. A. *et al.*, 2019; GUILHEN; MASEK*; et al.*, 2019; GUILHEN; ROVANI*; et al.*, 2019; HARTER *et al.*, 2019; MAGALHAES *et al.*, 2019; MEIRA *et al.*, 2019; MOREIRA *et al.*, 2019; PINTO *et al.*, 2019; ROSADO *et al.*, 2019; SOUZA, G. K. *et al.*, 2019; TEIXEIRA *et al.*, 2019; TRENTINI *et al.*, 2019; VISIOLI *et al.*, 2019; WANG *et al.*, 2019).
2020	Energy Fuels (27.12%)	Study of ultrasonic-mediated in situ transesterification for biodiesel; production of fatty acid methyl esters production through interesterification reaction; evaluation of calcium oxide as catalyst at different calcination temperatures for chemical interesterification of soybean oil; synthesis of renewable heterogenous acid catalyst for glycerol-free biodiesel production; using *macaúba* for biojet fuel and light biodiesel production; investigation of the presence of ethyl esters in transesterified *macaúba* and *pequi* oils; obtaining ethyl esters from *macaúba* pulp crude oil; processing of *macaúba* seed cake using slow pyrolysis to obtain bio-oil; fungal biocatalyst capable of efficiently hydrolyzing *macaúba* oil	21	(BARBOSA *et al.*; 2020; BRONDANI *et al.*, 2020; CARVALHO *et al.*, 2020; CERVI *et al.*, 2020; CRUZ, G. *et al.*, 2020; DA SILVA *et al.*, 2020; DE SOUZA *et al.*, 2020; DOS SANTOS *et al.*, 2020; MOREIRA, J. D. D. *et al.*, 2020; MOREIRA, S. L. S. *et al.*, 2020; NUNES; CASTILHOS, 2020; NUNES *et al.*, 2020; PASA *et al.*, 2020; PASCOAL *et al.*, 2020; SIMOES *et al.*, 2020; SOUZA *et al.*; WONG *et al.*; WONG *et al.*, 2020)

* Average value based on percentages of the respective years

3.2. Bibliometric Analysis of Countries

Figure 3 presents a three-field plot (Sankey diagram) with the top 10 countries, the 10 most frequent authors' keywords, and the top 10 journals (R CORE TEAM, 2020; RIEHMANN *et al.*, 2005). Brazil is the principal knowledge producer, responsible for 87.41% of the publications. This result is probably due to *macaúba's* large occurrence in Brazil. The second country is Spain (5.54% of the publications), followed by the United States of America (5.04%). Among the journals, Industrial Crops and Products (impact factor 4.244) is the most frequent publisher (27 documents), followed by Fuel (impact factor 5.578 and 12 documents), *Ciencia Rural* (impact factor 0.0644), and Renewable Energy (impact factor 6.274 and 9 documents each).

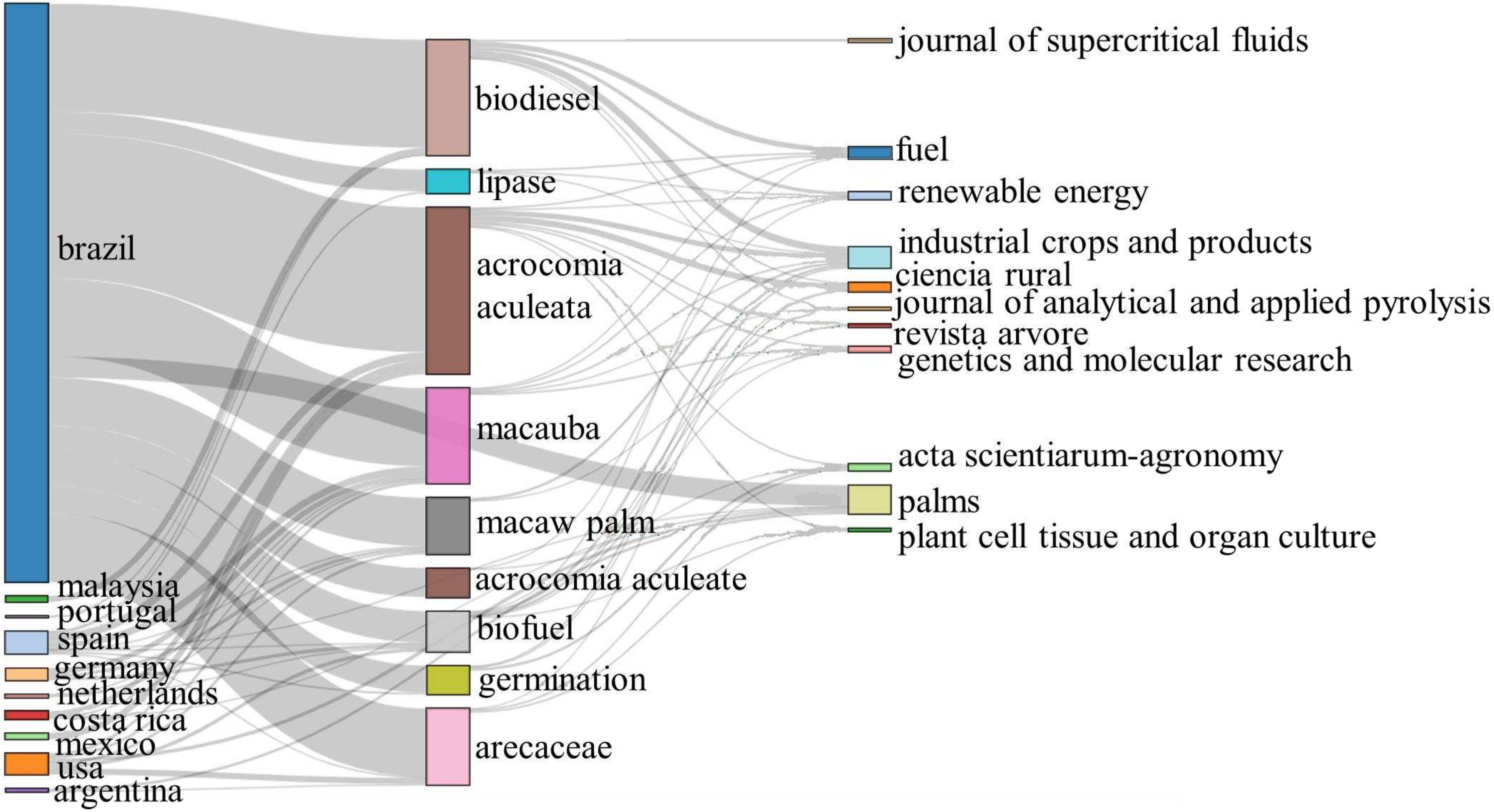


Figure 3. The three-field plot of *macaúba's* research relating the main countries, authors' keywords and journals.

Brazil is also the leader in the number of publications related to all the top 10 authors' keywords (**Figure 3**). The most used keyword is the scientific crop name (*Acrocomia aculeata*), followed by "biodiesel" and "macauba". Other keywords that provide insightful information on the main research areas are biofuel, germination and lipase. The authors' most frequent keyword is *A. aculeata*, that allows the scientific community to recognize the species studied since the common name given to "*macaúba*" vary across different countries and even across Brazilian states. The words "biodiesel", "biofuel" and "lipase" appeared as a consequence of the great potential in the use of *macaúba* oils to produce biodiesel, bio-jet fuel and biokerosene (DE SOUZA *et al.*, 2020; SILVA *et al.*, 2016; WANG *et al.*, 2020).

Table 2 presents the three most productive countries, the research fields, the most common authors' partnership and their respective countries. It is possible to notice the collaboration between Brazil, Spain and the United States of America, which represent 97.99% of the publications. This partnership is important to understand and evaluate the worldwide importance of *macaúba* and its applications in countries other than Brazil. The first publication associated with *macaúba* is from 1991, and it was developed in Brazil. The first document from the United States of America dates from 2004, while in Spain, the first study occurred only in 2014.

Brazil occupies the top position in the ranking of the most productive countries with the agriculture research field as the most frequent topic. Among the Brazilian publications, the most cited document presents 118 citations. With the increasing biodiesel production, an excess of crude glycerol was occasioned, so the most cited article presents a review and analysis of patents about glycerol use, showing extraordinary efforts to add value to glycerol from biodiesel production (MONTEIRO *et al.*, 2018). This article is not directly related to the application of *macaúba* itself, but it includes the plant as one of the feedstocks used for biodiesel production. Since biodiesel production is one of the most discussed topics, and glycerol surplus consists of a major bottleneck in the biodiesel production chain, it is reasonable that this work would have more citations.

The most discussed research field in Spain is plant sciences (**Table 2**). The most cited paper from Spain presents 79 citations. It reports the use of *macaúba's* endocarp to activated carbon production and the biochar characterization, aiming to remove Rhodamine B from aqueous solutions (LACERDA *et al.*, 2015). Rhodamine B is an example of an industrial pollutant dye with harmful properties. Synthetic dyes produce toxic, carcinogenic, mutagenic, and bio-accumulative compounds that contaminate the wastewaters, making it necessary to use non-conventional wastewater purification treatments (CHEN *et al.*, 2010; FORGACS *et al.*, 2004). In this document, the authors describe the production, characterization and use of activated charcoals obtained from three lignocellulosic waste materials, including *macaúba* endocarp, for the adsorption of contaminants in wastewaters. The contamination of water and wastewater with dyes, heavy metals and other chemicals consists of a current environmental problem, explaining the study's importance and several citations. The authorship includes some of the most important authors from Spain (refer to **Table 2**).

Among the publications from the United States of America, the most impacting research field is engineering (**Table 2**). The most cited article presents 39 citations. It is focused on seed dormancy presented by different *macaúba* palms species (BASKIN; BASKIN, 2014). Studies on seed dormancy, germination, embryogenesis and other agricultural/morphological traits on *macaúba's* development are indispensable to establish plantations for commercial purposes. This research area is one of the most prevailing, and the authors are not listed among the most productive from this country.

Table 2. Top countries with the highest number of publications, research fields, the most productive authors and partnerships among different countries.

Country	Research Fields	Authors	Partnerships
Brazil	Agriculture, Engineering, Chemistry, Energy Fuels, Plant Sciences, Food Science Technology, Biotechnology Applied Microbiology, Science Technology Other Topics, Forestry and Biochemist Molecular Biology.	Motoike, S.Y., Ribeiro, L. M., Da Silva C, Kuki, K.N., De Castro HF, Pimentel LD, Grossi JAS, Colombo CA, Garcia, Q.S. and Geraseev LC, Guilhen SN, Nelson DL	Spain, the United States of America, Colombia, Portugal, England, Germany, Ethiopia, Ireland and the Netherlands
Spain	Plant Sciences, Agriculture, Biotechnology Applied Microbiology, Chemistry, Energy Fuels, Environmental Sciences Ecology, Materials Science, Biochemistry Molecular Biology, Food Science Technology and Engineering	Martin-Gil J, Martin-Ramos P, Correa-Guimarães A, Navas-Gracia LM, Hernandez-Navarro S, Sanchez-Bascones M, Muller M, Munne-Bosch S, Del Rio JC, Garcia QS	Brazil, United States of America, Colombia, Panama, Angola, Argentina and Paraguay
United States of America	Engineering, Environmental Sciences Ecology, Plant Sciences, Energy Fuels, Zoology, Agriculture, Biotechnology Applied Microbiology, Evolutionary Biology, Chemistry and Food Science Technology	Berry EJ, Del Rio JC, Gorchov DL, Gutierrez A, Kim H, Ralph J, Rencoret J, Abad-Franch F, Adler HG, and Afonso CAM	Brazil, Spain, Germany, Argentina, Kenya, Panama, Colombia, Netherlands and Portugal

3.3. Most Productive Authors and Coauthors

The network of the 30 most expressive and most productive authors in the field is presented in **Figure 4**. The total number of authors collaborating in the 397 publications found on the WoS core collection is 1387. The most prominent circles indicate the higher number of documents published by each author. The lines represent the links between them, and the size of the line is proportional to its strength. It is possible to observe four different clusters not closely related to each other when the number of authors selected was 30. Simultaneously, the most extensive set of connections consisted of 10 items, with other authors isolated from these clusters.

Among the authors, Motoike, S.Y. has the highest number of documents, totalizing 27 publications. Considering both the number of publications and the number of citations, he is the most cited author globally, 405 citations, followed by Ribeiro, L.D. with 23 publications and 310 citations Kuki, K.N. with 13 publications and 179 citations.

The most cited article authored by Motoike, S.Y. (66 citations), published in 2010, deals with anatomy, histochemistry, and structure of *macaúba's* seed and its embryos using light and transmission electron microscopy, aiming to understand the seed post-harvest behavior and the establishment of plants from somatic embryos (MOURA *et al.*, 2010). The attention given to *macaúba* has been growing recently, and most part of publications are from the past ten years. Studies in this area are important due to the scarce information about the seed structure and its technological characteristics, resulting from the novelty of the topic under debate. The second most cited article, published in 2013, presented 65 citations. Other publications were related to harvest, plant and fruit characteristics and development, seed production and biofuel (ABREU *et al.*, 2011; CASTRO *et al.*, 2017; COSER *et al.*, 2016; COSTA *et al.*, 2017; COSTA, A. G. *et al.*, 2018; COSTA, A. M. *et al.*, 2018; EVARISTO; GROSSI; CARNEIRO*;* *et al.*, 2016;

EVARISTO; GROSSI; PIMENTEL; *et al.*, 2016; GRANJA *et al.*, 2018; LANES *et al.*, 2015; LANES *et al.*, 2016; LANES *et al.*, 2013; MATSIMBE *et al.*, 2015; MENGISTU *et al.*, 2016; MONTOYA *et al.*, 2016; MOURA, C. V. R. *et al.*, 2019; MOURA *et al.*, 2009; MOURA *et al.*, 2008; SIMIQUELI *et al.*, 2018; TILAHUN *et al.*, 2019).

The most cited document from Ribeiro L. M., published in 2011, 45 citations, exposed that dormancy (when the seed has favorable conditions but does not germinate) is not completely understood for most species of Arecaceae. Considering this, they have tested methods to find the best treatments to stimulate germination (RIBEIRO *et al.*, 2011). In the second most cited article, authored by Ribeiro, L.M., 43 citations, published in 2012, the collaborators examined the morphology and anatomy of *macaúba's* embryos and seedlings *in vitro* germination. Ribeiro's production was related to *macaúba's* seed, structure, germination, pretreatments, storage conditions and reserve mobilization (CARVALHO *et al.*, 2015; DIAS *et al.*, 2018; MAZZOTTINI-DOS-SANTOS *et al.*, 2017; 2018; MAZZOTTINI-DOS-SANTOS *et al.*, 2020; MOURA, A. C. F. *et al.*, 2019; OLIVEIRA, N. C. C. *et al.*, 2013; OLIVEIRA, T. G. S. *et al.*, 2013; RIBEIRO *et al.*, 2015; RIBEIRO *et al.*, 2010; RIBEIRO; OLIVEIRA; GARCIA, 2012; RIBEIRO; OLIVEIRA; CARVALHO; *et al.*, 2012; RIBEIRO *et al.*, 2013; RODRIGUES *et al.*, 2016; SILVA, R. S. *et al.*, 2014; SOUZA, J. N. E. *et al.*, 2019). The potential use of *macaúba* for biodiesel is necessary to accomplish commercial-scale plantations, which are currently limited by technological difficulties. This fact is explained by seed dormancy and the slow germination in low percentages. Considering the above discussed, studies conducted by Ribeiro L. M. are indispensable for the entry of *macaúba* in the market.

The third most productive author is Kuki, K. N., with 13 publications, most of them (84.62%) done with Motoike, S. Y. as a co-author or as the group's leader. The most cited work, 65 citations, published in 2013, was related to ecophysiological aspects of *macaúba* under semi-arid field conditions, like foliar content, gas exchange parameters, diel variation, light intensity and position within the tree canopy and rachis (PIRES *et al.*, 2013). Scarce data are available about the ecophysiology of *macaúba*, and often it refers to environmental conditions different from those found in the semi-arid region. The main importance of this study was to increase the knowledge of the species under semi-arid conditions.

Other publications of Kuki, K. N. evaluated the potential of *macaúba* as feedstock for solid biofuel; air drying to maintain its quality for biodiesel production; molecular characterization and population structure; patterns of fruit development; changes in morphology and storage compounds. Besides, methods to test and to predict the biomass of *macaúba's* fruit and genetic composition to support conservation programs and molecular biology were also found (CASTRO *et al.*, 2017; DE SOUZA *et al.*, 2016; EVARISTO; GROSSI; CARNEIRO*; et al.*, 2016; LANES *et al.*, 2015; LANES *et al.*, 2016; LANES *et al.*, 2013; MONTOYA *et al.*, 2016; SILVA, G. N. *et al.*, 2020).

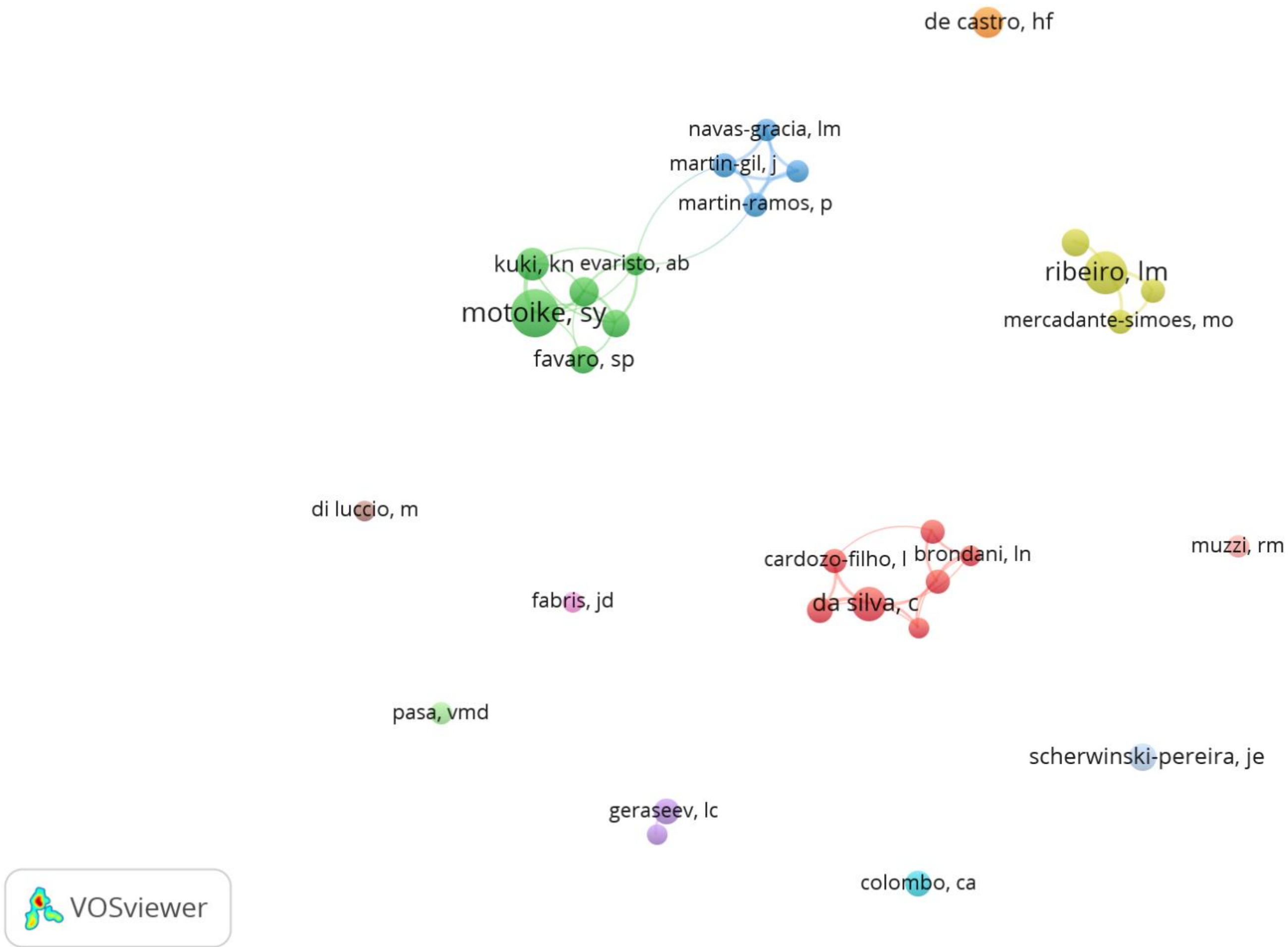


Figure 4. The 30 most expressive and most productive authors' network.

3.4 Patents

Table 3 presents the 14 patents related to *macaúba*. The most antique document dates from 2013, showing that the studies with this fruit are recent. Even with the growing interest in using *macaúba* for biofuel production, most of the patents are not associated with this research area. Only two patents connected to biodiesel were found (MACHADO DE CASTRO *et al.*, 2019; MACHADO DE CASTRO *et al.*, 2016). One patent stablishes the use of a broth obtained after grinding bark, leaves and fruit of *macaúba* and other palms to obtain a nutritive solution containing macronutrients for plant development, namely nitrogen (N), phosphorus (P) and potassium (K). This use of *macaúba* is of great interest to produce organic vegetables, avoiding industrial chemicals. Two patents focus on using a mixture of vegetable oils (SILVA, A. C. *et al.*, 2020) and only *macaúba* oil (SILVA; SCHONS SILVA, 2016) as collectors in minerals' flotation. These methods enable the separation of minerals more efficiently and sustainably. In the same line of using *macaúba* for separating materials, one patent establishes a process for obtaining biochar from the fruit endocarp (MARINHO DE FARIA, 2014). In contrast to other studies using *macaúba* for biochar, this patent offers a final product suitable for gaseous and liquid media. Consequently, it can be used for retaining particles present in the air.

One interesting patent developed in Brazil establishes a method for preparing nutrient tablets using the *macaúba* pulp (CLEMENTE *et al.*, 2017). This application is different from those reported in articles about using *macaúba* oil in the Food Industry (DA ROSA *et al.*, 2020; PRATES-VALERIO *et al.*, 2019; ROSA *et al.*, 2019), focusing on the use of the oil from the mesocarp and endosperm of the fruit. Another document presents the use of milled *macaúba* husks to produce and organic abrasive used for sandblasting with applications in automotive, aviation, subway, nautical and textile industries, presenting the advantage of easy disposal (DO BONFIM, 2013). Among the documents, a method for germinating palms was developed (SALES CARVALHO *et al.*, 2013). Given the great importance of finding the best way to implant a commercial scale plantation of *macaúba*, and considering the dormancy of *A. aculeata*, germination methods are indispensable and for identifying and separating *A. aculeata* and other species of *Acrocomia* (REGINA BAZZO *et al.*, 2020). In animal feed, only one patent was found, which consists of the production of a nutritional bulk using the pulp of *macaúba* (MACHADO DE CASTRO *et al.*, 2017). Finally, two patents are related to uses in the pharmaceutical industry. The first presents active ingredients for pharmaceutical composition, nutritional supplements and cosmetics for treating and preventing acute and chronic inflammation, increased oxidative stress, osteoarthritis, benign prostate hyperplasia and prostatitis (GAMEZ MENENDEZ *et al.*, 2013). The second one is a soap formulation from the *macaúba* pulp oil, and the use of the product is associated with skin texture improvement (ALVES NOGUEIRA DIAZ *et al.*, 2014). The diversity of areas in which intellectual protection was established proves the versatility and high applicability of *macaúba* for different purposes.

Table 3. Patents on *macaúba* research field from all databases on WoS.

Title	Year	Technology	Process conditions	Substrate	Product	References
Nutrient solution used for cultivation of commercial vegetable, fruits, flowers and microorganisms, comprises bark, leaves and fruit of palmeira such as *Euterpe oleraceae*, *Euterpe edulis*, *Bactris gasipaes* and *Archontophoenix alexandrae*	2015	Grind the substrates to extract the broth and separate the solids from the solution	-	Bark, leaves and fruits of *macaúba* and other species.	Nutritive solution containing nitrogen (N), phosphorus (P) and potassium (K), used for the cultivation of vegetables, fruits, flowers and microorganisms	(SOCCOL *et al.*, 2015)
Mixture of vegetable oils (*Glycine max*, *Jatropha curcas* and *Acrocomia aculeata*) used as collector for flotation of minerals comprises mixture of soybean oils, Macauba and Jatropha in flotation of ores, in binary and tertiary compositions	2020	The mixture of vegetable oils used in the flotation of ores	-	*Glycine max*, *Jatropha curcas* and *Acrocomia aculeata*	The mixture of vegetable oils used as a collector in the flotation of mineral	(SILVA, A. C. *et al.*, 2020)
***Macaúba* (*Acrocomia aculeata*) oil extracted from pulp or kernel of *macaúba*, used as anionic collector in flotation of minerals and as industrial natural reagent**	2016	Extraction of oil from pulp or kernel of *macaúba*	-	Pulp or kernel of *macaúba*	*Macaúba* oil as an anionic collector in flotation for the separation of minerals	(SILVA; SCHONS SILVA, 2016)

Flexible extractor device for use during removal of seeds of trees i.e. *Acrocomia aculeata*, has cylindrical tube and cable provided with protection part, and sharp blades formed with aperture and flow opening and sealed with plastic	2015	The construction of a device to easily remove seeds from *macaúba*	-	-	Flexible extractor device to remove seeds from *macaúba*	(SALES CARVALHO *et al.*, 2015)
Germinating palm, particularly dormant Acrocomia aculeata involves including five procedures that are obtaining seeds, surface disinfection of seeds, systemic disinfection, total removal of the lid, and incubation	2013 and 2018	Germination method including five procedures: obtaining seeds, surface disinfection of seeds, systemic disinfection, total removal of the lid, and incubation	-	Dormant *Acrocomia aculeata* seeds	Method for germinating palm, especially *Acrocomia aculeata*	(SALES CARVALHO *et al.*, 2013)
Identifying and separating *Acrocomia aculeata* and *Acrocomia* sp comprises performing synthesis of libraries from samples of macauba, identification of active transcripts, identification of gene microsatellites obtained from primers	2020	Molecular biology techniques	-	*Macaúba* samples, molecular primers and statistical methods	Method for identifying and separating *Acrocomia aculeata* and *Acrocomia* sp.	(REGINA BAZZO *et al.*, 2020)
Producing activated charcoal used as adsorbent for gaseous and liquid media for purification of undesirable materials, involves crushing fruit endocarp of *Acrocomia aculeata* to obtain carbonaceous powder, and than drying carbonaceous powder	2014	Involves crushing the endocarp to obtain the carbonaceous powder that is dried and immersed inactivating solution. The mixture is heated, washed,	-	Endocarp of *Acrocomia aculeata*	Activated charcoal (biochar) for adsorbent purposes	(MARINHO DE FARIA, 2014)

		filtered and dried; these processes are repeated twice. The dried material was carbonized, washed, filtered and dried to obtain the final product.				
Method for processing oil used for producing biodiesel, involves preparing fermented solid from fermentation by microorganisms *Rhizomucor miehei* in agroindustrial waste, such as babassu meal and separating oil with low acid content	2016	Solid fermentation of agroindustrial waste with *Rhizomucor miehei*. Lower alcohol is added, and the mixture is kept under stirring.	Temperature: 25-45 °C Added alcohol: methanol or ethanol.	*Macaúba* meal or babassu meal	Method for processing oil used for biodiesel production	(MACHADO DE CASTRO *et al.*, 2016)
Producing bulk animal feed involves grinding and sieving *macaúba* palm fruit pulp, pressing, extracting to obtain *macaúba* oil, adding to a fermenter under controlled temperature and relative humidity, and then adding supplement	2017	Grinding and sieving *macaúba* fruit pulp. The mixture is pressed and extracted to obtain *macaúba* oil. The mixture with a supplement of urea, glucose, water, inoculum is fermented for 10-120 hours.	0.1-5% urea and/or 0.2-10% glucose; adding water to reach moisture content of 40-80%; and inoculum Temperature: 2-6 °C	*Macaúba* palm fruit pulp	Production of bulk animal feed	(MACHADO DE CASTRO *et al.*, 2017)
Performing integrated process for production of biodiesel by enzymatic transesterification involves converting *macaúba* oil to biodiesel through use of	2019	Integrated process for the production of biodiesel by	Fermentation: inoculated with 107/g microorganism and incubated at 30-40 °C for 24-72 hours.	*Macaúba* oil	Biodiesel	(MACHADO DE CASTR

biocatalyst obtained by solid state fermentation of *macaúba* cake		enzymatic transesterification	Transesterification: mixing *macaúba* oil with alcohol and triglyceride in the presence of fermented *macaúba* cake. Reacting under stirring at 25- 45 ºC			O *et al.*, 2019)
Active ingredient used in pharmaceutical composition and cosmetics for treating and preventing acute and chronic inflammation, and benign prostate hyperplasia, is obtained from fruits of *Acrocomia crispa* or *Acrocomia aculeata*	2013 to 2020	-	-	Fruits of *Acrocomia crispa*, *Acrocomia aculeata,* or their mixtures	The active ingredient used in a pharmaceutical composition, nutritional supplement and cosmetics	(GAMEZ MENENDEZ *et al.*, 2013)
Organic abrasive used for sandblasting and cleaning plastic components and metal, such as propellers and wheels of aircraft, comprises abrasive material comprising particles of *macaúba* coconut shell in different particle sizes	2013	Milding *macaúba* husks to different particle sizes	-	*Macaúba* husks	Organic abrasive	(DO BONFIM, 2013)
Preparing tablet involves using pulp of fruit Acrocomia aculeata as main ingredient, aqueous solution of maltodextrin and water	2017	Food processing for preparing nutritional tablet, using *macaúba* pulp, maltodextrin and water	-	Pulp from *Acrocomia aculeata*	Nutritional tablet	(CLEMENTE *et al.*, 2017)
Manufacturing soap formulation for preparing personal cleaning products, involves harvesting, sterilizing, and	2014 and 2017	Harvesting, sterilizing and pulping the fruits.	Extracting the oil and directly adding it to glycerin with vitamin E to	Pulps of *Acrocomia*	Method for manufacturing soap	(ALVES NOGUEIRA

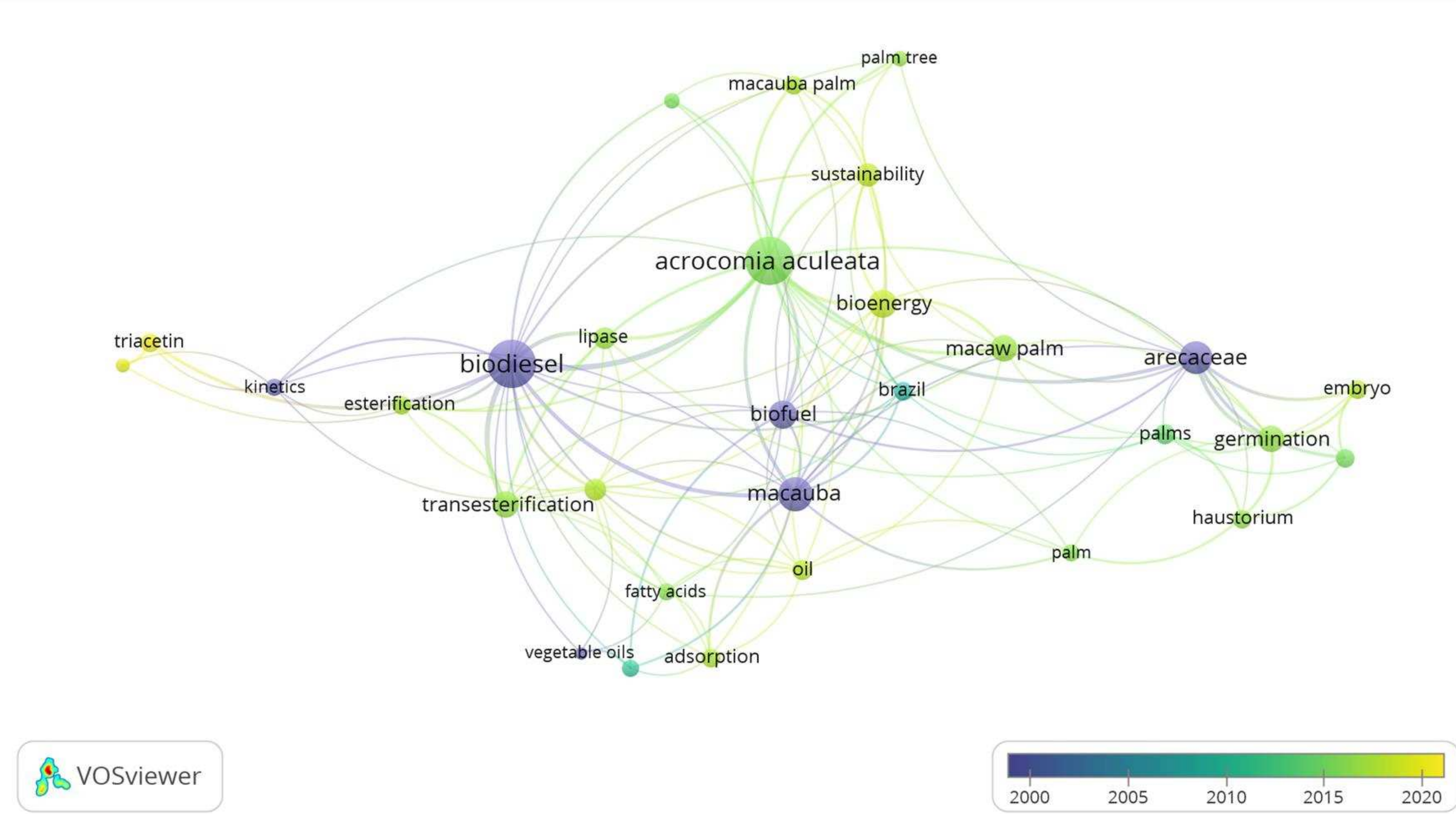
pulping fruits of *Acrocomia aculeata*, and then extracting to obtain oil	form a solubilized glycerin base.	*aculeata* fruits	formulation for preparing personal cleaning products	DIAZ *et al.*, 2014)

3.5. Most Frequent Authors' Keywords

Figure 5 presents 5 clusters for the 30 most frequent authors' keywords that appeared at least five times for the 397 selected documents. Among the 1144 authors' keywords, the most frequent, "*Acrocomia aculeata*", appeared 73 times, followed by "biodiesel" and "macauba" (53 and 36 times, respectively).

Cluster 1, the biggest (8 items), is formed by the words "biofuel", "macauba", "acrocomia aculeate", "pyrolysis", "fatty acids", "adsorption", "vegetable oils" and "oil", forming a group related to oil extraction and its application to biofuel production. The word "adsorption" present in cluster 1 brings to evidence a research area of great interest: the use of biochar from *macaúba* in the adsorption of water contaminants and even for the treatment of emerging contaminants (ALTINO *et al.*, 2017; BARBOSA *et al.*, 2020; DA SILVA *et al.*, 2017; DAMASCENO *et al.*, 2018; GUILHEN; MASEK*; et al.*, 2019; GUILHEN; ROVANI*; et al.*, 2019; MOURA *et al.*, 2018; OLIVEIRA *et al.*, 2014; VIEIRA *et al.*, 2012). In the cluster 2, "Arecaceae", "palms", "germination", "palm", "hastorium", "embryo" and "operculum" words are related to embryogenesis and seed studies. The cluster 3 is formed by the words "biodiesel", "esterification", "kinetics", "lipase", "methyl acetate", "transesterification" and "triacetin". This cluster is directly linked to energy fuels and Environmental Sciences area since "biodiesel" is intimately associated with renewable energy sources. In cluster 4 the most frequent authors' keyword "*Acrocomia aculeata*" was found, additionally, this cluster presents the words "genetic diversity", "macauba palm", "palm tree" and "sustainability". And, finally, cluster 5 is established by the words "bioenergy", "brazil" and "macaw palm".

The timeline bar in **Figure 5** makes it possible to follow the main explored issues from 2000 to 2020. In the early 2000's, keywords suggest the biofuel research area. In 2010, a transition to energy recovery is observed, following studies on adsorption and transesterification. Finally, in 2015 it is possible to follow a trend on germination and embryo studies, changing to bioenergy, biofuel and sustainability fields in 2020.



keyword	Occurrences
Acrocomia aculeata	73
Biodiesel	53
Macauba	36
Arecaceae	30
Macaw palm	19
Biofuel	16
Germination, palms	13
Acrocomia acualeate	12
Transesterification, lipase	11
Bioenergy	10
Pyrolysis	9
Macauba palm, triacetin, palm tree	8
Palm, vegetable oils	7
Sustainability, haustorium, adsorption, brazil, fatty acids, methyl acetate	6
Oil, embryo, esterification, kinetics, operculum, genetic diversity	5

Figure 5. The 30 most employed author keywords of 397 publications and the respective number of occurrences.

The current trend of using renewable materials to obtain cleaner energy is noticeable by the use of terms "bioenergy", "methyl acetate" and "triacetin" in the last years. During the processing, the mesocarp is removed and the oil is extracted through pressure, generating a protein-rich cake that can be used for bioethanol production (DA SILVA; RODRIGUES, 2014; MELO, 2012). The oils extracted from the mesocarp and endosperm are suitable for biodiesel production (PINTO *et al.*, 2012), for uses in chemical and food industries (DA ROSA *et al.*, 2020; PRATES-VALERIO *et al.*, 2019; ROSA *et al.*, 2019), and applications in the cosmetics and pharmaceutical industry (COIMBRA; JORGE, 2012). From the endocarp, a solid biofuel (biochar) can be obtained for thermal energy generation (EVARISTO; GROSSI; CARNEIRO*; et al.*, 2016; MELO, 2012) and also used as biosorbent, with possibilities for environmental purposes such as water/wastewater treatment/remediation (ALTINO *et al.*, 2017; BARBOSA *et al.*, 2020; DA SILVA *et al.*, 2017; DAMASCENO *et al.*, 2018; GUILHEN; MASEK*; et al.*, 2019; GUILHEN; ROVANI*; et al.*, 2019; MOURA *et al.*, 2018; OLIVEIRA *et al.*, 2014; VIEIRA *et al.*, 2012). The use of endocarp by-products as solid fuel has been studied to reduce the dependence on non-renewable energy sources, with particular attention given to the endocarp and the epicarp (EVARISTO; MARTINO*; et al.*, 2016). In contrast, the application as biosorbent is of substantial importance for removing hazardous pollutants from water/wastewater, favoring the environment (LACERDA *et al.*, 2015). However, *macaúba's* by-products are not used for oil extraction and could be converted into energy (for instance, biogas) or animal feed (refer to **Figure 6**).

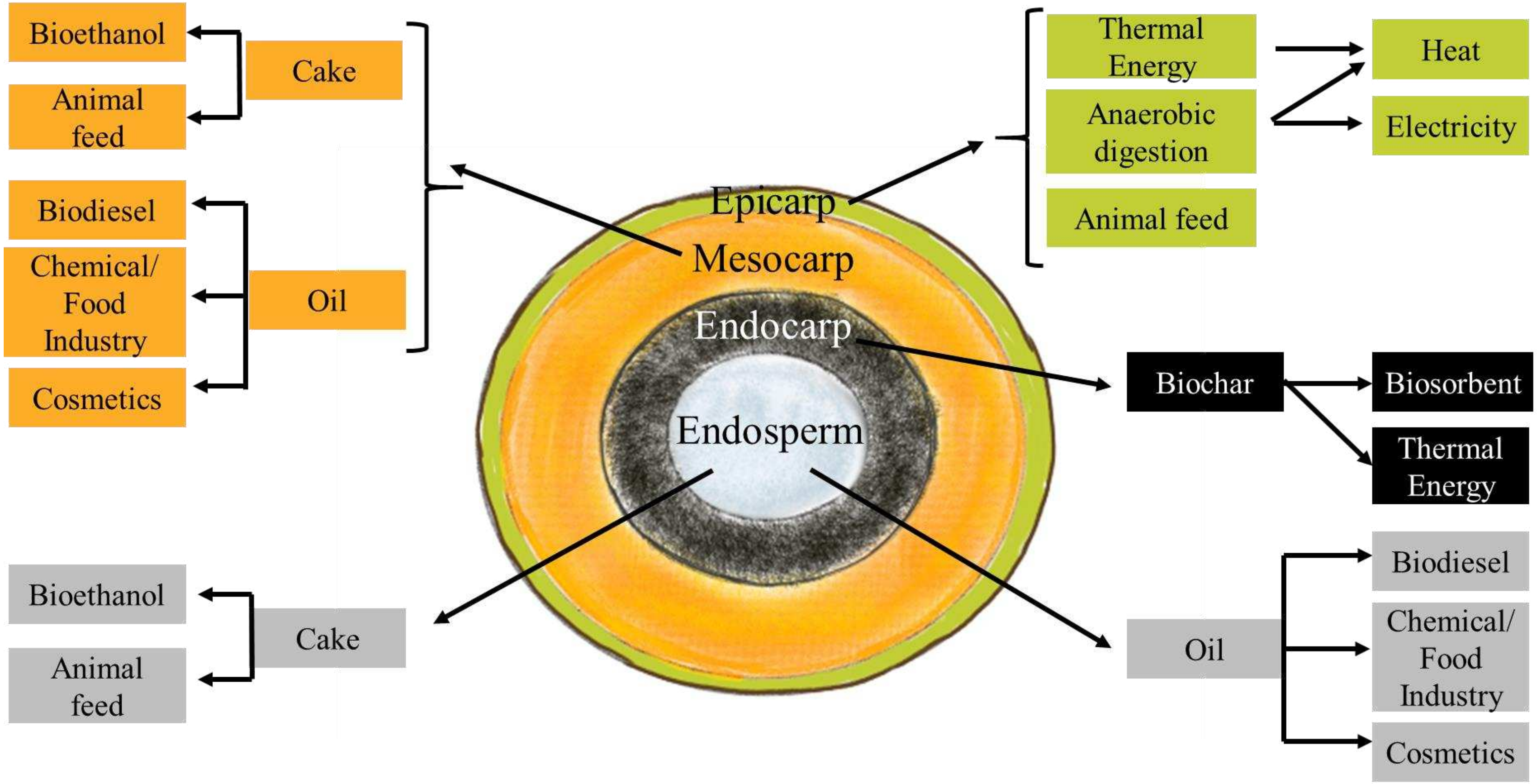


Figure 6. Representation of *macaúba's* fruit and the main products and co-products formed in the productive chain and its applications.

Although thermal energy from biomass combustion to produce steam is the main energy recovery route for *macaúba's* by-products, other technologies are possible. Biomass gasification produces gaseous fuels like hydrogen (H_2), carbon monoxide (CO), methane (CH_4), carbon dioxide (CO_2) and other gases that can be applied for heat, electricity and/or fuel. Pyrolysis generates a rich liquid hydrocarbon, biochar (solid carbon residues) and fuel gases. Esters and ethanol (C_2H_5OH) can be produced via esterification and fermentation, while anaerobic digestion produces biogas (rich in methane and carbon dioxide).

Anaerobic digestion is worldwide applied to treat organic wastes, and the biogas can be used up in manifold different ways, such as electric and thermal energy generation, and, when converted into biomethane, it is used as a vehicular fuel or can be injected into the natural gas grid (DEMIRBAS, 2004; DEMIRBAS, 2005; FERREIRA, S. F. *et al.*, 2019; JIMÉNEZ-CASTRO *et al.*, 2020; MACIEL-SILVA *et al.*, 2019; SAIDUR *et al.*, 2011; SCARLAT *et al.*, 2018). In general, it is possible to observe that the research on *macaúba's* by-products valorization was mainly developed to animal feed, biochar production and some paths for energy obtaining. No scientific information was identified on anaerobic digestion.

4. CONCLUSIONS

The bibliometric analysis indicated Brazil as the most productive country, contributing with 87% of the publishing on *macaúba*. It was also found that the publications are not focused on a specific research area. Even though it was possible to recognize the prominence of the following areas: agriculture, engineering, energy fuels, chemistry and plant sciences. Nevertheless, a strong collaboration involving Brazil, Spain and the United States of America was verified, which indicates a foreign interest in *macaúba*. No documents addressing the use of *macaúba's* by-products for biogas production, a promising energy source and environmentally friendly destination to the non-edible biomass, were identified. This knowledge gap indicates the possibility of energy recovery by a well-established technology, worldwide adopted for other agroindustrial by-products. Along with the research on *macaúba's* biodiesel production, other bioenergy sources could be employed to by-products energy recovery to leverage a greener development for this incipient industry. For the flourishing Brazilian *macaúba's* economy, and daring bioenergy and decarbonization state policies, new energy sources are especially attractive to establishing clean development mechanisms intimately associated with regional and world decarbonization targets.

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CAPÍTULO 3 - Valorização de coprodutos de macaúba da produção de biodiesel através de pré-tratamento de hidrólise em água subcrítica seguida de digestão anaeróbia

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Valorization of *macaúba* husks from biodiesel production using subcritical water hydrolysis pretreatment followed by anaerobic digestion

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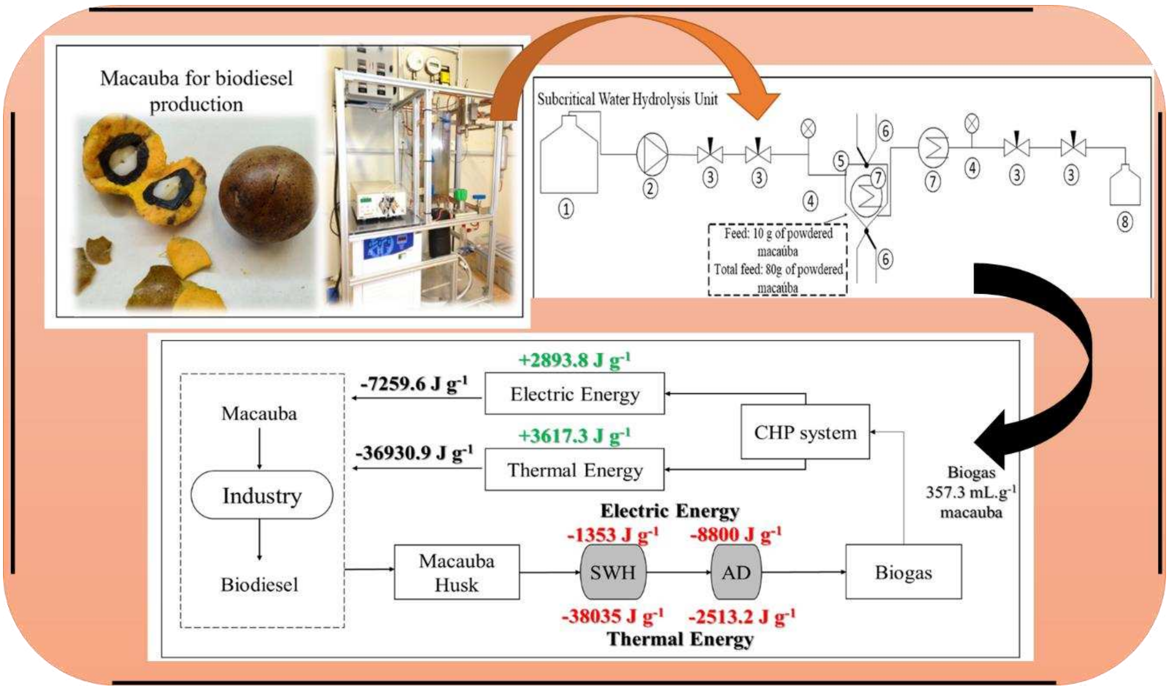
GRAPHICAL ABSTRACT



Abstract

Macaúba husks are inedible lignocellulosic wastes obtained after extracting oil extraction from the fruit for biodiesel production. The objective of this study was to valorize *macaúba* husks through subcritical water hydrolysis (SWH) pretreatment followed by anaerobic digestion (PT+AD) in comparison to a control reactor (AD). The methane yields for the two experiments were measured and used to assess the energy balance for use of the resulting biogas in a combined heat and power system (CHP) generating electrical and thermal energy. The semi-continuous SWH parameters were set as follows: 10 g of dried husk were loaded to the reactor; water was passed over the biomass at a flow rate of 10 mL min^{-1} at 200 °C and 14 MPa and for a total reaction time of 40 min. For AD, mesophilic conditions (35 °C) were kept for both experimental trials. For the AD experiment, digestion was performed for 38 days and for 39 days for the PT+AD experiment. The chemical oxygen demand (COD) removal for the PT+AD reactor was 48% and 43% for AD, indicating that the pretreatment improved digestibility of the organic feed. Similarly, the methane yield per unit of COD for 590 $mLCH_4$ g^{-1} for the PT+AD experiment compared with 57 $mLCH_4$ g for the AD experiment. The corresponding biogas yield was 161% greater than in the PT+AD experiment compared with the control. Energy analysis revealed a corresponding benefit from SWH for production of heat and power, and several recommendations were made for decreasing the heat required by SWH to make the process self-sufficient. *Macaúba* cultivation has promise as an energy crop that can be grown locally in Brazil and similar tropical locations for co-production of bio-diesel from the extracted oil and biogas from the husks, thereby avoiding greenhouse gas emissions by replacement of traditional fossil sources.

Keywords: *Lignocellulosic materials*, *Anaerobic digestion, Supercritical fluids, Biogas, GHG mitigation*

1. INTRODUCTION

In 2018, an estimated 33.1 Gton of carbon dioxide (CO_2) was released into the atmosphere due to energy use (EIA, 2019a), creating ecological and environmental burdens, especially as the driving force behind climate change (CHANDRA *et al.*, 2012; WAGNER *et al.*, 2018). The International Energy Outlook (EIA, 2019b) reported that the share of renewable energy was growing 3% per year. At the same time, global petroleum consumption is expected to decline from 32% to 27% between 2018 and 2050. New energy sources are needed to meet demand and decarbonize the energy sector.

One alternative source of energy is biomass, which can be obtained from crops (sugars/starches), cellulosic energy crops, food processing residues, urban food wastes, animal waste, and others (CHANDRA *et al.*, 2012; NUNES *et al.*, 2020). The most abundant renewable biomass for obtaining energy is mainly composed of lignocellulose (ALVIRA *et al.*, 2010; FORSTER-CARNEIRO *et al.*, 2013; SANCHEZ; CARDONA, 2008; SAWATDEENARUNAT *et al.*, 2015).

Among lignocellulosic materials, *macaúba,* a tropical palm tree belonging to the Arecaceae family, species *Acrocomia aculeata*, native of South America and present in the Brazilian *Mata Atlântica* region (COLOMBO *et al.*, 2018) is considered a promising energy crop. Because of its high quality oil, *macaúba* is used for biodiesel production (RENCORET *et al.*, 2018). After oil extraction an important by-product is the epicarp (husk), which corresponds to 22.6% of the fruit by mass (COLOMBO *et al.*, 2018; TEIXEIRA *et al.*, 2018).

The latest *macauba* production data in Brazil dates from 2017, in year which a total of 484 tons of *in natura* fruit were produced (IBGE, 2017). The production is predominantly extractive, and the governmental data include only this activity. In addition, some research and pilot projects for forest recovery using cultivated *macaúba* have been reported in the scientific literature (ALMEIDA CAMPOS *et al.*, 2015; MOTTA *et al.*, 2002).

Valorizing the energy content of the lignocellulosic biomass comprising the *macaúba* husk has potential to provide a new source of bioenergy to Brazil and similar locations. The growing interest in *macaúba* production and its application for biodiesel can increase the amount of by-products like husks, especially in *Minas Gerais* (MG), *Goiás* (GO) and *São Paulo* (SP) - Brazilian states where this species is endemic (CESAR *et al.*, 2015; MOTTA *et al.*, 2002). The current destination of husks is combustion for thermal energy recovery (TEIXEIRA *et al.*, 2018). The total lignin content in *macaúba* husks is reported at 35.26%, and the most common application of this by-product is for thermal energy (coal) (TEIXEIRA *et al.*, 2018).

Anaerobic digestion (AD) converts biomass, and organic wastes and by-products into biogas, which is a valuable energy end-product as it is rich in methane (CH_4) (SCARLAT *et al.*, 2018; WAGNER *et al.*, 2018). After purification, biogas can be used as a renewable fuel for light/heavy-duty vehicles and cooking, and also can be burnt in stationary engines to produce electricity and/or heat, while offsetting greenhouse gas (GHG) emissions relative to traditional fossil fuels (FERREIRA *et al.*, 2019; SCARLAT *et al.*, 2018).

Biogas from AD is considered an attractive renewable energy route, and decarbonizing the energy matrix is a current concern in Brazil, with the new RenovaBio national biofuels policy setting specific annual decarbonization targets for the fuel sector (ANP, 2017). Replacing natural gas (NG) by biogas could be part of a comprehensive decarbonization strategy, especially considering that, in 2019, NG alone was responsible for 59.7% of the total CO_2 emissions related to electric energy generation of the National Interconnected System of Brazil, an increase of 9.6% compared with 2018 (EPE, 2020).

AD is used around the world for energy production from organic food wastes, and solid by-products including lignocellulosic feedstocks (WAGNER *et al.*, 2018; YANG *et al.*, 2015; ZHANG *et al.*, 2018). Nevertheless, lignocellulosic byproducts like *macaúba* husks are challenging substrates for AD, mostly because lignin resists complete degradation under anaerobic conditions (WAGNER *et al.*, 2018).

Macaúba husk can be made to a suitable feed for AD with selection of an appropriate pretreatment method (SAWATDEENARUNAT *et al.*, 2015). Pretreatment of lignocellulosic biomass can increase biogas yields obtained from AD, with the greatest benefit observed for the lignin fraction of the biomass (PHUTTARO *et al.*, 2019). Different pretreatment methods have been evaluated, including physical, chemical, and biological methods (CHANDRA *et al.*, 2012). The most commonly studied methods involve alkaline, acids, and enzymes (ZHENG *et al.*, 2014). While these common methods can boost biogas yields, they have several disadvantages including: negative environmental impacts such as salinization and water pollution, hydrogen sulfide (H_2S) and molecular nitrogen (N_2) formation, and finally cost, selectivity, and efficiency issues (MACIEL-SILVA *et al.*, 2019; ZHENG *et al.*, 2014).

Hydrothermal pretreatment in sub/supercritical conditions promotes lignocellulosic materials degradation during AD (ALVIRA *et al.*, 2010; LACHOS-PEREZ; BROWN*; et al.*, 2017; MATSAKAS *et al.*, 2015). In particular, subcritical water hydrolysis (SWH) is a promising pretreatment to convert the lignocellulosic complex into short-chain sugars easily catabolized during AD (PRADO *et al.*, 2016). SWH technology is a thermal process, conducted at temperatures between 100-374 °C under pressure conditions sufficient to maintain the water in the liquid state (LACHOS-PEREZ; BROWN*; et al.*, 2017; LACHOS-PEREZ *et al.*, 2016; PRADO *et al.*, 2016; YOSHIDA *et al.*, 2015). Under these conditions, the behavior of water is qualitatively and quantitatively different than water at room temperature or supercritical conditions (DI DOMENICO ZIERO *et al.*, 2020; PRADO *et al.*, 2016), as subcritical water behaves as a mid-polar solvent with much greater self-ionization potential than either room-temperature or supercritical water (LACHOS-PEREZ *et al.*, 2018; LACHOS-PEREZ; TOMPSETT*; et al.*, 2017; MACIEL-SILVA *et al.*, 2019; MAYANGA-TORRES *et al.*, 2017; TORRES-MAYANGA *et al.*, 2019). The chief concern with SWH is the energy it requires, which must be sufficiently low to justify the pretreatment (LACHOS-PEREZ; BROWN*; et al.*, 2017). Unfortunately, the response of the *macaúba* husk to SWH pretreatment has not been studied previously, and no model exists that can predict AD performance of a given feed to SWH pretreatment. Only experimental measurements can fill this gap.

Accordingly, the current study aims to evaluate the effectiveness in SWH pretreatment for promoting biogas and methane yields obtained from anaerobic digestion of *macaúba* husk. A control experiment, consisting of AD without SWH pretreatment was performed to provide a basis of comparison. Energy balances for both experiments were performed to determine if the SWH pretreatment was an efficient use of energy; similarly, the potential electricity and heat generation were estimated for an assumed Combined Heat and Power (CHP) engine. Finally, the corresponding avoided GHG emissions for energy replacement in the Brazilian energy matrix were estimated. The results of this study can guide future research on AD of lignocellulosic substrates, especially for the valorization of *macaúba* byproducts.

2. MATERIALS AND METHODS

2.1. Raw material

Macaúba husks were provided by the Agronomic Institute of Campinas (IAC–SP, Brazil). The mesophilic inoculum was obtained from an Up-flow Anaerobic Sludge Blanket (UASB) reactor from a Brazilian brewery company (AmBev, Jaguariúna – SP, Brazil).

The husks were previously dried in the Agronomic Institute of Campinas. The samples were then size reduced until reaching a homogenous appearance in a mill (Marconi model, MA 340) equipped with a 1 mm sieve. The powdered husks were stored in plastic bags in freezers at −18 ºC until use.

2.2. Experimental setup for subcritical water hydrolysis and anaerobic digestion

Figure 1 shows the schematic diagram of SWH pretreatment combined with AD. First, the hydrolysis was carried out in a laboratory-scale subcritical water unit to obtain hydrolyzate from the husks. The resulting hydrolyzate was fed to the AD reactor (termed the PT+AD reactor). A control experiment was performed using the dry powdered *macaúba* husks as the feed without SWH pretreatment (termed the AD reactor).

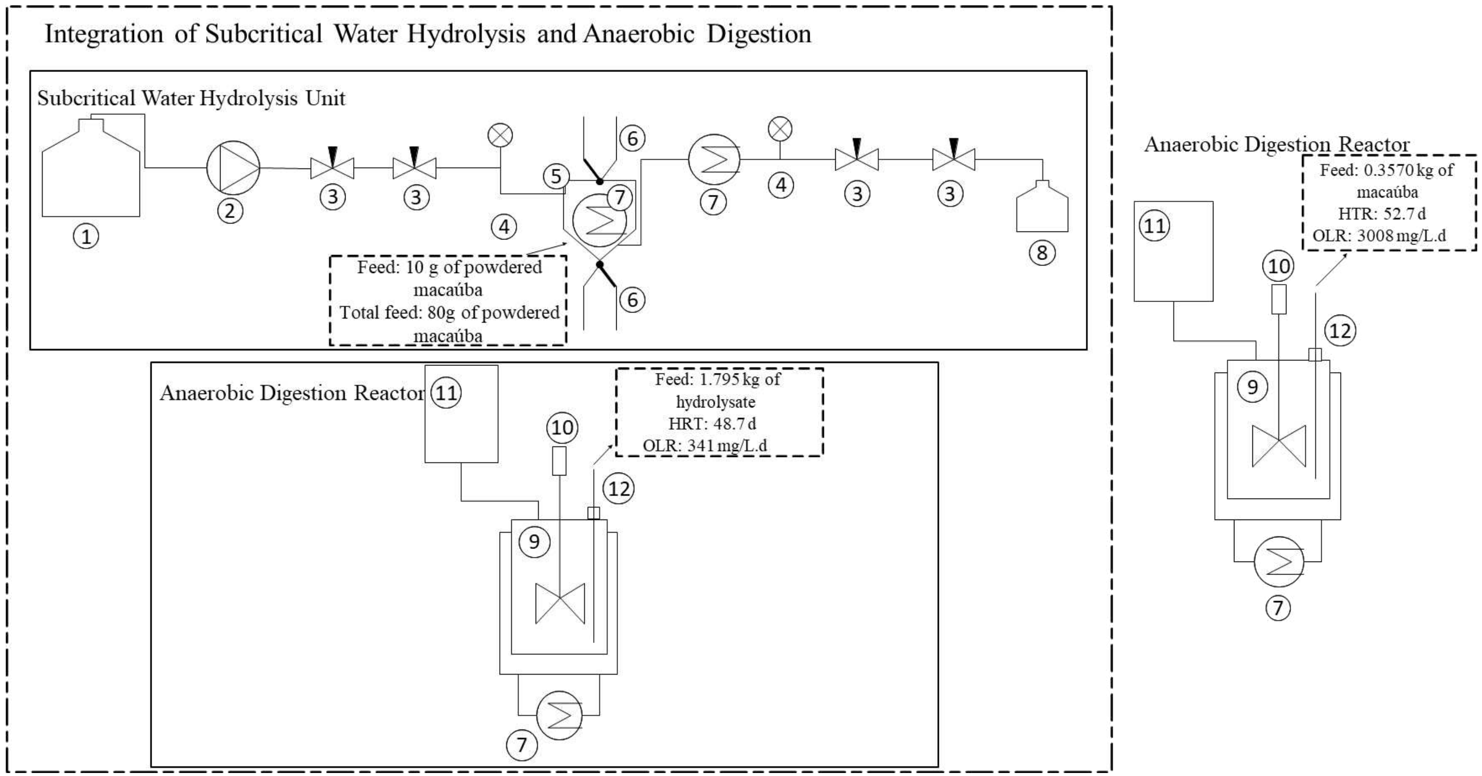


Figure 1. The schematic diagram for the combined process of subcritical water hydrolysis pretreatment with anaerobic digestion. (1) Water tank, (2) High pressure pump, (3) micrometric needle valves, (4) pressure gauges, (5) subcritical reactor, (6) thermocouples, (7) heat exchangers, (8) micrometer valve, (9) hydrolysate tank, (10) bioreactors, (11) Stirrers, (12) bags for biogas and (13) tubes for feeding, taking samples and pH control.

2.2.1. Description of subcritical water hydrolysis unit

The pretreatment was performed in a semi-continuous flow SWH reactor system (**Figure 1**). The SWH system consists of a high-pressure water pump (double piston pump, model Prep 36 Pump) to pressurize the water and feed it to the hydrolysis reactor vessel, which was a 316-stainless steel tube with an internal volume of 110 mL. The water fed the reactor is heated by an electric jacket type heat-exchanger (1500 W) insulated by ceramic fiber. The hydrolysis temperature is monitored by thermocouples (type K) positioned directly after the reactor entrance. After exiting the reactor, the hydrolyzate product is cooled in a second shell-and-tube heat exchanger coupled to a thermostatic bath (Marconi, model MA-184). The system pressure is controlled by a micrometer valve (Autoclave Engineers, model 10VRMM2812) positioned after the second heat exchanger.

At the start of each reaction, the reactor was loaded with 10 g of *macaúba* husk. Flow was initiated to reach the operating pressure. Heating was initiated to reach the desired temperature, and the reaction was performed for the desired time once the reactor had achieved a steady state temperature.

SWH operating conditions must balance biopolymer breakdown, primary product degradation, and product dilution. While predictive models do not exist to determine optimal SWH conditions for a given feed, prior studies provide guidance. Accordingly, SWH operating conditions were selected based on previous studies with sugarcane straw (LACHOS-PEREZ; TOMPSETT*; et al.*, 2017), orange peel (LACHOS-PEREZ *et al.*, 2018), coffee (MAYANGA-TORRES *et al.*, 2017), malt bagasse (TORRES-MAYANGA *et al.*, 2019) and *açaí* seeds (MACIEL-SILVA *et al.*, 2019). The hydrolysis temperature was maintained at 200 ºC and pressure at 14 MPa. The water flow rate was constant at 10 mL min^{-1} and the total reaction time was 40 min. The hydrolyzate obtained (500 mL of hydrolysate per 10 g of husks) was mixed with the final residue of the reactor; the pH of the resulting slurry was measured.

2.2.2. Anaerobic Digestion reactors

AD was performed in a 4.3 L stainless-steel stirred tank-type anaerobic reactors were fed either with hydrolyzate slurry (containing 2.2% solids loading obtained as the residue recovered from the SWH reactor) (PT+AD reactor) or powdered *macaúba* husk (solid), using the following procedures:

(i) The PT+AD reactor (wet-type) was initially fed with 1.795 kg of hydrolyzate (70 % V/V) and 0.794 kg of inoculum (30% V/V). The volume of this initial charge corresponds to 2.58 L, or 60% of the total volume of the reactor; the remaining 1.72 L is headspace for biogas production (40% of the reactor full capacity). Subsequent to the initial chare, the PT+AD reactor was fed at regular intervals fresh charges of 109.34 g (110 mL) of hydrolyzate slurry (ST= 0.87%, SV= 0.80%, COD= 7.44 mgO_2 mL^{-1}). The total amount of husk added to the reactor was 76.36 g (considering the initial addition of material and the further feedings). A total of 16 feedings and sample withdrawals were performed during the 38 days of the experiment.

(ii) For the AD experiment, 0.357 kg of *macaúba* husks (35% V/V) along with 0.9350 kg of inoculum (39% V/V), and 0.6060 kg of water (26% V/V) were initially charged to the digestor. The initial solids loading was 22%. The added material corresponds to 2.38 L or 55.35% of the total volume of the reactor, with the remaining 1.92 L available as headspace (44.65%). Subsequent feedings (ST= 22%, SV= 21%, COD= 52.18 mgO_2 mL^{-1}) consisted of 82.3 g (110 mL) of a slurry comprised of 16.3 g of powdered *macaúba* (40% V/V) and 66.0 g of water (60% V/V). The total mass of husk added to the reactor was 617.5 g. A total of 16 feedings and sample withdrawals were performed during the 39 days of the experiment.

In both experiments, samples were extracted at the same time as samples were extracted, three times per week on alternating days. Mesophilic conditions (35 °C) were maintained using a thermostatic bath (Tecnal, model TE-2005). Mechanical stirrers (Fisatom®, model 715) agitated the reaction mixtures. Biogas samples were extracted into Tedlar bags.

The hydraulic retention time (HRT) was calculated using **Equation 1**, considering the 16 sample takings multiplied by the effluent volume of 0.11 L, divided by the total days of the experiment.

$$HRT = V_{reactort} / Q_{effluent} \qquad \text{(Eq. 1)}$$

where $V_{reactor}$ is the reactor´s useful volume (mL) and $Q_{effluent}$ is the effluent volumetric flow rate (mL day^{-1}). For the PT+AD experiment, the calculated HRT was 48.7 days, whereas it was 52.7 days for the AD experiment – the difference in these two values is negligible for any meaningful comparison.

The organic load rate (OLR) was calculated using the average volumetric flow, the mass of substrate (hydrolysate for PT+AD reactor and *macaúba* plus water for AD reactor), and the volatile solids (VS) of the substrate (**Equation 2**).

$$OLR = \dot{m}_{effluent} \times VS / V_{reactor} \qquad \text{(Eq 2)}$$

where the units of OLR are mgSV $L^{-1}day^{-1}$, $\dot{m}_{effluent}$ is the mass flow rate (mg day^{-1}), VS is the fraction of total volatile solids content ($0<VS<1$), and $V_{reactor}$ is reactor volume occupied by liquid (L). The OLR was also calculated based on the chemical oxygen demand (COD) content of the feed (**Equation 3**).

$$OLR = Q_{effluent} \times COD \times V_{reactor} \qquad \text{(Eq 3)}$$

where the units of chemical oxygen demand are mgO_2 L^{-1}.

2.3. Analytical methods

All samples were analyzed for the following the protocols described in the Standard Methods for the Examination of Water and Wastewater (APHA, 1985): (i) pH (4500-H^+ B), (ii) total solids and moisture (2540B), (iii) total fixed and volatile solids (2540E), (iv) alkalinity (2320 B), (v) total ammonia nitrogen (4500-NH_3 C), and (vi) chemical oxygen demand (4520 D). Sample pH was checked at room temperature using a digital pH meter and the digester pH was corrected by addition of NaOH (6N) when necessary to maintain its value between 7 and 8.5. Prior to measurement of COD, alkalinity, and total ammonia nitrogen samples were diluted in distilled water (1:10 dilution), agitated at 25 °C and 200 rpm for 1 hour, and finally vacuum filtered. All samples were analyzed in triplicate.

Biogas composition was analyzed using a gas chromatograph (GC) (Shimadzu®, model GC 2014) equipped with a thermal conductivity detector (TCD) and a micro packed column (ShinCarbon, ST 50/80 mesh, 6 m length and 3 mm of internal diameter). Standards of molecular hydrogen (H_2), methane (CH_4), molecular oxygen (O_2), and carbon dioxide (CO_2) were used to calibrate TCD response. The GC injector and detector temperatures were held at 200 °C. The initial GC oven temperature was 50 °C where it was held for 3 min, and then increased by 5 °C min^{-1} until reaching 180 °C, where it was held for 5 min. The injected sample volume was 0.5 mL, and the carrier gas was molecular nitrogen (N_2) at 5 bar at a flow rate of 35 mL min^{-1}.

2.4. Efficiency of energy conversion, potential for electricity, and heat generation and avoided greenhouse gas emissions

The electric and thermal energy consumed in each part of the process in the PT+AD and in AD experiments were estimated to understand the effect of pretreatment on overall energy balance. Electricity consumption occurred during the use of stirrers in AD reactors and during the pump in SWH. Thermal energy was used to heat the water for SWH and to keep AD reactors at 35 °C. Heat recovery from SWH process and AD was not included. The objective of the energy analysis was to determine the specific electricity and heat consumption (J g^{-1}), the specific energy output associated with the methane (J g^{-1}), as well as the energy efficiency, defined as the ratio between the energy output attributed to methane and the energy associated with *macaúba* husk fed to the process. In both cases, estimates were based on the dry mass of husks.

The energy analysis for both experiments utilized the conservation of energy as stated in Equation 4 (CENGEL; BOLES, 1994).

$$(Q_{in} + W_{in} + \sum_{in} m.\theta) - (Q_{out} + W_{out} + \sum_{out} m.\theta) = (m_e e_e - m_b e_b) \quad \text{Eq. (4)}$$

where the subscripts "in" and "out" refer respectively to the condition of the mass entering and leaving the system; the subscripts "e" and "b" refer to final state and initial state of the system, respectively; m is the mass (g); Q is the energy in the form of heat (J); and W is the energy in the form of work (J); θ is the summation of specific enthalpy, kinetic and potential energies (J g^{-1}). For the *macaúba* husks and biogas, the higher heating value (HHV) was used in the place of specific enthalpy; and e is the summation of the specific internal, kinetic and potential energies (J g^{-1}). The HHV of *macaúba* husk was considered 20.24 kJ g^{-1} (EVARISTO *et al.*, 2016) and for the methane the HHV considered was 39,735 kJ Nm^3 (ABNT, 2008). Kinetic and potential energy terms were neglected, and no work was produced by the system (W_{out} =0).

The electric energy (W_{in}) consumption of the SHW pretreatment was estimated from the following variables: (i) mass of husks to be hydrolyzed (80 g); (ii) mass of water used (3,920 g), temperature, and pressure conditions during the pretreatment; (iii) time required to pressurize the system (5 min); (iv) kinetic time (40 min); and (v) pump electric power (45 W).

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The thermal energy used in SWH and in the AD was estimated from the assumption that the mixture properties (water, inoculum, and substrate) are equivalent to water at the same thermodynamic state. The temperature of the water entering the system was 20 °C and the mass of water used was 4,590 g for the PT+AD reactor and 4,140 g for the AD reactor. Electricity consumption (W_{in}) during AD in both cases occurred only during stirring, which was performed for 10 min before sample taking, with a 70 W rated electric power stirrer).

Equation 5 was applied to calculate the potential of electricity that could be generated from the total *macaúba* husks Brazilian production (CABRAL *et al.*, 2017; CAMPELLO *et al.*, 2020):

$$EG_{CH4} = Q_{biogas} \times LHV_{CH4} \times C_m \times \eta_e \times CF \qquad \text{(Eq. 5)}$$

where EG_{CH4} is the potential for electricity generation from biogas produced in the AD of *macaúba* by-products (MWh ton^{-1}husks); Q_{biogas} is the volume of biogas produced per mass of husks fed in the reactor (m^3 ton^{-1}); LHV_{CH4} is the lower heating value of methane (35.59 MJ m^{-3}); C_m is the concentration of methane in biogas (%); η_e is the CHP engine electrical efficiency (%), assumed as 34% (HEYWOOD, 2018); CF is the conversion factor from MJ to MWh (1/3600).

The potential thermal energy recovery (HG_{CH4}) from biogas by the CHP system was estimated from **Equation 6** (CLARKE ENERGY, 2020):

$$HG_{CH4} = Q_{biogas} \times LHV_{CH4} \times C_m \times \eta_H \qquad \text{(Eq. 6)}$$

where HG_{CH4} is calculated as MJ ton^{-1} of husks, and η_H is the heat recovery efficiency (%), assumed to be 50%.

Using experimental biogas and experimental methane yields, **Equations 5 and 6** were used to estimate the potential electrical and thermal energy generation, respectively, from biogas burning in a Combined Heat and Power (CHP) engine. For both estimations (EG_{CH4} and HG_{CH4}), biogas production and electricity and heat generation were assumed to take place on the *macaúba* production site.

For the potential energy conversion and greenhouse gas emissions estimations, the total mass of available *macaúba* was considered to be 750 ton year^{-1} and 900 ton year^{-1} (30 ha plantation with the production of 25 and 30 ton ha^{-1} year^{-1}) (FERNANDEZ-COPPEL *et al.*, 2018), and the mass of husks correspond to 169.5 ton year^{-1} and 203.4 ton year^{-1}, respectively. For the entire national territory, the adopted mass of husks is 109.4 ton.year^{-1} (22.6% of husks of 484 tons) (IBGE, 2017).

The avoided GHG emissions (A_{GHG}) were estimated from **Equations 7** and **8**. **Equation 7** is used in the specific case of electricity replacement from other sources for the electricity generated from biogas burning (DOS SANTOS *et al.*, 2017). Following the same approach, **Equation 8** provided the A_{GHG} due to biogas burning for heat generation.

$$A_{GHG\text{-}EG} = EF_{CO2\text{-}EG} \times EG \times m \qquad \text{(Eq. 7)}$$

$$A_{GHG\text{-}HG} = EF_{CO2\text{-}HG} \times HG \times m \qquad \text{(Eq. 8)}$$

where EG is the generated electricity (MWh ton^{-1}); HG is the generated heat (MJ ton^{-1}); EF_{CO_2-EG} is the emission factor of CO_{2eq} for 2019 national electric energy generation (MCTIC, 2019); EF_{CO_2-HG} is the emission factor of heat energy (IPCC, 2006); and m is the mass of husks produced in a year (ton year^{-1}) (IBGE, 2017).

The emission factor for the grid (EF_{CO_2-EG}), used to quantify the emissions of electricity that are being generated at a given time, was the annual average value (from January 2019 to December 2019), reported from official data of the Ministry of Science, Technology, Innovation and Communication (MCTIC, 2019), 0.075 tons of CO_{2eq} per MWh of electricity.

The emission factor of heat energy (EF_{CO_2-HG}) was taken to be 0.056 tCO_{2eq} GJ^{-1} (IPCC, 2006), which corresponds to replacement of natural gas with biogas in the boiler.

3. RESULTS AND DISCUSSION

3.1 Characterization of anaerobic digestion reactors

AD and PT + AD experiments were performed to evaluate the effectiveness of SWH pretreatment on biogas production from *macaúba* husks. Samples were extracted regularly throughout each experiment and **Tables 1** and **2** summarize relevant data, including data on the feed and inoclum. Overall, pH and HRT values show that the two digesters were operated under stable conditions that were comparable to one another (DAVID *et al.*, 2019; MAO *et al.*, 2015). In particular, HRT controls biological methane production efficiency in AD (KHAN *et al.*, 2016; MAO *et al.*, 2015). HTR is associated with microbial growth rate and consequently depends on process temperature (MAO *et al.*, 2015). In contrast, the OLR value for the PT+AD reactor was 341 mgSV L^{-1} day^{-1} and for the AD reactor it was 3008 mgSV L^{-1} day^{-1}. Unlike HTR, OLR depends on substrate composition (MAO *et al.*, 2015), as it depends on the COD and volatile solids content of the digester feed. The 8-fold increase observed for PT+AD therefore indicates the effectiveness in the SWH for converting *macaúba* husk solids into soluble organic molecules that are available for microbial catabolism.

Table 1. Physical and chemical composition for reactor with pretreatment of subcritical water hydrolysis (PT+AD) in the first and the last day of the experiment.

			Pretreatment +Anaerobic Digestion (PT+AD)					
Parameter	Macaúba	Inoculum	First Day	Last Day	Average	Highest Value	Lowest Value	Removal Yield (%)
pH	-	7.4	6.34	7.69	7.71	8.56	7.00	-
Alkalinity (mg $CaCO_3$/L)	25	206	17	312 ± 5.7	250	359 ± 5.7	17	-
Total Solids (%)	92 ± 0.22	12 ± 1	2.2 ± 0.7	0.98 ± 0.03	3.50	8 ± 0.3	0.9 ± 0.03	-
Total Fixed Solids (%)	3 ± 0.2	1,7 ± 0,1	0.50 ± 0.5	0.45 ± 0.01	0.67	1.5 ± 0.7	0.3 ± 0.4	-
Total Volatile Solids (%)	88 ± 0.1	10,3 ± 0,4	1.7 ± 0.8	0.53 ± 0.04	2.80	6.6 ± 0.2	0.5 ± 0.04	68
Moisture (%)	0.08	0,88	0.98 ± 0.01	0.99	0.96	0.99	0.92	-
Ammonia Nitrogen (mg/L)	48	144	144	221	142	221	96	-
Chemical Oxygen Demand (g/L)	255	7.6 ± 0.6	9.1	3.6	4.8	9.1	2.8	60
HRT (days)	-	-	48.7	-	-	-	-	-
Reactor Volume (L)	-	-	4.3	-	-	-	-	-
OLR (mgSV/L.days)	-	-	341	-	-	-	-	-

Values presented as mean ± standard deviation (in triplicates).

Table 2. Physical and chemical composition for conventional AD in the first and the last day of the experiment.

	Conventional AD					
Parameter	First Day	Last Day	Average	Highest Value	Lowest Value	Removal Yield (%)
pH	6.19	6.93	7.53	8.34	6.93	-
Alkalinity (mg CaCO3/L)	8.6	1040 ± 25	695	1100 ± 20	4.3	-
Total Solids (%)	22 ± 0.7	14.41 ± 0.98	16.8	22 ± 0.7	14.7 ± 0.6	-
Total Fixed Solids (%)	1 ± 0.5	2.3 ± 0.05	2.3	3.4 ± 1.36	1.00 ± 0.5	-
Total Volatile Solids (%)	21 ± 0.3	12 ± 1	14.5	21.2 ± 0.3	11.9 ± 1.2	43
Moisture (%)	0.78 ± 0.01	0.86 ± 0.01	0.8	0.86 ± 0.01	0.78 ± 0.01	-
Ammonia Nitrogen (mg/L)	48	415 ± 3.9	413	775	48	-
Chemical Oxygen Demand (g/L)	51.2 ± 0.26	42	57.8	74 ± 0.6	35 ± 1	17.9
HRT (days)	52.7	-	-	-	-	-
Reactor Volume (L)	4.3	-	-	-	-	-
OLR (mg SV/L.days)	3008	-	-	-	-	-

Values presented as mean ± standard deviation (in triplicates).

3.2 pH and alkalinity

Figure 2 provides digester pH measurements (after NaOH addition) and alkalinity. For the PT+AD reactor, pH values before correction ranged from 6.8 to 7.0. The necessary pH corrections (done only 9 times during the experiment) are consistent with the low-solids content of the PT+AD feed resulting from the SHW pretreatment. In contrast, the AD digester pH ranged from 4.6 to 6.3 before pH corrections and required adjusting 15 times by addition of NaOH 6N to maintain it in this range. These differences clearly demonstrate that the AD digester was both more acidic and less stable than the PT+AD digester.

Digester pH is one measurements of digester health (RAPOSO *et al.*, 2011) and directly affects the methane yield, influences the activity of enzymes and microorganisms, and the range changes during the different stages of AD (ANGELIDAKI; SANDERS, 2004; JAIN *et al.*, 2015; KHAN *et al.*, 2016). An acidogenic reactor activity reaches its peak at pH range 5.5-6.5 (KHAN *et al.*, 2016; MAO *et al.*, 2015). pH corrections aimed for pH between 7.0 and 8.0 (the optimum range for methanogenic microorganisms) to maintain constant biogas production (ANGELIDAKI; SANDERS, 2004; RAPOSO *et al.*, 2011).

The low pH of the AD reactor is consistent with hydrolysis of its high solids feed followed by formation and accumulation of organic acids from acidogenesis. Acid accumulation is undesirable as it can suppress methanogenesis and negatively affect the biogas production (CHEN *et al.*, 2014; IZUMI *et al.*, 2010; YANG *et al.*, 2015; YUAN *et al.*, 2006). Digester pH depends in part on the OLR of the initial startup, which was 8-times greater for the AD reactor than the PT+AD reactor. OLR values can be correlated with increasing biogas yields, though increasing OLR can sometimes lead to formation of excess acids that decrease the pH (JAIN *et al.*, 2015; MAO *et al.*, 2015). The observation that AD reactor pH is less than the PT+AD reactor pH therefore suggests that acetogenesis and methanogenesis are sufficient in the PT+AD reactor to prevent acids from accumulating and decreasing the pH.

Figure 2 presents the alkalinity values ($mgCaCO_3\ L^{-1}$) for both reactors. For the first 6 days of operation, alkalinity values in the PT+AD reactor were greater than the AD reactor. Starting on day 6, alkalinity values in the PT+AD reactor were much less than the AD reactor. After day 15, alkalinity values stabilized, with average values of 250 $mgCaCO_3\ L^{-1}$ for the PT+AD reactor and 695 $mgCaCO_3\ L^{-1}$ for the AD reactor.

Alkalinity is related to the digester buffering capability (i.e., the media capacity to neutralize acids), providing resistance to significant and rapid changes in pH (RAPOSO *et al.*, 2011). The difference in measured alkalinity can be explained by the NaOH addition in the AD reactor, which may have accelerated the formation of carbonates and bicarbonates, causing the alkalinity values to increase (ACEVES-LARA *et al.*, 2012; MACIEL-SILVA *et al.*, 2019). Correspondingly, the alkalinity in the PT+AD reactor fluctuated much less than the AD reactor, fluctuations, consistent with differences in the frequency of alkali additions to these two reactors (MACIEL-SILVA *et al.*, 2019).

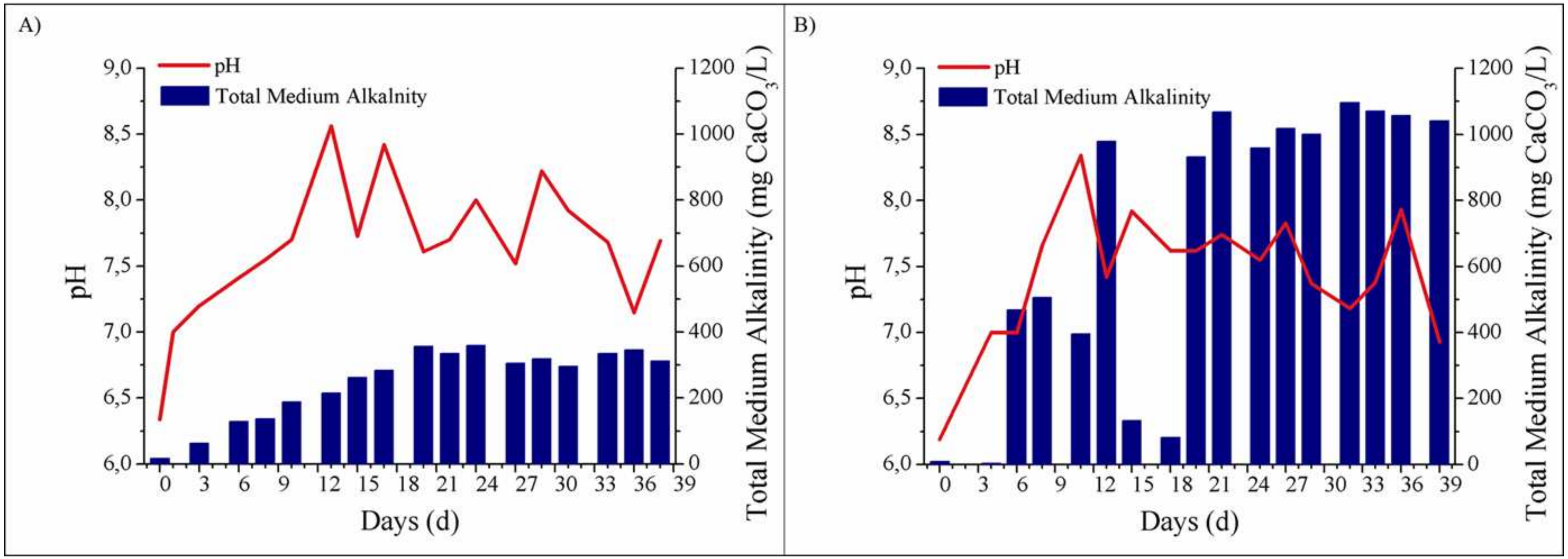

Figure 2. Evolution of pH and alkalinity: A) reactor with pretreatment (PT+AD) and B) reactor without pretreatment of subcritical water hydrolysis (AD).

3.3 Total and volatile solids and ammonia nitrogen

Figure 3 provides plots of Total Solids (TS), Volatile Solids (VS), and ammonia nitrogen (NH_3) measured for both reactors over the course of the experiments. The initial TS content of the PT+AD effluent was 2.2%, which corresponds to wet AD conditions; in comparison, the AD digester was initially operating under dry conditions, as its effluent contained 22% of TS (CHEN *et al.*, 2014). After 38 days, the TS in the PT+AD effluent decreased to 0.98%; for the AD reactor, the corresponding decrease in TS was to 14.41% after 39 days. These observations are consistent with solids hydrolysis to soluble products. Interestingly, the AD reactor did not continued to operate under dry conditions for the entire duration of the experiment, consistent with complete biomass utilization.

Between day 6 and day 22 the TS and VS increased in PT+AD reactor, which can be explained by microbial growth. The AD reactor did not exhibit a similar decrease in TS and VS values over this time. The difference is that the initial TS of the AD reactor was sufficient that it more affected by solubilization than microbial growth.

Over the course of the experiment the VS in the PT+AD reactor decreased from 1.7%, to 0.53% on the last day of the experiment, while for the AD reactor the decrease was from 21 to 12%. The VS are a portion of the total solids that describe the content of organic material in the feedstock, including fats, proteins, carbohydrates, and lignin (ANGELIDAKI; SANDERS, 2004; APHA, 1985; RAPOSO *et al.*, 2011). VS serves as a primary indicator of potential methane yield (RAPOSO *et al.*, 2011). The VS decreased by 68% in the PT+AD reactor and 43% in the AD reactor, indicating that VS removal was more efficient for the PT+AD reactor than for the AD reactor.

The initial and final NH_3 values in the PT+AD reactor were 144 mgNH_3 L^{-1} and 221 mgNH_3 L^{-1}, while for the AD reactor, they were 48 mgNH_3 L^{-1} and 415 mgNH_3 L^{-1}, respectively **(Figure 3a and 3b)**. During AD, ammonia is formed mainly because of the catabolism of VS, especially proteins and other nitrogen-carrying components. Additionally, ammonia is mostly present either in its free form (NH_3) or ammonium (NH_4^+) (ANGELIDAKI; SANDERS, 2004; APHA, 1985; YANG *et al.*, 2015). NH_3 is essential for bacterial growth, although in excess it may inhibit the methanogenesis (YENIGÜN; DEMIREL, 2013). The NH_3 value in the PT+AD reactor is less than the AD reactor due to aforementioned difference in solids loading.

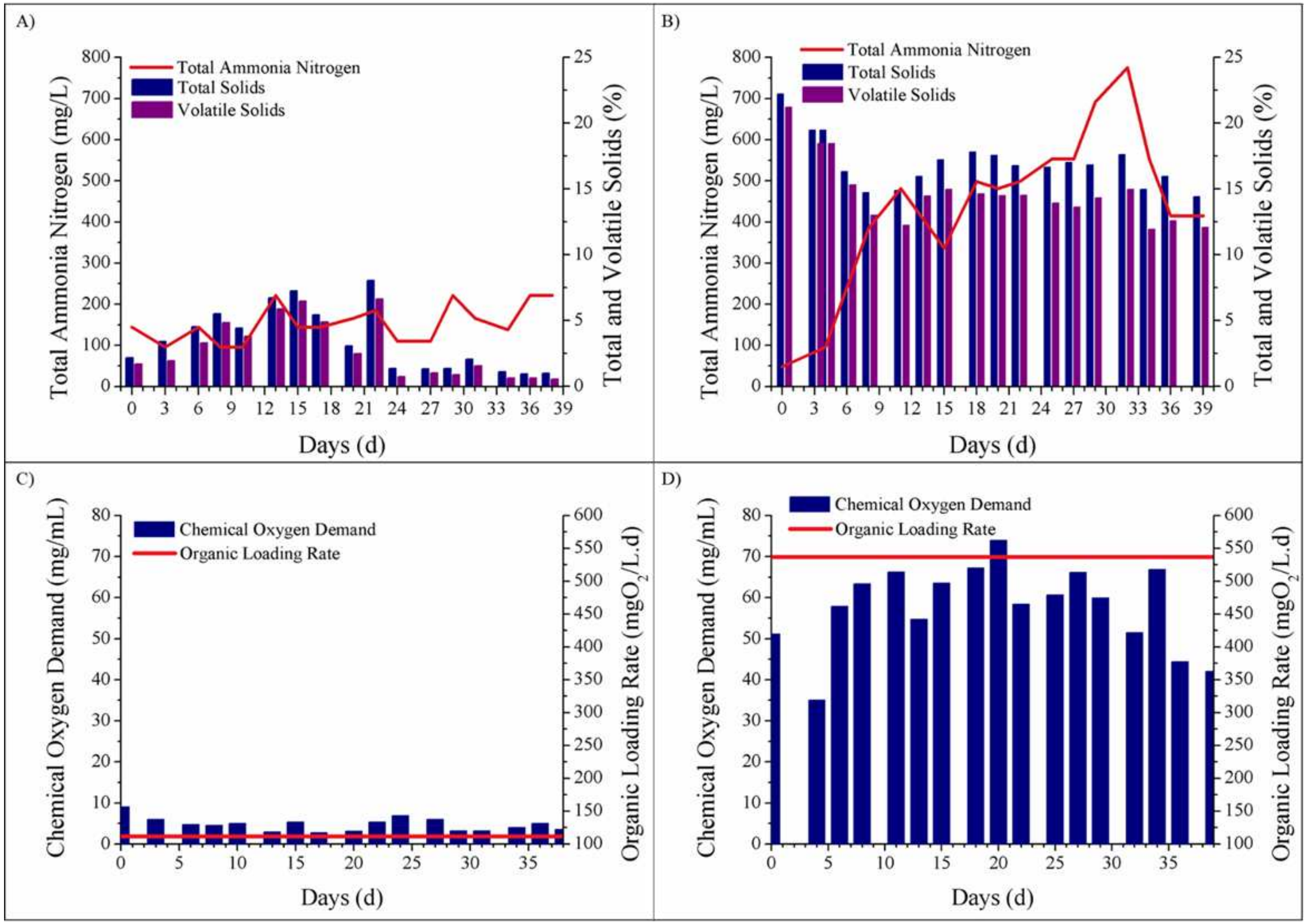

Figure 3. Evolution of the total ammonia nitrogen amount (mg/L), total solids (%) and volatile solids (%), evolution of chemical oxygen demand (COD), and the organic loading rate (mg O_2 $L^{-1}d^{-1}$ considering the reactor´s total volume) during experiment days: A) and C) reactor with subcritical water hydrolysis pretreatment (PT+AD); B) and D) reactor without pretreatment (AD).

3.4 Chemical oxygen demand (COD)

Figure 3c and 3d provides plots of COD measured in the PT+AD and AD reactors, respectively. COD is the amount of oxygen needed to completely oxidize the organic content of the digestate (ANGELIDAKI; SANDERS, 2004; APHA, 1985). For the PT+AD reactor, the greatest COD value (9.1 mg mL^{-1}) was obtained at startup and then fluctuated from 2.8 (day 17) to 6.0 mg L^{-1} (day 3) for the rest of the experiment. In contrast, the COD measured in the AD reactor increased from an initial value of 51 to 74 mg L^{-1} in the first 20 days of the experiment, consistent with hydrolysis and acidogenesis of solids in the feed to produce soluble products. After 20 days, the COD of the AD reactor decreased (42.0 mg L^{-1}), indicating COD removal by methanogenesis. While the COD of the PT+AD reactor COD was nearly constant, the COD values fluctuated widely for the AD reactor. The fluctuations observed in the AD reactor are consistent with the difficulties in regulating its operation, which were also evident in pH measurements of the AD reactor. Ignoring these fluctuations, the PT+AD reactor reduced the initial COD by 48% in the stabilization phase, and the corresponding value for the AD reactor was 43%. Again, comparison of the COD reductions observed for the PT+AD and AD reactors is consistent with improved digestibility after SWH. Similar results have been reported previously for AD of vegetable waste following thermal pretreatment.

3.5 Composition and volume of biogas

The previous discussion of results in **Figure 2** and **3** all are consistent with SWH improving the digestibility of *macaúba* husk. The next question to be answered was what effect SWH would have on biogas production. **Figure 4** provides plots of biogas composition measurements in the AD and PT+AD reactors, and **Figure 5** provides plots of accumulated biogas volume measurements. For the PT+AD reactor, the biogas initially consisted mainly of CO_2 (76%) followed by H_2 (24%) and O_2 (0.26%). CH_4 content increased over time and over the entire duration of the experiment, the average CH_4 composition in the PT+AD reactor was 57% with a peak value on day 21 (80%). Interestingly, in the AD reactor, the biogas initially consisted of CH_4 (57%), 41% of CO_2, and H_2 (1.8%). After the initial day, the biogas composition measured in the AD reactor fluctuated over a wide range; for comparison with the PT+AD reactor, the average CH_4 content over the course of the entire AD experiment was 43%, i.e. 14 percentage points less than observed for the PT+AD reactor.

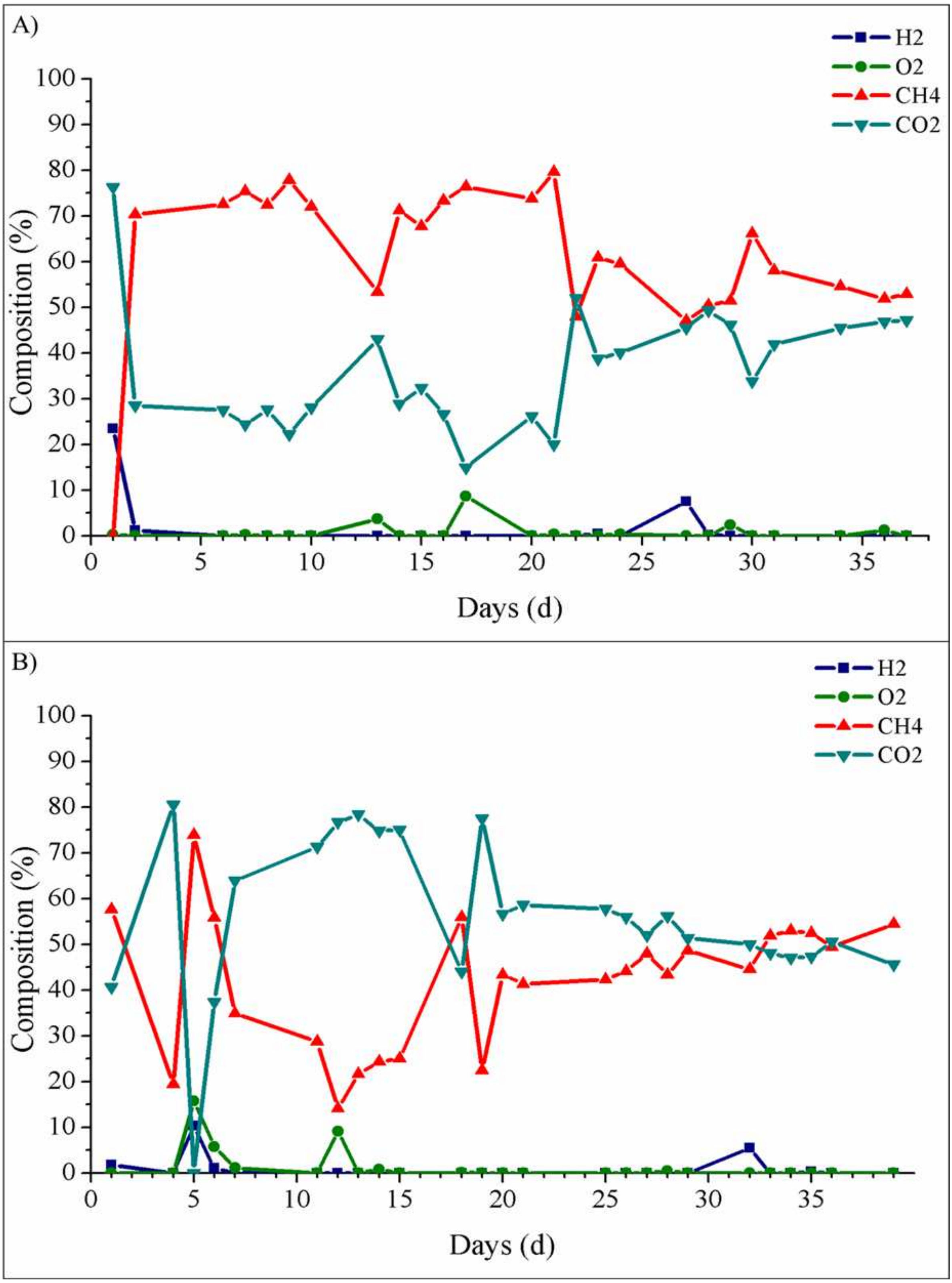

Figure 4. Evolution of biogas composition during anaerobic digestion: A) reactor with subcritical water hydrolysis pretreatment (PT+AD); B) reactor without pretreatment (AD).

Figure 5 shows that the PT+AD reactor produced 3,400 mL on the first day of the experiment, followed by a decline over days 2 and 3, followed by stabilization at a value of 670 mL/day with several noticeable peaks. The total biogas volume produced during the 38 days in the PT+AD reactor was 27,300 mL, corresponding to total CH_4 production equal to 15,500 mL. For the AD reactor, biogas production was initially delayed relative to the PT+AD reactor, with a spike on day 6, followed by stable operation for the remainder of the experiment. The total biogas production during the 39 days of the AD reactor was 22,000 mL, and the corresponding CH_4 production was 9,600 mL.

Directly comparing biogas and CH_4 production for the two reactors tells only part of the story. In fact, the total mass of biomass added to the two reactors was much different from one another, with 76.4 g added to the PT+AD reactor, considering the added material to start the reactor and all the feedings performed during the process, and 617.5 g added to the AD reactor. Accordingly, comparing biogas yield on a basis of added biomass clearly shows the improved digestibility of the feed after SWH relative to the native *macaúba* husk.

Normalizing biogas yields using VS and COD consumption data allows more direct intercomparison on a common basis. In terms of the mass of consumed VS, the CH_4 yield was 230 mL g^{-1} for the PT+AD reactor, which is more than 13-fold greater than observed for the AD reactor (17 $mLCH_4$ g^{-1}). In terms of the consumed COD, the methane yield for the PT+AD reactor was 590 $mLCH_4$ g^{-1}, while for the AD reactor it was 57 $mLCH_4$ g^{-1}. Similar observations are made for total biogas accumulation.

The biogas production depends on several variables, including retention time, temperature, pH, substrate composition and consistency of feed material, OLR, and particle size (CHANDRA *et al.*, 2012; IZUMI *et al.*, 2010; KHAN *et al.*, 2016; MAO *et al.*, 2015). Specifically, this work shows that the SWH pretreatment helps solubilize biomass components, and boost biogas yields that can be obtained from *macaúba* husk – similar to previous results reported for lignocellulosic biomass (CHANDRA *et al.*, 2012). Maciel-Silva et al. (MACIEL-SILVA *et al.*, 2019) reported similar findings for *açaí* seeds pretreated with SHW followed by AD, finding VS-normalized biogas yields of 792 $mLgVS^{-1}$ for the pretreated material and 7.8 $mL\ g^{-1}$ without pretreatment. On the other hand, the results presented here for *macaúba* husk indicate that SWH is much more effective in boosting biogas yields than has been reported for Nappier grass and sugarcane bagasse (BUITRÓN *et al.*, 2019; PHUTTARO *et al.*, 2019), indicating that the SWH benefit is very specific to the substrate.

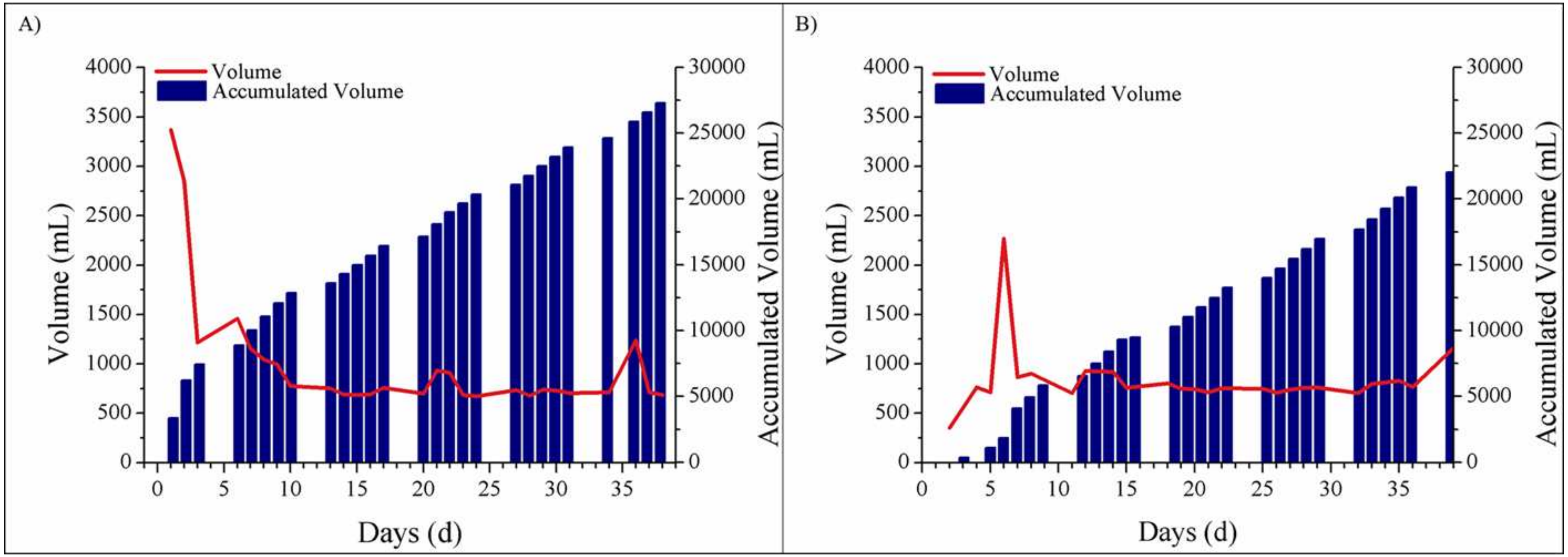

Figure 5. Evolution of biogas production and accumulated volume of biogas during the anaerobic digestion: A) reactor with subcritical water hydrolysis pretreatment (PT+AD); B) reactor without pretreatment (AD).

3.6 Electricity and heat generation and avoided GHG emissions

SWH clearly increase biogas yields; however, SWH is an energy intensive process and the benefit to biogas yields must be greater than the energy consumed by SWH to justify the additional step. **Table 3** summarizes the results of EG, HG and avoided GHG emissions obtained for the two experiments performed in this study (PT+AD and AD). SWH pretreatment followed by AD has the potential to replace 13-times the electricity and heat that is possible with AD alone, consistent with a benefit of the energy intensive SWH step.

Biogas electricity could be used on site to power *macaúba* processing facilities, and surpluses could be sold back to the energy grid. Both options contribute to GHG emission mitigation by replacing national grid electricity with a locally produced and renewable source. For the energy balance, the consumption and electric and thermal energy generation were estimated per unit mass of *macaúba* husks on a dry basis. In the transesterification process of palm oil, a total of 1,360 MJ is needed to produce 1 ton of biodiesel, and 0.0029 MJ of electricity is consumed for each MJ of biodiesel produced (HARAHAP *et al.*, 2019; LAM *et al.*, 2009; YEE *et al.*, 2009).

The results here presented refer exclusively to extractive *macaúba* production. *Macaúba* and husk production data in Brazil and governmental statistics on biofuel production are scarce. This preliminary study can therefore motivate adoption of a sustainable supply chain for *macaúba* as a commercial crop to support the recovery of degraded areas and with a much greater plant density than can be achieved using extractive methods (FERNANDEZ-COPPEL *et al.*, 2018).

Brazil has several state policies to support a transition from a fossil fuel economy to a renewable biomass-based one, thereby reducing pollutant emissions. Since March 2020, the government obligates mixtures of 12% of biodiesel in the diesel commercialized in Brazil, and this proportion is then scheduled to be increased in the future (ANP, 2020). Furthermore, RenovaBio (ANP, 2017), a Brazilian policy established to ensure the country's energy security and to help meet aggressive Brazilian decarbonization targets set on the 21st United Nations Climate Change Conference (COP 21), encompasses production of all types of biofuels, including biodiesel and biogas. Hence, a sustainable approach to increasing Brazilian production of biofuels is to use *macaúba* for production of both biodiesel and biogas, thereby reducing wastes while adding another source of biofuels to meet demand.

Table 3. Potential annual electricity and heat generated and avoided GHG emissions.

	Husks (ton $year^{-1}$)	EG_{CH4} (MWh $year^{-1}$)	HG_{CH4} (MJ $year^{-1}$)	A_{GHG-EC} ($tonCO_{2eq}$ $year^{-1}$)	A_{GHG-HG} ($tonCO_{2eq}$ $year^{-1}$)
PT+AD	169.5	136.3	613,134.4	10.2	34,335.5
AD	169.5	10.4	46,675.4	0.8	2,613.8
PT+AD	203.4	163.5	735,761.3	12.3	41,202.6
AD	203.4	12.4	56,010.5	0.9	3,136.6
PT+AD	109.4	87.9	395,676.1	6.6	22,157.9
AD	109.4	6.7	30,121.2	0.5	1,686.8
-	-	EG_{CH4} (MWh ton^{-1})	HG_{CH4} (MJ ton^{-1})	A_{GHG-EC} (ton CO_{2eq} ton^{-1})	A_{GHG-HG} (ton CO_{2eq} ton^{-1})
PT+AD	-	0.804	3,617.312	0.060	0.203
AD	-	0.061	275.371	0.005	0.015

Figure 6 presents the energy balance per unit of mass of husks for two scenarios: (i) scenario 1 corresponds to the PT+AD reactor and (ii) scenario 2, to the AD reactor. The PT+AD produces 10-times more biogas per unit mass of feed than the AD reactor. Similarly, the PT+AD reactor produces13-times more electricity and thermal energy than the AD reactor. An interesting approach to these results is to consider the percentage of the energy required to the whole processes that could be supplied by the energy recovered through the CHP system: for the PT+AD reactor, 28.5% of the total electricity required and 8.9% of the thermal energy needed could be supplied from the energy produced from biogas; for the AD reactor the respective values are 19.1% and 98.3%.

Considering both experimental results and energy analysis, the PT+AD strategy produces more biogas and electricity than the AD strategy, but the SWH consumes more heat than can be supplied by the CHP system. One way to improve performance is to use waste heat from biodiesel production to power the SWH process. Similarly, the adoption of a regeneration system, where the hot fluid that leaves the reactor is used to exchange heat with the liquid entering the reactor, with an average effectiveness of 75%, would reduce thermal energy requirements. The energy input would be lower, and the energy output from each of the routes (electrical or thermal energies) could be applied in the own *macaúba* biodiesel industry providing cleaner disposal to the by-products from the *macauba* biodiesel production.

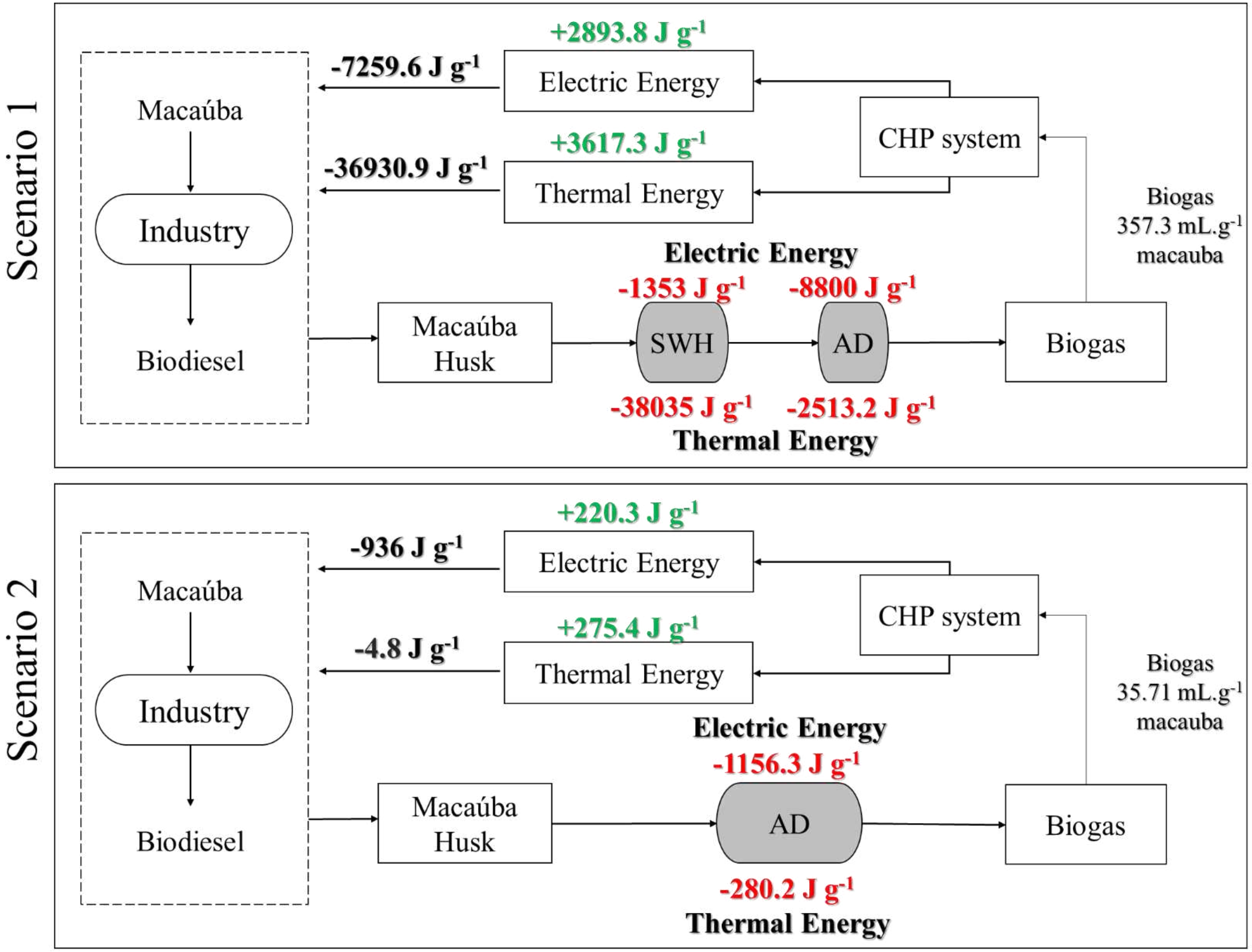

Figure 6. Energy balance per unit of *macaúba* mass (husks). Scenario 1: the biomass is pre-treated with subcritical water hydrolysis (SWH) before anaerobic digestions; Scenario 2: no pretreatments were applied before anaerobic digestion.

4. CONCLUSIONS

SWH pretreatment of *macaúba* husks efficiently converted lignocellulosic material into soluble forms for digestion, greatly boosting biogas yields. Comparison of COD reductions, pH, and alkalinity provides further evidence of the effect of SWH pretreatment, including improving digestion stability. The biogas could be used in a CHP cycle, and the resulting electrical and thermal energies could be used to offset *macaúba* processing requirements; any eventual surplus would be sold back to the energy grid. As configured in this lab study, SWH requires more thermal energy than can be produced in the CHP cycle and suggestions for heat recovery and improvement in heat use were suggested for the scaled technology. AD has a potential role in sustainable *macaúba* cultivation, resulting in a biorefinery that co-produces thermal energy, electricity, and biodiesel.

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CAPÍTULO 4 – Discussão Geral

Este trabalho buscou verificar as seguintes hipóteses:

- O processo de hidrólise em água subcrítica seguido de reatores anaeróbios consiste em uma integração de tecnologias ambientalmente favorável para a valorização de coprodutos orgânicos (biomassa) procedentes da produção de biodiesel de macaúba, mais especificamente a casca, para obtenção de produtos de maior valor agregado e energia;
- Os hidrolisados da etapa de pré-tratamento com água subcrítica possuem características químicas favoráveis para posterior digestão anaeróbia através de bactérias e archeas;
- A integração das tecnologias hidrotérmica e digestão anaeróbia através do uso dos hidrolisados, obtidos por tratamento subcrítico, nos reatores anaeróbios, permitirão a obtenção de maior rendimento de metano no biogás;
- Análise energética pode indicar alto rendimento de produção de energia elétrica e térmica para aplicação desta tecnologia sustentável.

Neste trabalho, verifica-se o crescente interesse na produção de macaúba e sua aplicação na extração de óleo, bem como na produção de biodiesel, podendo resultar no aumento da quantidade de coprodutos gerados no Brasil, dentre eles as cascas. A destinação final dos coprodutos de macaúba é a produção de carvão para conversão em energia térmica, não sendo relatados estudos do uso da hidrólise em água subcrítica como pré-tratamento de cascas de macaúba e sua posterior digestão anaeróbia. Considerando a valorização de cascas de macaúba para produção de biogás e seu potencial para geração de energia elétrica e térmica, à continuação apresenta-se uma discussão mais detalhada, e específica por capítulos.

4.1. Cenário mundial da macaúba: uma análise bibliométrica

Apesar dos avanços na produção de biocombustíveis, os resíduos e coprodutos da macaúba não são necessariamente recuperados como fontes de energia. A análise bibliométrica avaliou as potenciais aplicações da macaúba e investigou as novas alternativas para o aproveitamento de coprodutos sólidos, como cascas.

As análises tiveram como foco informações relacionadas aos campos de pesquisa mais explorados relacionados à macaúba e o estudo mostrou que de 1900 a 2020, 397 artigos e revisões bibliográficas foram publicados na coleção principal do banco de dados Web of Science. O Brasil é o maior editor, e as instituições brasileiras são as mais relevantes.

Apesar dos coprodutos oleico e proteico da macaúba serem aplicados como ração animal, foram identificadas algumas rotas de conversão relacionadas aos teores lignocelulósicos presentes nas partes não comestíveis, a saber: conversão térmica, combustão, gaseificação, pirólise, conversão bioquímica, fermentação, esterificação e digestão anaeróbica.

Na perspectiva agrícola, foram encontradas pesquisas sobre caracterização de plantas, germinação, embriogênese e desenvolvimento de sementes. A partir do estudo bibliométrico, avaliou-se o potencial de diferentes aplicações da macaúba para fins energéticos, farmacêuticos e alimentares, incluindo uma lacuna de conhecimento sobre a recuperação de seus coprodutos.

4.2. Valorização de coprodutos de macaúba da produção de biodiesel através de pré-tratamento de hidrólise em água subcrítica seguida de digestão anaeróbia

Neste trabalho verifica-se a valorização da casca da macaúba proveniente da extração de óleo (da produção de biodiesel) por meio do pré-tratamento de hidrólise em água subcrítica (10 g de alimentação, 200°C de temperatura, vazão de 10 $mL.min^{-1}$ durante 40 minutos e pressão de 14 MPa) seguido de digestão anaeróbia (regime semicontínuo e 35°C de temperatura).

Os resultados do hidrolisado obtido seguido de digestão mostram maior geração de metano e produção de biogás quando comparados com os reatores convencionais, sem pré-tratamento. Outros parâmetros operacionais, tais como demanda química de oxigênio, nitrogênio amoniacal, pH e alcalinidade também comprovam que o pré-tratamento com hidrólise em água subcrítica favorece um arranque de reator mais rapidamente e permite grande estabilidade de processo.

A análise energética indica que é possível obter-se energia elétrica e térmica a partir do biogás produzido durante a digestão anaeróbia. O ensaio com pré-tratamento de hidrólise em água subcrítica e digestão anaeróbia seria capaz de produzir 2893,8 J g^{-1} cascas de eletricidade e 3617,3 J g^{-1}cascas de calor a partir de coprodutos da extração do óleo macaúba, ambos treze vezes maiores que os valores obtidos para a D.A. somente. A produção de biogás por massa de cascas adicionadas é 10 vezes maior para o reator com pré-tratamento. Além disso, a energia gerada poderia ser utilizada no local da plantação de macaúba ou vendida ao Estado e contribuir para mitigar, ainda mais, as emissões de gases de efeito estufa.

Adicionalmente, o Brasil tem trabalhado na migração de combustíveis fósseis para combustíveis renováveis baseados em biomassa e na redução das emissões de poluentes. A macaúba poderia ser utilizada para a produção de biodiesel, e seus coprodutos aplicados na produção de biogás. Ou seja, poderia incluir o uso das mesmas fontes de calor utilizadas para a produção de biodiesel, já presentes na planta da indústria, que poderiam aquecer a água utilizada para o pré-tratamento da biomassa. Desta forma o aporte energético para a hidrólise em água subcrítica seria menor e a produção de energia de cada uma das rotas (energia elétrica ou térmica) poderia ser aplicada na indústria para proporcionar uma maior lucratividade e uma destinação mais limpa aos coprodutos de macaúba oriundos da produção de biodiesel. Um eventual excedente poderia ser revendido para a rede elétrica, desta forma a abordagem sugerida consiste numa fonte de energia renovável produzida localmente que contribui para a mitigação das emissões de gases de efeito estufa a partir da substituição de fontes fósseis tradicionais.

CAPÍTULO 5 – Conclusão Geral

Este trabalho verificou que existe uma lacuna de conhecimento e um grande potencial dos coprodutos de macaúba para recuperação energética com tecnologias sustentáveis. Nos últimos anos a atenção dada à bioenergia é crescente, à medida que aumenta o número de publicações nesta área. Para uma maior economia da macaúba brasileira e ousadas políticas estaduais de bioenergia e descarbonização, novas rotas de recuperação de energia são especialmente atraentes para o estabelecimento de Mecanismos de Desenvolvimento Limpo intimamente associados aos programas regionais e mundiais de desenvolvimento sustentável. Junto com a produção de biodiesel, outras fontes de bioenergia poderiam ser recuperadas dos coprodutos da macaúba para reforçar o desenvolvimento de energia mais limpa.

As seguintes conclusões gerais foram selecionadas para ambos os capítulos 2 e 3 deste trabalho:

- A análise bibliométrica apontou o Brasil como o país mais produtivo, contribuindo com 87% das publicações sobre macaúba, e as organizações brasileiras as mais envolvidas nas pesquisas de macaúba;
- Destacam-se as seguintes áreas nos trabalhos da literatura: Agricultura, Engenharia, Combustíveis Energéticos, Química e Ciências Vegetais;
- Os países com maior colaboração internacional são: Brasil, Espanha e Estados Unidos da América;
- Não foram identificados documentos que tratem do uso de coprodutos da macaúba para a produção de biogás, uma promissora fonte de energia e destinação ambientalmente correta para a biomassa não comestível;
- A hidrólise em água subcrítica, utilizada como pré-tratamento de coprodutos de macaúba da indústria de biodiesel, mostrou-se eficiente e adequada na degradação de material lignocelulósico recalcitrante;

- Os experimentos a 200°C, baseados em trabalhos anteriores, resultaram em melhores rendimentos durante o ensaio de digestão anaeróbia;
- A capacidade tamponante no reator PT+AD foi menor do que no reator AD, o que pode ser um efeito das repetidas correções de pH executadas para o reator AD;
- O teor de sólidos totais e voláteis e as concentrações de DQO apresentados pelo reator PT+AD foram inferiores aos valores apresentados pelo reator AD, um efeito direto da hidrólise em água subcrítica;
- Os menores valores de nitrogênio amoniacal apresentados pelo reator PT+AD ocorreram em decorrência de seu menor teor de sólidos inicial;
- Considerando o potencial de geração de energia e calor, os resultados obtidos para o reator PT+AD foram superiores aos do reator AD, confirmando a adequação do uso da hidrólise em água subcrítica como pré-tratamento para materiais lignocelulósicos;
- O ensaio com pré-tratamento e digestão anaeróbia foi capaz de gerar um total de 27,3 L de biogás obtido a partir de 76,36 g de cascas, e após passar por motor de utilização combinada de calor e eletricidade poderia ser convertido em 2893,8 J g^{-1} de energia elétrica ou 3617,3 J g^{-1} de energia térmica em um cogerador, com um saldo final de -7259,6 J g^{-1} ou -36930,9 J .g^{-1};
- O ensaio com reatores convencionais, a quantidade total de biogás produzido foi de 22,05 L, usando 617,47 g de cascas; e após passar por motor de utilização combinada de calor e eletricidade poderia ser convertido em 220,3 J g^{-1} de energia elétrica ou 2754,4 J g^{-1} de energia térmica, com um saldo final de -936 J g^{-1} ou -4,8 J g^{-1} em termos de energia térmica;
- Pelos cálculos mencionados, o volume total de biogás e de metano é maior quando o pré-tratamento é aplicado, porém o balanço não é favorável, o que torna importante o estudo de um scale-up para uma indústria, visando proporcionar uma melhor

recuperação energética ou evitar o consumo de energia pelo trocador de calor durante a hidrólise em água subcrítica;

- Conclui-se que a economia da macaúba brasileira e as políticas estaduais de bioenergia e descarbonização poderão criar novas rotas de recuperação de energia, permitindo o estabelecimento de uma economia circular e de Mecanismos de Desenvolvimento Sustentável.

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