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Clara Lisseth Mendoza Martinez

Assessment of agro-forest and industrial residues potential as an alternative energy source

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Assessment of agro-forest and industrial residues potential as an alternative energy source

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Clara Lisseth Mendoza Martinez

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To Bioenergy

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Resumo

A geração de energia a partir de fontes alternativas e renováveis são importantes para o desenvolvimento sustentável da bioeconomia mundial, pois seu uso mitiga questões ambientais como a emissão de gases de efeito estufa. Das fontes de energia disponíveis, a biomassa revela enorme potencial de expansão devido às reservas existentes e características versáteis, as quais auxiliam no abastecimento da demanda energética e a redução do acúmulo de resíduos. Vários países têm como objetivo promover e apoiar a expansão da bioenergia. No entanto, para aumentar a participação das energias renováveis, é necessário explorar as políticas, às novas tecnologias e a avaliação de biomassa sustentável. Esta tese investigou uma variedade de biomassa resídual, abrangendo agro-floresta, e processos industriais. Tais resíduos podem representar preocupação ambiental, se descartados de forma inadequada e sem tratamentos apropriados.
A diversidade considerável de fontes de biomassa e as diferenças em sua estrutura química requerem uma avaliação das propriedades e o impacto correspondente nos processos de conversão escolhidos. A qualidade da biomassa não tratada apresenta desafios para o seu uso e a conversão em produtos de valor agregado em grande escala. Esta tese teve como objetivo caracterizar a recuperação de resíduos estudando as alternativas de conversão de energia por meio de processos termoquímicos (carbonização hidrotérmica, gaseificação, pirólise, combustão direta) e físico-químicos (briquetagem). A caracterização de biomassas residuais da cadeia produtiva do café para fins energéticos foi estudada. Os resultados não disponíveis na literatura antes deste estudo são uma ferramenta fundamental para descrever o impacto dos componentes químicos na decomposição térmica e outras possíveis aplicações. Os resíduos sólidos de café apresentaram elevados teores de voláteis, celulose e hemiceluloses, características atrativas no processo de degradação térmica. O HHV entre 16-24 MJ kg^{-1} (base seca), análogo às biomassas comumente usadas na geração de energia, também foi observado nos resíduos de café.
O desempenho dos processos de conversão não depende apenas das características da matéria-prima, mas também dos parâmetros do processo. As tecnologias de conversão termoquímica foram estudadas através de balanços de massa e energia. Resultados como o potencial alternativo de geração de calor e eletricidade para áreas locais por meio da tecnologia de gaseificação, que reportou taxa de conversão de energia de 84 % para o pergaminho de café cereja, foram observados. Além disso, a avaliação da carbonização hidrotérmica (HTC) foi estendida a procedimentos experimentais usando várias biomassas de resíduos agroforestais e industrias de importância mundial. Como o processo requer o fornecimento de calor, a integração com plantas de calor e energia (CHP) foi simulada a fim de analisar o potencial do tratamento HTC como um processo atraente para biorrefinaria usando resíduos de biomassa. A integração do HTC permitiu um desenho de processo mais simples com um benefício eficiente, fornecendo um vapor de extração disponível em níveis de pressão suficientes. Além disso, os lodos primário e secundário das estações de tratamento de efluentes das fabricas de polpa celulosica, foi estudado através da tecnologia HTC, a integração ao processo da fábrica de celulose também foi avaliada a fim de aumentar as alternativas de captura de carbono. Propriedades físicas, mecânicas e químicas da densificação de biomassa também foram estudadas nesta tese, briquetes de resíduos agro-florestais produziram um combustível sólido de forma regular e alta densidade de energia e resistência, para uso em sistemas de queima na própria fabrica.

Palavras-chave: Biomassa residual, café, madeira, lodo, carbonização hidrotérmica, briquetagem, valorização energética, rentabilidade, integração.

Abstract

The generation of energy from alternative and renewable sources is of enormous importance for the sustainable development of the world bioeconomy, as its use mitigates environmental issues such as greenhouse gas emissions. Of the energy sources available, biomass has shown great potential for expansion due to existing reserves worldwide and its very versatile characteristics that can help to meet energy demands and reduce the accumulation of waste. Several countries aim to promote and support the bioenergy expansion, however to increase the share of renewables, policy goals, new technologies and sustainable biomass evaluation need to be explored. This thesis investigates a variety of different biomass-based residue streams, covering forest, agriculture and industrial processes. These residues may represent a serious source of environmental concern, if discarded inadequately and with poor management.
The considerable diversity of biomass sources and the differences in their chemical structure require detailed evaluation of the properties and the corresponding impacts on the chosen conversion processes. The quality of untreated biomass presents several challenges for its use and conversion into value-added products on a large scale. This thesis aims to characterize the residue recovery chain by studying the alternatives of energy conversion through a diverse thermochemical (hydrothermal carbonization, gasification, pyrolysis, direct combustion) and physicochemical (briquetting) utilization path. An extensive characterization of residual biomasses from the coffee production chain for energy purposes was evaluated. The results were not readily available in the literature before this study and are a fundamental tool to describe the impact of chemical components on thermal decomposition and further possible applications. Solid coffee residues showed high volatiles and cellulose and hemicelluloses content, suitable characteristics to thermal degradation. The HHV between 16-24 MJ kg^{-1} (db), analogous to biomasses commonly used in energy generation was also observed for coffee residues.
The performance of the conversion processes not only depends on feedstock characteristics but also on the process parameters. Thermochemical conversion technologies were studied through mass and energy balances. Results such as the alternative potential to generate heat and electricity to local areas trough gasification technology, which reported energy conversion rate of 84% for cherry coffee parchment, was found. Moreover, a hydrothermal carbonization (HTC) evaluation was extended to experimental procedures using several globally important woody and non woody waste biomasses. Since the process requires heat to be supplied, heat integration with combined heat and power (CHP) plants was simulated in order to analyze the potential of HTC treatment as an attractive process for a biorefinery using biomass residues. Integrating the HTC allowed a simpler process design, and an efficient benefit, provided that extraction steam is available at sufficient pressure levels. Additionally, sludge from pulp mill effluent treatment plants was studied through HTC technology, and integration with the pulp mill process was also evaluated in order to increase carbon capture alternatives. Physical, mechanical and chemical properties of densified biomass were also studied in this thesis, and agro-forest residue briquettes from coffee residues and pine produced a potential solid fuel of regular shape and high energy density and resistance, for use in local firing systems.

Keywords: Residual biomass, coffee, wood, sludge, hydrothermal carbonization, briquetting, energetic valorization, profitability, integration.

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Nomenclature

Acronyms

AC	Ash content
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CP	Coffee parchment
CS	Coffee shrub
CW	Coffee wood
EDF	Energy density factor
EMC	Equilibrium moisture content
ESR	Energy saving ratio
EU	European Union
EW	Eucalyptus wood
EY	Energy yield
FCC	Fixed carbon content
FLW	Food loss and waste
GB	Giant bamboo
GHG	Greenhouse gas
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen sulfide
HHV	High heating value
HTC	Hydrothermal carbonization
IEA	International Energy Agency
IRENA	International energy agency
K_2O	Potassium oxide
LHV	Low heating value
MC	Moisture content
Mtoe	Million tonnes of oil equivalent
MY	Mass yield
N	Nitrogen
NO_x	Nitrous oxides
OECD	Organization for Economic Co-operation and Development
PC	Principal component
PCA	Principal component analysis
pH	Potential of hydrogen
PLS	Partial least squares
PV	Photo-voltaic
REmap	Renewable energy roadmap analysis
RMSE	Root mean square error
S	Sulfur

SCG	Spent coffee ground
SO_2	Sulfur dioxide
TPES	Total primary energy supply
VM	Volatile matter

Greek alphabet

η_{LHV}	LHV-basis net efficiency
$\mathrm{P}_{el,in}$	Power consumption
$\mathrm{P}_{el,net}$	Power generation
θ_{HC}	Hydrochar output
$\theta_{b,HTC}$	HTC feedstock
$\theta_{b,boiler}$	Boiler fuel

Other symbols

EDF	Energy density factor
ESR	Energy saving ratio

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List of publications

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Publication I

Mendoza, C.L.M., Rocha, E.P.A., Carneiro, A.C.O., Gomes, F.J.B., Batalha, L.A.R., Vakkilainen, E., and Cardoso, M. (2019). Characterization of residual biomasses from the coffee production chain and assessment the potential for energy purposes. *Biomass & Bioenergy*. 120, pp. 68-76.

Publication II

Mendoza, C.L.M., Saari, J., Melo, Y., Cardoso, M., Almeida, G.M., and Vakkilainen, E. (2021). Evaluation of thermochemical routes for the valorization of solid coffee residues to produce biofuels: A Brazilian case. *Renewable and Sustainable Energy Reviews*. 137, 110585.

Publication III

Mendoza, C.L.M., Sermyagina, E., Saari, J., Jesus, M.S., Cardoso, M., Almeida, G.M., and Vakkilainen, E. (2021). Hydrothermal carbonization of lignocellulosic agro-forest base biomass residues. *Biomass & Bioenergy*. 147, 106004.

Publication IV

Mendoza, C.L.M., Sermyagina, E., Carneiro, A.C.O., Vakkilainen, E., and Cardoso, M. (2019). Production and characterization of coffee-pine wood residue briquettes as an alternative fuel for local firing systems in Brazil. *Biomass & Bioenergy*. 123, pp. 70-77.

Publication V

Mendoza, C.L.M., Kuparinen, K., Martins, M., Cardoso, M., Vakkilainen, E., and Saari, J. (2020). Negative carbon dioxide emissions from eucalyptus pulp mill including biosludge HTC treatment. In: *Proceedings of 53rd Pulp and Paper International Congress and 9th International Colloquium on Eucalyptus Pulp*, Virtual Platform.

Publication VI

Martinez, C.L.M., Jesus, M.S., Vakkilainen, E., Cardoso, M., and de Almeida, G.M. (2019). Bioenergy technology solutions in Brazil. *Brazilian journal of wood science*. 10(2), pp. 112-121.

Author's Contribution

Mendoza C.L.M. is the principal author and investigator in all publications. Professor Vakkilainen, Professor Cardoso, Professor Almeida, Dr Sermyagina and Dr Carneiro supervised the work and gave valuable comments and suggestions during the course of the research. Publication V was written based on the previous research work of Dr. Kuparinen, and the calculations and HTC integration were done by Dr. Kuparinen and Dr Saari. In Publication III, the work related to HTC simulation integration was done by Dr. Saari.

Relevant Publications (not included in the thesis)

Mendoza, C.L.M., Jesus, M.S., Sermyagina, E., M.S., Cardoso, M., Almeida, G.M., and Vakkilainen, E. Use of principal component analysis to evaluate thermal properties and combustibility of coffee-pine wood Briquettes. Accepted manuscript to Agronomy Research Journal.

Saari, J., Mendoza, C.L.M., Kuparinen, K., Saari, J., Kähkönen, S., Hamaguchi, M., Cardoso, M., and Vakkilainen, E. (2021). Novel method to integrate biosludge handling and HTC to pulp mill energy generation. Accepted manuscript in proceedings of International Chemical Recovery Conference (ICRC).

Mendoza, C.L.M., Mashlakov, A., Jesus, M.S., Cardoso, M., and de Almeida, G.M. (2019). Carbonização hidrotérmica de resíduos do café (Hydrothermal carbonization of coffee residues). In: *Proceedings of the IV Congresso Internacional de Biomassa - CIBIO*. Curitiba-PR, Brazil. (In portuguese)

Mendoza, C.L.M., Mashlakov, A., Jesus, M.S., Cardoso, M., and de Almeida, G.M. (2019). Carbonization of coffee wood for charcoal production. In: *Proceedings of the V Fórum Nacional Sobre Carvão Vegetal e III Seminário de Energia da Biomassa Florestal*. Belo Horizonte-MG, Brazil.

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Jesus, M., Carneiro, A.C.O., Mendoza, C.L.M., Nava, D.S., de Magalhaes, M.A., and de Vital, B.R. (2019). Wood thermal profile during the pyrolysis process. *Revista Brasileira de Energias Renováveis*. 8(3), pp. 538-546.

Jesus, M., Mendoza, C.L.M., Costa, L.J., Pereira, E.G., and Carneiro, A.C.O. (2020) Thermal conversion of biomass: a comparative review of different pyrolysis processes. *Brazilian Journal of Wood Science*. 11(1), pp. 12-22.

1 Introduction

1.1 The role of biomass in the transition towards sustainable and renewable energy

The use of renewables as an alternative energy source has been increasing in the last decades. They currently account about 13.7% $\left(1{,}882 \text{ million tonnes of oil equivalent (Mtoe)}\right)$ of the world total primary energy supply (TPES) (IEA, 2018), and are predicted to reach 2,741 Mtoe in 2040 (IEA, 2019). The significant growth in renewables is led by solar photo-voltaic (PV) and wind power, which grew at average annual rates of 37% and 24%, respectively (from a very low base in 1990). Biofuels were responsible for 9.5% of the total world renewable energy supply in 2017 - providing four times the contribution of solar PV and wind combined (IEA, 2018). Despite this, the share of fossil fuels in the global primary energy demand remains above 80%, with oil representing the highest contribution (32%) of the world TPES. Nonetheless, oil markets are facing major challenges, which have been evidenced in the sharp reduction on the 1.5 mb/d annual pace since 2010 (IEA, 2020a), followed by the negative growth in 2020 due to the pandemic outbreak. The major challenge for the fossil fuels markets is the ongoing clean energy transition in order to mitigate the risk of climate change, mainly caused by the anthropogenic emissions of greenhouse gases (GHGs), such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxides (NO_x) (IPCC, 2018).

Bioenergy plays an important role in the transition to a low carbon energy approach. Several policies and strategies have been implemented to accelerate the bio-based economy, mainly focusing on agriculture, forestry, industry, energy, environment, climate change, research and innovation. In the European Union (EU), the initiative *Stepping up Europe's 2030 climate ambition*, proposes a framework for the actions to develop a efficient, productive and sustainable economy by 2030 (Commission, 2011). In South America, Brazil has developed the incentives *Brazil's national climate change plan* (Brazil-CIMC, 2008), *2030 national energy plan* (EPE, 2007), and *Decennial Plan* (EPE, 2020) to determine certain targets for the reduction of GHGs and increasing renewable energy generation with particular focus on bioenergy and hydropower on a large scale. In general, the transition towards all-renewable energy is a complex issue, involving technology, economics and politics. The priorities for tackling this challenge depend on the specific assumption of strict sustainability regulations.

A commonly used definition of sustainability given by the United Nations World Commission on Environment and Development is *"development that meets the needs of the present without compromising the ability of future generations to meet their own needs"* (White, 2013). Moreover, the term sustainable is very abroad, and has different implications when applied to different subjects. With the purpose of assessing the sustainability on renewable energy sources, elements such as flexibility, low cost, safety, transportability, efficiency, high energy density, together with the possibility to solve crucial task like improving energy supply reliability and organic fuel economy, increase the standard of living and level of employment, fulfil the international agreements relating to environmental protection (Panwar et al., 2011), among other factors must be considered to define sustainability for energy applications. However, Costanza and Patten (1995) noted that the definition must be more specific with regard to what

particular system or subsystem to sustain and for how long. For example, the conflicts of the terms "sustainable" and "renewable" caused by the large-scale hydroelectric dams, which the energy source is renewable but cannot be considered sustainable due to populations displacement, downstream fisheries degradation and environmental damage (Ascher, 2021). Therefore, sustainability must be evaluated on a case by case basis.

1.2 Bioenergy trends and residues management

The potential for energy utilization from biomass, including forest, agriculture and waste to varying extents depend on land availability. Figure 1.1 provides the definitions and shows the regional participation of global land use. Currently, agricultural land accounts for the largest share of world land use with 37%, divided into arable land, permanent crops and permanent grassland and meadow (FAOSTAT, 2020). Forestry with a 31% share of the total world land, supplies wood-based industries, including pulp and paper manufacturing, furniture, and charcoal production, among others (FAOSTAT, 2020). In this sense, the use of biomass for energy purposes is projected to compete with the existing uses of land, leading to increased food prices and intensified competition for additional resources (water, nutrients). Nonetheless, enhancing the treatment of agro-forestry residues could be a land-related sustainable option to increase bioenergy generation, including the manufacture of wood pellets or liquid biofuels as well as biogas production from agricultural residues feedstock. However, biomass energy from the agro-forest sector must overcome some obstacles concerning sustainability and economics. The availability of residual biomass depends on the production cycle, and in agriculture on the production season. The reliability of supply is also uncertain, although residues originally have little value, the prices can rise once the demand has developed. Transportation also suggest a logistic problem, as well as the current high dependence on fossil fuels for powering machinery in biomass collection (Bardi et al., 2013).

For the future prospects the renewable energy roadmap analysis (REmap) reported by the international energy agency (IRENA), aims to map out the energy scenarios and review data by using a framework of complex models. The REmap assess low-carbon and energy transition pathways, including the infrastructure and biomass supply (IRENA, 2018). The share growth of renewables is target to increase to approximately 60% by 2030 and 85% by 2050 from the around one-quarter reported in 2015 for energy sector decarbonisation. For this, the growth rate need to raise more than double of the 0.7% growth rate that have been reported over the past five years (Gielen et al., 2019). Biomass alone can contribute to the transport (liquid fuels), industry and buildings (conversion into electricity and district heat) sectors, mostly accounting for two-thirds of direct use of renewable energy in 2050; around 116 EJ in terms of annual bioenergy supply levels. To reach those targets, shift away from traditional biomass use to modern technologies have to be implemented, mainly for heating applications and liquid biofuels production. For example, the program *proalcool* from Brazil, which use sugarcane to produce alcohol for consumption or bioethanol for fuel use. This initiative started in 1975 and expanded rapidly due to several policies that evolve over time to address the need of supply and demand sides (Gielen et al., 2019). The use of sugarcane ethanol has been estimated to reduce in about 86% GHG emissions when compare to petrol (CCC, 2018). However, economics and government priorities may affect the long-term development of the sector. Likewise, in northern Italy

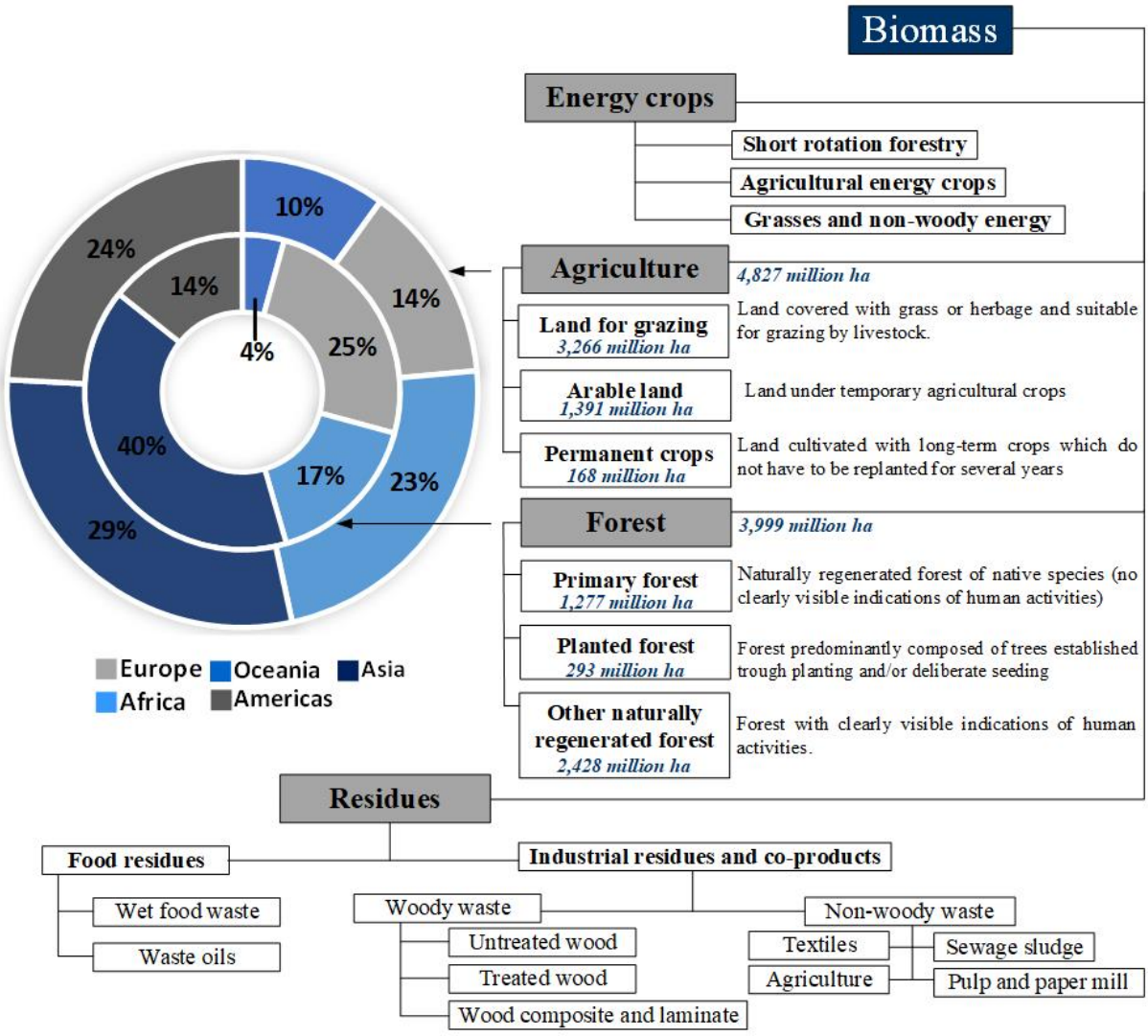


Figure 1.1: Land use and classification of sources of biomass. Data from FAOSTAT (2020).

from double-cropping (second crop after main food crop is harvested), animal manure and other farm waste and residues, are used to produce biogas through anaerobic digestion. The biogas is combusted to generate electricity that is then selled to the national grid (CCC, 2018).

The prediction of the renewable energy use by sector and source, and reduction targets of CO_2 emissions for year 2050 is showed in Figure 1.2. The data was collected from the published reports by IRENA (2018), and compared to the reference case, year 2015. The prediction model may look ambitious in some extend but the energy potential of the renewables is highly attractive to reach the established targets. The transition however is not obvious and economics are not entirely sustainable. Different sectors such as iron and steel making, cement, chemical and petrochemical have significant challenges, especially in the feedstock supply. According to Gielen et al. (2019) these sectors require the mobilisation of about 1000 million tonnes of affordable and reliable feedstock. Biomass as a renewable energy carrier with carbon content that can be stored with a high energy density, plays a fundamental role in the urgent need to develop alternative technologies in the full-scale energy transition of the end-use sectors such as iron and steel, cement, chemical, and petrochemical. Infrastructure will need to integrate technologies and the decarbonisation can stimulate employment and economic growth.

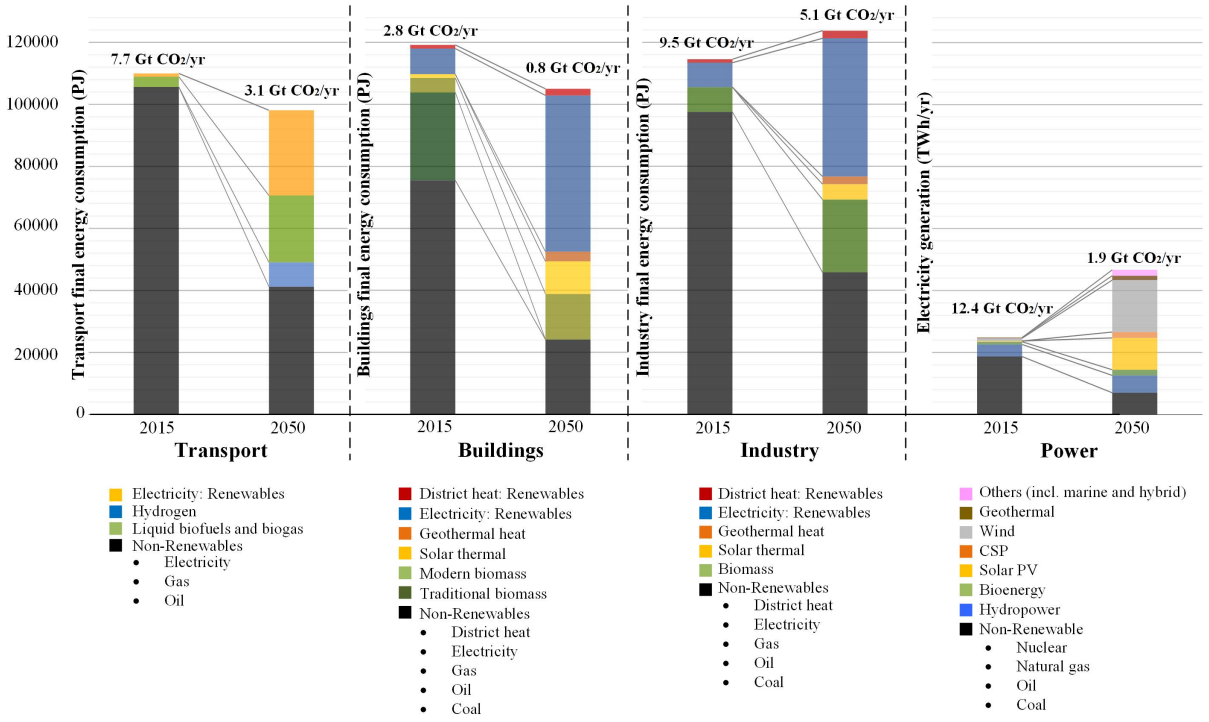


Figure 1.2: Global energy transformation: a roadmap to 2050. Data from IRENA (2018).

1.2.1 Global trends

From the latest data available reported by the International Energy Agency (IEA), the potential for electricity and heat generation from solid biofuels and municipal-industrial waste in 2017, was $502 \cdot 10^3$ GWh and $1{,}037 \cdot 10^3$ TJ, respectively (IEA, 2020b). The total energy potential of different sources of biomass for electricity and heat is presented in Figure 1.3. Converting municipal waste to heat and electricity is significantly utilized in the members-states of the Organization for Economic Co-operation and Development (OECD), while a large shift in the industrial activities included in industrial waste generation can be observed in the non-OECD countries. Solid biofuel sources including wood chips, wood pellets and agro-forestry residues make an important contribution to global bioenergy production accounting for more than half of the total electricity and heat generation from biomass worldwide. Non-OECD members generate the largest share of electricity from solid biofuels. Brazil for example contributed with $51 \cdot 10^3$ GWh in 2018 (IEA, 2020b).

The biomass usage data available is typically not complete or consistent, especially to quantify agro-forestry residues and industrial waste, due to the differences in management practices. However, a theoretical estimate by Kummamuru (2016) is that in 2014, 3.6 - 17.2 billion tonnes of agricultural residues were used worldwide (including straw, husks, cobs, kernels and leaves), and more than 777 million tonnes from the forestry sector (including logging, sawmilling, plywood and particle board manufacture). Rapid urbanization, economic development and population growth, suggest even higher values. Regarding the waste obtained from municipalities and industries, 2.01 billion tons of global food loss and waste (FLW) were produced in 2016. This makes food and green residues the highest source of waste (44%) worldwide. Currently, just a small part of agro-forestry residues and waste become feedstock for

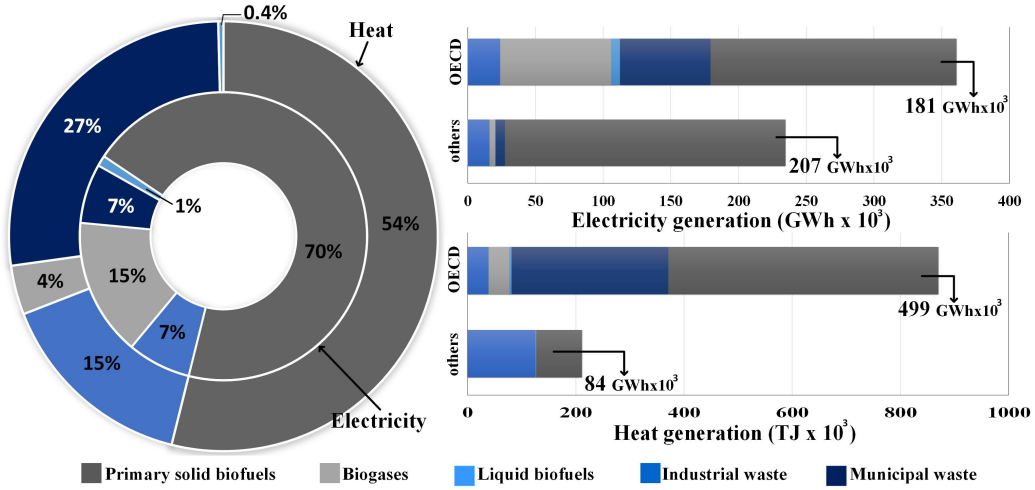


Figure 1.3: Electricity and heat generation from biomass worldwide in 2017. Data from IEA (2020b).

industrial applications and electricity generation, especially in European Countries. Their use is supported mainly through legal requirements and low cost of collection and further processing.

The residual collection and disposal differs between countries according to income (Kaza et al., 2018). Waste collection rates in high-income countries are nearly 100%, through which more than half of all waste is recycled, composted or incinerated, and 39% of the total disposal is attributed to landfill. In low-income countries, only 35% of waste is collected, and open dumps remain a major disposal option (Kaza et al., 2018). From agro-forestry activities, most of the residues are used for household cooking and compost, or burned in the field, due to prices usually above the energy netback. Conversion technologies of residues into valuable goods may play a key role in the future. Compounds such as antioxidants, enzymes, cellulose, starch, lipids, proteins, pigments and vitamins can be produced from agro-forest residues and municipal-industrial waste. In the energy sector, fuels at a competitive cost, e.g. pellets, briquettes, charcoal, bio-oil and biogas can also be obtained. In doing so, large-scale sustainable biomass use and new technologies linked to sustainable development such CO_2 capture and sequestration, can emerge.

1.2.2 Trends in Europe

High-level strategies focused on the green economy concept have implicated the use of biomass as an opportunity to achieve several benefits simultaneously, such as improved food security, reduced natural resource scarcity and fossil resource dependence as well as the mitigation of climate change (Scarlat et al., 2015). The primary supply potential comes from forestry, agriculture and the waste sector, which are projected to be higher than the amounts that will be required for bioenergy in a near future (Bogaert et al., 2017). According to Bogaert et al. (2017), 45 to 64 Mtoe in agriculture, 76-110 Mtoe, which is very close to the total supply in the forestry sector, and 78% in municipal-industrial waste, will be consumed as bioenergy by 2030.

In March 2020, the European Commission published a new circular economy action

plan, including many proposals to contribute towards the EU becoming a cleaner and more sustainable economy, as well as climate neutral. Several limitations need to be considered and measures need to be taken in order to achieve such goals. One of these focuses on waste, which is still landfilled. Trends of waste-to-energy still lie in incineration (and energy recovery), which does not have a good reputation due to released toxins and greenhouse gases. A number of new market technologies, such as anaerobic digestion, pyrolysis, gasification and hydrothermal carbonization provide the potential to recover products from waste streams. However, environmental analysis and efficiency still need further studies. The biobase chemical industry, which is characterized by strong growth, is seeking novel industrial materials. Several studies consider waste and also agro-forestry residues as an attractive source (Thorenz et al., 2018; Bogaert et al., 2017).

The agricultural sector provides a large amount of residues as a biomass supply for energy, which is likely to be used for biogas. To enhance their potential, a biobased economy must be developed for the agricultural sector. According to Thorenz et al. (2018), less than 8% of the theoretical potential of straw, which provides the largest amount of residues in the agricultural sector in the EU, is recovered from fields, which means that just 29 Mt out of 390 Mt is recovered. EU countries, led by Spain, France, Poland and Germany, that account for more than half of agricultural supply potential, perceive agricultural residues as an opportunity to generate profit and contribute to the biobased economy. However, agricultural residues-to-energy limitations such as the low energetic density and high heterogeneity, suggest a need for applications of technologies and treatments to generate high-quality and low-cost products.

In the forestry sector, more than half of the share of forest biomass supply comes from Germany, France, Sweden, Finland and Poland. Softwood is almost completely used for industrial or manufacturing purposes, leaving between 1-44 Mm^3 available for energy, while hardwood utilization ranges from 60 to 110 Mm^3 (Bogaert et al., 2017). Nonetheless, several residues from forests have interesting potential such as bark, sawdust and logging residues or other low value biomass from silvicultural and harvesting operations. These are typically left in the forest or discarded due to transport costs. One of the most relevant markets in the EU that uses woody residues is the pellet market. In 2017, the EU became the largest producer (17.8 Mt), consumer (23 Mt) and importer (14.6 Mt)/exporter (9.4 Mt) of pellets in the world (IRENA, 2019).

1.2.3 Trends in South America: case Brazil

Brazil ranks sixth among the countries with the highest GHG emissions in the world. The main emissions have historically been concentrated in agriculture, forestry and other forms of land use related to deforestation, cultivation and livestock (La Rovere et al., 2018). In 2017, Brazil reported total emissions of about 436 $MtCO_2$-eq (EPE, 2018), the mitigation of which seems very difficult to achieve, mainly due to turbulent events including the economic and political crisis. This has currently lead to slowing the progress on climate and energy policy. However, Brazil has a high potential in the energy scenario due to the widespread use of clean energy sources and its implementation of renewables in the electricity generation matrix, which is demonstrated in the high usage of energy from hydro power (64%) and biomass (8%) (EPE, 2018). The Global Energy Network Institute, reported that the energy potential through the

use of biomass in Brazil is between 250-500 EJ. However, more conservative studies refer to a potential for bioenergy around 11,690-13,930 PJ, considering the average productivity between 20-80 tons of agricultural culture per hectare.

In the latest survey of agricultural production in Brazil by IBGE (2018), the northeast region accounts for 7.87% of total production. The north, southeast and mid-west are responsible, respectively, for 2.40%, 13.30% and 32.03%, and the southern region represent the highest share of 44.40%. An average growth of 12.22% in comparison to the previous harvest in 2019, was observed. The main crops in the country are sugarcane, corn, soy, rice and coffee. Their total production in 2019 accounted for 667, 101, 114, 10 and 2 million tons, respectively. From them, large amount of residues are produced, mainly in the field, resulting from the activities of harvesting. Some residues are used for energy due to existing technologies. But currently, Brazil does not use more than 200 million tons of agro-industrial residues. Part of the residues not used for energy are used for animal feed, medicine and fertilizer. However, a significant part is burned in the field due to transportation costs and most importantly due to the lack of sustainable standards that enhance the use of residues.

In the forest energy context, the area occupied by forest plantations in Brazil totalized in 7.8 million hectares for energy purposes, of which 84% corresponded to wood from planted forests. The country's total wood production is concentrated in the pulp and paper industry, followed by the segments of firewood, sawnwood, coal-fired steel, industrialized wood panels and plywood. The industries in this forestry sector generate a significant volume of residues during the various operational phases, ranging from the forest harvest to the final product, which can be considered as an important source of biomass. However, most of the time these residues are wasted for lack of well-developed markets or non-existent information from the producer and consumer agents and lack of clear public policies aimed at their best use. This situation is observed mainly in the Amazon and central regions of Brazil, where non-competitive prices associated with long transport distances, delay the bioeconomy development. On the other hand, alternative technologies have been implemented for agro-forestry residues in the country, basically for two main purposes: as raw materials for products with higher added value and as energy sources. In the energy sector, direct combustion or incineration is typically used in industries that work in the agroforest sector. The residues generate vapor that consequently produces heat and electricity. Gasification, pyrolysis (biocoal production) and briquette or pellet production for subsequent combustion, are also part of the current residue treatments.

1.3 Motivation and objectives

The high dependency on fossil fuels and the urgent transition to renewable energy sources present bioenergy as a possible alternative to maximize the value of biomass. However, biomass has restricted potential, environmental and social implications. Residues minimize these negative impacts when are sustainably used, i.e., leading to the production of power, heating, alternative fuels, among other applications. Three principal topics were examined; the characterization of residual biomasses, then thermochemical and physicochemical conversion technologies including evaluation and optimization. Figure 1.4 summarizes the contents of six publications related to different aspects of the research. Also, in light of the general objective, the following key research questions (RQs) guided this study, focused on to the biomasses

studied in this dissertation:

RQ 1: How does the composition of the residual biomass affect its behaviour for energy applications?

RQ 2: How can the hydrothermal carbonization process and densification treatments enhance the residual biomasses properties for the generation of value added products?

RQ 3: What are the effects of integrating an hydrothermal carbonization (HTC) plant in an industrial process?

RQ 4: Is the energy potential of residual biomass attractive for the bioeconomy?

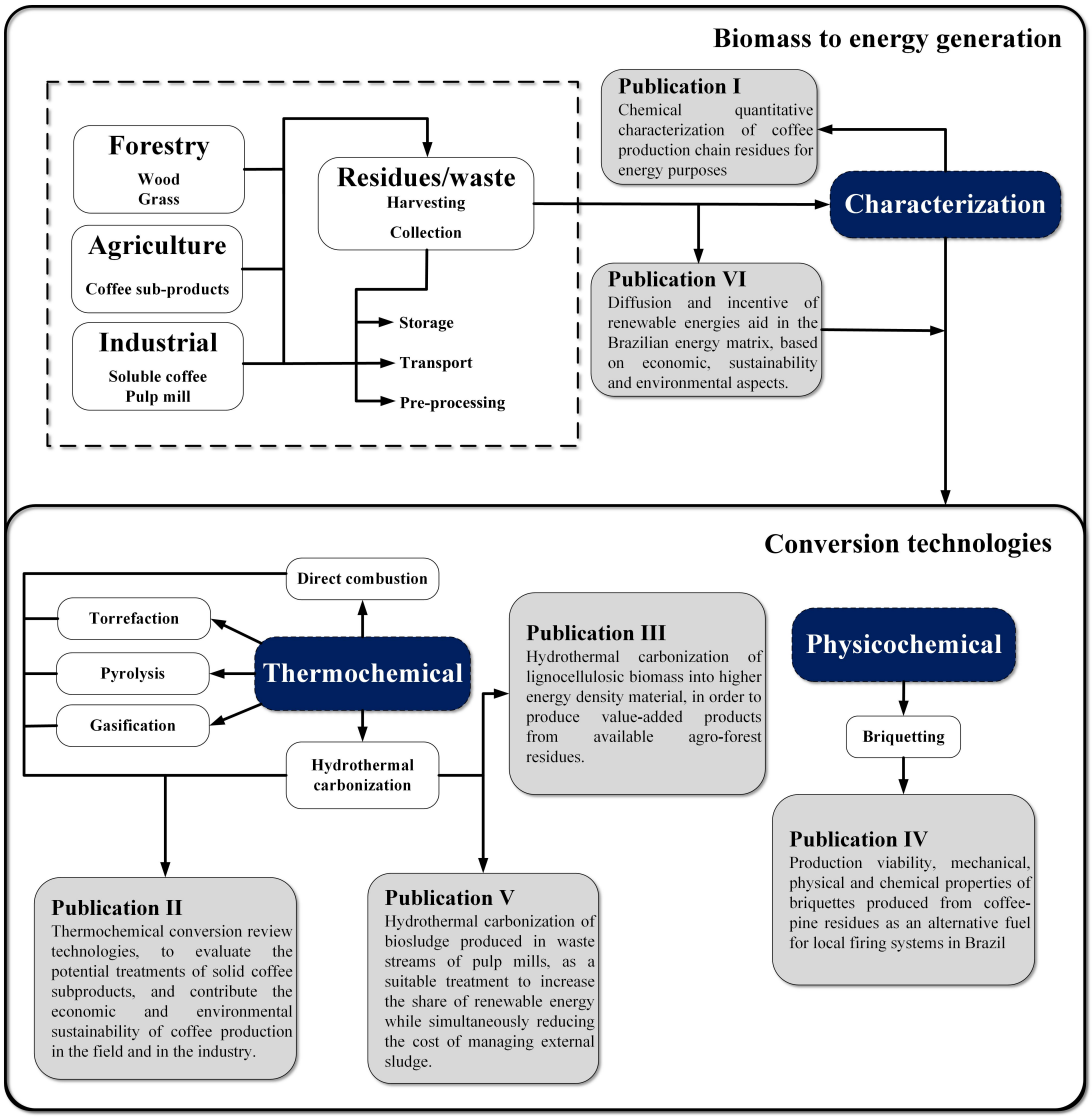


Figure 1.4: Types of residual biomass included in this dissertation together with the conversion routes for energy and other applications studied in **Publications I-VI**.

The research related to residue management was motivated as an alternative solution to overall environmental sustainability. Through the years, recovery systems of residues have been intensified to mitigate their negative effects in fields and water courses. Currently, recycling has been strongly adopted by diverse industries due to the possibility of achieving economic and

environmental benefits. However, residues will often require treatment for further applications, ranging from transportation through to conversion technologies. **Publication VI** presents an overview of the Brazilian energy sector with background, challenges and the degree of sustainability in the production of energy, based on economic and environmental aspects of its production. Around half of energy in Brazil, as the largest renewable energy market in Latin America, is generated by natural inputs. Most of the biomasses studied in this thesis were collected in the production chain of different industries in Brazil. It was considered important to diversify the energy sources in the country and to contribute to the development of the energy industry, where despite having a renewable energy matrix, new investments to encourage research and develop new technologies heading to sustainability are still needed.

Within this thesis, research question RQ 1 can be considered as the first step of the process in finding alternative solutions for residual biomass applications. An extensive characterization of different source/residual biomass through the behavior of the physical and chemical properties identified their most important quality indices. Some of the parameters evaluated were: the lignocellulosic structure, moisture content, proportion of carbon in organic matter, ashes, concentration of nitrogen and sulfur. Due to the large amount of possible residual biomass, only selected large sources were studied. **Publication I**'s main objective was to report a broad characterization of coffee shrub (CS) residues (*coffea arabica*), in order to identify alternative applications in the energy matrix of countries where the coffee industry is one of the major agricultural activities, with the main focus on Brazil. **Publications II** to **V** also quantify properties of raw material from agricultural, forestry and industrial sources, as described in Section 2, for the further generation of value-added products.

A variety of available treatment and conversion technologies, each associated with different process parameters and product yields can create suitable energy carriers between the raw biomass feedstock and the final energy use. Research question RQ 2 examines diverse physicochemical and thermochemical routes in the interest of conversion treatments of selected sources of biomass for energy generation, as in **Publication II**. This quantifies the potential of solid coffee residues for efficient production of energy through direct combustion, pyrolysis, gasification, torrefaction and HTC technologies. The information collected to a single source and the development of mass and energy balances for solid coffee residues treatment trough different thermochemical technologies, was first time evaluated.

Questions RQ 3 and RQ 4 concentrate on the operation of HTC, for which detailed reaction mechanisms for different feedstocks and the characterization of HTC products are not yet completely understood and only a few itemized reports have been published. HTC technology is broadened in **Publication V** to include biosludge as an industrial residue from pulp and paper mills, and **Publication III** to evaluate selected agro-forest residues. Physicochemical technology is studied in **Publication IV** to evaluate the utilization of coffee residues mixed with pinewood in the briquetting process in order to produce a solid fuel with a regular shape and high energy density and resistance for use in local firing systems.

1.4 Outline of the thesis

This thesis consist of four sections, which present the background of the study and a summary of the key findings. Furthermore the publications are introduced. The content of the

sections can be summarized as follows:

Section 1 Introduction. Provides an overview of the background of the global challenge to achieve sustainability through renewable energies and the importance of disposing of agroforest and industrial residues in a sustainable way. This section continues by stating the motivation, research objectives and scope of the thesis.

Section 2 Residual biomass. Addresses properties of diverse lignocellulosic biomasses. Reviews the most relevant parameters with respect to energy conversion treatments though chemiometric analysis. Introduces diverse conversion pathways for lignocellulosic biomass. Evaluates the process parameters and product yields of diverse thermochemical and physicochemical conversion technologies in order to generate value-added products.

Section 3 Results. Describes the laboratory evaluation of the residual biomasses. Test results of biomass characterization, HTC and densification conversion processes are discussed, together with the integration of hydrothermal carbonization schemes.

Section 4 Conclusions. The key observations in response to the stated research objectives are summarized in this section. Scientific contributions and future research prospects are also presented, followed by the list of references and publications.

2 Lignocelulosic biomass for energy application

The main sources of biomass that can be used for energy production are represented by a wide group of materials and are divided into energy plantations, agricultural crops, forest, animal, municipal and industrial waste. Biomass has unique potential among the other renewable energy sources to provide solid (coal-like products), liquid (biodiesel, bioethanol, pyrolysis oil) and gaseous (biogas, syngas) energy streams. The determination of the biomass properties is fundamental for understanding the necessary conversion processes and for establishing the quality of the final product characteristics, as well as for developing technologies capable of transforming the energy contained in the biomass in an efficient and environmentally friendly way. This section reviews and evaluates physical, mechanical, anatomical and chemical characteristics to indicate the capacity of biomass for the manufacture of high-quality and high-yield products.

The residues generated from agricultural-forestry-industrial production chains not only represent unused potential, but landfilling or burning can have significant negative environmental impacts (e.g., emission of large quantities of volatile organic compounds in the case of combustion, and contamination of ground-water in the case of landfill). The unused residues treatments often generates high costs that producers want to avoid. Figure 2.1 shows the studied biomasses and displays their production and approximate distribution worldwide. The amount of total residues generated are difficult to estimate due to the differences in management practices in the field and in industry.

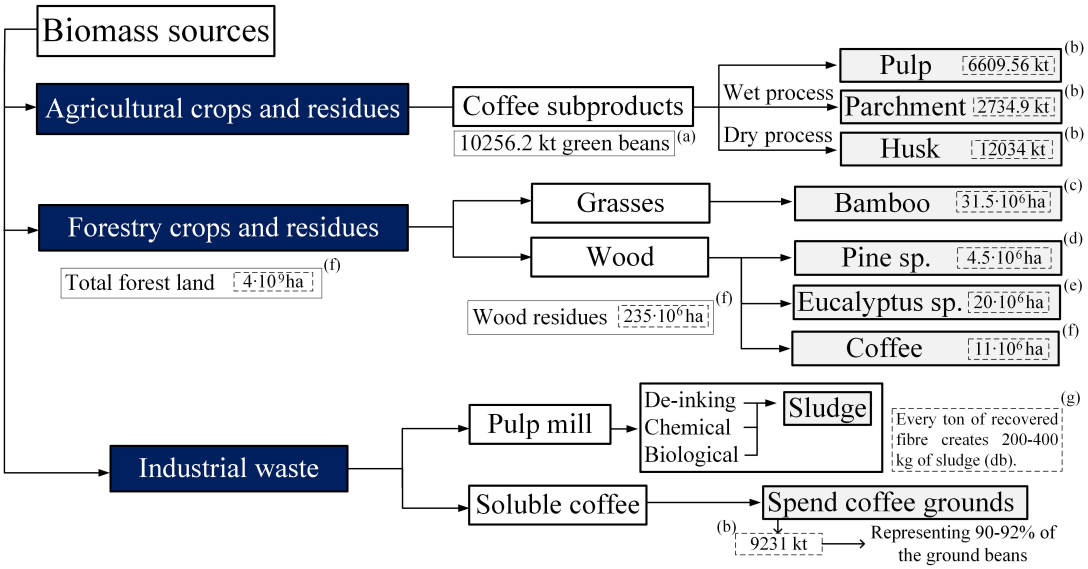


Figure 2.1: Biomass sources studied in this dissertation. (a) coffee production 2018/2019 from ICO (2020); (b) calculated: pulp 29% db, parchment 12% db wet process, and husk 52.8% db dry process of coffee cherry, and spend coffee grounds 90% db of coffee beans; (c) covered land from Yuen et al. (2017); (d) covered land from Diekmann et al. (2002); (e) covered land from Ferreira et al. (2019); (f) area harvested from FAO (2020); (g) data from Tarnawski (2004). Data worldwide.

2.1 Biomass sources

2.1.1 Coffee production

Coffee is one of the most consumed beverages in the world, and also one of the most important agricultural crops (ICO, 2020). The cultivation, industrialization and commercialization of this agrobusiness product represents great importance for the development of countries like Brazil due to the large numbers of jobs and foreign exchange generated (Kruger, 2007). In 2019, the world production of coffee beans reached 10 million tons, where Brazil was the largest producer (37%), followed by Vietnam (18%) and Colombia (8%) (ICO, 2020). According to the Brazilian Institute of Geography and Statistics (IBGE, 2018), in 2017, Brazil had 1.8 million hectares of coffee plantations (*coffea arabica* and *coffea robusta* species), from which final destination of coffee beans collection was to produced soluble coffee for sale.

The high consumption of coffee is associated with the production of a large amounts of low-value waste. Only 6% of the coffee harvest is used in the preparation of the beverage. The remaining 94% correspond to residues, mostly originating during the washing and depulping stage of processing the coffee fruit. According to Veenstra (1995), processing 60 million kg of coffee beans produces about 218 kt of fresh pulp and mucilage (coffee residues), resulting in a wastewater chemical oxygen demand similar to that generated in one year by 1.2 million people. For the purpose of this study, coffee processing is described in Figure 2.2.

The generation of residues and by-products is unavoidable for the coffee industry. Furthermore, lack of knowledge of the quantity, physical and chemical characteristics and technologies available for using the residues has been a hindrance to finding an alternative that conserves energy and contributes to sustainable development. Before the extensive selected coffee residue characterization reported in **Publication I** no readily available information was published. The obtained results are fundamental to quantifying the effects of coffee properties on conversion technologies, including the thermochemical processes described in **Publication II**, and extended for hydrothermal carbonization technology in **Publication III**. Briquette production as a physicochemical conversion route is discussed in **Publication IV**. These are also studied as promising energy applications.

2.1.2 Forest crops

Wood is an important source within the energy matrix in different countries. In Brazil, for example, the high forest productivity in the forest-based industry promotes the economic growth of the country through diverse sectors such as pulp and paper, steel and charcoal, wood panels and laminates, and solid wood products (IBÁ, 2020). Unlike most other industries, forest-based industries are fortunate to be able to use their residues to help meeting their energy needs, generally through the combustion for heat or power generation. Although, handling, treatment and combustion equipment, together with labor and maintenance can be a costly

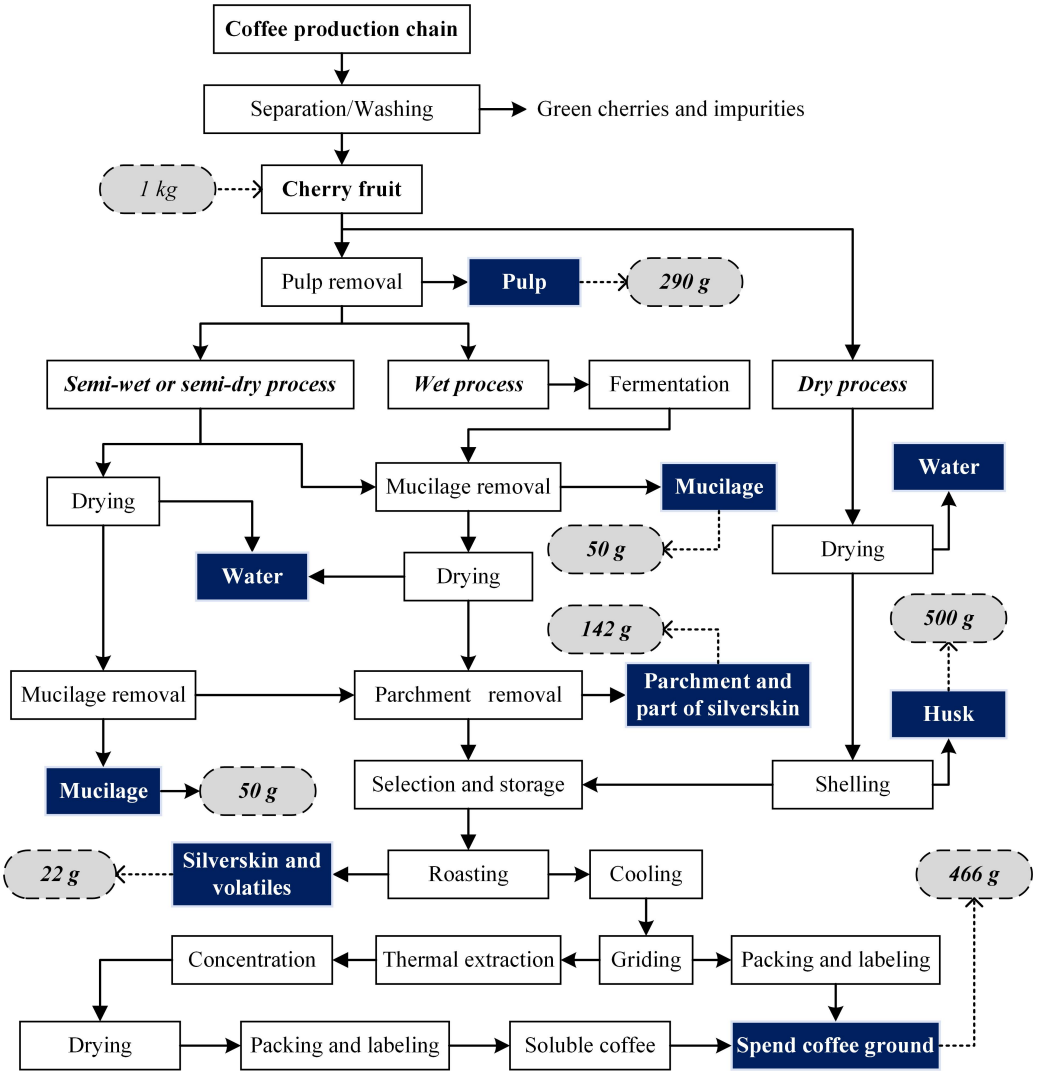


Figure 2.2: Flowchart of post-harvest coffee processing and generated waste (Mendoza Martinez et al., 2021a).

adjunct to a plant's operating costs, the implementation of alternative technologies and the integration of physicochemical and thermochemical residue treatment can be considered an economically viable investment. Bamboo, eucalyptus, pine and coffee wood residues were collected in this study for further analysis and alternative applications.

Bamboo represents the major wood grass species found in the tropical and subtropical regions of the Asia-Pacific region, as well as in continental Africa and the Americas. Due to its fast-growing characteristics (attaining stand maturity within five years) (Banik, 2015; Ogunjinmi et al., 2009), technological properties, easy handling and availability, bamboo has various uses as a plant and specially for structural constructions, interiors, furniture, handicrafts, musical instruments, panels, paper, textiles, medicines and pesticides among other applications (Bystriakova et al., 2004). Its widespread use generates a large amount of residues, which can serve as a breeding ground for fungi, thereby endangering forests and the bamboo industry unless effectively disposed of. **Publication III** examined the HTC treatment of bamboo as an alternative means of residual recovery, and showed suitable applications of hydrochar as a fuel. Schneider et al. (2011) found similar results for HTC bamboo treatment with additional to high concentrations of nutrients, especially nitrogen, phosphorus and potassium in an aqueous solution, which was attractive characteristic for soil amendment applications.

Another fast-growing species in commercial plantations is Eucalyptus, representing a

hardwood biomass. This species is particularly found in the tropical and subtropical regions. Eucalyptus provides raw material particularly for the pulp and paper industry (Domingues et al., 2011), as well as other uses such as building materials or charcoal (de Jesus et al., 2019; Jesus et al., 2018). Pine classified as a softwood biomass, also provides a good quality material for the production of pulp, in addition to presenting adequate technological characteristics for use in sawmills and for resin extraction. Contrary to eucalyptus, pine is native to the northern hemisphere, from which various species have been introduced to temperate and subtropical regions. The high consumption of eucalyptus and pine in the forest industry generates large amounts of residues, originating from the stemwood, leaves and bark during logging and wood processing. Typically, residues are either left in the forest, or burned in biomass boilers within pulp and paper mills (Domingues et al., 2011). Alternative solutions were presented in **Publication IV** for pine, and **Publication III** for eucalyptus, through briquetting and HTC treatments, respectively.

Coffee wood is collected from the periodically pruned and stumped coffee shrub. According to De Oliveira et al. (2013), a full-grown coffee shrub weighs on average 15 kg (dry wood). Approximately 25% of the shrub becomes solid waste during pruning, which occurs approximately every five years. The pruning frequency depends on the agronomic management practices, production and shrub growing stage. To prune, the secondary and tertiary branches should be cut from the shrub, leaving more space for the primary ones to grow. This rejuvenation should occur after four to five harvests, which means that an average of 32 million tons of residual wood are generated from coffee plantations in Brazil annually. Coffee wood is generally burned in field. **Publications I** to **VI** implement different conversion routes for coffee wood.

2.1.3 Industrial waste

Pulp mills generate various by-product streams. In addition to internal recycling, some of these can be sold, refined, or used on site for energy production, but some, such as the biosludge generated in wastewater treatment, cannot be reused or disposed of, easily. Biosludge has accounted for over 50% of overall wastewater treatment costs in some mills, and is typically disposed of in landfills, by composting or burning in a recovery or biomass boiler, all of which can be in some ways problematic. Likewise, environmental legislation has requirements for industries to achieve environmental certifications such as various solutions that comply with environmental laws and, at the same time, make their products competitive in the market. Treating the pulp mill sludge by HTC is reported in **Publication V** as an alternative solution for further applications.

In the coffee industry process, the roasted and ground beans are cooked in hot water to extract the water-soluble solids and volatile compounds. The remaining insoluble residues form the spent coffee grounds (SCGs), representing 90-92% of the ground beans (Karmee, 2018). According to Durán et al. (2017), SCG has attracted a great deal of attention since large quantities are constantly generated, about 4.5 tonnes for each ton of soluble coffee produced. Currently, SCG when not deposited in dumps, is used as fuel in boilers, generally in the industry itself, presenting several problems in the emission of dust and particles. Several alternatives of use have been tested for these residues, and some of them are evaluated in **Publication II**.

2.2 Biomass characterization

2.2.1 Chemiometric analysis of biomass composition

In this thesis sampling, preparation and laboratory procedures for characterization and conversion, aimed to gain a better understanding of the connection between the composition of biomass and its thermal behaviour. During the development of this thesis, tools for data analysis were implemented. Typically, chemical analyses are performed with using classical methods. These procedures, despite being very useful, are slow, laborious and have low sensitivity. The increasing demand for analytically safe data in all areas of science is increasing the studies on the exploration of different phenomena that could result in the improvement of the methods of analysis (Petrozzi, 2012).

Chemometrics is the most recent area of analytical chemistry that is emerging as a result of the search for mathematical and statistical tools that were able to convert the analytical signal derived from modern instrumental techniques into useful information through appropriate methods. These tools can be subdivided into three main areas: design of experiments, pattern recognition and multivariate calibration. This dissertation applies principal component analysis (PCA) and a partial least squares (PLS) method to evaluate the data obtained from the experimental procedures and data available in the literature (Figure 2.3).

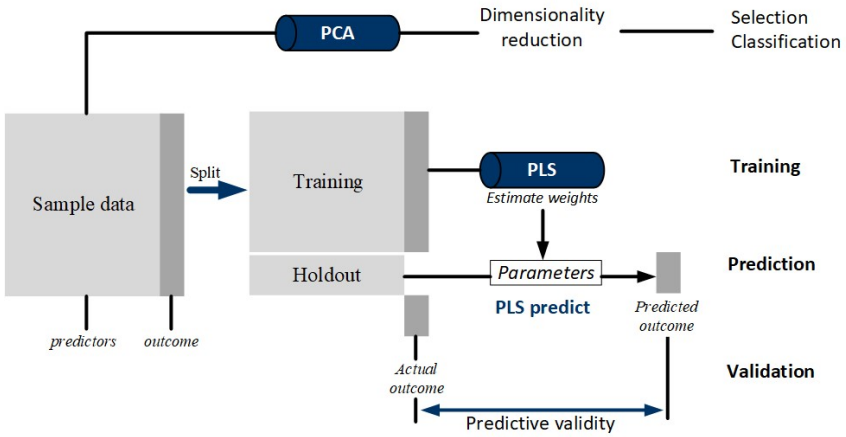


Figure 2.3: Methodology PCA and PLS data analysis.

PCA is the most widely used unsupervised technique and is considered the basis of multivariate analysis. The main objective is to reduce the dimensionality of the data with maximal variance by transforming the original variables into their principal components (PCs), which are a set of unrelated orthogonal vectors knowing as eigenvectors of the covariance matrix ($\sum$). In general terms, PCA seeks a linear mapping **M**, which maximizes the objective function trace ($M^T \sum M$), where $\sum_{ij} = cov(x_i, x_j) = \mathbb{E}[(x_i - \mu_i)(x_j - \mu_j)]$. Research question Q5 points to patterns of characterization similarities existing between biomass samples interpreted in the projected data. This data comprehension was possible due to the PCA's ability to group variables that provide similar information into clusters. In the analysis, the main components are built in a decreasing order of variance, so generally the most relevant information is concentrated on the first components, facilitating data interpretation.

The PLS method was also used to develop models from the multivariate calibration, offering the possibility of analyzing data as spectra which show overlapping signals and simultaneous determinations of diverse variables. The structural base of the PLS models is presented by the following equations: $\boldsymbol{X=TP^T+E}$ and $\boldsymbol{Y=UQ^T+F}$, where **T** and **U**, **P** and **Q**, and **E** and **F** are the scores, loadings and residues of **X** and **Y** matrix, respectively (Wold et al., 2001). The models were validated by cross-validation and a new test data group. When removing one or more samples from the calibration of the set of samples a cross-validation was performed, since the calibration models were elaborated with remaining samples for several PCs and the excluded samples participated in each model with their determined values. The whole process was repeated, until the values were determined for all the samples, thus optimizing the total error for a given number of PCs. Similarly, the models were evaluated using a test group, where a different set of samples were used for validation. This way model improves its accuracy and reliability, since it uses unknown samples.

2.2.2 Proximate composition

The proximate composition quantifies the chemical characteristics: moisture content (MC), ash content (AC), fixed carbon content (FCC) and volatile matter (VM) content contained in the biomass material. Figure 2.4a shows the resulting scatter plot using the scores of the first two principal components, preserving 51.1 and 31.6% of total variance, respectively. Data for coal, lignite and sub-bituminous coal, which are highly used in energy generation have been also plotted as a reference. Agro-forest residue samples form a relatively compact cluster, while samples from coal and industrial waste are more diverse, reflecting their different composition from plant material.

The moisture content varies over a wide range of 10-70% depending on the type of biomass. A high MC may cause difficulties in the utilization of biomass from the point of view of transportation, handling, and processing, as well as ignition and combustion problems (Mendoza Martinez et al., 2019a). A pre-drying stage is required before processing the feedstock through thermochemical conversion such as gasification, pyrolysis, and direct combustion. However, for hydrothermal technologies and biological conversion routes, raw materials with a high moisture content are desirable, since water acts as a catalyst for higher energy potential (Xiao et al., 2012).

The volatile matter is quantified by measuring the mass fraction of volatiles during heating a sample in an inert atmosphere at temperatures up to 900ºC. On a dry basis, VM typically has higher values than fossil fuels, ranging from 48 to 86% (Mendoza Martinez et al., 2019a). The VM content influences the fuel reactivity and the formation of condensable gases during heat treatment processes. The VM composition includes light hydrocarbons such as: CO, CO_2, H_2 and H_2O. The fixed carbon content refers to the mass remaining after the release of VM, excluding the ash and moisture content. This generally varies by a range of 1-38% depending on the standard process conditions (García et al., 2013). The FCC is a useful parameter to evaluate the calorific value of a fuel. Samples with high VM and low FCC contents are more susceptible to thermal degradation, which makes biomass an attractive feedstock for thermochemical conversion (Mendoza Martinez et al., 2019a).

The ash content establishes the amount of inorganics in the fuel per kilogram of biomass.

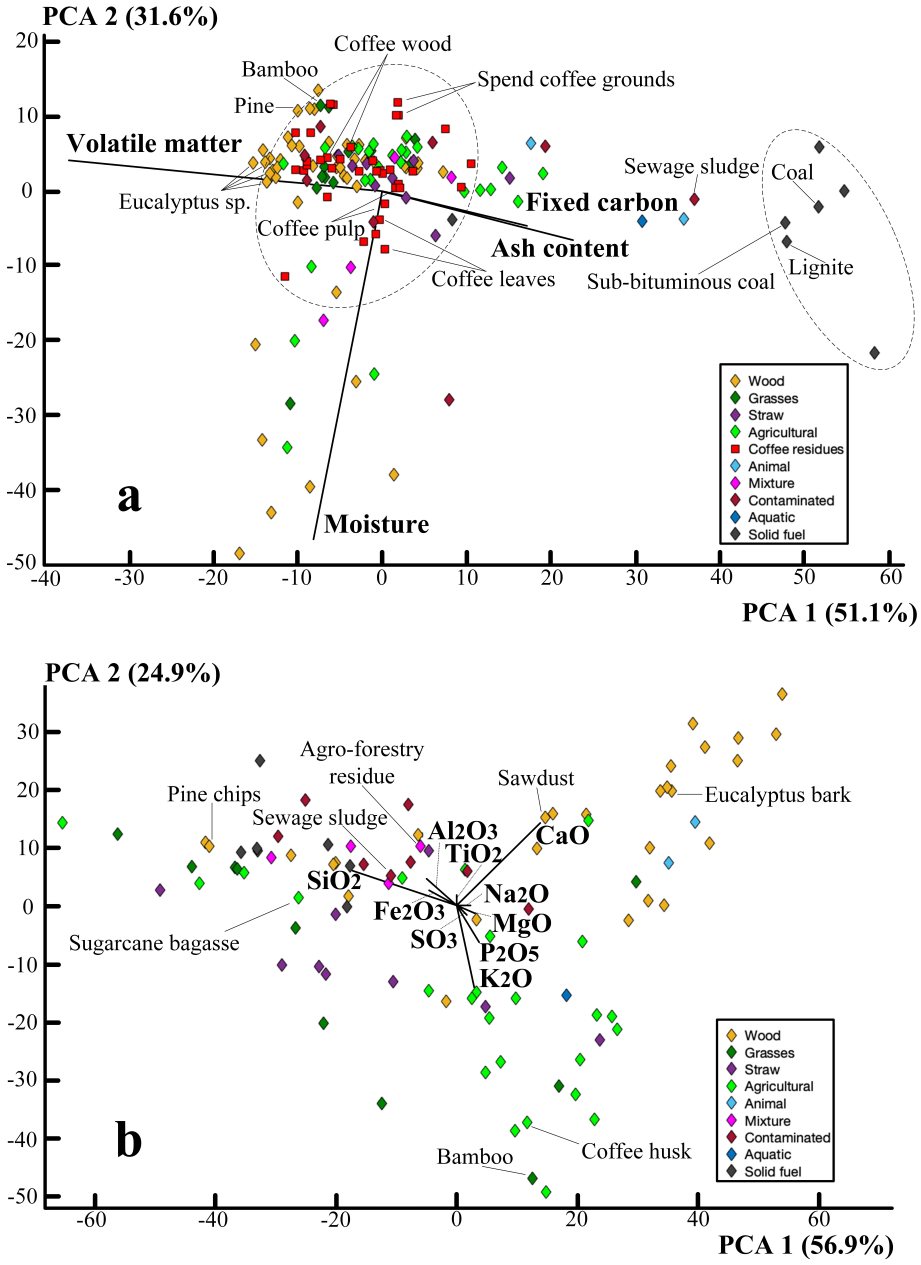


Figure 2.4: PCA score plot for 156 samples characterized by volatile matter, moisture, ash and fixed carbon content (a), PCA score plot for 95 samples characterized by the main ash compounds (b).

AC is one of the most studied parameters in characterization of biomass, but unfortunately it is also not completely understood. The complex nature of this parameter is due to its simultaneous production from organic and inorganic sources during the energy conversion processes (Masiá et al., 2007). The AC value influences the available energy content in the biomass, making it difficult to transfer heat by acting as an insulator. Despite its limitations, the ash content is an important parameter to approximate: (I) the mass of the inorganic matter, (II) the affinity between the elements and compounds from the organic and inorganic material of the biomass and (III) the possible contamination of the biomass.

Figure 2.4b shows the composition of the main ash compounds found in 95 samples including biomass and coal (named solid fuel) as a reference. The scores of the first two principal components accounted for 56.9 and 24.9% of total variance, respectively. As observed in Fig-

ure 2.3a, agricultural residues typically generate significantly more ash than woody biomass, indicating the higher presence of K_2O in agricultural samples. In general, AC represent a potential problem when biomass is degraded at high temperatures, due to slagging and fouling of burners and boilers from ash deposition (Mendoza Martinez et al., 2019a). On the other hand, ash from biomass can stimulate microbial activity and mineralization of the soil by improving both the soil's physical and chemical properties. For example, AC from woody biomass has a high alkalinity, which raise the pH of acidic soils (da Costa et al., 2020).

2.2.3 Elemental chemical composition

The elemental chemical composition of biomass is the percentage of the mass of the main chemical elements that constitute the samples. The composition of biomass involves five main elements: approximately 50.26%–54.41% dry basis (db) of carbon (C) , 35.52 %–42.29% db of oxygen (O), 6.13%–6.59% db of hydrogen (H) and small amounts of nitrogen (N) and sulfur (S) in the organic phase (Mendoza Martinez et al., 2019a). A biomass with high values of C and H, contributes the most to the calorific value of the fuel. Figure 2.5 shows 142 biomass samples characterized by the contents of C, H, O, N and S. The first and second principal components account for 89.4 and 6.8% of the total variance, respectively.

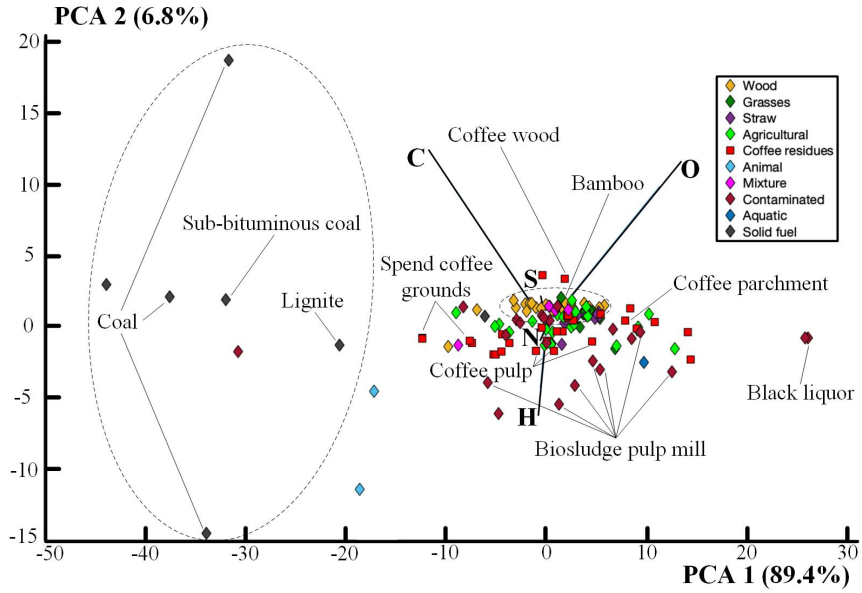


Figure 2.5: PCA score plot for 142 samples characterized by carbon (C), oxygen (O), hydrogen (H), nitrogen (N) and sulfur (S).

Elements O and N, contribute negatively to the energy processes due to the ability of carbon to form oxidized nitrogen compounds. The O content in the biomass usually decrease in the order: agricultural biomass > agricultural residues > forest biomass > animal biomass. High O contents can be commonly found in biomass such as soybean hulls and coffee hulls. The presence of N and S in the biomass have a direct impact on the environmental pollution due to the formation of harmful oxides (NO_x, SO_x) from volatile compounds (Wilson et al., 2011). The N content varies in the range of 0.1 - 12% and usually decreases in the order: animal

biomass > agricultural residues > agricultural biomass > forest biomass, in the same way as the S element. S varies in the range of 0.01 - 2.3% in biomass and plays an important role in the formation of boiler deposits, causing equipment wear due to its corrosive behavior, while S facilitates the mobility of many inorganic compounds, in particular potassium, contributing negatively to energy conversion systems (Vassilev et al., 2010).

2.2.4 Energetic content

The thermal power of biomass is a parameter of fundamental importance in the evaluation of the feasibility of the use of biomass for thermochemical conversion. The heating value is divided into low heating value (LHV) and high heating value (HHV), and the difference between HHV and LHV consists of the amount of energy required to evaporate the water formed from the oxidation of the hydrogen of the fuel. The HHV is affected by the elemental chemical composition of matter, and its value increases with the greater proportion of oxygen and hydrogen compared to carbon, due to the lower energy contained in C-O and C-H, than in C-C bonds (McKendry, 2002). Figure 2.6 shows a Van Krevelen diagram that can be used to compare the chemical structure with respect to the influence of the O:C and H:C ratios on calorific power. In this graph, the lower the atomic ratio O:C and the greater the atomic ratio H:C, the better the energy properties of the fuel. The calorific value is also affected by the moisture content, since high humidity values generate insufficient energy during the drying stage, reducing the evaporation efficiency of the material and energy production in the form of heat (He et al., 2013). Ash negatively influences the calorific value of the biomass, since for every 1% of ash contained in the biomass a reduction of about 0.2 MJ/kg occurs. The AC does not contribute to the generation of heat, although some components of the ashes can act as catalysts in the process of thermal degradation (Loy et al., 2018).

The heating value of fuels is one of the most important parameters for the planning and the control of power plants, and in general for energy production. Early mathematical models relating HHV to the elemental composition have been published for coal and municipal solid waste, and some attempts have been made to do so for biomass as a fuel (Hosseinpour et al., 2018; Parikh et al., 2005). This thesis suggest empirical equations to relate the heating value of plant-base biomass to C, H, N, O, S and the AC content (in mass% of dry material) - corresponding to features $x_1, ..., x_p$, respectively. The dataset reported in the EU 7^{th} Framework Programme (2020), was used to increase the information on the composition of different biomass samples. The selection of the samples of different biomass origin were divided into 6 groups as shown in Table 2.1.

Models for prediction were calculated by PLS regression (Table 2.2). Cross validation of all samples and data divided into calibration (75% of the total data) and validation sets (remaining 25% of the total data) were applied to estimate prediction errors and model selection. The performance of the model was evaluated by the coefficient of multiple determination R^2 and the root mean square error (RMSE) as follows:

$$R_a^2 = 1 - \frac{\sum_{i=1}^{n_a}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n_i}(y_i - \overline{y_i})^2}, \tag{2.1}$$

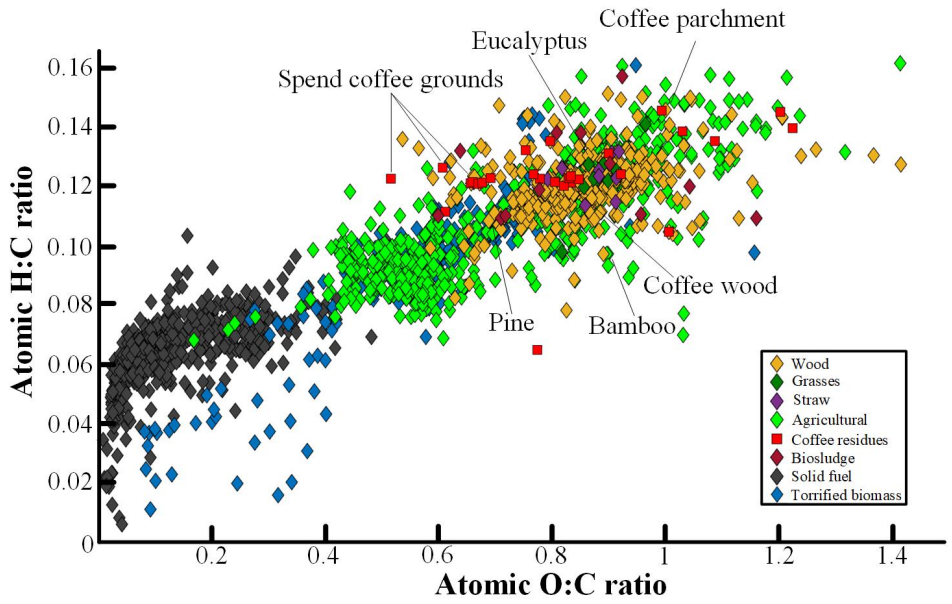


Figure 2.6: Van-Krevelen diagram for different materials.

Table 2.1: Composition (%, w/w) of biomass samples for HHV calibration and prediction.

Properties	Parameters	Biomasses						
		Wood residues	Wood material	Grasses	Agricultural	Food industry waste	Horticultural waste	Coffee residues
	n	162	291	202	114	133	112	122
C	Max	58.02	58.46	54.09	58.70	60.09	49.74	56.02
	Min	47.62	42.42	42.40	42.29	30.06	47.39	44.52
	Mean	52.04	50.42	49.34	50.89	50.07	48.57	51.15
	SD	2.06	1.86	1.55	2.96	5.63	1.18	2.81
H	Max	6.99	8.90	9.13	10.01	9.12	6.44	6.79
	Min	4.85	4.12	4.88	4.80	5.75	6.24	3.53
	Mean	6.05	6.08	6.16	6.35	6.70	6.34	6.19
	SD	0.34	0.43	0.71	0.75	0.77	0.10	0.70
O	Max	46.32	52.51	51.10	49.90	59.71	49.61	48.38
	Min	33.51	34.54	36.93	29.92	24.76	43.17	34.31
	Mean	41.62	42.98	43.31	41.55	40.80	46.39	40.66
	SD	2.36	2.11	2.14	3.53	6.31	3.22	3.77
N	Max	1.70	3.41	4.28	6.42	3.83	1.33	3.54
	Min	0.08	0.02	0.10	0.10	0.25	0.74	0.22
	Mean	0.44	0.38	1.06	1.14	1.44	1.04	1.73
	SD	0.33	0.49	0.86	1.03	0.77	0.29	1.02
S	Max	0.19	17.61	2.21	0.87	1.06	0.30	1.02
	Min	0.01	0.01	0.01	0.01	0.01	0.12	0.03
	Mean	0.05	0.13	0.14	0.15	0.19	0.21	0.28
	SD	0.04	1.03	0.19	0.16	0.22	0.09	0.21
AC	Max	12.42	13.70	22.91	16.20	15.68	9.90	7.39
	Min	0.10	0.02	0.90	0.20	0.20	5.50	0.60
	Mean	3.56	1.65	5.77	4.54	5.77	7.70	3.45
	SD	3.10	2.02	3.36	3.64	3.87	2.20	2.13
HHV	Max	23.21	23.06	21.47	26.75	27.49	19.87	23.77
	Min	17.48	17.33	16.90	15.12	12.58	18.43	16.00
	Mean	20.52	20.02	19.60	20.54	20.78	19.15	18.93
	SD	1.02	0.92	0.75	1.68	2.77	0.72	1.54

$$RMSE_a = \sqrt{\frac{\sum_{i=1}^{n_a}(y_i - \hat{y}_i)^2}{n_a}}, \tag{2.2}$$

where, a refers to calibration c and prediction p.

The best model in Eq. (5) was obtained with the five features C, H, O, S, N. The model accuracy is plotted in Figure 2.7, showing the predicted HHV versus experimental values and

Table 2.2: Equations for fuel HHV (MJ kg^{-1}) calculation

Eq.	$HHV = f(C, H, O, S, N, AC)$	CV 1-out	Calibration		validation	
		$RMSE_{CV}$	$RMSE_c$	R^2_c	$RMSE_p$	R^2_p
(1)	$HHV = -1.142C + 0.014C^2 + 41.222$	1.14	0.84	0.59	0.70	0.46
(2)	$HHV = 0.314C + 0.63H + 0.385$	1.17	0.81	0.77	0.73	0.70
(3)	$HHV = -0.217C + 0.005C^2 + 0.636H + 13.817$	1.38	0.81	0.76	0.75	0.64
(4)	$HHV = 0.326C + 0.738H - 0.015O - 0.237$	1.69	0.82	0.85	0.77	0.68
(5)	$HHV = 0.233C + 0.565H - 0.117O - 0.855S - 0.101N + 10.026$	1.46	0.79	0.85	0.64	0.71
(6)	$HHV = -0.306C + 0.005C^2 - 0.682H + 0.026CH + 0.007N + 20.092$	1.36	0.81	0.76	0.71	0.63
(7)	$HHV = 0.304C + 0.432H - 0.095N - 0.042S + 0.035AC + 2.007$	1.22	0.84	0.68	0.88	0.41
(8)	$HHV = 0.091C - 1.479H - 0.038N - 0.006O + 0.040S + 0.002AC + 12.224$	1.50	0.84	0.85	0.87	0.54
(9)	$HHV = 0.284C + 0.447H - 0.089N - 0.076O - 0.035S + 0.004AC + 6.285$	1.75	0.85	0.84	0.77	0.55

residuals. Factors such as biomass composition and properties related to species, field location, rain and sun exposure, harvesting time, among others, are challenging problems for using chemometrics to obtain accurate model prediction.

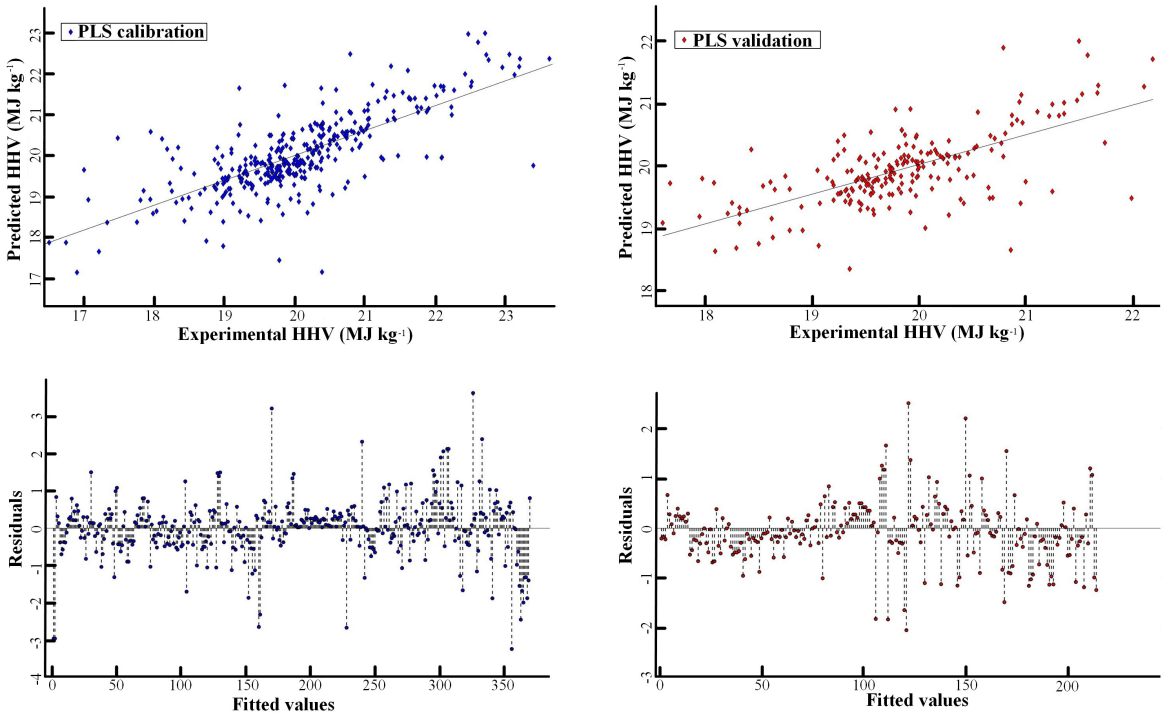


Figure 2.7: Predicted vs. experimental HHV. Calibration and residuals (PLS, model type 5 in Table 2.2) (left), Validation and residuals (right).

The results of the PLS analysis was compared to different equations summarized in Maksimuk et al. (2020) for biomass fuel. The results are showed in Figure 2.8. The calibration and validation data used in this study, together to new data for a total of 1430 biomass samples was combine to determine the best equation fit. Equations proposed by Mendeleev (1897) as the first universal formula for HHV calculation, together with equations proposed by Graboski and Bain (1979), Ebeling and Jenkins (1985), Ozyuguran et al. (2018), Merckel et al. (2019) and Channiwala and Parikh (2002), which reported an average absolute error of 1.45% and bias error of 0.00%, were used to be compared to the one proposed by this study. The highest R^2 was for the Eq. (5) reported in Table 2.1.

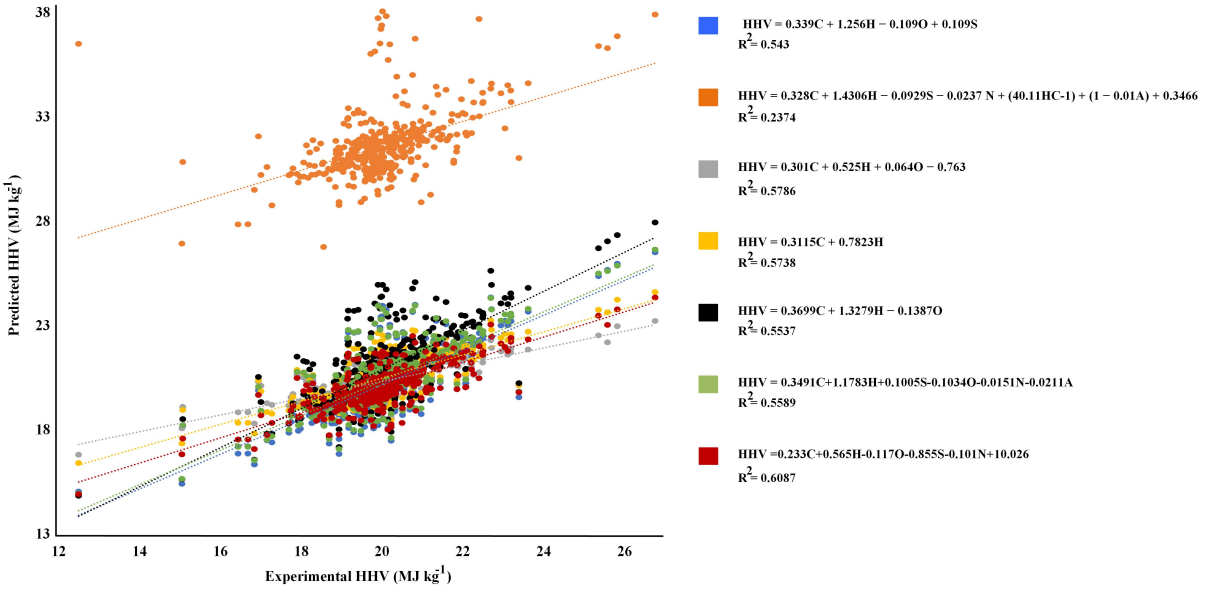


Figure 2.8: Predicted vs. experimental HHV proposed by different studies.

2.2.5 Structural chemical composition

Considering the structural chemical composition, biomass is defined as a complex mixture of natural polymers known as cellulose, hemicellulose, lignin, lipids, proteins, sugars, starch, hydrocarbons, among others. These polymers vary in their concentration depending on the species, tissue type, age and growth conditions. In plant-based biomass, independent of its origin, the structural composition consists mainly of cellulose, hemicellulose, lignin and a smaller amount of extractives and inorganic materials (Basu, 2010). Figure 2.9 shows 115 biomass samples characterized by the contents of the main structural compounds. The first and second principal components account for 58.1 and 23.4% of the total variance, respectively.

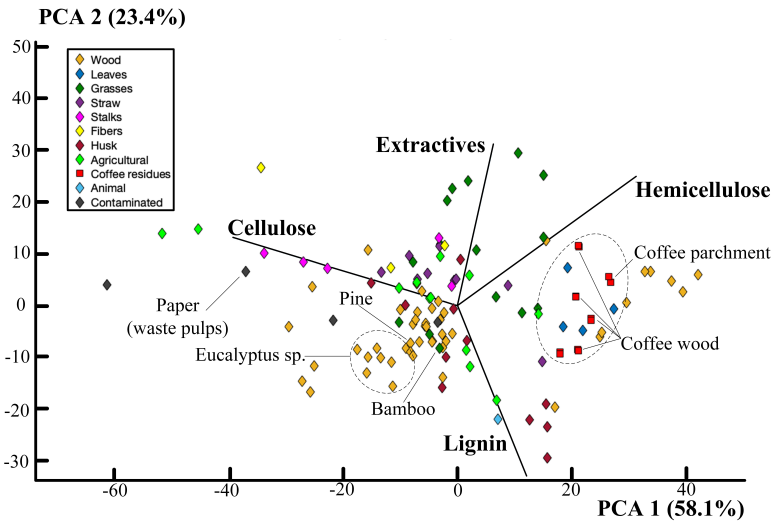


Figure 2.9: PCA score plot for 115 samples characterized by their cellulose, lignin, hemicellulose and extractives composition.

Lignin, cellulose and hemicelluloses are basically constituted of carbon, hydrogen and oxygen. Hemicelluloses (polioses) are the main non-cellulosic polysaccharides present in the biomass. They are generally amorphous polymers with a low molecular weight, formed by several types of sugars, the hexoses: D-glucose, D-manose, D-galactose; and the pentoses: D-xylose and L-arabinose, and smaller amounts of L-D-glucuronic acid,acetic acid, D-galacturonic acid, 1,4-anhydro-D-xylanopyranose and furfural, as well as small fractions of methanol and acetone (Peng et al., 2011).

Cellulose is composed of about 50% carbon, while lignin contains 61-67%. The calorific value of the cellulose is 0.73-0.80 times lower than the lignin, whose value varies between 21-27 MJ / kg. However, it is important to take into account the stability of the polymers in thermal degradation. In the case of cellulose, the main component of the cell wall of plants consisting of a linear high molecular weight polymer composed exclusively of β-D-glucose, it decomposes at temperatures between 260 and 370 °C, where it is relatively stable up to 294 °C and degrades rapidly at 370 °C. This degradation process produces volatile fuels such as acetaldehyde, propenal, methanol, butane- dione and acetic acid, which at the time of biomass burning are heated and exothermic combustion occurs. These low temperature values in which the thermal degradation of the cellulose occurs, identify it as a low yield polymer in some energy conversion processes such as carbonization (Mendoza Martinez et al., 2019a).

Lignin is a macromolecular structure with a three-dimensional, heterogeneous, amorphous and branched structure, with phenylpropane as the basic unit, bonded by ether bonds (C-O-C) and carbon-carbon (C-C) bonds. Lignin has a high resistance to thermal degradation when compared to cellulose and hemicelluloses due to its high aromaticity level, size and structural arrangement (Ghaffar and Fan, 2013). The degradation occurs over a wide temperature range, which, according to some investigations, starts at temperatures from 100 °C to 900 °C (Pecina et al., 1986).

2.3 Conversion pathways for lignocellulosic biomass

The conversion of biomass to energy can involve different routes according to the biomass characteristics. Diverse pre-treatments and conversion technologies, each associated with different process parameters and product yields, are available to create suitable energy carriers between the raw biomass and the final energy use. Figure 2.10 classifies the conversion technologies according to the type of transformation used, biochemical, physiochemical and thermo-chemical:

Biochemical conversion relies on the processes of anaerobic digestion, fermentation, distillation and hydrolysis, in which the feedstock biomass molecules are broken into smaller molecules through the action of bacteria or enzymes (Naik et al., 2010). This type of conversion requires a longer time than the thermochemical routes, but it can be achieved with a smaller amount of external energy. Physicochemical conversion encompasses the densification of biomass into pellets or briquettes (Mendoza Martinez et al., 2019b), as well as physical extraction of oils by compression. This can be followed by esterification, in which the oils react with an alcohol in the presence of a catalyst, to produce biodiesel, for example (Vardon et al., 2013). The thermochemical conversion route involves the use of heat to promote the chemical transformation of biomass into energy and chemical products. In the following sections the

thermochemical and physicochemical conversion routes are described in more detail.

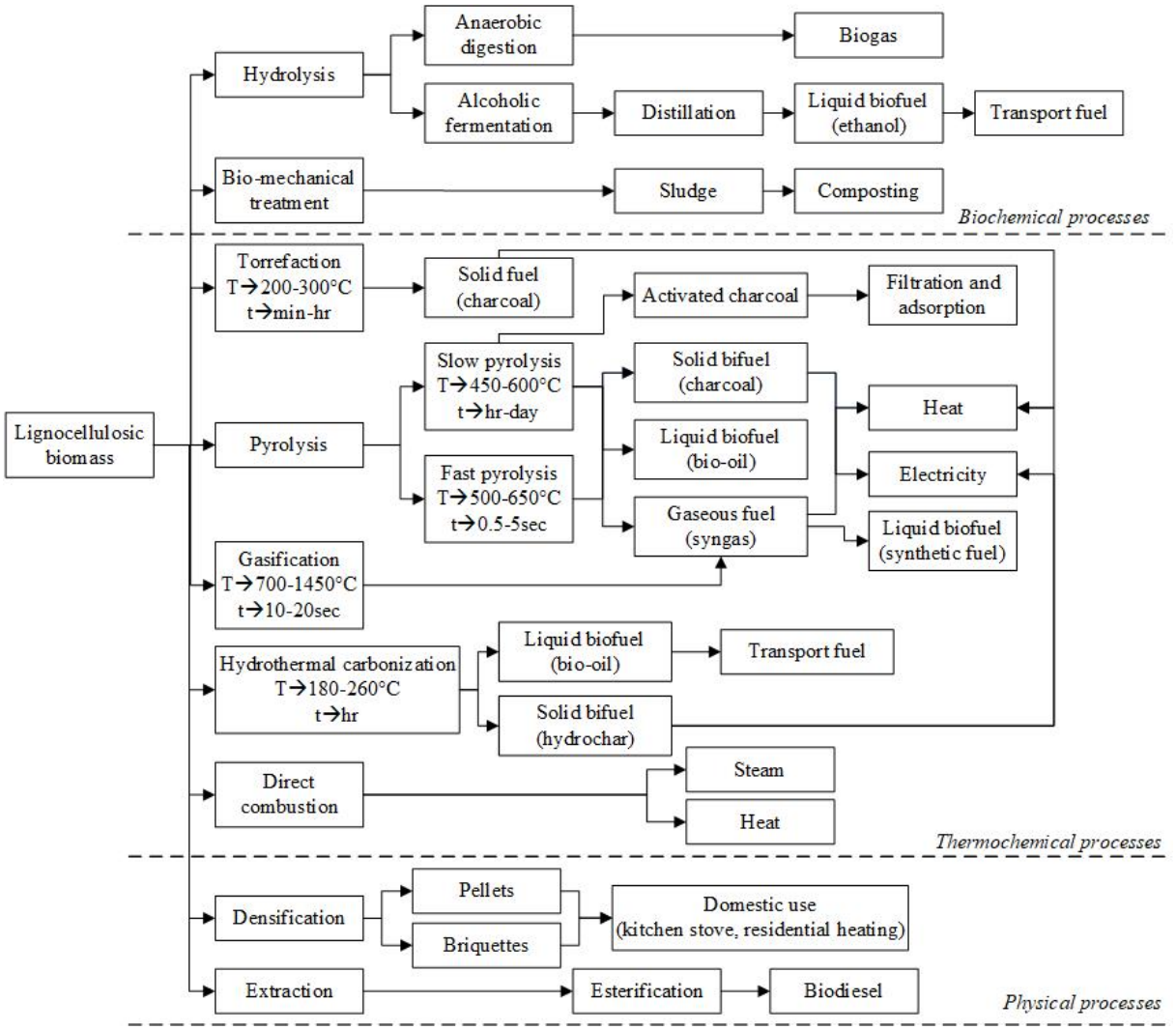


Figure 2.10: Conversion routes of biomass for value-added products generation (Mendoza Martinez et al., 2021a).

2.3.1 Thermochemical conversion

Feedstock preparation is essential in the case of solid biomass for any thermochemical method. The size distribution, particle shape, moisture content, bulk and particle densities, compressive and compact ratio are the main properties considered in the preteatment of lignocellulosic biomass (Pandey et al., 2015). The particle size has a major influence on the degree of flowability, specific mass, porosity, fluid dynamics, terminal velocity and heat and mass transfer rates (Vidal et al., 2011). Smaller particles provide a larger surface area per unit mass, enabling a higher producer gas quality, a reduction in the reactor size or a lower space residence time to achieve a complete cracking of the heaviest and condensable fractions. A smaller particle size in the pyrolysis process in a free fall reactor leads to an increase gas yield and decrease char and tar yields (Mlonka-Medrala et al., 2019). The gasification process, which is mainly controlled

by the reaction kinetics of smaller particles, as the particle size increases, kinetic control gives way to heat transfer control (Hernández et al., 2010).

Drying is also a fundamental pretreatment of feedstock for thermochemical conversion technologies such as pyrolysis, gasification, combustion and torrefaction, and the reduction of moisture yield higher efficiencies. At high fuel/air ratios and high moisture content in gasification processes, the water shift reaction leads to the formation of hydrogen and increase concentration of CO_2. For pyrolysis, the initial moisture content contributes to the water content in the bio-oil and above around 10% moisture, the bio-oil produced will separate into two phases (Oasmaa et al., 2010). Failing to dry the samples will consume energy to vaporize the moisture of the fuel during conversion. For the same reason, dried biomass is usually preferred in thermochemical processes (Mendoza Martinez et al., 2019a). Otherwise, technologies such as hydrothermal carbonization upgrade the biomass in an aqueous environment, thus a high moisture content is desired (Sermyagina et al., 2015a).

Additionally, the basic density influences the combustion behavior and burn-out time, since the presence of voids controls the movement of oxygen inside the feedstock (Rhen et al., 2007). During the thermochemical conversion process, the release of volatiles rich in hydrogen and oxygen, such as water and carbon dioxide will improve the biomass quality as an energy source through an increase in the energy density since more oxygen than carbon is lost in form of volatiles (Rhen et al., 2007). Temperature has highest impact on energy density of thermochemical converted biomass, while the effect of the residence time and moisture is much less expressed. The density of the feedstock also affects the production capacity of the carbonization sites, because for a given volume the use of a denser sample results in greater mass production. During the thermochemical conversion, changes in the basic density of the sample may occur due to changes in the thickness of the wall of the fibers, reduction of the flame or increase in the length of the fibers and in the extractive content (Lu et al., 2008).

After feedstock preparation, the subsequent step is the thermochemical conversion. Diverse technologies for lignocellulosic biomass conversion have been evaluated and commercialized. Figure 2.11 shows the input and output streams of the gasification, torrefaction, pyrolysis, direct combustion and hydrothermal carbonization technologies. In general, the thermochemical conversion of biomass refers to the use of elevated temperatures to produce new improved energy carrier products and/or heat. A variety of process parameters can be utilized depending on the desired products as shown in Table 2.3. In addition, characteristics of the feedstock affect the process performance to a great extent. A comprehensive assessment of both the chemical and physical properties of biomass is essential for the evaluation of the potential of certain biomass feedstock with respect to the considered methods.

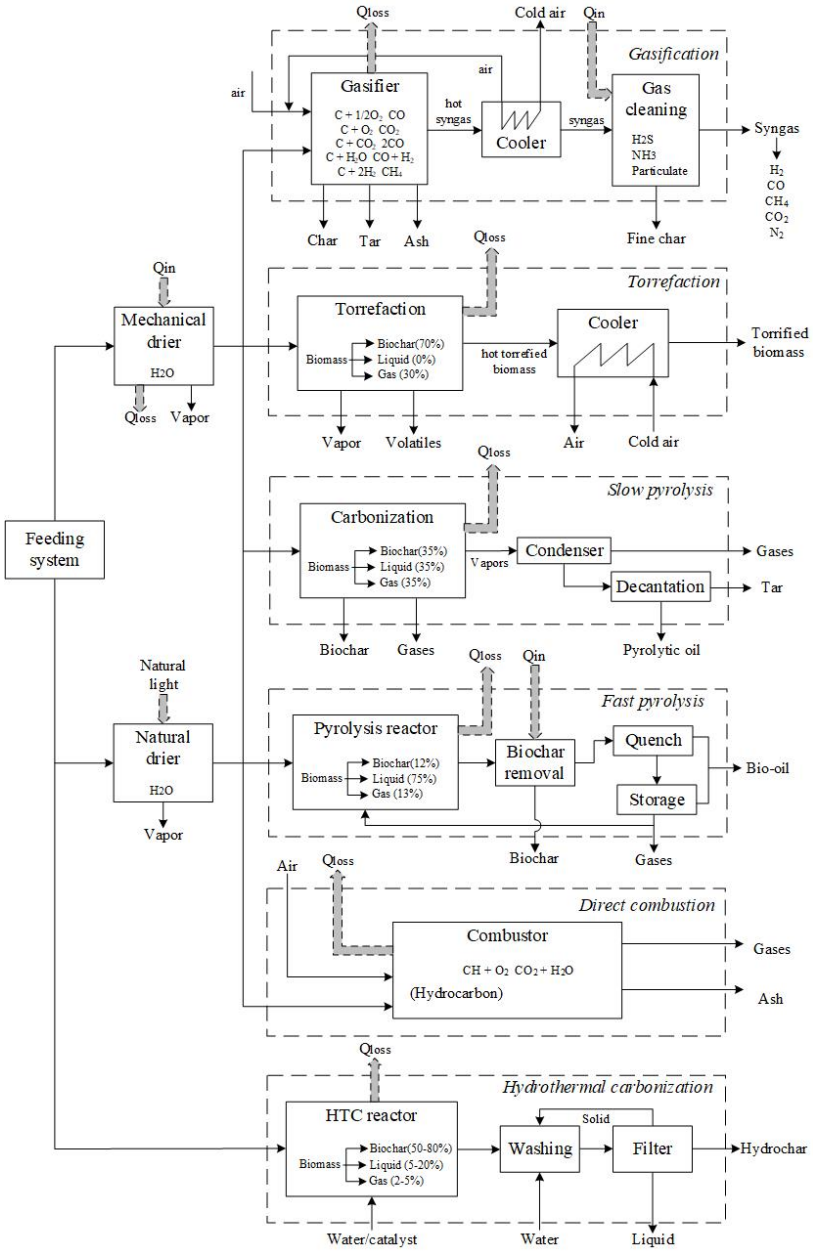


Figure 2.11: The flow balance of thermochemical conversion technologies (Mendoza Martinez et al., 2021a).

Table 2.3: Thermochemical processes operation conditions, reaction mechanism, main products and technology feasibility.

Technology	Operation conditions	Reaction mechanism	Products	Technology feasibility
Direct combustion	Oxidizing agent greater than stoichiometric supply of oxygen; Temperature range 800°C to 1200°C; Carbon conversion >99%	The combustion begins with a drying stage followed by volatilization. The process is defined as an exothermal reaction between the fuel and oxygen. The goal of the process is near-total combustion conversion of biomass into H_2O and CO_2, with minimal loss of heat value with unburnt carbon and gaseous hydrocarbons.	Heat and flue gas.	The most widely used thermochemical conversion route. The scale of equipment can vary from domestic stoves to industrial boilers of several hundred megawatts. Low moisture content biomasses with high calorific value are suitable for grate-fired or, if the fuel is sufficiently brittle and grindable, pulverized combustion, while fluidized bed combustion permits the use of high-moisture, low or mixed quality biomasses.
Gasification	Takes place at 700-1450°C in the presence of a controlled amount of oxidizing agent; carbon conversion 80-95%; drying necessary. Yields: 5% L, 10% S and 85% G.	Process aims to produce high yields of syngas containing mainly H_2,CO, CH_4, CO_2, H_2O, N_2 and tar. The gasifying medium can be air, oxygen or steam, or a combination of them. The process involves drying, pyrolysis and tar cracking.	Combustible syngas and heat.	Mature technology of biomass conversion into heat and power, already commercialized. Gasification requires higher temperatures leading to high energy consumption to operate. Tar cracking in particular is an important consideration, as the production of tars not only reduces the gas yield, but also poses additional problems in the form of equipment fouling and environmental pollution.
Fast pyrolysis	Moderate temperature 450-500°C; short hot vapor residence time 1s; absence of oxygen. Moisture of the feedstock is a limiting factor. Short residence time necessitates small particle size yields: 75% L, 12% S and 13% G.	High heating rates to moderate temperatures followed by rapid cooling promote higher fractions of liquid products. Primary reactions occur through the adsorption of thermal energy during pyrolytic process, leading to the breakdown of the weak bonds, followed by depolymerization of the lignocellulosic chemical structures.	Main product bio-oil. Combustible gas and bio-char are also produced.	Biomass is heated so rapidly that it reaches maximum operating temperature peak before decomposition. The short residence time also contributes to non-formation of non-condensable gaseous products, preventing thermal and catalytic fragmentation of the vapors, and minimization of charcoal formation.
Slow pyrolysis	The process involves long residence times, hours up to several days, in an inert atmosphere at temperatures of 450-600°C; yields: 30% L, 35% S and 35% G.	The residues are initially dried for several days prior to feeding into a pyrolysis reactor, then the material is heated above decomposition temperature, breaking chemical bonds in the lignocellulosic material structure. Up to 100-600°C decomposition of sugars, cellulose, lignin and other compounds occur. Solid mineral residue (ash) remains once combustion of the carbonaceous residues is complete.	Main product bio-char. Condensable and non-condensable gases are also produced.	The heating rate has a direct influence on the porosity of the charcoal. In general, micropores are favored by slow heating, while high rates benefit macroporosity, due to the rapid exit of volatiles. Ashes retain hazardous constituents and metals, requiring subsequent treatment and controlled disposal.
Torrefaction	Takes place at relative low temperatures between 180-300°C; atmospheric pressure in the absence of oxygen, with residence times from 30 min to a couple of hours. Yields: 0% L, 80% S and 20% G.	Torrefaction produces a gas-phase mixture consisting of significant fractions of CO_2, CO, H_2O, vapor, H_2, CH_4 and organic compounds (e.g. acetic and formic acids), while the remaining solids are the main resulting product. The ratio of CO_2 to CO decreases with reaction time, leading to the formation of CO during secondary reaction of CO_2 and H_2O with porous char.	Main product bio-char. Fuel gas also produced.	The released torrefaction gas can be combusted to cover a part of process heat requirements. Torrefaction does not reduce corrosive deposits on boiler tubes (all ash components of biomass are still in the sample). Torrefaction improves transport, handling and storage of the biomass due to higher bulk and energy density, homogeneity and hydrophobic properties when compared to the raw materials.
Hydrothermal carbonization	The process occurs in an aqueous environment at relatively low temperatures, usually in the range of 180-260°C, in a closed system under autogenous pressures of 1–5 MPa, long residence time (hours) and external heat supply; drying unnecessary. Yields: 5-20% L (dissolved in process water, TOC), 50-80% S and 2-5% G.	The process takes place in a aqueous medium, the organic compounds remain dissolved in the liquid. The HTC technology involves a complex sequence of reactions (dehydration, decarboxylation, and hydrogenation of functional groups, etc.). At high temperatures (260°C), the exothermic reactions of sugars such as monosaccharides will dominate the process.	Hydrochar, aqueous coproducts and reaction water as main products. Non-condensable gases are also produced.	Technology with significant potential in upgrading materials with a high moisture content without preliminary drying. Hydrochar typically holds 55 to 90% of the initial mass of the feedstock and 80 to 95% of its energy content. The process removes alkali and alkaline metals from the biomass, unlike dry torrefaction. Due to the relative novelty of the technology detailed reaction mechanisms for different feedstocks are not fully understood, only a few comprehensive reports have been published.

L-liquid; G-gas; S-solid.
References:Tillman (2000); Overend (2009); Demirbas (2007); Basu (2010); Bridgwater (1999, 2012); Williams and Besler (1996); Van der Stelt et al. (2011); Chen et al. (2015); Funke and Ziegler (2010); Libra et al. (2011); Reza et al. (2014)

2.3.2 Physicochemical conversion routes

The densification of residues in the form of briquettes and pellets contributes to high volumetric concentrations of energy, improving the handling and reducing the volume and resulting storage and transport costs (dos Santos et al., 2015). This solid fuel is widely used for any type of thermal application such as steam generation in boilers, heating, drying, food processing industries, brick making units and gasifier systems (Lubwama and Yiga, 2018). Currently, the high demand for briquettes and pellets is driven, significantly by governmental policies and incentives. The EU as the main consumer, accounted for 80% the global biomass briquette market and reported around 20 million tons of wood pellet production, since the solid fuel is used also in non-industrial environments, such as domestic heating and commercial boilers, on a small scale (FAO, 2020).

The briquette is one of the cleanest and most environmentally friendly solid fuel on the market today. Its emissions of nitrogen and volatile organic compounds are lower than the feedstock. Likewise, the moisture content and CO_2 released, when under thermochemical conversion processes, are also significantly reduced, improving the efficiency of the transformation. Briquettes are generally produced in a piston (mechanical or hydraulic) press by applying load on a die to biomass particles. Additional binder and heat treatment can be applied depending on the properties of the feedstock. Generally, the densification is carried out at high pressures in the order of 1200 Psi, which causes an increase in the process temperature, usually in the range of 100-140 °C, causing the "plastification" of lignin, that acts as an agglomerating element, which is strongly influenced by the humidity of the material, which is typically between 8-15% (Mendoza Martinez et al., 2019b).

Agro-forestry residues are the more commonly used for the formation of briquettes and are generally compacted in the order of 5 times. A notable advantage in the use of briquettes is the reduction of time in the production of fuels and the implementation of residual raw material, thus reducing the rate of deforestation (Pallavi et al., 2013). Several studies have evaluated the diversity of agro-forest waste as by-products for briquetting, such as, rice residues (Yank et al., 2016; Lubwama and Yiga, 2018); rice and coffee husks briquettes for domestic cooking applications (Amaya et al., 2007); production of activated carbon briquettes from rice husks and eucalyptus wood (Muazu and Stegemann, 2015), coffee-pine wood briquettes as an alternative fuel for local firing systems in Brazil (Mendoza Martinez et al., 2019b), explained in **Publication IV**. This rational use of biomass tends to promote the development of less economically favored regions, through the creation of jobs and reduction of external energy dependence, based on local availability (dos Santos et al., 2015).

In order to produce good quality briquettes/pellets, the pretreatment of the feedstock plays a fundamental role. The particle size, moisture content, apparent density, use of binders and process variables such as the pressure and temperature are parameters that need to be measured and controlled. The feedstock should be composed of a mixture of particles of various sizes, where the maximum particle size must not exceed 25% of the equipment matrix, and the percentage of powder component (<4 mesh) must be in the range of 10 - 20% (Grover and Mishra, 1996). The presence of particles of different sizes improves the mechanical behavior, contributing to the high strength of the product (Vidal et al., 2011). The final density of the solid fuel is also affected by the particle size, higher density and less compaction forces can be reached with a small particle size. However, this can lead to low porosity in the solid fuel, as well as mass transfer during drying, devolatilization and combustion (Hernández et al., 2010).

The moisture content also highly influences the manufacture of briquettes/pellets. The presence of water favors heat transfer, promoting the softening of lignin and, consequently, the connection between particles (Grover and Mishra, 1996). Depending also on the type of feedstock and compaction process, an adequate moisture range is typically 8 - 12%. According to Grover and Mishra (1996), this moisture content, briquettes/pellets are generally resistant and free from cracks. On the other hand, very dry material affects the particles' connections, which impairs the briquette's stability and resistance. Moisture percentages that exceed 15% must go through a drying process, otherwise they may compromise the efficiency of combustion process of the briquettes due to possible explosions due to the formation of water vapor inside the interstices (Yaman et al., 2000). The high density of the feedstock is also not attractive due to little gains in densification, and low density biomasses demand greater energy for their adequate compaction. Therefore, a possible solution is a mixture of biomasses that increase the energetic and mechanical characteristics of the briquette, taking into account proportions that produce a lower percentage of ash and pollutant gas emissions in the thermochemical conversion processes. Pressure is another relevant factor in the final properties of the product which is responsible for the compaction and transfer of energy between the particles. The internal and external friction caused by the pressure, produces heating in the material which increases the process temperature.

3 Energy potential of residual biomass

3.1 The effect of biomass for energy applications

In order to achieve efficient utilization of biomass, the most appropriate characteristics according to the final application, need to be selected. This section of the thesis evaluates the main parameters which influence the residual biomass in the coffee production chain for energy purposes. The concern for the increase of coffee bean productivity has ignored the variation of the residues provided by the coffee production chain. Additionally, little or only partial information currently exist in the literature. The obtained results reported in **Publication I** and **Publication II** can be used for the evaluation of the applicability of coffee residues for various energy production pathways.

Based on a chemical and thermal characterization analysis and the available data on different treatment technologies, the characterization parameters obtained for coffee solid residues, the effects of the properties of biomasses evaluated in diverse conversion routes, as well as their impact on operational and economic parameters are summarized as follows (Mendoza Martinez et al., 2019a):

- The high moisture content of coffee pulp would be a drawback for most of the thermochemical conversion routes except for HTC, since a large amount of energy would have to be spent on water evaporation. The high ash content is also a drawback that may cause sintering at high temperatures. The high fractions of cellulose, hemicellulose and phenolic compounds in the chemical composition of the pulp are a favorable for obtaining bioethanol, proteins, enzymes, vitamins, amino acids, lactic acid and acetic acid through hydrolysis and biodegradation (Mussatto et al., 2011).

- For combustion, biomass with a high basic density (> 500 kg·m^{-3}) results in more concentrated fuel energy, due to the greater mass of the fuel contained in the same unit volume (Obernberger and Thek, 2004). Thus, coffee wood is a desirable material for charcoal production. Moreover, a high charcoal density can be achieved, resulting in greater strength and higher energy per volume.

- The coffee wood shrub holds a high economic potential for energy applications. The low moisture content means low transport and storage costs (Hamelinck et al., 2005). Additionally, the energy consumption in the drying stage when subjected to processes such as gasification, combustion and pyrolysis, is low.

- For the production of bio-oil in a fast pyrolysis process, the biomass is subjected to high temperatures and short vapor residence time. High ash content generates secondary vapor cracking, reducing the bio-oil quality and liquid yield. However, the presence of inorganic components such as potassium favors the formation of charcoal (Rocha et al., 2015). As a result, leaves from the coffee shrub and parchment of the coffee cherry are desirable biomasses for the fast pyrolysis process.

- During combustion, sulfur is converted into H_2S and SO_2, which are strong sources of contamination. The leaves of the coffee shrub are poor in the respect the high content of sulfur.

Moreover, high nitrogen contents have also been reported for coffee leaves, resulting in the formation of nitrous oxides.

- A drawback of coffee parchment as a biochar feedstock is the ash content. The ash not only reduces the heating value, but alkali metals and chlorine can be problematic due to the formation of alkali chlorides. These can cause agglomeration, fouling, and corrosion in high-temperature processes such as gasification and combustion.

- Hydrothermal carbonization can be an attractive solution to turn raw coffee parchment into a valuable product, i.e. soil conditioner, activated carbon or an adsorbent agent. Further analysis of coffee cherry parchment HTC products should be performed.

- Some characteristics of the husks obtained in the coffee dry treatment route are suitable for thermochemical and physicochemical conversion. The high content of polysaccharides, proteins and minerals can also make them suitable as a substrate support in the fermentation process for the extraction of compounds for the food and pharmaceutical industries, in addition as a material for composting applications. Value-added applications of coffee husks are already commercialized, mainly in bioprocessing, detoxification and vermicomposting.

- Spent coffee grounds include large amounts of carbon with a low ash content, which are factors that contribute to the production of fuels with a high calorific value through thermochemical conversions. Additional advantages of SCG for energetic conversion are the high heating value and low sulfur and nitrogen content. The high content of volatile matter in SCG involves a large number of compounds that can be devolatilized, which increases the ignition speed of the feedstock. Moreover, their high lignin and low extractive content indicate a potential application in physical processes such as the production of briquettes/pellets.

- The phenolic and organic compounds in the chemical composition of the SCG, such as lipids improves extraction and hydrolysis processes, which is an advantage for biochemical and physical conversion routes. Among the applications, SCG is used as raw material for the production of bio-oil and biochar by slow pyrolysis, biogas through anaerobic co-digestion, solid fuel for direct combustion in boilers, bio-alcohol by fermentation, biodiesel production through transesterification, biofuels, biopolymers, antioxidants and biocomposites. Additionally, SCG also has other applications such as fertilizer in the agro-industry, production of activated carbon, animal feed and as an adsorbent.

- The residues in the coffee production chain consists of desirable materials for densification processes, especially coffee parchment, wood and spent coffee grounds due to the relative high lignin content, that promotes agglomeration (Obernberger and Thek, 2010). Briquettes increase the energy density of waste materials and reduce storage and transportation, which are desirable factors for the energy industry.

3.2 Hydrothermal carbonization of agro-forest residues

Due to the relative novelty of HTC technology, detailed reaction mechanisms for different feedstocks during HTC are not completely understood yet and only a few reports have been

published. Even fewer studies have investigated the properties of the HTC liquor, which contains valuable substances such as organic acids, furans and phenols that can be used for various industrial applications (Hoekman et al., 2013; Eseyin and Steele, 2015). Recent studies have mainly focused on the effects of HTC operational parameters on mass and energy yields and hydrochar characteristics. Differences in biomass composition also result in significant variations in the decomposition behaviour during the HTC treatment.

In general, the carbonaceous structure of hydrochar becomes more stable and compact compared to the feedstock. Aromatic functional groups, and C-C and C-O bonds gradually increase during the thermal degradation (Wang et al., 2020). Characteristics such as the ignition energy, reactivity, heating value and morphological structure, and therefore, potential uses of the final product, depend also on the composition of the feedstock material. Results of studies on HTC process have been published for rice hulls and sugar cane bagasse (Hoekman et al., 2013), agricultural residues (Oliveira et al., 2013), wheat straw (Funke et al., 2013), food waste and packing materials (Li et al., 2013), municipal solid waste (Berge et al., 2011), coconut fiber and eucalyptus leaves (Liu and Balasubramanian, 2012), microalgae (Heilmann et al., 2010), cellulose (Sevilla and Fuertes, 2009), bamboo (Schneider et al., 2011), eucalyptus (Sevilla et al., 2011), among others. Pilot plants are still being tested, while a few industrial-scale plants have already been built, mainly for wastewater treatment.

This section aims to characterize HTC chars and HTC liquors resulting from the hydrothermal carbonization of several globally important widely unused woody and non-woody waste biomasses as reported in **Publication III**. Then, the section provides evidence of the coffee residues potential as a fuel with enhanced properties due to the HTC process. Laboratory scale experiments were performed to determined the morphological, chemical and physical characterization of the obtained HTC products at different temperatures. Then, two different industrial-scale HTC plants, a stand-alone plant and one integrated to a small biomass-fired power plant, were simulated in order to analyze the potential of HTC treatment as an attractive process for biorefinery using biomass residues. The integration of two processes utilizing the same feedstock can often bring advantages in terms of efficiency improvement, process simplification, and cost savings.

3.2.1 HTC experiments

Hydrothermal carbonization of selected lignocellulosic biomasses, coffee parchment (CP), coffee wood (CW), eucalyptus wood (EW), and giant bamboo (GB) were performed in the laboratory facilities of LUT University of Technology, Finland, in four main stages: feedstock preparation and characterization, HTC treatment, liquid-solid separation and product characterization. The experimental procedure is presented in Fig. 3.1, the parameter details are explained in **Publication III**.

The experimental results showed that HTC produced a hydrochar with improved energy carrier properties compared to the raw feedstock. As the HTC temperature increases, the high heating value and fixed carbon increase, while reducing the volatile matter, and the ashes become partially dissolved into the liquid phase; this all combines to improve the characteristics of the hydrochar as a solid biofuel. The gradual increase of HHV with the increasing temperature, demonstrated the energetic improvement of hydrochar due to the processes of chemical

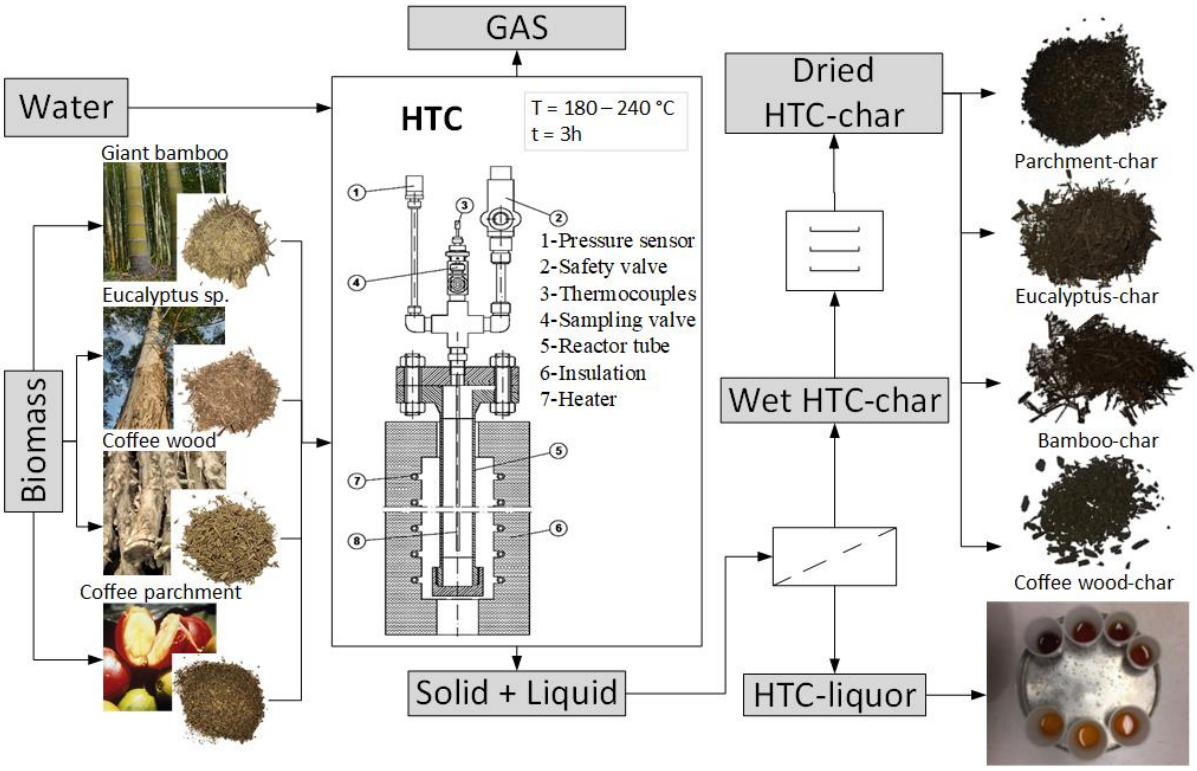


Figure 3.1: HTC experimental unit (Mendoza Martinez et al., 2021b).

dehydration and decarboxylation. Devolatilization/depolymerization processes also took place during HTC, increasing the carbon concentration, observed in the fixed carbon content of the different treated samples. Biomass degradation also occurred in the structural composition of the samples, due to the release of low molecular weight products from the hemicelluloses, cellulose and lignin chains, as well as slight disintegration of water extractives at low temperatures (250 °C). The changes in the VM and FC contents were less with coffee residues than with eucalyptus wood (EW) and giant bamboo (GB) as shown in Figure 3.2. This indicates that eucalyptus and bamboo samples are more susceptible to thermal degradation, requiring less time for a thermochemical conversion, while coffee residues are more stable for HTC process conditions, probably due to differences in chemical-structural composition.

The removal of inorganics from the feedstock after the HTC process was efficient, because the inorganics became partially dissolved in the liquid phase (Reza et al., 2013). This phenomenon was more evident during the HTC conversion process of coffee residues, which showed a significant reduction of 75% for CP and 56% for CW for $HTC_{240°C}$ in comparison to the raw feedstock. Slight AC increases, were also observed, probably associated with the precipitation of minerals in the ash while the temperature increased (Gao et al., 2016). Some inorganic compounds may be organically bound, form insoluble salts, adsorbed on the hydrochar, or dissolved in liquid but remain in the hydrochar during thermal drying. The ash content is also related to the reactivity of the samples due to the deposition of inorganic compounds on the sample surface, contributing to the hydrochar from higher HTC temperature being more reactive than its lower HTC temperature counterpart.

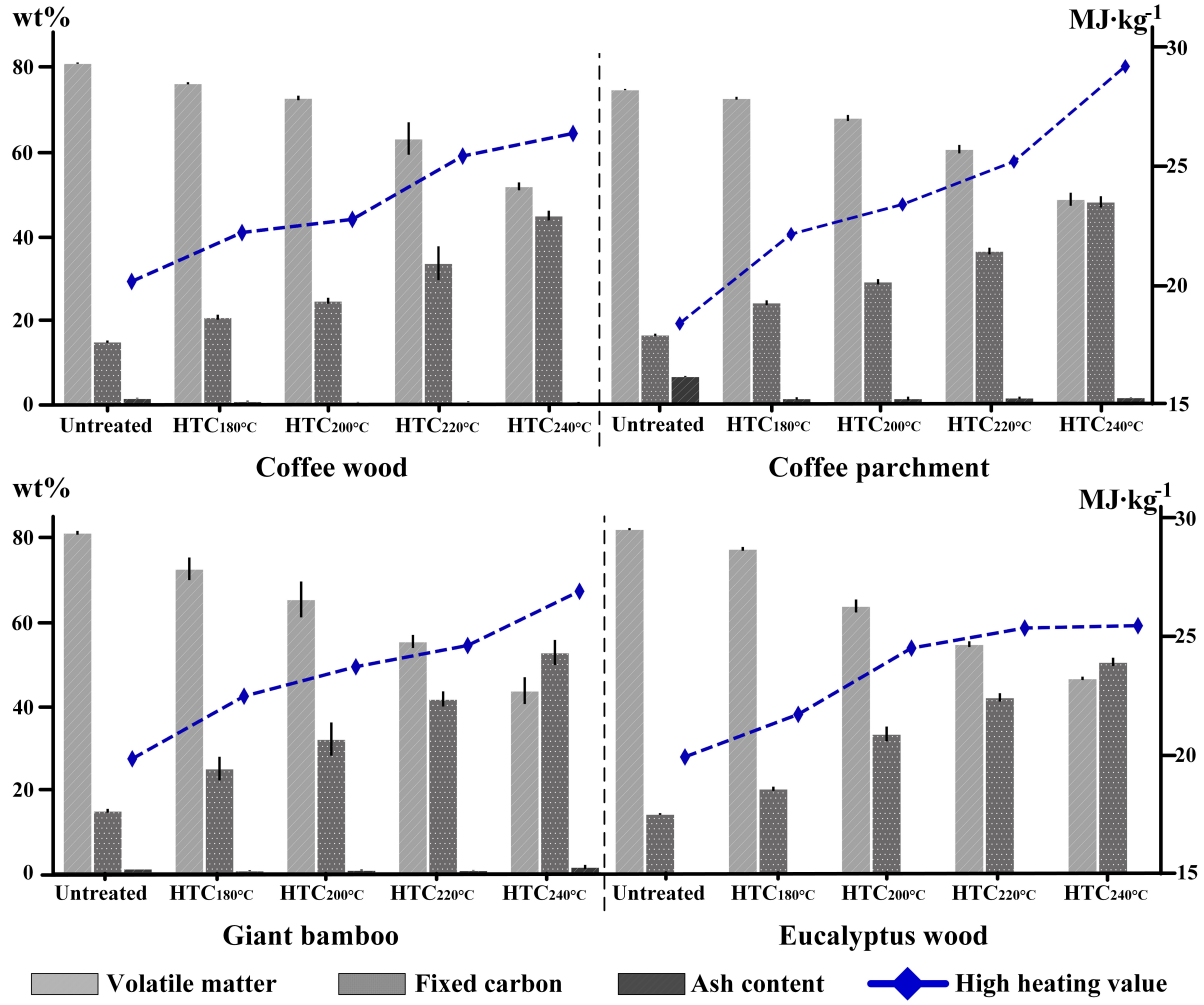


Figure 3.2: Chemical analysis of feedstock and hydrochar samples.

3.2.2 Temperature effect on mass and energy yield

To extent of the feedstock decomposition during pre-treatment process can be evaluated with the mass yield (MY) and energy yield (EY), defined by Eq. (3.1) and Eq. (3.2), respectively.

$$MY = \frac{(Mass_{hydrochar})_{db}}{(Mass_{feedstock})_{db}} \cdot 100\% \tag{3.1}$$

$$EY = (MY) \cdot EDF \tag{3.2}$$

where, the energy density factor (EDF) is defined by Eq. (3.3).

$$EDF = \left(\frac{HHV_{hc}}{HHV_b}\right)_{daf} \tag{3.3}$$

The experimental results described the dependence of MY and EY on the temperature. A regression model (Eq. 3.4) was created and analyzed in order to explained the percentage of variation for all four feedstocks. The coefficients and corresponding R-squared values are described in Figure 3.3.

$$Y = 100 - a(T - b)^c \tag{3.4}$$

The mass yields obtained for the biomasses were considered satisfactory in comparison to previous findings. For example, the hydrochar yield obtained for Eucalyptus sp. did not exceed 46.4% (conditions at 220-300 °C for 0.5-10 h) (Gao et al., 2016), while MY values of approximately 50-71% were found for wood samples (Hoekman et al., 2013), which are values supported by pine wood studies (Sermyagina et al., 2015a). For agricultural residues such as sugarcane bagasse, corn stover and rice hulls, MY values of 36-72% at HTC temperatures of 200-300 °C have been reported (Hoekman et al., 2013). Similar trends of an MY decrease with an increasing temperature were observed in this research (Figure 3.3)

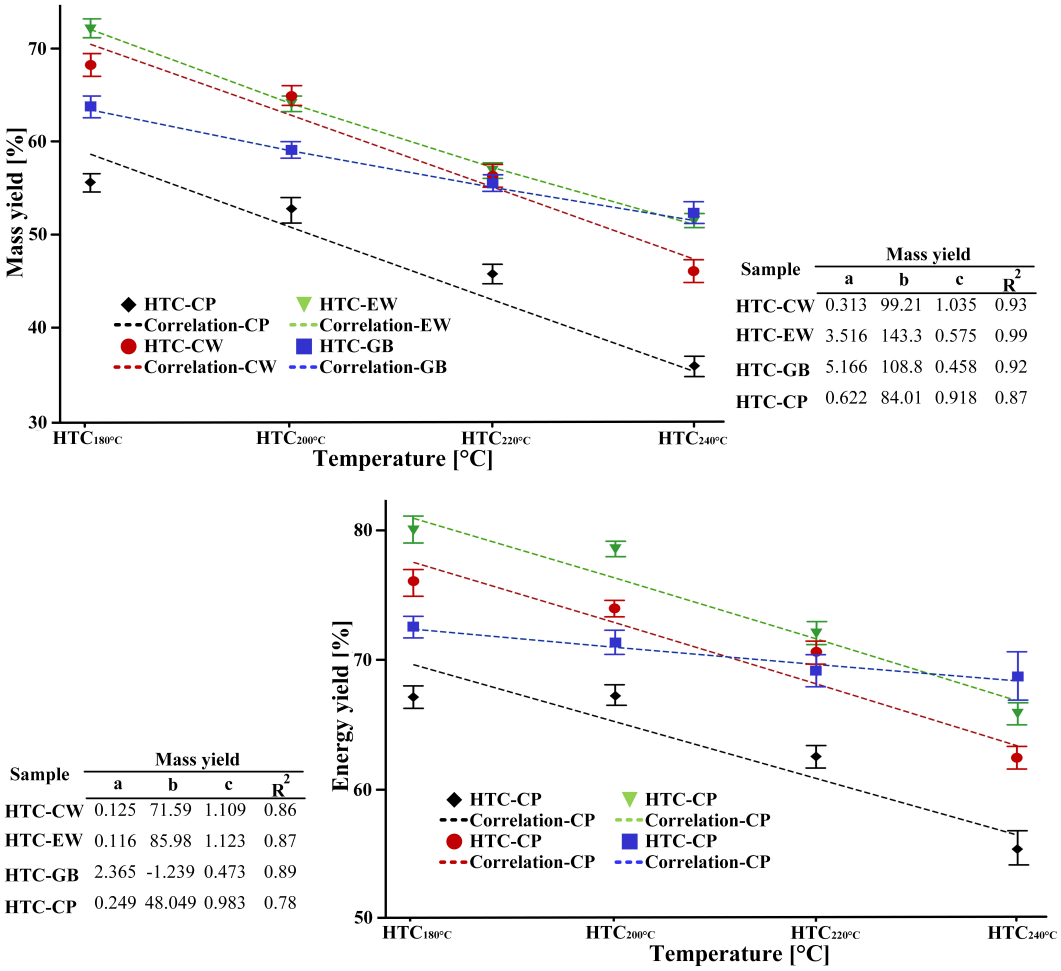


Figure 3.3: Temperature effect on mass and energy yield. Hydrochar from CW, eucalyptus wood (EW), giant bamboo (GB), CP.

The mass yield reduction is connected to the deoxygenating reactions and volatiles conversion, as the hydrogen and oxygen contents become lower at higher temperatures. For all four biomasses, increasing the temperature in the range of 180-240 °C increased the mass loss, from 45% to 66%, 32% to 54%, 28% to 48%, and 36% to 48% for CP, CW, EW and GB, respectively. The energy yield EY of the process is a product of two factors: the mass yield and energy densification (relative increase of heating value).

The total EY within the studied HTC temperature resulted in values ranging from 61-79% for woody biomass and 54-69% for CP. The energy yields indicate solid matter energy content reductions of 31% to 45%, 25% to 39%, 21% to 34% and 27% to 31% for CP, WC, EW, and GB samples, respectively. The results are consistent with literature reports for woody biomass (66-85%) (Sermyagina et al., 2015a; Hoekman et al., 2013) and agricultural residues

(56-78%) (Hoekman et al., 2013). The type of biomass influenced the yield distribution. Woody biomass produces more solid matter, and consequently less tar, water and gas, than agricultural residues. This finding is in qualitative agreement with previous studies, where higher energy and solid yields from wood residues were attributed to higher lignin content and lower amounts of anhydrosugars and inorganics (Singh et al., 2015).

3.2.3 Morphological structure analysis

Morphological transitions of the biomasses under different HTC temperature conditions are shown in Figure 3.4. As expected, the shapes, arrangement of the pores and their radii, and the fibers of the samples were all modified during the HTC treatment. Surface changes are associated with the reduction in organic compounds and volatilization, which results in the formation of the hydrochar matrix (Cantrell et al., 2012). The feedstock samples displayed a typical cellular structure of a lignocellulosic biomass with continuous smooth thick surfaces. As a consequence of the HTC treatment, the lignocellulosic structure ruptured into small fragments, due to the presence of easily decomposable polymers such as hemicelluloses in the samples. Protuberances in the hydrochar, which are likely to be cell wall changes caused by thermal degradation, can also be observed. Literature reports indicate that at high temperatures the dissolution of anhydrosugars followed by polymerization of monomers and fragments in the liquid phase can result in the formation of carbonaceous spheres on the hydrochar surface (Xiao et al., 2018). These are known as secondary hydrochar. The number of heterogeneous fragments increases as the temperature is increased, and for the same temperature, new microsphere structures and pores are formed on the hydrochar surface. When the cellulose and hemicellulose contents of the biomass are high, the hydrochar becomes more fragmented, and the presence of carbonaceous microspheres, esters and hydroxyl groups on the hydrochar surface increases (Xiao et al., 2018).

The porosity increases due to gas emissions from volatile matter, fragmentation of biomass composition (Gao et al., 2016) and reduction of the parenchyma cells. The parenchyma cells have thin primary walls and are easily degraded by temperature (Krigstin and Wetzel, 2016). The higher porosity can be explained by the difficulty of dissolving and dispersing lignin and cellulose into the aqueous phase at low temperatures. In summary, the formation of hydrochar can be described as a conversion of non-dissolved lignin and/or cellulose and dissolved fragments through homogeneous hydrocarbonization (Gao et al., 2016). It can be seen that the fibres were the most affected cells during the hydrocarbonization and changes in the cell walls were easily discernible. As the temperature increased, the reduction in the cell wall thickness of the fibers increased. The fibers exhibited a glassy and brittle appearance after hydrocarbonization, which was also observed by Yildiz and Gümüşkaya (2007).

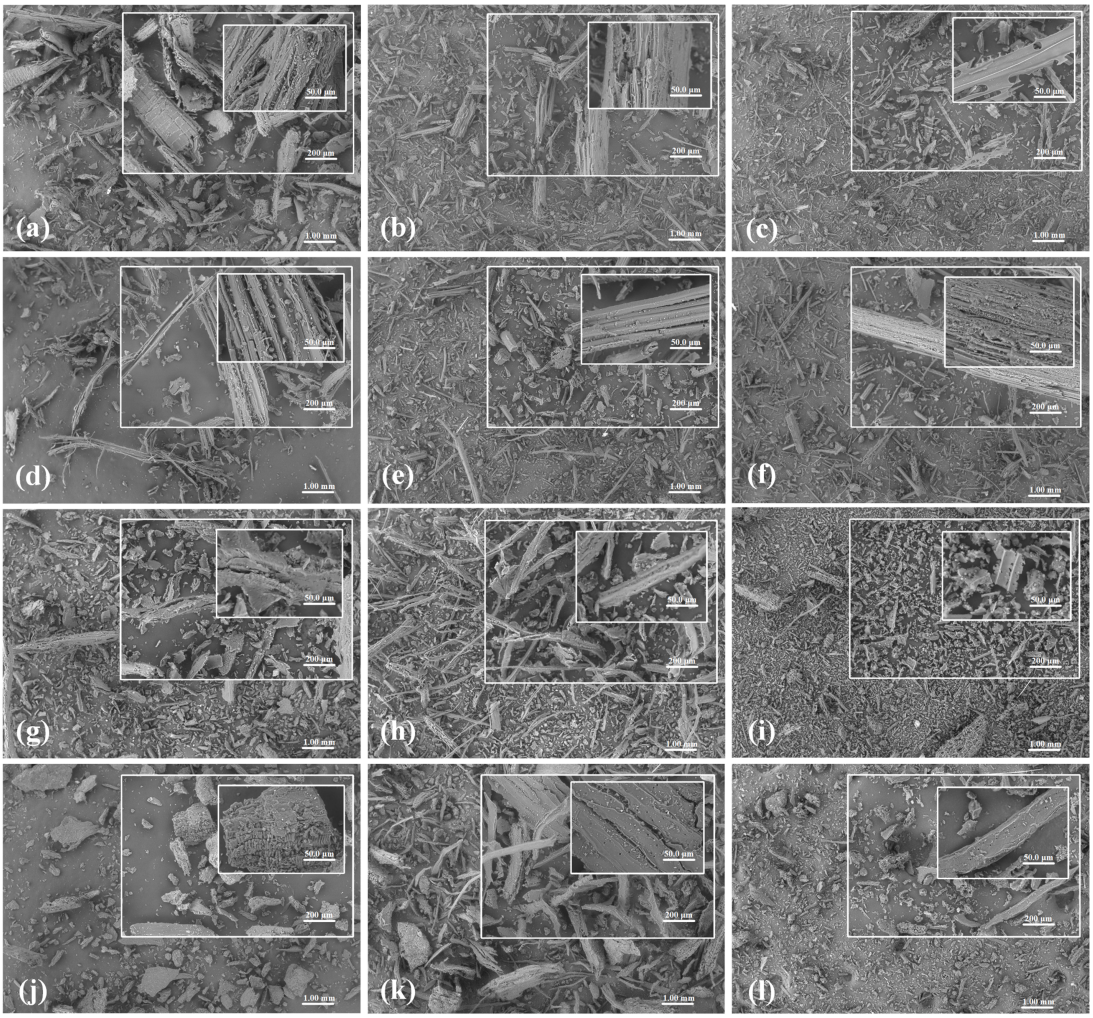


Figure 3.4: SEM images of eucalyptus sp.: (a) raw, (b) HTC180ºC and (c) HTC240ºC; bamboo: (d) raw, (e) HTC180ºC and (f) HTC240ºC; coffee wood: (g) raw, (h) HTC180ºC and (i) HTC240ºC; coffee cherry parchment: (j) raw, (k) HTC180ºC and (l) HTC240ºC. (Mendoza Martinez et al., 2021b)

3.2.4 Integration of HTC process and a CHP plant

Several studies have evaluated different integration possibilities of biomass conversion processes with other industrial cycles, forming so-called polygeneration systems. Combined heat and power (CHP) plants are an efficient proven technology. The integration of a sawmill with a pellet plant and a CHP plant in Anderson and Toffolo (2013) reported that thermal energy and electricity produced in the CHP by burning part of the sawmill biomass output can be used for the heat and power requirements of the other two industries. Sermyagina et al. (2015b) found for the integration of a torrefaction and CHP plant, that the boiler capacity in CHP could cover the torrefaction heat demand and simultaneously increase the electricity generation. Additionally, an economic evaluation has proved that the combined plant can be profitable at certain price relations between biomass and fossil fuels in a short-time perspective (Saari et al., 2016; Tsupari et al., 2016).

Different plant configurations and operating schemes were considered, including stand-

alone, and integration to the steam cycle of either a small biomass-fired condensing power plant, or the CHP plant of a large kraft pulp mill. The HTC process requires heating and pressurizing a large mass of water along with the feedstock. Recovering most of this heat is vital for a reasonably efficient process. Accomplishing this with a relatively simple plant configuration was the main goal of the process design part of the study. An extended explanation of the integration case can be found in **Publication III**.

A stand-alone plant, and one integrated with a small bio-fired power plant, is shown in Figure 3.5. The main energy parameters of the plants at full-load operation are presented in Table 3.1. The integration allows a simpler process design, while yielding a small but positive energy saving ratio, as well as removing the need for the pre-treatment drying required by most thermochemical technologies is an advantage for the integration process with a biomass-fired steam power plant. The plants were simulated using IPSEpro simulation software. The process models are based on those presented in Saari et al. (2018).

LHV-basis net efficiency η_{LHV}, and energy saving ratio ESR were used as the key indicators for quantifying the performance of the simulated HTC plants. The net efficiency is defined in Eq. (3.5) for the stand-alone HTC plant, and in Eq. (3.6) for the integrated plant.

$$\eta_{LHV} = \frac{\theta_{HC}}{\theta_{b,boiler} + \theta_{b,HTC} + P_{el,in}} \tag{3.5}$$

$$\eta_{LHV} = \frac{\theta_{HC} + P_{el,net}}{\theta_{b,boiler} + \theta_{b,HTC}} \tag{3.6}$$

The ESR is defined as

$$ESR = \frac{(\theta_{b,boiler} + \theta_{b,HTC})_{sep} - (\theta_{b,boiler} + \theta_{b,HTC})_{co-gen}}{(\theta_{b,boiler} + \theta_{b,HTC})_{co-gen}}, \tag{3.7}$$

where subscripts *sep* and *co-gen* refer to the fuel and feed consumptions of separate stand-alone, and integrated co-generation of hydrochar and electricity, respectively.

Table 3.1: Energy inputs and outputs of a stand-alone HTC and integrated case plant.

Properties	Stand-alone HTC plant				Integrated plant			
	EW	CW	CP	GB	EW	CW	CP	GB
Boiler fuel $\theta_{b,boiler}$ [MW$_{LHV}$]	2.7	2.6	3.2	2.9	30.9	30.9	30.9	31.8
HTC feedstock $\theta_{b,HTC}$ [MW$_{LHV}$]	11.2	11.1	11.7	12.0	11.2	11.1	11.7	12.0
Power consumption $\mathrm{P}_{el,in}$ [MW$_{el}$]	0.40	0.39	0.41	0.40	-	-	-	-
Hydrochar output θ_{HC} [MW$_{LHV}$]	10.3	9.4	9.7	10.0	10.3	9.4	9.7	10.0
Power generation $\mathrm{P}_{el,net}$ [MW$_{el}$]	-	-	-	-	8.55	8.56	8.43	8.72
Net energy efficiency η_{LHV} [%]	72.5	66.7	63.3	65.1	44.8	42.8	42.5	42.6
Energy saving ratio ESR [%]	-	-	-	-	1.6	1.5	2.1	1.9

The thermodynamics of a power cycle dictate that a condensing power plant inevitably has a far lower net energy efficiency η_{LHV}, than an HTC plant; consequently, the overall efficiency of an integrated plant is lower. Despite the lower efficiency values for the integrated cases, the positive values of the energy saving ratio (ESR) show that the integration not only allows considerable simplification of the process, but also yields a slight efficiency benefit in the overall conversion efficiency of the biomass.

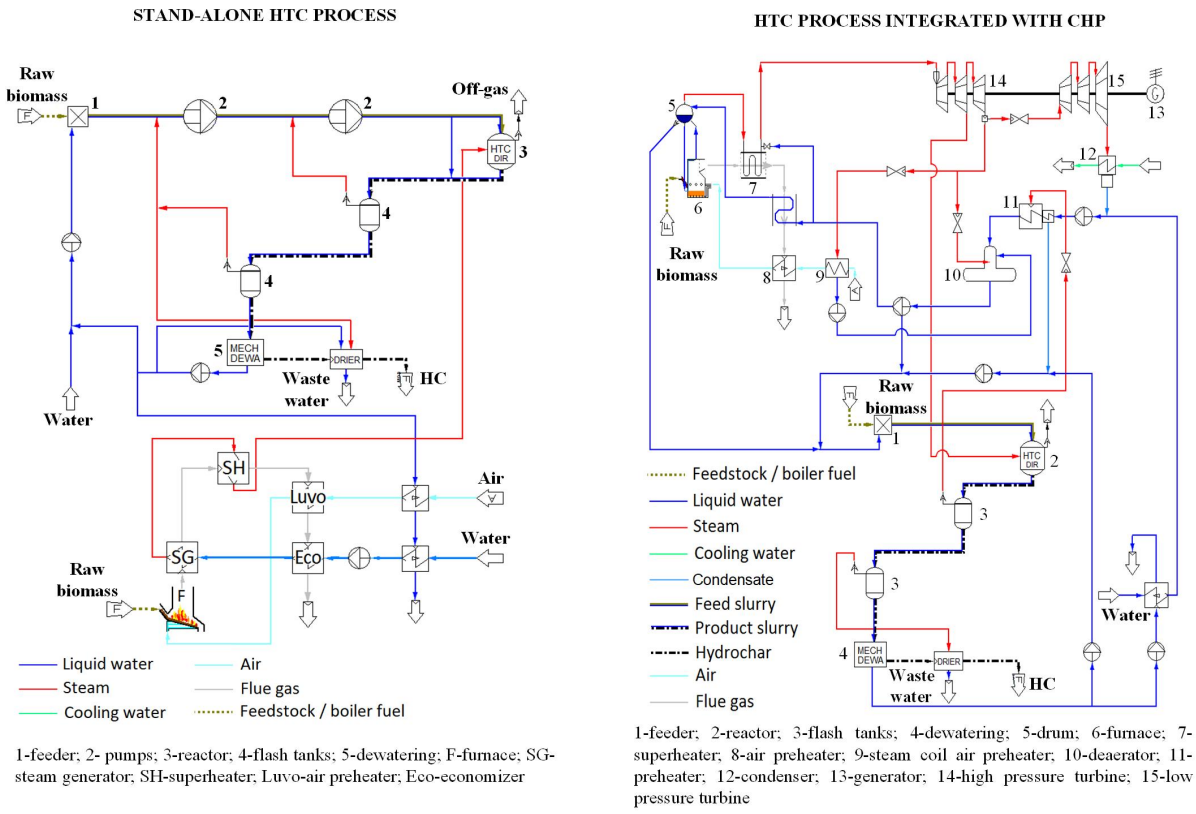


Figure 3.5: Design model of stand-alone HTC process and HTC process integrated with a CHP plant.

3.3 Hydrothermal carbonization of industrial waste

Sludge has been a challenging residue to dispose of for the pulp and paper industry, due to its high moisture content and poor dewatering characteristics. According to Canales et al. (1994), sludge disposal has been reported to be as high as 60% of the total wastewater treatment plant operating costs. The sludge in the forest industry is normally incinerated, land applied and land filled. Tightening legislation has increased interest in alternative sludge disposal options. Problematic characteristics, such as high moisture content of 85-90% and presence of chlorine, make sludge a challenging fuel for incineration in boilers, while the high inorganic and heavy metals content may limit potential use as a fertilizer (Mäkelä et al., 2012).

The effluents of pulp mills are rich in suspended solids, dissolved organics, color and, above all, organochlorine compounds (in factories that use chlorine and derivatives in bleaching), giving them high polluting potential. Liquid effluents are generated at different points in the pulp and paper process during woodhandling, at the digester, on the fiber line and during bleaching, drying, evaporation, recovery boiler, causticization and calcination (Mendoza Martinez et al., 2020). The treatment of those liquid effluents is composed of a sequence of four distinct stages with different objectives: removal of coarse solids, removal of suspension solids, removal of biodegradable organic matter and toxicity, and color removal (Stephenson and Duff, 1996). Incineration in a recovery boiler is a potential way to dispose of sludge. Recovery boilers are designed for challenging fuels and have advanced monitoring and control systems, which are an advantage for sludge combustion. Sludge incineration results in some additional

costs due to the moisture content, however: moisture vaporization requires a significant amount of energy, flue gas flow rate, boiler losses, ash transportation, treatment costs and significantly increased maintenance. Mäkelä et al. (2016) reported that the use of subcritical water under elevated temperatures and pressure does not require the prior drying of sludge and improves respective drying properties and destroys potential sludge pathogens.

3.3.1 HTC experiments

Sludge is produced mainly in primary (fiber) and secondary (biological) waste treatment. The primary sludge contain fibers, mineral fillers such as carbonate, ink, calcium, clay and adhesives from the converting processes, some of which still have insufficient research regarding their environmental impact (Leuenberger et al., 1985). Primary sludge is formed in wastewater primary clarifiers and contains compounds that settle easily, such as fibres. The secondary sludge, or so-called biosludge, is produced in the bioreactors and separated from treated effluent in the secondary clarifiers in mills with a biological wastewater treatment plant. Biosludge has proven resistant to attempts to reduce its moisture content mechanically or thermally (Coimbra et al., 2015).

HTC is a particularly attractive concept for treating biosludge for several reasons. While techno-economically feasible and environmentally friendly processes for biosludge treatment are greatly needed, HTC offers a low emission and low waste toxicity technology for treating and upgrading diverse feedstocks. HTC treatment, can also be applied even when biosludge has a high moisture content and no preceding, energy-intensive drying is needed. The process results in a hydrochar with heating value increased over that of raw sludge solids, while reducing some organic pollutants that may be suitable not only for use as an energy carrier, but also as e.g. soil conditioner, absorbent or in carbon sequestration (Mäkelä et al., 2016). A possible flow chart of the HTC process is presented in Figure 3.6. The sludge is mechanical dewatering to increase the percentage of dissolved solids, and according to Mäkelä and Yoshikawa (2016) mechanical dewatering of sludge increased process efficiency as the energy required for reactor heating and carbon losses to the liquid are minimized.

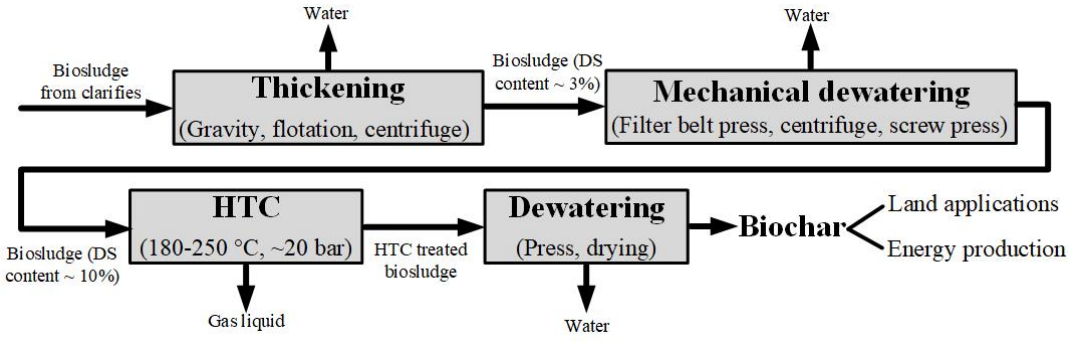


Figure 3.6: Flow chart of the HTC process for pulp and paper sludge.

Primary sludge and biosludge were hydrothermally carbonized under same conditions as the agro-forest residues discussed in previous section. The characterization of the waste is

showed in Figure 3.7. High moisture and ash content in the samples reduced the heating value. Thus, when considering the application of raw sludge for energy generation by combustion the properties are far from attractive. Biosludge can also be treated in a digestion process to reduce its volume and mass to produce biogas as a byproduct (Wood et al., 2009). Biogas can be used for energy production and the digested sludge can be used for land applications or incineration. Dewatering the digestate can be more difficult than the original sludge, which can complicate its incineration (Karlsson et al., 2011). Typically, the problem is minimize by mixing primary sludge with the digestate.

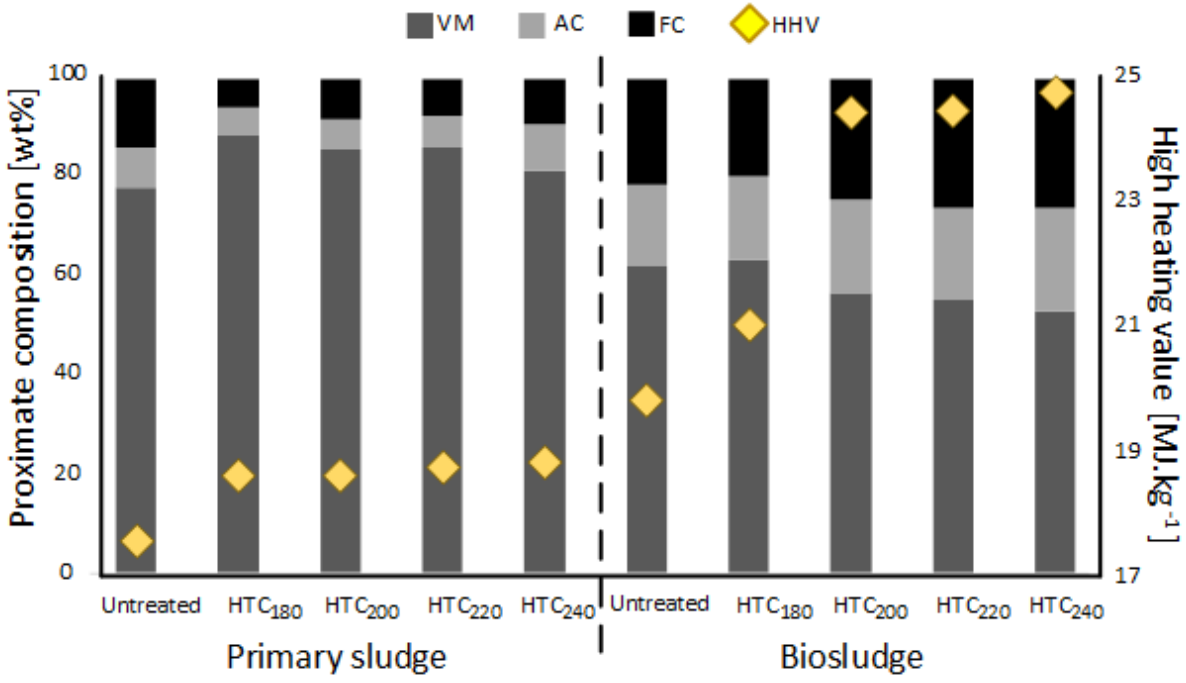


Figure 3.7: Chemical analysis of sludge feedstock and hydrochar samples.

This research focused on the alternative of treating sludge through a hydrothermal carbonization process, mainly because the recent carbon balances of the industrial units have been under lively discussion due to increased concern regarding climate change and its implications. Pulp mills among other industrial operators are looking for options to reduce their carbon dioxide emissions. In the case of a modern pulp mill, relatively small amounts of carbon capture and storage could make a pulp mill a carbon sink instead of a carbon source (Kuparinen et al., 2019). If HTC-treated biomass is used as soil conditioner, the carbon in the biosludge is then stored and not released in the atmosphere. For a pulp mill, this can offer a way to get closer to negative emissions. Additionally to reduce corrosion problems especially in boilers, caused by alkali compounds, chloride, among other harmful components present on sludge.

3.3.2 Integration of HTC process and Eucalyptus kraft pulp mill

The potential to reduce the CO_2 emissions and manage residual streams of a modern eucalyptus (Eucalyptus globulus) kraft pulp mill located in South America through hydrothermal carbonization technology, was analyzed via case studies. The implementation of HTC was compared to traditional biosludge disposal processes (case 0) where the biosludge is combusted in the recovery boiler after introducing the sludge into black liquor in the evaporator. Two integration cases were considered. In both, the sludge was first mechanically dewatered prior to being fed to the HTC plant. Unlike in HTC processes using solid feedstocks, no water other than the flash vapor from the product slurry is added to the feed slurry; even then, the final water-to-dry ratio in the HTC reactor becomes relatively high at approximately 16:1. The HTC reactor operates at 200 °C under 16 bar pressure, with a 3 hour slurry residence time. Mechanical dewatering to a 35% wet-basis dry solids content (case A) and thermal drying to 90% dry solids (case B) was considered. Details of the operational parameters and integration process can be found in **Publication V**. Figures 3.8 – 3.10 show the main process flows in the considered cases.

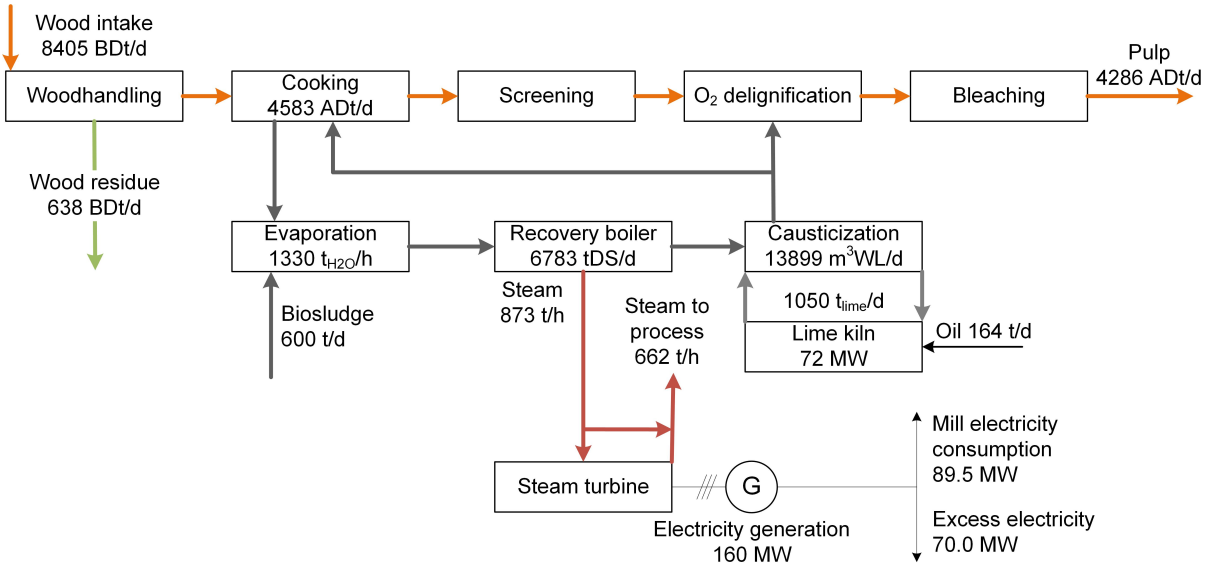


Figure 3.8: Flow diagram model of Eucalyptus kraft pulp mill case 0 (Mendoza Martinez et al., 2020).

In general, the impact of the moisture of the biosludge on the operation of the recovery boiler is clear; this was demonstrated earlier in (Kuparinen et al., 2019) by calculating the steam production of the boiler. When the share of biosludge is 1% of the total fuel mass flow rate, the steam production changes for moisture contents of 75%, 85%, and 95% are 0.16%, 0.31%, and 0.47%, respectively. The effect on the recovery boiler's operation may appear small, but in the long run the amount of lost steam is notable. In the HTC integration, when biosludge is combusted in the recovery boiler it increases the boiler load. If the recovery boiler is the bottleneck of the pulping process, biosludge disposal using other methods would enable pulp production to increase.

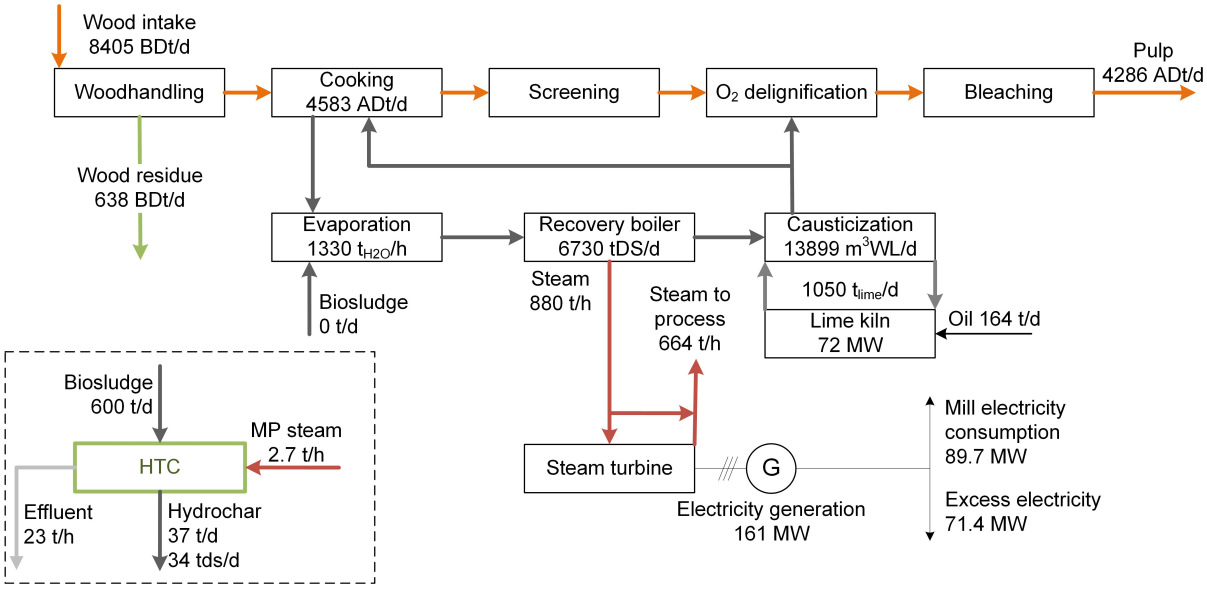


Figure 3.9: Flow diagram model of the integration of an HTC process and Eucalyptus kraft pulp mill - case A (Mendoza Martinez et al., 2020).

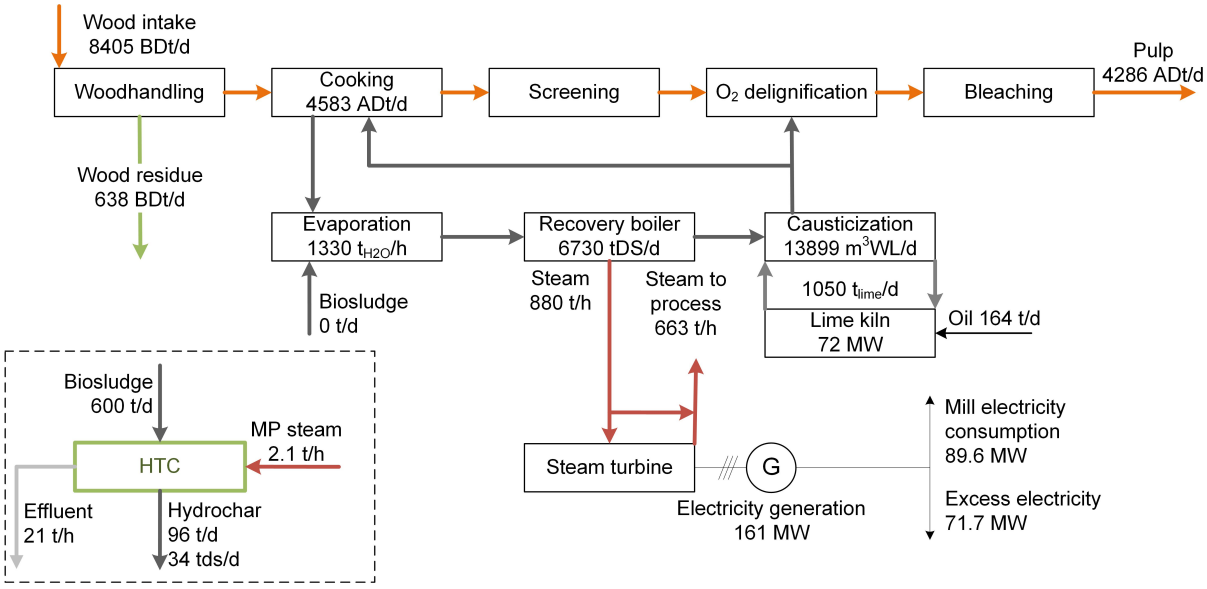


Figure 3.10: Flow diagram model of the integration of an HTC process and Eucalyptus kraft pulp mill - case B (Mendoza Martinez et al., 2020).

3.4 Densification of agro-forest residues

The physical, chemical and mechanical properties of briquettes produced with different proportions of coffee residues (coffee wood parts, i.e, the stem, branches, and parchment of coffee cherries) and pine, were evaluated in this thesis as a potential route to produce sustainable alternative for energy, specifically as an alternative fuel for coal firing systems in Brazil (**Publication IV**). Typically, briquettes in Brazil are used as substitutes for firewood in bakeries, food establishments, pizza restaurants, as well as factories with fuelwood-burning furnaces, such as red brick factories. Briquetting activities in Brazil are limited to those few regions with

high wood residues concentrations, such as the states of Sao Paulo, Santa Catarina and Mato Grosso (Mendoza Martinez et al., 2019b). Nevertheless, the quest for sustainability and the so-called green economy has contributed to expanding consumption, and consequently, the production of briquettes. This expansion primarily depends on three factors: residue availability, adequate technologies and the growing market for briquettes.

As mentioned in the previous sections, for coffee by-products themselves, there is still very little information about the energy potential. According to De Oliveira et al. (2013), the energy potential of coffee residues - coffee husks and coffee wood - in Brazil annually may reach 11.3 PJ and 49.5 PJ, correspondingly. However, a significant part of is not used. For briquette production, chemical and physical properties of the coffee residues need to be improved. The use of coffee residues along with traditional biomasses already utilized in the production of briquettes, such as pinewood, may considerably improve the potential of coffee residue utilization. Pine cultivation areas occupy a significant amount of land in Brazil, so the availability of feedstock would not be a limiting factor (da Silva et al., 2018). Additionally, pinewood is rich in natural resins that increase its calorific value (Brito et al., 2008). It also has a high lignin and silica content. Briquette production would not require any additional binders since lignin acts as a natural binding material during the pressing process. Figure 3.11 shows some of the briquetting treatments for the mixture of residues from the coffee production chain and pinewood to produce a solid fuel of regular shape and high energy density and resistance, for use in local firing systems.



Figure 3.11: Briquettes produced from coffee wood mixed with pinewood in different ratios.

3.4.1 The physical-chemical potential of briquettes

The briquettes produced from coffee residues and pinewood in ratios of 25%, 50%, 75% as well as the briquettes from each individual biomass sample showed a satisfactory visual appearance: good uniformity, the absence of cracks, with smooth and shiny surfaces. The average values of the equilibrium moisture content (EMC), compressive strength, apparent density and energy density of briquettes are illustrated in Fig. 3.12 and the main finding are summarized (Mendoza Martinez et al., 2019b).

- The briquettes with a low equilibrium moisture content (5–12 wt%) are better suited for transportation not only with respect to the lower concentrations of water carried in the bio-

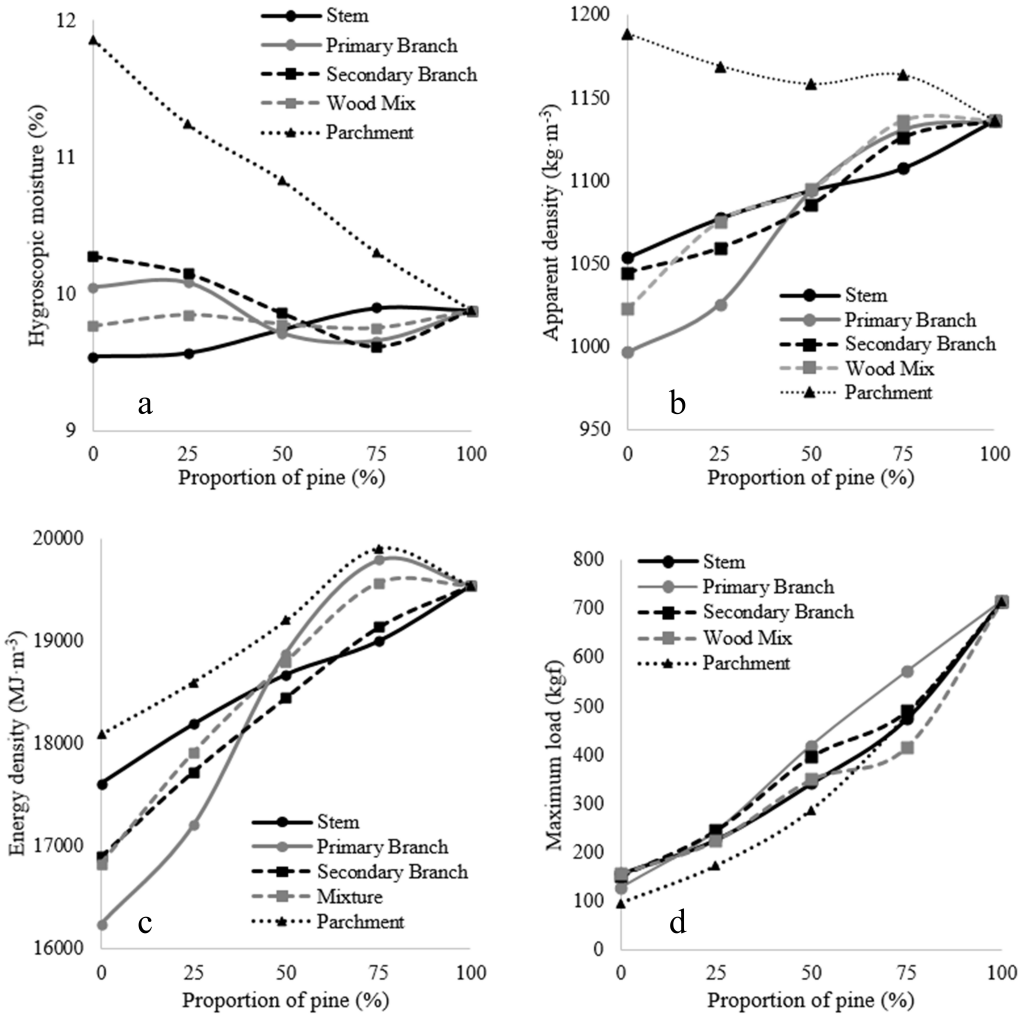


Figure 3.12: Properties of briquettes produced with the studied biomasses. (a) Equilibrium moisture content, (b) apparent density, (c) energy density and (d) compressive strength (Mendoza Martinez et al., 2019b).

mass material but also due to increased physical and mechanical resistances.

- Higher EMC complicates the ignition of the fuel and leads to lower energy density values due to the inverse relationship between the EMC and the heating value.
- The EMC for the majority of the produced briquettes was observed to be in a relatively narrow range between 9 and 10.3 wt% with little effect from the pine addition.
- A lower density raises the costs of transportation and reduces the energy density. The apparent density of the briquettes of coffee wood increases with the share of pine in the mixture.
- The tensile strength of diametric compression and maximum force is related to the ability of the briquettes to withstand mechanical impacts during storage and transport. The briquettes with low resistance tend to disintegrate more quickly, which can causes problems during their combustion.
- The resistance to diametric compression and maximum force increased in conjunction with the increase of the pine briquette content for all studied materials. This result is probably

due to the low volumetric expansion after the densification of the mixtures because of the presence of fines, low EMC and high lignin contents of the pine.

The obtained results for coffee-pine briquettes were compare with diverse biomass-base briquettes as showed in Table 3.2. Values were in the range of the ones found in the coffee-pine briquettes.

Table 3.2: Physiscal and thermal properties of briquettes

Feedstock	Properties				Ref.
	HCM [%]	Apparent density [kg m^{-3}]	Energy density [MJ m^{-3}]	Maximum load [kgf]	
Saw dust 40% + castor deoiled cake 60%	12.50	1140	-	-	Singh (2004)
Coffee pulp	11.4	1000	-	479.73	Cubero-Abarca et al. (2014)
Charcoal+cellulose	10.78-11.35	1701-663	-	-	Martins et al. (2016)
Cardboard/sawdust	5.7-7.6	1039.8-1380	-	-	Lela et al. (2016)
Cashew shell+rice husk+grass	6.81-8.43	895-1109	-	-	Sengar et al. (2012)
Banana leaves	7.17-13.47	990	17523	-	de Oliveira Maiaa et al. (2014)
Eucalyptus bark	-	1310-1340	21460-22090	-	Sette Jr et al. (2018)
Eucalyptus wood	-	1320	25520	-	Sette Jr et al. (2018)
Spruce sawdust	6.8	758.5	-	593.5	Brožek et al. (2012)
Pine bark	8.1	806.3	-	321.2	Brožek et al. (2012)
Birch chips	6.3	692.4	-	273.3	Brožek et al. (2012)
Poplar chips	7.2	776.2	-	828	Brožek et al. (2012)

HCM-Hygroscopic moisture

3.4.2 Thermal properties and combustibility

The thermal decomposition of the biomass briquettes is one of the main characteristics used to evaluate their energy potential, which is an important parameter for the planning and control of industries that use this type of fuel. As examples, a combustibility analysis was employed for the design of boilers, gasifiers and pyrolysis reactors, as well as in the optimization of thermochemical conditions (Tabarés et al., 2006; Di Blasi, 2009; El-Sayed and Mostafa, 2014). Combustibility is directly related to high temperatures and long burning times. Heat and mass transfer limitations, physical and chemical heterogeneity, and systematic errors also influence the combustibility properties of the fuel.

Weight loss and temperature variation analysis is the most commonly applied thermoanalytical technique in solid-phase thermal degradation studies (Jesus et al., 2018). The combustion system developed to evaluate the combustibility of the briquettes is presented in Figure 3.13. This technique can be implemented for different purposes, such as to determine the energy potential of biomass through thermal decomposition profile and thermal behavior of lignocellulosic fuels for energy applications. Figure 3.14 shows the main parameters typically collected in the TGA: weight loss curves along with their derived parameters and the temperature profile during devolatilization of the briquettes.

the behavior of the briquettes, given the same proportion of coffee residues, are quite similar: the weight loss and the highest peaks of temperature occur almost at the same time period. The briquettes solely composed of pine showed the highest temperature, longest burning region and slowest weight losses. The briquettes from the mixture of primary and secondary branches exhibited the lowest temperatures and shortest rapid burning regions. While the briquettes with coffee stem in its composition reached temperatures of 550 °C and 601 °C for

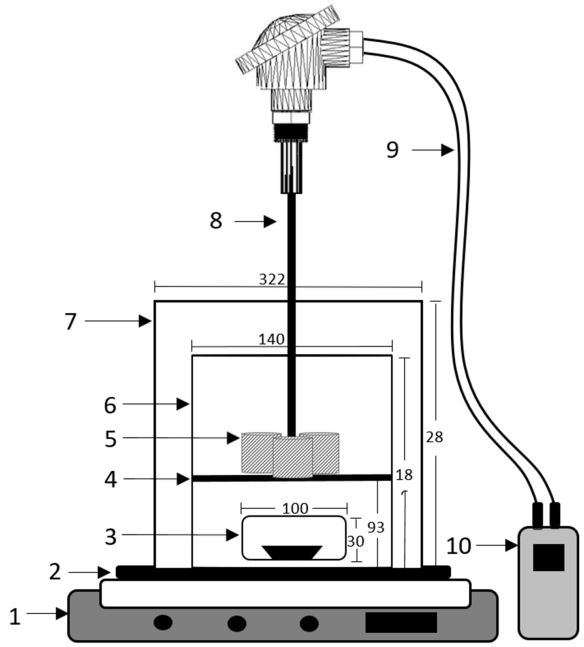


Figure 3.13: Scheme of the combustion system (dimensions in mm). (1) digital balance, (2) wooden base, (3) ignition chamber, (4) grate, (5) briquettes, (6) combustor, (7) combustor bulkhead, (8) thermocouple, (9) compensation cables, and (10) temperature recorder.

100% and 25% stem, respectively. As expected, briquettes with lower percentages of coffee residues showed higher and longer time range combustion temperatures probably because of lower ash and higher volatile contents in the pinewood.

Ignition and peak temperatures are the most important thermal characteristics of a combustion profile. By the place where the burning profile undergoes a sudden rise, the ignition temperature can be determined, namely 150 °C for 100% stem, 120 °C for 100% primary branch, 117 °C for 100% secondary branch, and 110°C for 100% pine briquettes. The release of volatile matter causes superficial structure modifications in the briquettes with a decrease in the free sites for an oxidative reaction, which promotes the ignition effect (Tognotti et al., 1985). In that sense, the lower ignition temperatures are favorable since they decrease the energy requirement to initiate the combustion process. As for the maximum combustion temperature, it corresponds to the place where the weight loss rate due to combustion is at the maximum level.

The reactivity R_a [min^{-1}] was calculated from the specific reaction rate *k* by splitting the defined range of a burnout into a series of discrete intervals as described in Eq. (3.8).

$$R_{a,x\%} = \frac{\sum(k \cdot \Delta W)}{\sum(\Delta W)} \tag{3.8}$$

Where ΔW [g] is the briquette weight loss in a 0.5min interval, and *k* is defined by Eq. (3.9):

$$k = \frac{1}{w} \cdot \frac{dw}{dt}, \tag{3.9}$$

where *w* is the instantaneous mass [g], and *dw/dt* is the mass loss rate [$g.min^{-1}$]

The *k* values increased in the range of 6-18 minutes, due to the temperature increment as showed in Figure 3.15. Right after this interval, the *k* values decrease steadily due to the briquette burnout, meaning that the combustion reaction rate depends on the velocity gradient of the mass of the unburnt combustible material remaining in the fuel.

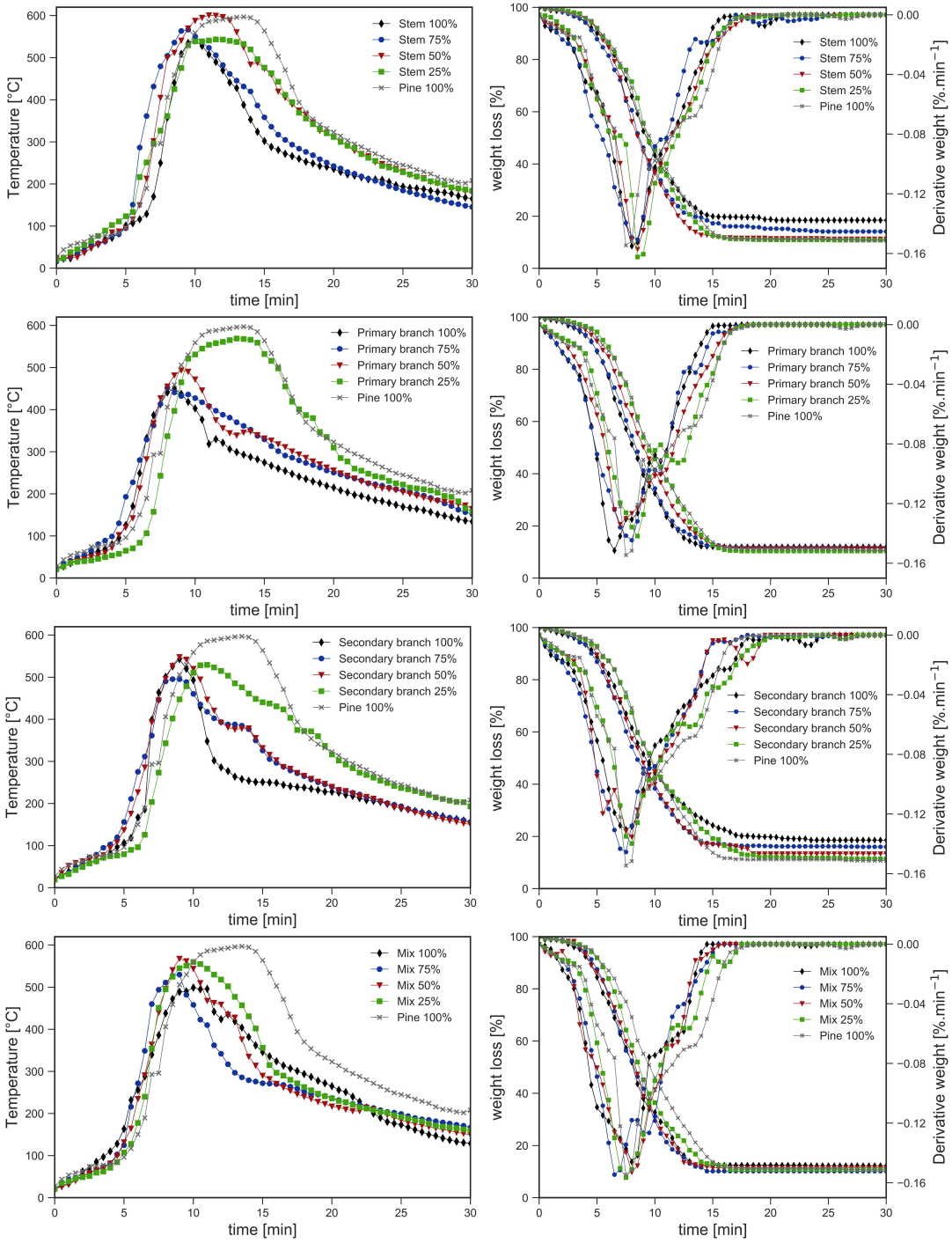


Figure 3.14: Weight loss along with their derived parameter curves (right) and temperature profiles (left) versus time for coffee-pine briquettes.

Higher amounts of coffee residues in the briquettes reduced their reactivities. In addition, low reactivity can also be attributed to a low volatile matter content, challenging the combustibility performance of the briquettes. Concerning the combustibility properties, it can be acknowledged that all produced briquettes are an alternative solution to maximize the thermochemical properties of coffee-pine-based biomass residues. However, coffee-pine briquettes composed of coffee stems and secondary branches displayed the highest combustibility potential, given their peak temperatures at over 550 °C and burnout times over 20 minutes. Properties such as high volatile matter (82.5 wt%) and low ash contents (0.7 wt%) in pinewood favor the

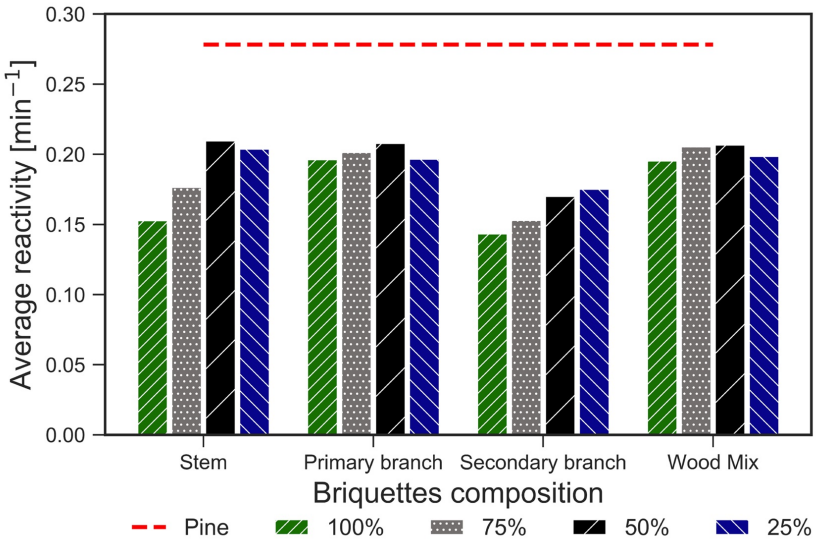


Figure 3.15: Average reactivity of coffee-pine wood briquettes.

combustion process and the energy potential of the briquettes.

4 Conclusions

Throughout this work it was shown that residual biomass can play a part as a renewable form of energy. It can be considered an environmentally benign solution to the problem of GHG emissions. The decentralized production characteristics of residual biomass promotes the use of existing residues and encourages the development of energy crops and new plantations, generating job opportunities and income in rural areas.

In addition, residual biomass implementation in industrial processes for heat and electricity generation is attractive due to low-cost feedstock. However, a large part of these residues have been wasted or underutilized due to the lack of incentive policies and lackluster environmental laws, among other factors. One of the reasons for this incipient use is the fact that these residues often do not have right conditions for efficient burning or even for other applications. In this context, technologies for the efficient use of biomass and the improvement of existing processes, as well as the development of new processes, are fundamental.

4.1 Main contributions

The overall contribution of this research is to expand the utilization of biomass resources to access energy markets. The contribution to climate mitigation strategies by reducing CO_2 emissions, and alternative sustainable disposal treatments of residual materials in industrial processes, are addressed. This study provides contributions for the first time within the field of conversion processes from woody and non-woody biomass, more specifically from coffee production chain residues for energy purposes. Prior to this study no information had been collected or evaluated on applications for solid coffee residues, except for few reports on industrial coffee by-products.The detailed characterization of several residues and a comparison of their properties for understanding and predicting the decomposition process during pretreatments, were also analyzed.

Hydrothermal carbonization as a relative new and currently developing technology was evaluated using different types of biomass in order to increase the knowledge about the technology and the effects of the process parameters. Solid and liquor products collected in experimental procedures were partially characterized for further possible applications. Generally, liquor analyses have been underestimated in the literature. The integration of HTC technology, has been evaluated in already published reports. This was confirmed in this study, which reported net energy efficiency values between 64.1–77.2% on the stand-alone cases and positive values in the energy saving ratio of 1.003–1.118 in the integration simulations of both, the recovery boiler cogeneration plant and the condensing power plant. The integration not only allows considerable simplification of the process, but also yields efficiency benefits in the overall conversion of biomass.

4.2 Main findings

Q1. How does the composition of biomass affect their behaviour for energy applications?

Biomass for energy production has some advantages over fossil fuels. Out of which stands out the fact that biomass is a source of clean energy and is renewable. Biomass has less impact on corrosion in process equipment and is considered a source of energy that can be produced by simple processing. Its implementation allows the reduction of dependence on oil in the less developed countries, which will lead to a decrease in industrial waste and reduced implementation and maintenance costs. However, some of biomass properties are inconvenient, requiring sometimes complex energy production processes. The high moisture content and, consequently, low calorific value, make biomass use economically unfeasible, i.e. resulting in high expenses for transportation and storage difficulties. Additionally, some biomasses possess a tenacious and fibrous structure and a heterogeneous composition. Therefore, an extensive characterization of residual biomasses for energy purposes is a critical factor for the optimal selection of alternatives which may be applicable to the energy matrix of diverse countries. For example, a high content of cellulose and hemicelluloses in the biomass are favorable for conversion through biochemical processes, and high lignin and low extractive contents are attractive for physical processes such as densification.

Publication I evaluated the applicability of coffee residues for energy generation as an alternative use where coffee is one of the major agricultural activity. Through physical and chemical analyses the most important quality indices, the interactions between them, as well as the quantification of energetic properties, were identified. In general, residual biomasses from the coffee production chain could be classified as suitable feedstock for thermochemical conversion processes with a low moisture content, with an average higher heating value, and volatile matter content. Additionally, it was also found, that ash composition is not detrimental to use, and a low sulfur content corresponds to good environmental performance. The composition of residual coffee shrub biomasses can lead to good product quality such as charcoal. The characterization of the samples shows that thermochemical conversion and densification technology is an environmentally friendly alternative. It can be used to upgrade the large quantity of waste generated by the coffee industry into energetic valued residues thus improving their management.

Q2. How can the hydrothermal carbonization process and densification treatments enhance the residual biomasses properties for the generation of value added products?

Conversion processes are viable alternatives to generate energy, even in remote locations, and their implementation can help sustainable energy development, reducing the current dependence on fossil fuels. The extended review in **Publication II** summarized the alternative thermochemical routes and the potential of their implementation for residual biomass. **Publication III** studied the application of hydrothermal carbonization of different globally important woody and non-woody residual biomasses. HTC produces a hydrochar with improved energy carrier properties compared to raw feedstock. The higher temperature promotes an increase in the hydrochar heating value and the destruction of functional groups, a factor that can improve the dewatering characteristics. In addition, HTC also increased the fraction of fixed carbon while reducing the volatiles and dissolving some of the ashes into the liquid phase, all of which combine to improve the characteristics of the hydrochar as a solid biofuel. In general, all the biomasses studied could be considered suitable feedstocks for HTC treatment. Coffee wood and

coffee parchment hydrochars exhibited suitable properties for use as adsorbent agents, activated carbon synthesis precursors or soil conditioners, while bamboo and eucalyptus was suitable for use as solid fuels. HTC technology was also evaluated on sludge produced in pulp and paper mills as described in **Publication V**. The HTC process showed some notable advantages for sludge treatment. The energy consumption of an HTC process with efficient heat recovery was significantly lower than that of the water content being evaporated in an evaporator plant and/or in the boiler furnace, offering the possibility to improve the energy efficiency. The hydrochar produced in the process could either be used at the site in the mill as a much-improved fuel compared to the original sludge, possibly even to be sold as a product.

Residues from the coffee production chain such as coffee wood and the parchment of coffee cherries can also be used to produce briquettes for combustion processes when mixed with pine wood residues, creating a new source for the utilization of undervalued residual biomasses as described in **Publication IV**. The resulting briquettes presented a regular format and homogeneous constitution, characteristics which indicates better quality and durable products after handling, transportation and storage. Additionally, the high energy density of the briquettes produced presented an attractive advantage for increasing the Brazilian energy production matrix using densified material.

Q3. What are the effects of integrating an HTC plant into an industrial process?

In the scenarios evaluated in this study, **Publication V** explained that the feasibility of the HTC treatment of pulp mill sludge production depends on the operational environment, such as the local regulations related to waste management, and mill-specific details for sludge final disposal. In a pulp mill where the recovery boiler and evaporator plant are the bottlenecks of the pulp production and biosludge is disposed of by combustion with the black liquor, HTC process can offer a novel way to increase the pulp production capacity. **Publication IV** also indicates that the integration of HTC in a pulp mill plant can bring benefits in the form of increased steam production and thereby power generation. Even after accounting for the steam and power consumption of the HTC plant, the change in the net generation of sellable electricity was clearly positive in the evaluated case. Additionally, the growing concern with the environmental impacts generated in pulp mills has induced the development of new methods that help to understand, control and, or reduce, for example CO^2 emissions and landfilling. Carbon capture, storage and utilization are attractive technologies for climate change mitigation and can be a way to achieve negative CO_2 emissions in kraft pulp mills. In the case of a modern pulp mill, a relatively small amount of carbon capture and storage could make a pulp mill a carbon sink instead of a carbon source. If HTC-treated waste biomass as a sludge, and used it as a soil conditioner, the carbon in the biosludge would then be stored and not released in the atmosphere. For a pulp mill, this can offer a way to get closer to negative emissions.

Another scenario evaluated in this study was reported in **Publication III**, which evaluates the heat integration possibilities of the hydrothermal carbonization process and a combined heat and power plant. The integration allows considerable simplification of the HTC process by removing preheating of the feed slurry. Instead, the main condensate stream of the power plant steam cycle serves as a heat sink for the flash steam from the high-pressure flash tank, yielding a small but positive energy saving ratio. Removing the need for the pre-treatment drying required by most thermochemical technologies is an advantage of HTC over other thermochemical conversion processes.

Q4. Is the energy potential of residual biomass attractive to the bioeconomy?

Considerable transformations in the political, social, environmental and economic fields are continuously happening worldwide. Several key trends act together and influence the development stages and living standards of societies. Successful countries will be those that could

adapt to these trends and discover how to turn them into opportunities. Energy consumption is one of the main indicators of country performance. The energy challenge has been faced by several countries with two strategies: maintaining a renewable energy matrix, and promoting energy efficiency and energy conservation through various government programs. A growing focus on sustainable development for resource conservation and environmental enhancement has resulted in a considerable number of new bio-based initiatives and support for biotechnology. Bioeconomy means using renewable sources from land and sea to produce food, materials and energy. According to the European commission (EC, 2021), stronger development on bioeconomy will help to accelerate progress towards a circular and low-carbon economy. This concept, of the circular bioeconomy promises new value chains and widening connections between small- and large-scale industries that may help climate change mitigation and future carbon neutrality, while protecting biodiversity and the environment. Opening new markets and producing new materials from the available feedstocks are essential for the bioeconomy development.

Biomass residues are expected to play an important role in supplying the feedstock needed for sustainable bioeconomy pathways. The scientific community has reported several results on the theoretical potential of diverse residual materials which would enable a comprehensive analysis of residual streams for different sustainable applications. For example, such applications could include straw residues for animal feeding, mushroom production and in the long-term soil quality by putting carbon into the soil. **Publication VI** presents an overview of the Brazilian energy matrix, background, challenges and degree of sustainability in the production of energy, based on economic and environmental aspects of its production. Due to hydroelectricity and bioethanol, Brazil is still in a privileged position compared to many other countries in South America. However, the main obstacle the country is facing in the energy sector is the absence of public policies that would ensure the establishment of public actions to encourage the development of the renewable energy industry.

4.3 Recommendations and future research

Several questions and assumptions were made during the development of this thesis. Thus, different future lines of research are proposed for more detailed study and analysis:

During the HTC process, the aqueous phase was collected and partiality characterized. This phase acts as a heat transfer medium, solvent and reactant. Thus, it participates actively in the degradation of carbohydrates during hydrolysis. According to the literature, the liquid may contain organic compounds at the end of each HTC experiment, mainly sugars, organic acids, furfural and phenols, among other components. The sugars are monosaccharides such as xylose, glucose, sucrose, mannose, arabinose and fructose, as well as others, resulting from the hydrolysis and dissolution of hemicellulose and cellulose. Of the organic acids, acetic, formic and lactic acids can be found in largest concentrations, but also others such as maleic, malonic, methane sulfonic, levulinic, glutaric and oxalic acids. The furfurals are a result of the dehydration of hydrolysis products, particularly pentoses such as xylose. Those compounds may be attractive to industries such as the food, cosmetics and biomaterials. However, the separation process could be highly intensive, so the quantification and further application should be analyzed.

One of the challenges for the application of HTC is the respective integration to existing industrial environments and the management of the generated process water. An alternative is to treat the separated filtrate to recycle it back to the wastewater treatment plant, generating a circulating carbon load between wastewater treatment and the HTC reactor. However, no research has been published on the effects of HTC conditions on the filtrate properties that are important for industrial wastewater treatment. Additionally, recycling the separated filtrate back to the reactor may increase the char mass and energy yields where additional water for HTC is required. Alternative options for HTC liquor disposal as well for hydrochar should be evaluated in future research due to their importance as valued-added products in the market. Hydrochar typically has soil improving qualities by supplying nutrients and trace elements. Sludge from pulp mills and obtained HTC products may have attractive applications in material recovery and soil enhancement. Nevertheless, the possible organic chlorine compounds in its composition and their environmental behavior are to some extent unknown. Furthermore, possible heavy metals might prevent land application use. The time period for land spreading is limited to specific months, and hence the storability of a fertilizer is a key property. In some EU countries land spreading of sludge may be permitted but completely banned in others. Some examination of this scenario should be made.

Further future work could involve an economic analysis of the briquetting and the hydrothermal carbonization processes for further applications. The economic analysis could be influenced by the assumption of feedstock, electricity and heat prices. The limited available data on the hydrothermal carbonization market is also a source of uncertainty, and prices are bound to fluctuate depending on the applications of the products. Different scenarios extended to an operational and economic analysis of different feedstock, integration concepts and applicability forecast may allow increase environmental incentives and improve the profitability and sustainability of residual biomass utilization.

Considering the wide variety of residual biomasses and conversion technologies, experimental procedures and the development of prediction models would be highly beneficial for understanding the residual biomass behavior during pretreatments. Advances in this regard are already being made. Partial results have been obtained for fast pyrolysis applications of EW in the pulp industry and CS in coffee plantations. The physicochemical characterization of raw materials has indicated that in general, residues exhibit different important parameters for fast pyrolysis technology, such as high calorific values, high carbon contents, and low ash contents. Furthermore, the pyrolytic behavior of wood was investigated under inert and oxidative conditions at the heating rates of 10, 25 and 50 °C min^{-1}. The thermal decomposition of samples presented three stages in the two atmospheres analyzed. In nitrogen: drying, active pyrolysis (devolatilization), and passive pyrolysis (carbonization) stages. In oxidative atmosphere: drying, active oxidative pyrolysis (devolatilization), and char combustion stages. In oxidative atmosphere the different decomposition stages occurred at lower temperatures and led to a higher rate of decomposition than decomposition in a nitrogen atmosphere, and this was more pronounced for eucalyptus residues.

The pyrolysis of eucalyptus wood and coffee shrubs in a pilot-scale plant (feed rate capacity of about 20 kg h^{-1}) was successfully carried out. For eucalyptus wood, the process produced 37.7% gases, 22.64% heavy bio-oil, 17.07% light bio-oil and 15.35% bio-char, and for coffee shrubs, the process produced: 47.35% gases, 14.67% heavy bio-oil, 23.2% light bio-oil, and 14.75% bio-char. As the biomass pyrolysis occurred in an oxidative atmosphere, the overall results for the liquid yield were good compared to the other biomasses in literature. Bio-oils have a higher energy density than the raw materials, 6.3 times higher for EW and 3.5 for CS. For bio-char a high heating value was reported of 26.1 MJ kg^{-1} for CS and 26.2 MJ kg^{-1}

for EW, enabling it to be used as fuel. In conclusion, the characterization of Brazilian residues and products from oxidative fast pyrolysis ensures that these biomasses are potential candidates for bioenergy production by fast pyrolysis. Therefore, the Brazilian residues have the potential to favorably compete with other conventional biomass sources such as sugar cane straw, pine wood and banana leaves and in thermochemical conversion technologies.

Slow pyrolysis from diverse wood samples was also tested. The results show that thermochemical treatment allows biomass conversion into charcoal with enhanced after-treatment characteristics in the heating value and energy density. Charcoal produced from slow pyrolysis is an important source of renewable energy and currently has several uses in the chemical (activated carbon), agricultural (soil conditioning), domestic (commercial establishments such as pizzerias, steakhouses, residences) and fuel sectors, for the cement industries , ceramics and especially steel. For countries like Brazil, charcoal has a critical application on an industrial scale, since it is the world's largest coal and sole pig iron producer. From this point of view, energy efficient conversion of agroforestry residues produced nowadays in considerable amounts have great potential for industry as the form sustainable development. Experimental results of charcoal production using coffee wood, bamboo, pine and eucalyptus residues at 300 °C, 400 °C, 500 °C and 600 °C temperatures revealed relatively high charcoal yield values, about 28–36%, 27–54%, 30–49% and 27–35% for bamboo, pine, eucalyptus and coffee wood residues, respectively. Additionally, properties such fixed carbon and high heating values also reported attractive energy potential.

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Research paper

Characterization of residual biomasses from the coffee production chain and assessment the potential for energy purposes

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ABSTRACT

Chemical quantitative characterization of biomass is relevant for waste to energy recovery technologies. In the present work, selected agroindustry solid residues from coffee crops – parchment and coffee shrub, i.e., stem, branches and leaves – were characterized. Properties such proximate, ultimate and biochemical composition, energy content, and thermogravimetric analysis, were evaluated. Results showed high values of higher heating value and volatile matter content. The silica contents are small for all samples. Additionally, the high content of extractives and lignin, reveal that these residual biomasses are more suitable for charcoal than cellulose pulp production. The extensive residue characterization provided valuable data that helped in outcome of the evaluation of different conversion technologies as being an environmentally friendly alternative, contributing to sustainable, reliable, carbon-neutral form of modern energy and upgrade the large quantity of waste generated by the coffee industry into energetically valued residues, by improving their management.

1. Introduction

Brazil, Vietnam, Colombia and Indonesia are the largest bulk coffee beans producers in the world, responsible for more than 50% of world production. The coffee production chain generates a large quantity of residues from the cherries and shrub. Large scale around the world. It is estimated that the annual world production of coffee generates over ten million tons of residues yearly (solid and liquid). This amount excludes the residues of cultivation (pruning leaves) which are difficult to estimate due to the differences in agronomic management practices [1]. Organic residues from coffee production represent a serious source of environmental concern, if discarded inadequately and with poor management.

With exports amounting to 30.2 million bags of 60 kg in 2017, Brazil is the largest producer and exporter of bulk coffee beans in the world [2,3]. The gross amount of bulk coffee beans (*Coffea arábica* and *Coffea robusta*) produced in Brazil (2017) was 2.78 million tons according to [4], and the total area planted in the country with coffee shrubs (*Coffea arábica* and *Coffea robusta*) in 2017 was 2.21 million hectares, where 1.86 million hectares (84.16%) were in production [5]. As can be seen in Table 1, Southeastern Brazil, is the main region of bulk coffee beans production (84.44% of total bulk coffee beans produced). The environment and climate provide there ideal growing conditions for coffee shrub.

Coffee shrub should be periodically pruned and stumped. According to [6], a full-grown coffee shrub weighs on average 15 kg (dry wood). Approximately 25% of the shrub becomes solid waste in the pruning, which occurs approximately every five years. The pruning frequency depends on the agronomic management practices, production and shrub growing stage. To prune, the secondary and tertiary branches should be cut from the shrub, leaving more space for the primary ones to grow. This rejuvenation should occur after four to five harvests, which means that an average of 32 million tons of residual wood is generated in the from coffee plantations of Brazil annually. To stump, the shrub should be cut down 30 cm in height. The frequency of stumping is linked to the number of shrubs within a given unit of area

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Table 1
Data of estimated amount of planted area, harvested area, total coffee beans produced and residues generated in coffee plantation in Brazil (2016/2017) [4].

Region	Planted area ($ha \cdot 10^3$)[a]	Harvested area ($ha \cdot 10^3$)[a]	Total coffee produced ($t \cdot 10^3$)[a]	Residues generated ($t \cdot 10^3$)	
				Wood	Parchment
Brazil	2270	1914	2777	31654	607
North	90	78	154	1286	34
Northeast	165	148	184	2449	40
Southeast	1942	1621	2345	26795	512
South	46	46	72	762	16
Central-west	27	22	23	362	5

[a] Systematic Survey of Agricultural Production - December 2017.

(planting density): at a sowing density of 2500 to 3000 shrub·ha^{-1}, the production level will start to decrease after 10 years, at 5000 shrub·ha^{-1} after 7 years and at 10,000 shrub·ha^{-1} after 4–5 years after planting.

The coffee plantations in Brazil are mostly high-density (5000 shrub·ha^{-1}). Several reports have indicated that coffee beans production may be more suited for high-density plantings; indeed the high productivity, less erosion due to complete land cover, low cost of weeding, better use of the resources, greater efficiency in the workforce, recycling of the organic material when coffee shrub is harvested [7]. Some evidences suggest that optimal plant density is of about 5000 shrubs ha^{-1} for *Coffea arábica*, and no more than 4000 shrubs ha^{-1} for *Coffea robusta* [7–10].

Furthermore, in bulk coffee beans production, approximately 55% of the coffee cherry are converted into grain, and the parchment represents 12% of the fruit on a dry basis [11]. Consequently the estimated production of parchment was 605.81 thousand tons in 2017 in Brazil (December 2016/2017). Therefore, the bulk coffee beans production represents over 2.3 million tons of solid residues being generated per year. As a result of having the greatest bulk coffee beans production, southeastern Brazil is the region with the highest waste generation from coffee plantations, producing more the 80% of the total amount of waste produced in the country. This amount excludes the leaves (fallen and pruning). However, under normal cultivation conditions, coffee leaves have an average duration of 1.5 years, with defoliation caused by different factors such as inadequate nutrition, water deficiency in the soil, excessive plant burden, disease and crop. When bulk coffee beans are cultivated in full sun, as in Brazil, in the post-harvest period, the leaf defoliation occurs in plants with a normal 30–70% drop in leaves. Thus, the *Procafe* foundation, in a survey in the state of Minas Gerais (Brazil), estimated that on average 5500 kg (dry basis) per hectare of leaves fall annually in different conditions of *Coffea arábica* coffee plantations.

The large amount of waste generated by the agricultural industries is a problem that exists in almost all regions of Brazil. Thus, the waste management is often considered potentially problematic, because its disposal or proper use usually generates high costs that producers often want to avoid. The thermochemical conversion technologies for recovery of energy from wastes can play a vital role in mitigating the problems caused by the large amount of residual waste. In this sense, the residues from bulk coffee beans production can be used to generate thermal energy to dry agricultural products or to heat animal facilities, or as fuel to generate mechanical or electrical energy. However, knowledge of the quantity, physical and chemical characteristics and technologies available for use of residues has been an hindrance to find an alternative that conserves energy and contributes to sustainable development.

The concern with the increase of coffee bean productivity has ignored the changes to the characteristics to the residues provided by the coffee production chain, additionally, little or partial information exist about its use in the generation of value-added products. In order to solve some limitations in relation to the use of bulk residual coffee biomass, such as low energetic density, high content of moisture, high heterogeneity that leads to difficulties in handling, transport and storage, agricultural/forestry companies and research centers, suggests solutions for reducing these problems, trough treatments that produce homogeneous, high yielding, high quality and low cost products, such as biodiesel, biogas, source of sugars [12], and precursor for production of activated carbon [13,14].

The aim of this study was to present an extensive characterization of residual biomasses from the coffee production chain for energy purposes, increasing knowledge about the alternatives applicable to the energy matrix of countries where the coffee industry is one of the major agricultural activity, through physical and chemical analyzes that identify the most important quality indices, the interactions between them, as well as the quantification of its importance. An extensive characterization of the residues presented in this work is not readily available in the literature and these results are fundamental tools for the qualification and quantification of the effects of their properties on conversion technologies that include thermochemical processes such as pyrolysis, gasification, and combustion, and physical processes such as briquetting and pelletizing.

2. Materials and methods

2.1. Sampling and preparation for characterization process

Residues from coffee shrub (*Coffea arábica* L.) cultivation: parchment, leaves and wood, provided by a rural farm in the municipality of Paula Cândido, MG, Brazil (20°49′50.0″ S 42°55′03.3″ W) were used. The plantation was established in 1986, and due to low productivity, stumping of new plant formation was required. The wood collected was 11 years old (from after the last stumping period), from a 30-years-old plantation.

The biomasses were ground in an industrial mincing Lippel® brand, and posteriorly in an electric hammer mill, motor Weg® mark of 10 CV and 3520 rpm, which was coupled with a screen opening of 2 mm. For samples intended for chemical analysis it was necessary to further reduce the particle size, using a knife mill type Wiley® Mill Model 4. The biomasses were finally classified into superposed screen with openings of 40 mesh and 60 mesh according to the American Society for Testing and Materials (ASTM), 1982.

The experiment was conducted according to a randomized design with six biomasses and two replicates for each characterization. Data were subjected to analysis of variance (ANOVA). For the large number of tests and variables involved, Bonferroni-corrected alpha value ($\rho = 0.001$) was employed to reduce the likelihood of spurious correlations. Statistical analyzes were performed on the IBM SPSS® software platform, 2015.

2.2. Stock estimation of the coffee shrub wood parts

The wood samples were previously separated into (I) stem, (II) primary branch and (III) secondary branch according to their diameter, 10 ± 2 cm, 2 ± 1 cm and 1 ± 0.5 cm, respectively, for individual properties analysis and stock estimation.

2.3. Laboratory procedures for biomass characterization

An extensive characterization of the solid fuel was performed, evaluating their properties, including proximate and ultimate composition, energy content, several biochemical composition (polysaccharides, lignin, extractives, uronic acids and acetyl group) and thermogravimetric analysis of each residue group.

2.3.1. Basic density

The measurement for basic density of wood sample (stem) was determined according to the Scandinavian Pulp, Paper and Board (SCAN-CM) 43:95 (1995) standard procedures of 25 disks obtained from different cut sections on the main axis of the shrub. The drying analysis of wood parts of the coffee shrub, (stem, primary branch and secondary branch) with dimensions of 30 cm length and variation of the diameter for each wood part, was conduct in a climate-controlled room with temperature (23 °C-24 °C) and relative humidity (60 %–70% RH) control. The mass loss of the samples was monitored by periodic weightings until reaching anhydrous mass.

2.3.2. Ultimate analysis

The ultimate analysis shows the content of five major elements: carbon (C), oxygen (O), hydrogen (H), nitrogen (N) and sulphur (S) in the organic phase. The content of these elements was measurement using a Vario Micro Cube CHNS−O equipment with helium as a carrier gas and oxygen as an ignition gas according to the German Institute for Standardization (DIN EN) 15104:2011-04 (2011) standard procedure. The molar ratios of oxygen and hydrogen to carbon were also determined.

2.3.3. Proximate analysis

The equilibrium moisture content (EMC) was determined by mass difference. It was considered that equilibrium was reached when the sample weight difference between two successive days was less than the balance accuracy. The volatile matter (VM) analysis was performed according to DIN EN 15148:2010-03 (2010). Ash content (AC) was determined according to DIN EN 14775:2010-04 (2010). Fixed carbon (FC) was calculated as the difference between 100 and the sum of VM and biomass AC. The silica content of the biomasses was measured according to the Technical Association of the Pulp and Paper Industry (TAPPI) T245 cm-98 (1998) and the contents of sodium (Na), iron (Fe), copper (Cu), manganese (Mn), potassium (K), calcium (Ca) and magnesium (Mg) were determined by atomic absorption spectroscopy, according to the SCAN CM 38:96 (1996) procedures. The chloride content was determined by potentiometry using automatic titrator equipped with HI 4107 combination chloride electrode.

2.3.4. Heating value

The high heating value (HHV) has determined according to DIN EN 14918:2014-08 (2014) standard procedure, in duplicate, using a bomb calorimeter adiabatic IKA300. The net heating value (NHV) of dry matter was determined according to equation (1) of the annex E of the DIN EN 14918:2014-08 (2014).

$$NHV\ (J{\cdot}g^{-1}) = (HHV\ (J{\cdot}g^{-1}) - 212.2 * \text{Hydrogen content (\%)} - 0.8 * (\text{Oxygen content (\%)} + \text{Nitrogen content (\%)}) * (1–0.01 * EMC\ (\%)) – (24.43 * EMC\ (\%)) \quad (1)$$

2.3.5. Chemical composition

The chemical composition of studied biomass samples was evaluated within the following procedure. The milled samples were extracted successively with ethanol/toluene (1:2 v/v), ethanol and finally water following the TAPPI method T264 cm-97 (1997). This extracted sample (extractive free sawdust) was conditioned in a temperature and relative humidity-controlled room (23 ± 1 °C, 50 ± 2% RH) until an equilibrium moisture was achieved. The extractions were carried out in duplicate, and the extraction yields were expressed in percentage in relation to the biomasses dry weight. The contents of uronic acids and acetyl groups and anhydrosugars (anhydroglucose, anhydromannose, anhydrogalactose, anhydroxylose and anhydroarabinose) in the extractive-free biomass were determined according to [15,16] and SCAN-CM 71:09 (2009) standard procedure, respectively. Sugars were measured by a Shimadzu HPLC, coupled to a refractive index detector (RID-10 A), equipped with a Bio-Rad Aminex HPX-87H column (300 × 7.8 mm), and operated at 60 °C with a mobile phase of sulfuric acid 5 mM at rate of 0.6 mL min^{-1}. On the extractives-free biomass, the acid insoluble lignin and acid soluble lignin were determined according to TAPPI T 222 om-11 (2011) standard procedure and [17], respectively.

Thermogravimetric analysis was applied to evaluate the gradual rate of mass loss of the biomass as a function of the constant temperature increase. Tests were performed using a TGA analyzer (SHIMADZU DTG60 Series), by heating a typical sample mass of 4 mg in a purge of nitrogen (30 ml min^{-1}), at heating rates of 10 °C min^{-1} with final temperature at 1000 °C.

Table 2
Stock estimation of the woods parts (stem, primary branch and secondary branch) of the coffee shrub.

Estimation	Wood Parts of coffee shrub			
	Stem	Primary Branch	Secondary Branch	Total
Diameter (cm)	9.8[a]	2.3	1.8	
Biomass (kg·coffee shrub^{-1})	4.10[a]	2.24	2.54	8.88
Biomass (%)	46.17[a]	25.22	28.61	100

[a] Significant difference, using a Bonferroni-corrected alpha value (p = 0.001).

3. Results and discussion

3.1. Stock estimation of the coffee shrub woods parts

Table 2 shows stock estimation of the biomass (stem, primary branch and secondary branch) in the coffee shrub.

The analysis of Bonferroni presented significant difference between the stem and the branches for diameter and proportion. The stem has greater diameter as it is responsible for sustaining the plant and supporting the weight of the branches with its foliage and fruit. The coffee shrub represents on average 8.88 kg wood·coffee $shrub^{-1}$, the greater contribution is from the stem, followed by secondary branches and primary branches, respectively. The branches represent more than 50% of the total weight of the shrub, a fact that explains the great importance of the branches in the structure of the system, as it is on which the fruits grow. The growth of the shrub is influenced by age, planting density, cultural practices and weed competitions [7]. The pruning of the shrub occurs approximately every five years to increase the shrub productivity [6]. For energy, the transport of the raw material is a fundamental stage in the chain of energy production. In this way, the stem provides more amount of stacked biomass than the branches, as a result of the significant difference between the densities.

3.2. Characterization of residual biomasses from the coffee production chain

Table 3 shows a chemical analysis of the residual biomasses from the coffee production chain.

3.2.1. Basic density of coffee wood

In the average value of basic density of coffee wood (598.7 kg m^{-3}), negligible variations between the base and the top of the stem were observed. For energy, high wood density is preferred, resulting in higher mass production for a given volume of wood [18]. Operational advantages, such as gains in harvesting and forest transport processes can be achieve, due to the fact that larger volumes of harvested wood will generate greater specify mass values [19]. According to the measures suggested by Ref. [20], wood basic density for charcoal

Table 3
Properties of residual biomasses from the coffee production chain.

Components	Biomasses						
	Leaves	Primary branch	Secondary branch	Stem bark	Stem	Parchment	SD[c]
Basic density (kg m^{-3})	*nd*	*nd*	*nd*	*nd*	598.7	*nd*	–
Ultimate elemental[b] (wt % dry)							
C	53.97	50.31	51.82	54.41	50.64	50.69	1.80
H	6.55	6.13	6.40	6.59	6.12	6.23	0.21
O	35.50*	42.28	40.06	36.66*	41.16	42.05	2.87
N	3.54*	0.92	1.51	2.13*	1.86	0.82	1.00
S	0.43*	0.36*	0.21	0.21	0.21	0.20	0.10
H/C	1.46	1.46	1.48	1.45	1.48	1.45	0.01
O/C	0.49*	0.63	0.58	0.50*	0.62	0.61	0.06
Proximate composition(wt %)							
EHM	16.35	8.70*	9.28*	18.11	10.96	11.09	3.88
VM[a]	74.71	80.62*	75.31	75.63	83.70*	74.07	3.90
FC[a]	18.12	16.95*	21.23	20.03	14.62*	20.09	2.45
AC[a]	7.17*	2.42*	3.45*	4.33*	1.67*	5.84*	2.08
Silica (% of ash)	0.10	0.10	0.10	0.40*	0.15	0.35*	0.14
Minerals (g kg dry^{-1})							
Ca	4.65	4.49	6.41	20.96*	6.29	3.73	6.55
Fe	0.18	0.05	0.11	0.57*	0.07	0.24*	0.19
Mn	0.03	0.04	0.02	0.01	0.01	0.03	0.01
Mg	2.05*	1.17	1.68	2.23*	1.07	1.77	0.46
Cu	0.05	0.02	0.04	0.06	0.02	0.04	0.02
K	10.86*	6.74*	7.96*	2.94*	4.06*	12.20*	3.65
Na	1.19*	0.36*	0.69	0.95	0.68	0.73	0.28
Cl	4.36	7.26	6.80	5.98	3.08*	3.16*	1.83
Heating value (MJ kg dry^{-1})							
HHV	19.45	19.20	19.20	19.20	19.00	18.30*	0.40
NHV	14.68	16.10	15.92	14.11*	15.44	14.81	0.77
Chemical composition (%)							
Extractive	24.72*	13.09	13.95	12.19	10.58	21.95*	5.80
Insoluble Lignin[b]	35.52	26.73	29.32	40.98	27.33	24.52*	6.26
Soluble Lignin[b]	3.59*	3.12*	2.93	2.19	2.24	2.07	0.61
Total Lignin[b]	39.11	29.85*	32.25	43.17	29.57*	26.59*	6.37
AnhydroGlucose[b]	19.65*	33.25	29.05	17.90*	31.65	29.60	6.46
AnhydroXylose[b]	5.30*	11.85	10.30	6.25*	12.20	14.55	3.61
AnhydroGalactose[b]	2.50*	1.15	1.45	1.20	0.90*	1.65	0.56
AnhydroMannose[b]	1.10	2.55*	1.70	0.90	3.30*	1.00	0.97
AnhydroArabinose[b]	4.50	1.55	2.90	4.25	1.35	3.45	1.33
Uronic acids[b]	4.80	3.80	4.70	5.20	3.30	5.50	0.84
Total sugars[b]	37.85*	54.15	50.10	35.70*	52.70	55.75	8.70
Acetyl group[b]	1.00	1.8	1.8	1.00	2.80*	2.85*	0.82
Others[b]	14.87	11.78	12.40	15.80	13.26	8.97*	2.42

*significant difference, using [a] Bonferroni-corrected alpha value (p = 0.001).
[a] Dry basis.
[b] Dry ash free basis.
[c] Standard deviation. *nd*-not determined. EHM-Equilibrium Hygroscopic Moisture. VM-Volatile matter. FC-Fixed Carbon. AC-Ash content. HHV-Higher Heating Value. NHV-Net Heating Value.

production should exceed 500 kg m^{-3}. The value found for coffee wood is similar to values reported in the literature for Eucalyptus wood, that presents basic density between 436 and 668 kg m^{-3} for the species *Eucalyptus pellita, Eucalyptus urophylla* and *Eucalyptus grandis*, traditionally used for energy conversion, including firewood and charcoal [21].

3.2.2. Ultimate analysis

The biomasses collected are basically composed of carbon (50.26 %–54.41%, dry basis), hydrogen (6.13 %–6.59%, dry basis) and oxygen (35.52 %–42.29%, dry basis). Small amounts of nitrogen and sulfur were also observed. Biomass with high values of carbon and hydrogen, contributes the most to the calorific value of the fuel [22]. The energy generated by thermal reactions is associated with the enthalpy of carbon, hydrogen and sulfur [23]. The presence of nitrogen and sulfur in the biomass have a direct impact on the environmental pollution, due to the formation of harmful oxides (NO_x, SO_x) from volatile compounds [24]. The content of sulfur observed in the elemental composition was low (0.20 %–0.43%). Generally, the S content in biomass varies in the interval of 0.01 %–2.3% [25].

The coffee shrub is highly N-demanding, the nitrogen requirements increases with shrub age especially at the beginning of grain production. If there are not limiting factor, the nitrogen will promote rapid plant development specifically through the increase in number of plagiotropic branches per shrub, number of nodes per branch, and number of fruiting nodes, flowers and leaves per node, which, taken together, are associated with higher yields in coffee beans [26,27]. Hence the coffee shrub presents high potential for nitrate assimilation in leaves as well as in roots. That is the reason of the highest levels of nitrogen in leaves with significant difference between the other biomasses. The supporting, slowly growing parts have the lowest nitrogen content. The nitrogen content in biomasses varies in the interval of 0.10 %–12% [25,28]. The values of nitrogen and sulfur found in this study are similar to other biomasses used for energy, which are environmentally more advantageous than other sources of thermal energy such as mineral coal.

The molar ratios of oxygen and hydrogen to carbon for the residues studied are shown in Fig. 1. Oxygen is generally present in plant-based

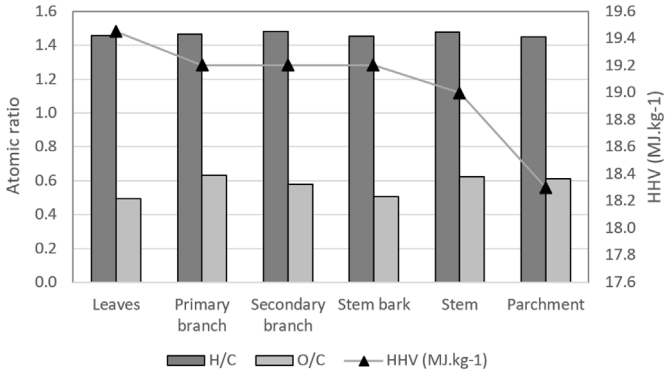


Fig. 1. Molar ratios of hydrogen and oxygen to carbon and high heating value for studied residual biomasses from the coffee production chain.

fuels, and its presence decreases the calorific value [29]. Therefore, low H/C and O/C ratios are desirable for the use of biomass for energy. The samples with low O/C ratio, also have more energetic content because C—C bonds have higher chemical energy than C—O bonds [30]. In the biomasses collected, higher O/C ratio can be observed in the primary branch (O/C = 0.63) with no significant difference among biomasses. In H/C ratio, secondary branch and stem have the highest value (H/C = 1.48), no significant difference between the biomasses were found for this property. Parchment appears to have a low value for the heating value considering the relatively high O/C ratio. This fact may be also associated with high AC. According to [22], higher proportion of oxygen, hydrogen and inorganic elements, compared with carbon, tend to decrease the HHV of the fuel.

3.2.3. Heating value

[31], reported that heating value is one of the most important parameters for energy modeling and simulation in thermochemical conversion processes. For the HHV, Table 3 shows mean values between 18.30 and 19.45 MJ kg^{-1} (dry basis) similar values are found in literature (18.60–21 MJ kg^{-1}, dry basis) for residues from coffee production chain and are analogous to biomasses commonly used in energy generation [6,32,33]. NHV shows mean values between 14.11 and 16.10 MJ kg dry^{-1}. Primary branch has the higher value of NHV with no significant difference with the other biomasses, mainly due to its low moisture content and its high HHV, influenced by low AC and mineral composition. (Table 3).

3.2.4. Proximate analysis

The proximate analysis aims to quantify the moisture, volatiles (condensable and non-condensable), fixed carbon and ash biomass content. The FC content is of special interest since this indicates the potential for charcoal generation from devolatilized biomass. The FC content in the samples varies in the interval of 14.62 %–21.23%; secondary branch presents the highest values of FC content with no significant difference among the biomasses. The biomasses studied presents high values of FC, similar to FC content mentioned in the literature for biomasses more commonly used in energy generation, such eucalyptus wood [34,35]. For VM, the range of values was 74.07 %–83.70%. The primary branch presents the highest volatile matter content (83.7%), significance difference between the other biomasses, and similar to solid fuels as eucalyptus (82.62%) and bamboo (84.65%) [36,37]. Solid fuels with high VM and low FC content are more susceptible to thermal degradation [38], requiring less length of time on a thermochemical process, making the biomass degradation faster compared to fuels with high FC and low VM content.

Ash is the inorganic solid residue left after the fuel is completely burned [39]. In the data obtained for ash content, it was observed that the residual biomasses from the coffee production chain had low ash contents in the range of 1.67 %–4.33%, except for the parchment and leaves, which had higher values of 5.84% and 7.17%, respectively. According to [40,41], in the coffee production chain, the residues from the coffee cherry typically generate significantly more AC than the coffee woody biomasses, supporting the data obtained. Few results of coffee shrub leaves have been reported; however, studies from leaves of different species show that ash content is significantly high compared to the tree and shrub wood from which it comes: for example [42] reported 16.8 g kg^{-1} - 67.8 g kg^{-1} AC of leaves in different trees and shrub species.

The mineral composition of ash (Table 3) shows that potassium (K), calcium (Ca), chlorine (Cl) and magnesium (Mg) present dominants levels in the ashes, and manganese (Mn), iron (Fe), copper (Cu) and sodium (Na) appeared in small quantities. The values of the minerals showed significant difference in the analysis of Bonferroni between the biomasses for some of the samples. Stem bark, parchment and leaves were the biomasses with more significant difference in the minerals content analysis, this is because the mineral concentration in crop-related biomass is strongly influenced by the type of biomass (herbaceous biomass, wood, fruit and crop residues), and also the harvest time and fertilization practices [43]. The parchment shows the highest content of K (12.09 g kg^{-1}) followed by the leaves. However, these residues and the stem present the lowest values of Cl, 3.16, 4.36 and 3.08, g kg^{-1} respectively. The stem also evinces low content of K (4.06 g kg^{-1}) as the stem bark (2.94 g kg^{-1}) does.

These minerals indicate potential ash-related problems at high or moderate thermal conversion temperatures [39,44–48]. The release of Cl and K is a main concern due to their effect on corrosion when biomass is combusted or gasified [49,50]. They also affect the deposit formation or fouling of heat transfer surfaces [51,52] and deactivation of Selective Catalytic Reduction (SCR) [53]. Emissions of hydrogen chloride (HCl), methyl chloride (CH_3Cl), Cl_2, or alkali chlorides, mainly potassium chloride (KCl), sodium chloride (NaCl), and calcium chloride ($CaCl_2$) are not desirable [54–56]. It is preferable to have a chloride content at or below 0.2% to prevent ash fouling in the thermochemical processes [57]. Furthermore, the literature report that in the biomass thermochemical conversion processes, Cl is primarily released during the devolatilization [58]. [59] found that 60–80% of Cl contained in woody biomass are released during the devolatilization phase in a fixed bed reactor at low temperature. [32,60,61] also observed the reduction of Cl during low temperatures pyrolysis by 20 %–50% or more.

The silica contents are quite small for all biomass samples (0 %–0.4%). The influence of the silica on combustion and gasification processes has been reported at temperatures higher than 873 °C because of the ash deposition propensity in thermal fuel conversion systems. The presence of minerals increase both, the tendency for ash particles to stick to heat transfer surfaces and the subsequent rate of strength build-up in ash deposits. These operational problems are closely related to the chemical composition of the AC. The gasification process requires a feedstock with less than 5% ash content, preferably less the 2%, in order to prevent the formation of clinkers [62]. To mitigate the negative effects of minerals in thermochemical conversion processes [63], suggested a pre-treatment to reduce their concentration in the fuel, e.g. fuel leaching.

3.2.5. Chemical composition

Another important characteristic of biomass is the composition in terms of the main structural chemical compounds. Data of chemical composition is presented in Table 3. The dried biomass is composed mainly of about 40%–60% of cellulose (composed of units of Anhydroglucose linked by glycosidic bonds β1-4), 15%–30% of hemicelluloses (matrix polysaccharides) and 4 %–35% of lignin (cross-linked phenolic polymers) [39,64]. However, residues from coffee production chain contain several other components, including lipids, tannin, polyphenols and nitrogenous compounds [65–67]. These minor components were not evaluated in this study, but were considered in the mass balance presented in the Table 3.

The carbohydrate fraction range for the studied samples were 17.90 %–33.25%; 5.30 %–14.55%; 0.90 %–2.50%; 0.90 %–3.30%; 1.35 %–4.50% for anhydroglucose, anhydroxylose, anhydrogalactose, anhydromannose and anhydroarabinose, respectively. These values are within in the ranges found in studies carried out for biomasses used in energy production, where the anhydroglucose represent, on average, 46.6% of the chemical composition of biomass, varying from 44.5% to 50%, the anhydroxylose are the dominant fraction of the hemicelluloses and represent 10.8%–13.2%, on average of 12.2% of the biomass. The other carbohydrates (anhydrogalactose, anhydromannose and anhydroarabinose) contributed with approximately 0.7%, 0.6% and 0.2%, respectively [68].

The chemical composition of the biomass exerts a great influence on the results of energy conversion, affecting the thermogravimetric performance of the process. The hemicelluloses are more susceptible to the reactions of thermal degradation because of the presence of hydroxyls connected to its main chain and the absence of crystalline agglomerates [69]. The branched chains of the hemicelluloses and cellulose are easily degraded at low temperatures, having maximum peaks loss at approximately 275 °C for hemicelluloses and 350 °C for cellulose [70].

For lignin, higher content in biomass leads to more sustainable biofuel production, because lignin is the chemical component that has a greater thermal stability due to the C—C bonds between monomeric units of phenyl-propane, and consequently has more stability in its aromatic matrix contributing for charcoal and products like methanol and bio-oil formation [71]. The acid insoluble lignin content of the samples evaluated in this study varied from 24.52% to 40.98% and soluble solids from 2.07% to 3.59%, similar to the reported values for soluble and insoluble lignin from biomasses used in energy production such *Eucalyptus grandis, Eucalyptus globulus, Eucalyptus dunnii and Eucalyptus urophylla* [72], and higher values than those reported in the literature for *Coffea arábica* residues [40].

The total extractive content ranged from 10.57% to 24.72%. Leaves of the shrub of *Coffea arábica* present a total extractive significantly higher than the other lignocellulosic materials (Table 3). The high extractive content of the leaves (24.72%) is mainly due to the residual fraction of amino acids, sugars and mucilage of low molar mass not removed during the milling of the biomass, because the extraction with ethanol/toluene only extracts substances such as waxes, fats, resins, phytosterols and non-volatile hydrocarbons [73]. The lowest levels of total extractives were found in the samples of the coffee shrub wood, corresponding to approximately 50% of the total extractives verified for the leaves. Because of high extractive content its use in processes such as the production of cellulose pulp is not attractive due to the increase in the expense of reagents.

The extractives play an important role in the use of biomass, because they influence the physical and energetic properties. Depending on their thermal stability, these substances can contribute to the increase in the yield of charcoal. Some of the extractives are volatile and therefore they are important in the direct burning of the biomass, because they react faster and help to maintain the combustion flame. For the production of charcoal, the high volatile extractive content in the biomass is detrimental because it provides lower gravimetric yield in charcoal due to the degradation of these substances at low temperatures [74].

3.2.6. Thermogravimetric analysis

Fig. 2 shows the thermal behavior of the residual biomasses of the coffee production chain by Thermogravimetric analysis (TG) and Differential thermogravimetric analysis (DTG).

It is observed that the thermal degradation profiles of the biomasses were similar, with small differences in the temperatures corresponding to the maximum peaks of the curve, mainly related to the degradation of the hemicelluloses and cellulose. The thermogravimetric data (TG) curves and the first derivate data (DTG) curves, usually show three bands of thermal degradation, which the first one is attributed to the drying of the biomasses and the other two to the degradation of its main components; it should be emphasized that each biomass components degrades in different temperature ranges. The second temperature range corresponds mainly to the thermal degradation of the hemicelluloses and of cellulose and lignin in smaller proportions. The third thermal degradation range was then initiated, this temperature range corresponded mainly to the degradation of the cellulose. The loss of mass for the cellulose needs a greater amount of energy than the hemicelluloses, due to the depolymerization of the cellulose chain and the breakdown of its monomer [75], that is the reason the degradation of the cellulose occurs after the degradation of the hemicelluloses. The degradation peak of lignin is absent, due to the fact that its thermal decomposition occurs in a wide temperature range [69,76]. Table 4 shows the measurements of the mass losses (%) obtained for each biomass, according to the temperature ranges from T_i (initial temperature) to 600 °C, with intervals of 100 °C.

As presented in Fig. 2, the combustion process of the samples could be divided into two stages. The first stage extended from 33°C to 127 °C; 23°C-105 °C; 32°C-107 °C; 31°C-101 °C; 27°C-121 °C; 25°C-102 °C for leaves, primary branch, secondary branch, stem, stem bark and parchment, respectively, which represented the dehydration by evaporation. The second stage was from 233°C to 424 °C; 243°C-380 °C; 237°C-422 °C; 242°C-384 °C; 233°C-464 °C; 280°C-364 °C for leaves, primary branch, secondary branch, stem, stem bark and parchment, respectively, which represent the liberation of the volatile compounds. A similar phenomenon was shown in the combustion characteristics of oil palm fiber and eucalyptus in torrefaction [77]. From Table 4, the mass loss percentage of the first and second stage in the total mass loss was approximately 8.04% and 45.02%; 13.76% and 58.00%; 7.63% and 55.99%; 9.73% and 46.00%; 7.04% and 64.01%; 8.00% and 50.57% for leaves, primary branch, secondary branch, stem, stem bark and parchment, in the first and second stage, respectively. As coffee shrub residues are biomasses, the main composition of the biomasses are cellulose, hemicelluloses and lignin. Therefore, the combustion of coffee shrub residues corresponds to the combustion of other biomasses. Cellulose rapidly decomposes between 300 °C and 350 °C; lignin decomposes between 410 °C and 540 °C and hemicelluloses decompose between 198 °C and 398 °C [76–78]. Therefore, the mass loss in the second stage of the thermal degradation samples was because of the decomposition of cellulose and hemicelluloses. The stem and primary branch of the coffee shrub present higher mass losses in the second stage. Probably these biomasses have higher rates of cellulose crystallite. The opposite is observed for leaves, which have the lowest degradation rate and are responsible for the greatest residual mass.

3.3. Biomass potential for energy purposes

Alternative routes for the waste use have been continuously studied and proposed to generate attractive and competitive products, such as solid. Liquid and gaseous fuels (briquettes, pellets, charcoal, bio-oil, biogas), as well as several chemical products, such as natural antioxidants, enzymes, vitamins, cellulose, lipids, proteins, and pigments. Knowing the characteristics of the biomass is a very important factor to understand its influence on the appropriate process of energy conversion. According to the data obtained, the following section describes the effects of the properties of biomasses evaluated in thermochemical and physical processes, as well as their impact on operational and economic parameters:

- For direct combustion, wood with high basic density (> 500 kg·m-3) results in more concentrated fuel energy, due to the greater mass of fuel contained in the same unit volume [79]. In this sense, coffee wood is a desirable material for charcoal production. In addition, the charcoal density will also be higher, resulting in greater strength and higher energy per volume.
- High volatile content shows high potential for bioenergy production

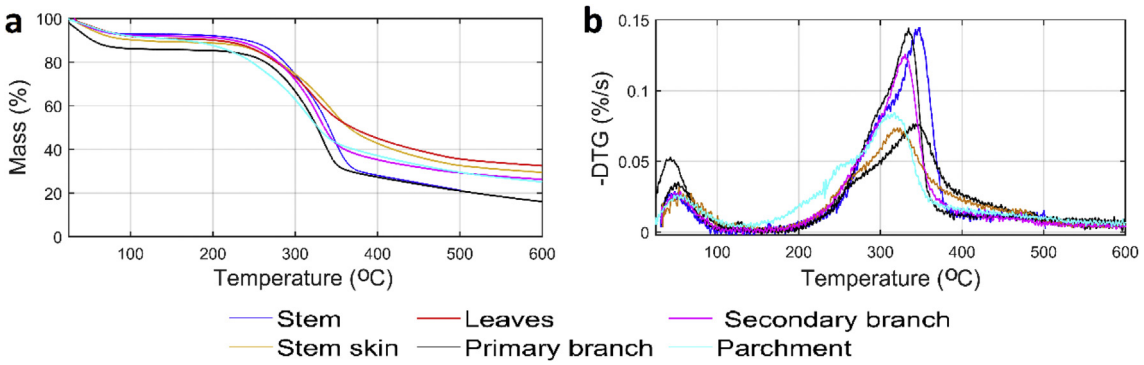


Fig. 2. TG (a) and DTG (b) of the residual biomasses of the coffee production chain.

Table 4
Values of mass loss of biomasses in function of the temperature ranges, in percentage.

Biomasses	Temperature rates (°C)						Residual mass (%)
	T_i - 100	100–200	200–300	300–400	400–500	500–600	
	Mass lost (%)						
Leaves	8.04	1.85	16.94	28.08	9.47	3.16	32.46
Primary branch	13.76	0.92	18.68	39.32	6.34	4.90	16.08
Secondary branch	7.63	1.08	19.45	36.54	6.02	3.00	26.26
Stem Bark	9.73	1.49	14.22	31.78	10.17	3.13	29.47
Stem	7.04	0.82	17.66	46.35	6.86	4.99	16.00
Parchment	8.00	4.31	24.80	25.77	7.61	4.44	25.07
SD[a]	2.48	1.31	3.52	7.65	1.71	0.94	6.84

[a] Standard deviation.

through the direct conversion of raw material [80]. Charcoal and ash are the main residues obtained from the thermochemical conversion processes. The high volatile content of the stem and primary branch of the coffee shrub, as well as its low percentage of ash compared to the other evaluated biomasses make them desirable as feedstock for combustion.

- Woody parts of the coffee shrub have high economic potential for energy applications. The low moisture content reduces transport and storage costs [81]. Additionally, the energy consumption in the drying stage when subjected to processes such as gasification, combustion and pyrolysis, decrease.
- For the production of bio-oil by fast pyrolysis process, the biomass is subjected to high temperatures and short vapor residence time. High ash content generates secondary vapor cracking, reducing the bio-oil quality and liquid yield. However, the presence of inorganic components such as potassium favors the formation of charcoal [62]. As a result, leaves and parchment are desirable biomasses for fast pyrolysis process.
- During the processes of combustion, the sulfur is converted into H2S and SO2, which are strong sources of contamination. In this sense, leaves of the coffee shrub are the least qualified because of the higher content of sulfur. In addition, the sample has the highest nitrogen content, resulting in the formation of nitrous oxides.
- For the charcoal production, biomass with lower fractions of cellulose and hemicelluloses should be preferred. The parchment of coffee cherry, stem, primary and secondary branch of coffee shrub experienced a greater thermal degradation than the other biomasses at low temperatures, probably, due to the high anhydrosugars content in its chemical composition
- The high content of cellulose and high calorific value of the parchment of the coffee cherry makes it an attractive biomass for use as a direct combustion material.
- Waste of the coffee production chain are desirable materials for the densification processes, due to them lignin content and humidity, conditions that favoring agglomeration [82]. Briquettes increase energy density of waste materials and reduce storage and transportation, desirable factors for the energy industry.

The literature does not provide enough information of the evaluated biomasses due to the complexity relation of the sample properties and the conversion processes. However, now it is possible to create a database that allows to classify the energetic potential of the waste from coffee production chain based on its physico-chemical characterization.

4. Conclusions

Residual biomasses from the coffee production chain could be classified as suitable feedstock for thermochemical conversion processes with low moisture content, carrying an average higher heating value, and volatile matter content. Additionally, it was also found, that ash composition is not detrimental to use and low sulfur content corresponding to good environmental performance. The composition of residual coffee shrub biomasses will lead to good product quality for charcoal. Therefore, the characterization of the samples shows that the thermochemical conversion and densification technology is an environmentally friendly alternative. It can be used to upgrading the large quantity of waste generated by the coffee industry into energetic valued residues thus improving their management.

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Publication II

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Evaluation of thermochemical routes for the valorization of solid coffee residues to produce biofuels: A Brazilian case

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Evaluation of thermochemical routes for the valorization of solid coffee residues to produce biofuels: A Brazilian case

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ABSTRACT

Coffee production in Brazil creates significant amounts of residues. The goals of this study are to evaluate the characteristics of these residues (parchment, husk, pulp, spent grounds, silverskin and defective beans); to discuss their potential for conversion to improved biofuels via thermochemical methods; and to develop mass and energy balances of the processes to help determine the value of residues for direct combustion, fast and slow pyrolysis, gasification, hydrothermal carbonization and torrefaction.

Particularly the pulp, but also husk and parchment, are characterized by high moisture, as well as high contents of cellulose (41–64%) and hemicellulose (27–35%). These residues are suitable for several conversion routes, albeit with the drawback of drying need for the dry methods. The ash of these also creates a risk of fouling, corrosion and agglomeration with high-temperature and fluidized bed technologies. The silverskin and some of the defective beans are available at lower moisture. The spent coffee grounds appear a particularly advantageous residue for energy use: while moisture varies, the roasted product dries easily and has the highest heating value of the residues. For defective beans, little thermochemical treatment data is available.

Among the technologies, for wet feedstocks hydrothermal carbonization has the advantage of post-conversion drying. Gasification appears advantageous for parchment with a high syngas yield and heating value. Fast pyrolysis of biomass suffers from the oxygen content of the liquid, requiring additional treatment; slow pyrolysis may be more appropriate. In conclusion, coffee residues have potential as feedstocks for a number of thermochemical conversion processes.

1. Introduction

Climate change has received increasing attention in academic studies, government policies, as well as in public and private sector actions. According to the Intergovernmental Panel on Climate Change [1], the main cause of global warming is the anthropogenic emissions of greenhouse gases (GHGs), such as carbon dioxide (CO_2), methane (CH_4) and nitrous oxides (NO_x). An estimated 1.0 °C warming over the pre-industrial temperature levels has been reached in 2019, and increasingly severe consequences are predicted if the warming trend is not stopped to 1.5 or 2.0 °C [1]. Brazil is the fourth largest GHG emitter in the world, with agriculture, forestry and other forms of land use the main sources of emissions [2]. The anthropogenic emissions associated with the Brazilian energy matrix reached 436 MtCO2-eq in 2017 [3]. On the hand, there is also a large potential to curb emissions through the use of renewable energy [4]. Hydroelectricity currently accounts for 68% of the total electricity supply [5]. Hydropower alone cannot meet the predicted growth of power demand, however. At the current expansion rates, Brazil will reach the maximum obtainable capacity of hydroelectric generation in the next decades [6,7]. Heavy reliance on hydropower is also a risk for security of supply in case of the droughts, which was already experienced in the recent years [6]. The future Brazilian energy system should thus be more balanced, using also other low-emission sources [6,7].

Sustainably produced biomass has been identified as having significant potential for GHG emission mitigation [8]. In Brazil recent incentives i.e. 'National Climate Change Plan' [9], '2030 National Energy Plan' [10] and 'Decennial Plan' [11], determine targets for the reduction

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of greenhouse gas emissions and increasing renewable energy generation, with a particular focus on large-scale use of bioenergy. The energy policies implemented in Brazil are mainly aimed at supporting the use and production of liquid biofuels [12]. At the same time, it is estimated that plantation crops as feedstock for biofuel production will become the dominant biomass source category according to a forecast until 2030 [13]. Biomass can also facilitate decentralized production near the demand, thereby creating work and income opportunities in rural areas. Particularly when it can be used in industrial processes for combined heat and power generation (CHP), biomass can provide a highly efficient and low-cost energy source.

The availability of large amounts of residual lignocellulosic biomass and the high productivity of the agricultural and forestry sectors in Brazil combine for a significant potential to increase the share of bioenergy, while simultaneously reducing the costs of managing the residues [14]. According to The Global Energy Network Institute, Brazil is the largest user of biomass for industrial heat; 1.6 EJ of heat was generated in CHP plants in 2018. Most of this was sugarcane residues from sugar production [15]. Coffee production is also one of the biggest agroindustries in Brazil, and responsible for a considerable side stream of residues. Several studies have indicated a potential for profitable applications of coffee residues, their high availability for collection, as well as their rich compositions in carbohydrates, proteins, pectin, and bioactive compounds such as polyphenols [16]. Currently the residues are largely discarded and not used productively, however. This is due to several reasons, including shortcomings of Brazilian agricultural policies and the coffee crop coming from small farmers, lack of specialized support of financing, and lack information on the treatment of residues among the farmers. The international companies and large roaster which constitute the majority of the global coffee market prioritize the quality of the green coffee and the international trade. The collection and treatment of residues is not a priority, and opportunities of the coffee growers to find solutions to reduce costs are limited [17].

The main coffee residue and the one most frequently studied for biofuel production is the spent coffee grounds [18–21]. Pulp, parchment, husk, and defective coffee beans have also been studied; reported potential applications include adsorbent materials [22], biofuels [23, 24], fertilizer [25], livestock feed [26], compost [25], among others. Nonetheless, more research is still needed, e.g. for defective coffee beans, which could be suitable for the production of solid biofuels [24]. Failing to take advantage of the residues generated from coffee production chains can cause environmental problems, since unused residues are often discarded without treatment [23]. To produce 60 million kg of dried coffee beans generates approximately 218 million kg of fresh pulp and mucilage, resulting in a sewage water chemical oxygen demand similar to that generated by 1.2 million people in one year [27].

This research addresses the potential of coffee solid residues for efficient production of energy through thermochemical conversion technologies. Information collected to a single source for solid coffee residues applications has not yet been evaluated, except for a few studies reporting the potential and characterization of industrial coffee by-products [16,25]. The primary objective and the novelty of this work is to collect the mass and energy balances for different thermochemical routes using solid coffee residues as a feedstocks, in order to determine the viability of possible applications viability. Due to the limited availability of comprehensive information on the mass and energy balances in processes using coffee residues, an extensive review of composition and characterization of coffee by-products is also reported. In addition, the energy conversion processes implemented to treat the coffee residues were studied. The evaluated technologies - pyrolysis, gasification, hydrothermal carbonization and torrefaction - were chosen due to their flexibility in the use of raw material, fast conversion rates, and diversity of products.

2. Coffee

Coffee shrubs belong to the family *rubiaceae*, of the genus *coffea* dicotyledonous. Over 103 species of the sub-genus *coffea* have been reported [16]. However, just two account for the majority of commercial beverage production, *coffea arabica* (Arabica) and *coffea canephora* (Robusta), with 64% and 35% shares of the all global production, respectively [25]. Coffee cherries are the raw fruit of the coffee shrub. They are composed of two coffee beans covered by four other structures (Fig. 1): (i) outer skin, formed by the outermost layer of the fruit, (ii) mucilage, a thin layer (0.5–2 mm) composed of a liquid colloidal system, (iii) parchment, a cartilaginous membrane, and (iv) silverskin, thin layer that surrounds the bean [25].

The cultivation, industrialization and commercialization of coffee production has evolved significantly throughout the course of Brazil's development, especially in terms of location of production. Currently, the coffee industry supports a large number of jobs and generates a significant foreign trade income for Brazil [28]. In 2019 the world production of coffee beans reached 10 million tons, where Brazil was the largest producer (37%), followed by Vietnam (18%) and Colombia (8%) [29]. The production of coffee in Brazil takes place in fifteen states, and comprises in total 1.8 million hectares of coffee plantations (*c. arabica* and *c. robusta*) [30]. The southeastern region of the country accounted for 84% of the total production in 2017 [30]. Minas Gerais, Espírito Santo, São Paulo, Bahia, Goiás, Paraná and Rondônia are the main Brazilian producing states of *c. arabica* and *c. robusta*. Considering the external market, United States, Germany, Italy, Japan and Belgium are currently the main buyers, acquiring both coffee beans and soluble coffee [31].

2.1. Coffee agro-industrial process

The production chain of coffee includes several stages of processing, production, and distribution. For processing, the beans are separated from the outer layers as soon as possible after harvesting to avoid natural fermentation, which may have a negative impact on the coffee quality. The separation can take place by dry, wet and semi-wet methods. Fig. 2 summarizes the mass balance of the residues of processing 1 kg of coffee cherry in dry basis (db).

In Brazil the most common way of coffee processing is the dry method, where the fruit are dried naturally by the sun or artificially in an oven. Depending on the type of harvest and the processing conditions, the fruit can be separated from impurities (stones, sticks, leaves) and also by maturation in washer/separators. In order to obtain the beans,

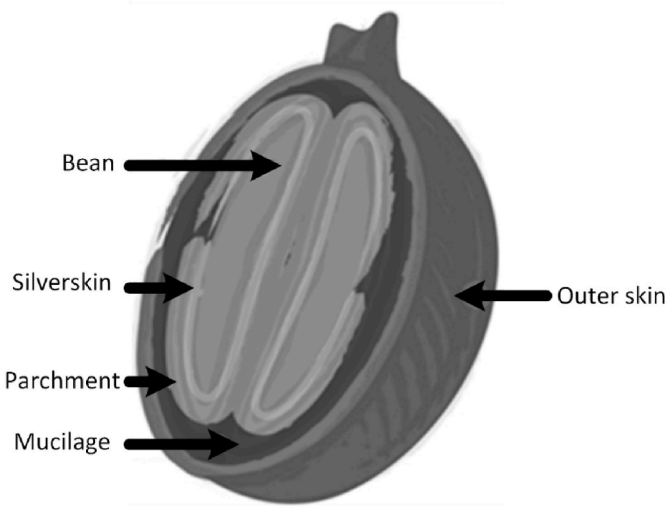


Fig. 1. Cross-section of the coffee cherry.

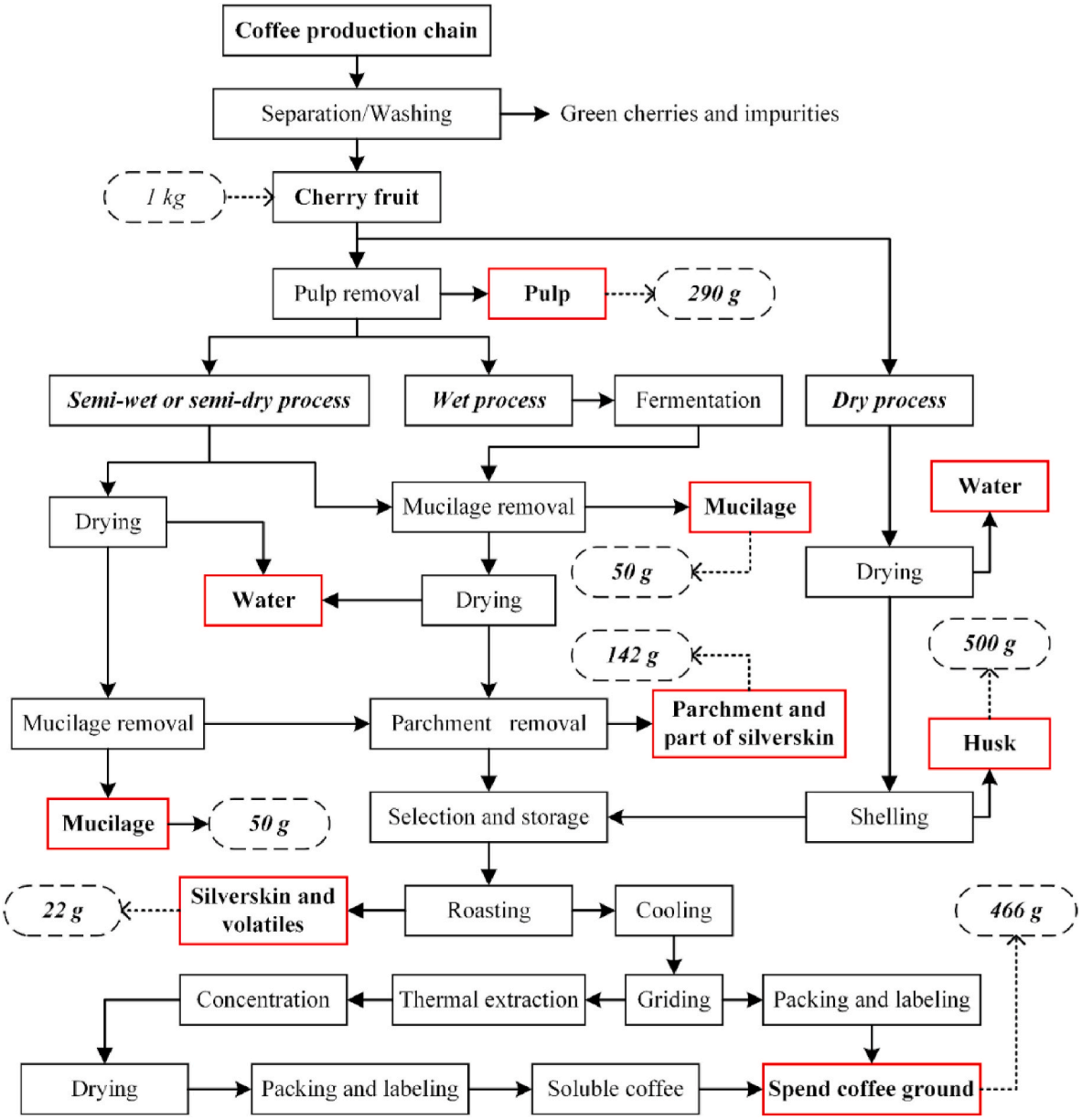


Fig. 2. Flowchart of post-harvest coffee processing and generated waste.

the outer skin, mucilage and parchment are removed by peeling. These residues, known as the husk, constitute 50–60% of the dried fruit [25]. The wet coffee processing is more common in Brazil's main competitors, Colombia and Vietnam. The advantage of the wet method is better preservation of the intrinsic attributes of the coffee bean and a homogeneous green coffee product; this results in higher consumer acceptance and thus higher prices in the international market, offsetting the higher production cost of the wet method. As shown in Fig. 2 the fruit are washed, mechanically depulped, demucilled, fermented and dried naturally or artificially to a moisture content of approximately 12% [32]. During the depulping stage, the outer skin and part of the mucilage are removed. The mucilage that remains adhered is digested in the fermentation tank. The remaining parts of the cherry structure are placed to dry, followed by sorting and classification. In this last step the parchment and part of the silverskin of the bean are stripped, the impurities separated, and the beans are classified by shape, weight and size. Finally, roasting takes place, separating the silverskin from the bean. This process influences significantly the final product, as the transformation of the polyphenolic components leads to several changes in the chemical and biological composition.

Eventually the beans proceed to roasting, followed by a granulation stage, in which the dried beans are crushed and ground, for soluble coffee and capsule industries. Brazil's main product in the international market is the green coffee, accounting for 89% of the 2.4 million tons of total coffee exports in 2019; in comparison, soluble coffee and roasted coffee reached just 10% and 0.1%, respectively [33]. While the growing sector searches for better quality coffee [34–36], the industry has not kept up with the pace of innovations, failing to add value to the product in the industrial phase.

2.2. Solid coffee residues

Global coffee consumption has increased by approximately 6% during the last five years, with Europe as the main consumer accounting of 3.3 million tons [29]. The increasing demand generates an increasing amount of waste from the processes. Often the waste is not properly treated, and the functional properties of the residues are left unexploited.

Pulp (the outer skin and part of the mucilage) is the first residue generated in the processing of the coffee cherry and represents approximately 44% of the fresh cherry weight, or 29% on dry basis [37]. Due to its composition and typically high moisture content, the pulp decomposes fast, and is a source of pollution to the soil and groundwater, causing chemical and physical changes. Mucilage represents approximately 5% of the dry weight of the cherry [25]. If it is allowed to be in prolonged contact with the coffee bean, the mucilage can cause grain deterioration and quality control problems [25]. Together with coffee pulp, it can act as an excellent substrate for the growth of fungi, bacteria and other micro-organisms [25]. The parchment and the silverskin represent approximately 12% (db) and 2.2% (db) of the coffee cherry, respectively. If discarded to the environment, the pollution hazards include not only the considerable oxygen demand of the biological decomposition, but also the additional risks caused by the presence of high quantities of toxic organic substances, such as caffeine, tannins, and polyphenols [23,25].

Defective and immature beans collected during the harvesting and preprocessing are also considered solid residues. These beans, known as "PVA defect" in Brazil for Preto (black), Verde (green) and Ardido (sour), can result in a significant loss of quality in the final coffee drink unless separated from the process. Approximately 20% of Brazilian coffee production are defective beans [38]. These are usually separated from the exported coffee, and incorporated in the domestic market, thus reducing the quality of some of the roasted coffee consumed in the country. The spent coffee grounds (SCG) obtained after producing the beverage are the final residue considered. The insoluble SCG residue represents 90–92% of the ground beans [39]. SCG is generated in large quantities, approximately 480 kg per each ton of soluble coffee produced, and consequently has attracted considerable attention recently [40].

2.3. Chemical composition of coffee solid residues

In order to determine the energy potential of a fuel the main chemical and thermal characteristics must be known. For solid residues of the coffee production chain, these properties are presented in Table 1. The reported values of some of the properties vary greatly due to the conditions of the samples before the measurements.

According to Ref. [61], the moisture content (MC) of fresh coffee cherry varies from 63.5 to 71.6% and that of coffee pulp between 52.4 and 60.2%. Higher values can also be found due to the plantation conditions. The MC in SCG is also high, due to the short time between coffee boiling and moisture measurement. In contrast, relatively low values (<12%) were reported for parchment, husk, silverskin and PVA since drying is needed before their collection. High MC may cause difficulties in the utilization of solid coffee residues in transportation, handling, and processing, as well as ignition and combustion problems [37]. A pre-drying stage may be required before processing the feedstock through thermochemical conversion, except for hydrothermal carbonization process, where high MC is desired.

Fixed carbon (FC) content is of particular interest since it indicates the potential of charcoal generation from devolatilized biomass [23]. FC content of the solid coffee residues were similar to those biomasses commonly used in energy generation, such as eucalyptus wood (<20 wt %) [62]. Volatile matter (VM) is the portion of fuel released in the form of gases; high VM is associated with high reactive and fast rate of combustion [23]. Solid coffee residues have suitable characteristics for thermochemical conversion processes, since high VM and low FC contents make them more susceptible to thermal degradation. Ash content (AC) is the fraction of non-combustible inorganic materials in a fuel. A high ash content can cause a variety of problems, depending on the composition of the ash, such as fouling, erosion, corrosion, and agglomeration. The AC values found in the literature for all coffee residues varied, but were clearly higher than for the woody biomass from the coffee shrub [25]. Residues from the coffee cherry have higher contents of alkalis and silica compared to coffee shrub wood parts [23].

Coffee solid residues are mainly composed of carbon (C), making up from 30 wt% to 60 wt% (db), hydrogen (H), comprising typically 5–6 wt % and oxygen (O) 30–40 wt%. High fractions of C and H increase the higher heating value (HHV) of the fuel [63]. Table 1 shows HHV mean values between 16 and 24 MJ kg−1 (db), analogous to biomasses commonly used in energy generation [64,65]. Pulp, with high contents of both moisture and ash, has the lowest values of HHV. Small amounts of nitrogen (N) and sulfur (S) were also observed. The presence of N and S in the coffee residues have a direct impact on the environmental

Table 1
Elementary, proximate and high heating value of coffee production solid residues.

Biomass	Elementary[a] (wt%)					Proximate (wt%)				HHV ($MJ \cdot kg^{-1}$)	Ref.
	C	H	O	N	S	FC	VM	MC	AC		
Pulp	38.7	5.4	54.3	1.6	–	–	88.3	76.7	7.4	15.9	[41]
	47.8	6.3	43.0	1.9	1.0	20.0	73.6	11.3	6.0	18.2	[42]
	50.1	6.8	39.9	2.9	0.3	17.4	77.0	8.2	5.6	17.9	[43]
	51.3	6.8	38.7	3.0	0.2	–	–	10	0.6	16.0	[44]
Parchment	50.3	5.3	43.8	–	–	16.0	72.7	10.1	1.2	18.7	[45]
	46.5	6.8	46.2	0.4	0.01	15.5	76.6	7.2	0.7	17.9	
	50.7	6.2	42.0	0.8	0.2	20.1	74.1	11.9	5.8	18.3	[23]
	47.7	6.3	41.6	1.8	0.05	–	85.2	10.3	2.5	–	[46]
Husk	48.5	6.0	44.7	–	–	16.4	81.9	9.2	1.7	–	[47]
	50.7	6.2	42.3	0.8	0.07	14.3	83.2	10.1	2.5	18.34	[48]
	46.8	4.9	47.1	0.6	0.6	14.3	74.3	10.4	1.0	16.5	[49]
	44.5	6.0	48.4	0.78	0.29	8.84	79.8	10.1	1.2	18.74	[50]
	54.4	3.5	42.1	0.22	0.28	13.6	80.9	9.96	5.47	18.6	[51]
CS	–	–	–	–	–	16.1	80.7	7.5	3.2	17.8	[52]
	45.8	8.1	43.7	2.4	–	14.8	79.3	–	5.9	18.6	[53,54]
	48.2	6.3	40.0	5.5	–	–	–	–	6.3	–	[55]
	47.7	6.2	32.7	3.3	0.2		75.9	9.3	9.9		[46]
PVA	45.9	6.6	45.0	2.4	–	21.2	69.2	6.5	3.1	19.4	[24,56]
	46.5	7.0	38.3	3.2	0.1	12.7	77.3	5.0	4.9	20.3	[57]
SCG	57.7	7.8	31.7	2.4	0.2	20.8	75.5	75.5	3.7	24.15	[58]
	53.5	6.6	37.0	2.8	0.05	16.7	71.8	0.5	1.0	22.0	[59]
	56.0	6.2	34.3	3.1	0.03	19.3	69.4	9.3	2.0	23.8	
	59.5	7.3	30.7	2.5	–	13.9	83.5	5.7	2.7	21.8	[60]
	56.2	7.1	34.1	2.4	0.2	–	–	–	–	24.3	

[a] Ash free and db. CS-Coffee silverskin; PVA-defective coffee beans; SCG-Spent coffee grounds; FC-Fixed carbon content; VM-Volatile matter; MC-Moisture content; AC-Ash content; HHV-High calorific value.

pollution, due to the formation of nitrogen oxides (NOx) and sulfur compounds (SO_X, H_2S, COS) and the occurrence of fouling and slagging in thermal conversion systems [23,66]. Generally, S in biomass varies in the interval of 0.01–2.3% and N in 0.1–12% [67]. The reported values for solid coffee cherry residues are inside these ranges, and can be considered as an environmentally less harmful than for example fossil coal [16,25].

The structural composition plays an important role in the decomposition of the residues and the final distribution of the products generated in the conversion processes. The basic structure of all lignocellulosic biomass consists of extractives and three basic polymers: lignin, cellulose and hemicelluloses i.e. glucose, xylose, galactose, mannose, arabinose and fructose [64]. The reported average composition is shown in Table 2.

The hemicelluloses present in pulp are mainly arabinose (35.4%) and glucose (24%), [16,65,68]; for parchment, glucose (29.6%) and xylose (14.5%); for husk glucose (20.8%) and xylose (13.5%); for CS glucose (17.8 g/100 g) and xylose (4.7 g/100 g), and for spend coffee grounds, glucose (35.8%) and mannose (9.3%). No information on the hemicellulose composition was found for PVA. Coffee pulp, husk, PVA and SCG also contain some amounts of caffeine and tannins, making them toxic in nature and thereby a disposal problem. The high content of glucose and xylose in the coffee residues indicates attractive route for bioethanol production. While 1 ton of glucan is estimated to yield 1.11 tons of C6 sugars, xylan yields 1.14 tons of C5 sugars, producing 650 and 666 L of bioethanol, respectively, after fermentation [74].

3. Conversion of solid residues into energy

The conversion of biomass to energy can involve different routes according to the biomass characteristics. The end use of the energy is typically electricity, heat or mechanical energy, but there are a variety of available treatment and conversion technologies, each associated with different process parameters and product yields, to create suitable energy carriers between the raw biomass feedstock and the final energy use. The biomass conversion technologies can be classified according to the type of transformation used, as indicated in Fig. 3. The three main categories of conversion are biochemical, physiochemical and thermochemical.

Biochemical conversion relies on the processes of anaerobic digestion, fermentation, distillation and hydrolysis, in which the feedstock biomass molecules are broken into smaller molecules through the action of bacteria or enzymes. This type of conversion requires a longer time than the thermochemical routes, but it can be achieved with a smaller amount of external energy [75]. The most common example is the production of bioethanol from lignocellulosic biomass. Currently, bioethanol is the most produced biofuel at 45-50 Mtoe (more than 100 million m^3) globally per year [76]. Brazil and the United States account for almost 85% of the total global production, using mainly sugarcane and corn as feedstock, respectively [76]. Several studies have indicated also coffee residues as a potential feedstock for bioethanol production. Concentration of bioethanol varies depending on process conditions such as substrate loading, yeast strain, concentration, temperature and pH, among others. The concentration values reported for bioethanol from coffee pulp (11.28 g L^{-1}) [77], coffee husk (8.20–12.19 g L^{-1}) [78], and spent coffee grounds (19 g L^{-1}) [79], all fall within the range typically found for sugarcane (3.36–31.5 g L^{-1}).

Table 2
Chemical composition (wt% db).

Biomass	Extractives	Lignin	Hemicelluloses	Cellulose	Ref.
Pulp	26	17.5	26.6	63.5	[16,65,68]
Parchment	21.9	26.6	34.8	41.2	[23,65]
Husk	38.0	24.3	31.5	43.8	[16,69–71]
CS	15.9	28.6	19.3	22.8	[53–55]
PVA	52	3.4	6.0	28.8	[24]
SCG	22.3	33.6	24.20	36.5	[16,72,73]
	–	24.5	33.4	12.3	[53]

Physicochemical conversion encompasses the densification of biomass into pellets or briquettes [80], as well as physical extraction of oils by compression. This can be followed by esterification, in which the oils react with an alcohol in the presence of a catalyst, to produce for example biodiesel [21]. Defective coffee beans can be a potential feedstock for biodiesel production, since the extracted oils were successfully converted to fatty acid methyl and ethyl esters according to Ref. [81]. Satisfactory results for biodiesel production were also found for SCG [82]. Likewise, a number of studies concluded that pelletizing and briquetting processes of coffee residues are a convenient alternative to increase the energy density from the raw material [46,80,83–86]. With. coffee husk the energy density increases from 7.5 GJ m^3 of the raw material to 13.2 GJ m^3 in the form of pellets [83].

This work is on thermochemical conversion routes, where heat is used to promote chemical transformations of biomass for higher-quality products. Pyrolysis, torrefaction, hydrothermal carbonization, direct combustion, and gasification, were selected to evaluate and discuss the conversion potential of coffee residues for biofuels. The following sections describe the main characteristics of the technologies and their utilization in coffee residue treatment.

3.1. Thermochemical processes

Thermochemical conversion of biomass refers to the use of elevated temperatures to produce new improved energy carrier products and/or heat. A variety of routes and process parameters can be utilized depending on the desired products and the characteristics of the feedstocks; residence times vary from less than 1 s to days, temperatures from 180 to 1500 °C, the process may take place under oxidizing or reducing conditions, and may consist of endo- or exothermic reactions. The different processes and their typical characteristics and implementations are briefly outlined in the following. In addition, comparative experimental reports of coffee solid residues are summarized for the different conversion routes in Table 4. Due to limited studies of energy generation from coffee production chain residues, only partial information describing the efficiency of thermochemical process implementations on coffee residues conversion, has been found.

3.1.1. Direct combustion

At its simplest, thermochemical conversion can be direct combustion taking place under oxidizing conditions, with excess oxygen. Currently direct combustion of the raw biomass is still by far the most widely used thermochemical conversion route of biomass [87]. The combustion begins with drying, followed by devolatilization, combustion of gases, and char burning. The goal of the process is near-total combustion of the biomass into water and carbon dioxide, with minimal loss of heating value with unburnt carbon and gaseous hydrocarbons. The scale of equipment can vary from domestic stoves to industrial boilers of several hundred megawatts. The only direct product is heat, which can be the end use of the energy or implemented to generate mechanical work and from it, electricity.

A variety of combustion technologies are available for different types of biomass. Low moisture content biomasses with high calorific value are suitable for grate-fired or, if the fuel is sufficiently brittle and grindable, pulverized combustion, while fluidized bed combustion permits high-moisture, low or mixed quality biomasses to be used. For coffee residues, partial description of husk, pulp and spent coffee grounds direct combustion, and thermogravimetric analysis of defective coffee beans in oxidizing atmosphere, reported in Tables 4 and 5, was found in the literature. The husk and pulp are mostly either burnt in the farm or used as organic fertilizer, due to the absence of structured commercial markets. In the soluble coffee production, SCG is used as solid fuel in the boiler to generate steam. Before combustion the moisture is reduced to about 25–30% to improve the combustion efficiency

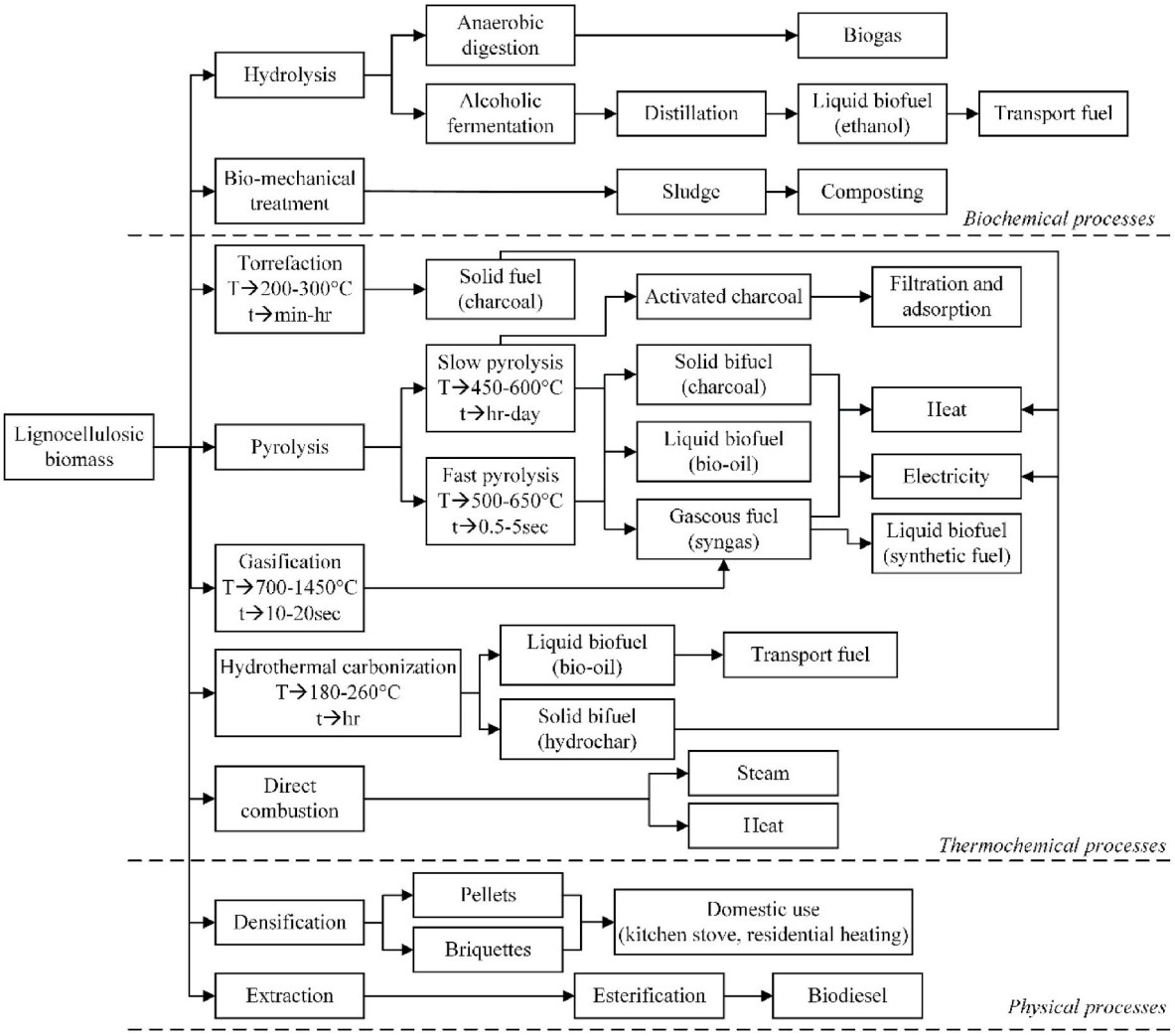


Fig. 3. Conversion route technologies.

[88]. Although wet residues as SCG could be burned in a suitable boiler, that would require large combustion chambers, more excess air and auxiliary fuel to maintain high enough temperature [89]. This would make the combustion of wet SCG inefficient and expensive.

3.1.2. Gasification

As the term suggests, gasification is a conversion route aimed at producing high yields of gaseous product, so-called syngas, by partial oxidation of the feedstock. The gasifying medium can be air, oxygen or steam, or a combination thereof. The process takes place at between 700 and 1450 °C and is typically net exothermic due to the partial oxidation taking place in the gasifier [90].

The process of gasification involves several stages. Typically, the raw biomass is dried before feeding into the gasification reactor, but final drying of the last fractions of moisture can only take place in the gasifier as the biomass particles are heated to over 100 °C temperature. As the temperature of the particles increases towards the reactor temperature, drying is followed by pyrolysis, which produces gaseous, liquid (condensable gas, tar) and solid products. The final reactions involve tar cracking, char gasification, partial combustion and shift reactions between H_2O and CO, and CO_2 and H_2 [91]. Tar cracking in particular is an important consideration, as the production of tars not only reduces the gas yield, but also poses additional problems in the form of equipment fouling and environmental pollution [92].

Operating parameters and composition of the produced syngas from husk, parchment, pulp, silverskin and SCG through gasification is shown in Tables 4 and 5 The syngas product has significant fractions of CO, CO_2 and H_2, and lower fraction of CH_4, results supported by Ref. [91]. The findings demonstrate the high energetic potential of coffee residues. A high gasification temperature results increases the gas-phase yield of the process. Approximately half of the molar fraction was N2; excessive diluting of the syngas with nitrogen can be prevented by the use of oxygen and/or steam as the gasification medium. The effect can be as much as doubling the HHV of the gas [93]. The syngas product can be cleaned and used as-is for engine fuels, industrial processes or heat and power industry, or further upgraded to gaseous or liquid fuels for example through Fischer-Tropsch process [94]. Syngas produced by eucalyptus sp., common biomass used in Brazil for energy generation, which generally contains 38% of H_2, 27% of both CO and CO_2 and 5% of CH_4 under conditions explained in Ref. [95], when compared with coffee residues content, higher percentage in eucalyptus were found, except for H_2 production, where for example parchment reported around 50% H_2.

3.1.3. Pyrolysis

Biomass pyrolysis is the process of thermal decomposition in the absence of oxygen. The process is endothermic, but if the oxygen has not been excluded at 200–300 °C, exothermic combustion of carbonaceous residue may take place. The fractions of gaseous, liquid and solid products can vary significantly depending on the implementation and

Table 3
Influence of biomass parameters during thermochemical conversion processes.

Parameter	Characteristics	Ref.
Moisture content (MC)	• MC promotes the formation of solid bridges during conversion process. • MC may reduce the reaction temperature and degrade the thermochemical conversion performance. • For gasification, acceptable moisture content can be as high as 20% or 30% • At high fuel/air ratios and high moisture content in gasification processes, the water shift reaction tends to the formation of hydrogen and carbon dioxide, increasing the CO_2 concentration under these conditions. • Variations in humidity hinder the carbonization and combustion control. • In combustion, fluidized bed technology allows using up to 65% MC fuels. • In pyrolysis, initial MC contributes to the water in the pyrolysis oil; above approximately 10% MC, the oil produced will separate into two phases. • For hydrothermal conversion, wet biomass can be used without drying.	[111–118]
Particle size (PS)	• PS influences decisions on biomass storage and transportation. • With a few exceptions, studies demonstrate that PS affects lignocellulose conversion, with small size correlating with high conversion. • Decreasing PS improves heat and mass transfer. • In gasification, the small particles produce more gas per kg of biomass than large particles; consequently, powdered biomass is most suitable for gasification • Water-gas, carbon gasification, secondary cracking and boudoir reactions are facilitated by small PS, increasing hydrogen and CO content in the product. • Reducing PS affects cellulose conversion positively. • Larger PS implies a reduction in the fuel pretreatment costs, and also the possibility of using available and inexpensive feeding systems such as screw feeders • PS plays important role in all the successive reaction steps (fuel heating, reactant and product diffusion between the particle and the reaction atmosphere, and solid–gas reactions) during the conversion process. • In gasification, smaller PS enables high gas quality and a reduction in the reactor size or a lower space residence time to achieve a complete cracking of the heaviest and condensable fractions. • In the pyrolysis process in a free fall reactor, a small PS increases the gas yield and decreases the char and tar yields • Reaction kinetics dominate gasification process at small particle size, shifting to heat transfer dominance as PS increases. • In a model of downdraft moving bed gasifiers, the larger the PS, the lower its surface temperature, and thus higher the required heat for the reactions to take place.	[119–129]
Density	• Low bulk density and low energy density reduce the feasibility of long-distance transportation. • The release of volatiles rich in hydrogen and oxygen during thermochemical conversion will improve the biomass energy density, since more oxygen than carbon is lost with the volatiles. • Process temperature has highest impact on energy density of thermochemically converted biomass; the effects of residence time and moisture are clearly less. • The density of the material affects the production capacity: for a given volume, a denser sample results in greater mass production. • Denser biomass produces higher density coal with advantages for energy use. • The changes in the basic density of wood during the thermochemical conversion process may be due to changes in the thickness of the wall of the fibers, reduction of the flame or increase in the length of the fibers and in the extractive content. The density of the material affects the production capacity of the carbonization sites, because for a given volume the use of the denser sample results in greater mass production. • Denser biomass produces higher density coal with advantages for energy use. • The changes in the basic density of wood during the thermochemical conversion process may be due to changes in the thickness of the wall of the fibers, reduction of the flame or increase in the length of the fibers and in the extractive content.	[112,130, 131]
Chemical composition	• Greatly influences the design of boilers and heat exchangers involving oxidation processes. • High ash content (>5%) lowers the calorific value and may cause problems such as fouling and corrosion. • When the biomass is heated above the glass transition temperature, the lignin becomes soft and exhibits heat-curable properties.	[69, 132–135]

process parameters. Very high heating rates to moderate temperatures followed by rapid cooling have been found to promote higher fractions of liquid products, high heating rates to high temperatures increase the fractions of gas, while slower heating rates and lower temperatures result in high solid yields [96,97]. Different types of pyrolysis exist; their classification is based on the operating conditions i.e. slow, fast, flash, intermediate and vacuum [98,99]. Due to availability of data, only slow and fast pyrolysis mass, and energy balances of some of the coffee residues could be reported; the findings are shown in Tables 4 and 5

Slow pyrolysis, earlier also known as conventional pyrolysis or just pyrolysis [100], aims at the production of solid char. The process involves treating the biomass over long residence times, up to several days, in an inert atmosphere at temperatures of 450–600 °C [101–103]. While the char is the main product, significant yields of liquid and gas are also produced. The residues are initially sun-dried for several days prior to feeding to a pyrolysis reactor [104]. HHV of 31 MJ kg^{-1}, was found for SCG [21]. Most of the information available in the literature for slow pyrolysis of coffee residues is reported for biochar formation from briquette/pellet, from where the residues are either first densified or treated through slow pyrolysis [104–106]. For briquettes, calorific value in the range of 18.5–19.5 [MJ·kg^{-1}], flame duration of 81–207 [min], ash content of 8.4–9.8 [wt%], fixed carbon of 45–59.3 [wt%] and volatiles of 22.6–33.5 [wt%], were reported.

Fast pyrolysis, sometimes also known as thermolysis, aims at a high yield of liquid product. Typical process parameters are approximately 1 s residence time and 500–650 °C temperatures [100]; the very short residence time necessitates very small particle size. Liquid yields as high as 75 wt% can be obtained [100]. Bio-oil yields of 56–62 wt% were found for husk and SCG, with 24 MJ·kg^{-1} oil HHV [100].

3.1.4. Torrefaction and hydrothermal carbonization (HTC)

Torrefaction and hydrothermal carbonization (HTC) are both mild thermochemical processes taking place at relatively low temperatures of less than 300 °C in the absence of oxygen. The processes are not significantly endo- or exothermic. They can be considered mild forms of pyrolysis, aimed at upgrading the solid raw biomass, with only small yields of liquid and gaseous products. For coffee residues, the products, torrefied biochar and hydrochar, have higher carbon contents and heating values than the feedstock. Compared to untreated feed, both are hydrophobic, brittle, and less prone to decay. The significant difference is that in torrefaction the reactions take place at approximately atmospheric pressure in an inert gas, while in HTC the feedstock is in a pressurized water slurry, typically at saturated state. For torrefaction, energy potential of the biochar obtained from eucalyptus sp., typical biomass used in Brazil for energy generation, was lower than the HHV reported for coffee residues, between 20.3 and 22.6 MJ·kg^{-1} at

Table 4
Alternatives for energy generation of residues of coffee harvest and processing.

Feedstock	Process	Parameters	Results	Ref.
Pulp	**Gasification**	t [min] = 200 mi [kg] = 9 t[h]: 1.11–8.15 air flow[kg h-1]:12.43–15.97	Char[%] = 18 Low production of tar Reduction temperature[C]:583.8–645.3 Experimental mole fractions [%]: 11–20 (CO2); 11–20 (CH4); 20–30 (CO); 15–18 (H2); 21–31 (N2) ΔG0 = −27 and −45 kJ/mol convergence range	[136] [137]
		T[C]:900 t[h]:1 O2 concentration[%]:5,10,15,21	T_X_{99}[min]:10.9–23.3 T_X_{50}[min]:2.5–9.3 R_{50}[min-1]:0.11–0.45 Gas yield [min mg-1]: 3.3x10-2 (CO2); 2.3x10-3 (CH4); 1.8x10-2 (CO); 0.5x10-3 (H2).	[138]
	Pyrolysis	T[C]800 heating rate [C.min-1]:40	Residue yield [%]: 9.40 T_{comb} [C]: 130 (dw/dT)max (wt%/oC): 0.44 (T = 110–350C); 0.35 (T = 350–510C); 0.49(T = 550–800).	
Husk	**Gasification**	Gasifying agent: air $T_{combustion-zone}$ [C]:755 $T_{gasification-zone}$ [C]:755	Syngas HHV [MJ Nm−3]: of 7.76 ± 1.27 Syngas composition [%]:12.14 ± 1.02(CO2); 13.81 ± 1.49 (CO); 14.77 ± 3.38 (CH4); 6.64 ± 1.42 (H2).	[139]
		T[C]: 790 and 815 Air flow rate[NM3 h-1]: 72-80	Syngas HHV [MJ Nm-3]: 3.07–3.34 Syngas composition [%]:17–18.7(CO2); 10.6–11.4 (CO); 1.6–2.4 (CH4); 7.5–12.4 (H2).	[140]
		T[C]: 815 Air flow rate[NM3 h-1]: 75	Syngas composition [%]:18.7(CO2); 11.4 (CO); 1.6 (CH4); 12.4 (H2); 52.3 (N2).	[141]
		T[C]: 839 Air flow rate[kg h-1]: 18	Syngas composition [%]:8(CO2); 8.2(CO); 14 (H2).	[49]
		T[C]: 700-740 Air flow rate[kg h-1]: 20.5	Syngas LHV [MJ Nm-3]: 3.42–3.61 Syngas composition [%]:7.1–7.2(CO2); 9.49–9.84(CO); 7.68–8.74 (H2); 3.88–3.97(CH4)	[142]
	Fast pyrolysis	Heating rate [°C/min]: 22 Residence time [min]: 4 T [°C]: 500	Yield [%]: SY (26.2); LY (56.5); NCGY (17.3) LHV biochar [$MJ.kg^{-1}$]: 23.2 LHV bio-oil [$MJ.kg^{-1}$]: 24.9	[64]
Silverskin	**Torrefaction**	Termogravimetric analysis Nitrogen flow rate [Lmin-1]: 3.5 T[C]: 200, 260 and 300 t[min]: 20,40,60	Weigh loss [%]: 8.6–16.3 (T = 220C); 38.4–44.9 (T = 220–300). HHV[MJ kg-1]: 20.6–25.5	[53]
PVA	**HTC**	T[C]: 150 t [min] = 40	HHV [MJ kg-1]: 20.2 SY[%]: 61.2 EY_{solid} [%]: 60.8	[57]
		T[C]: 200 t [min] = 40	HHV [MJ kg-1]: 22.82 SY[%]: 41.7 EY_{solid} [%]: 46.5	
		T[C]: 250 t [min] = 40	HHV [MJ kg-1]: 29.1 SY[%]: 34.2 EY_{solid} [%]: 49	
	Torrefaction	T[C]:210 t[min]: 6 and 15	Higher number and volatile compounds compared to control beans were reported.	[38,143,144]
SCG	**Gasification**	T[C]: 650-850 heating rate [C.min-1]:20	HHV[MJ.kg-1]: 16-34 Syngas [%]: 50–80 = H_2 and CO; 10 = CO_2	[145]
		T[C]: 585-720 Air flow rate[NM3 h-1]: 24.3	HHV [MJ Nm-3]: 3.05–3.95 Syngas composition [%]:17.7–18.4(CO2); 9.6–14.7(CO); 5.36–7.55 (H2); 3.13–4.23 (CH4); 56.9–62.8 (N2)	[60]
		T[C]: 765-799 Air flow rate[NM3 h-1]: 30.6–35.1	HHV [MJ Nm-3]: 2.7–3.64 Syngas composition [%]:14.2–17.6(CO2); 8.3–11(CO); 5.46–7.31(H2); 2.98–4.09(CH4); 62.9–65.4 (N2)	
	Torrefaction	Termogravimetric analysis Nitrogen flow rate [Lmin-1]: 3.5 T[C]: 200, 260 and 300 t[min]: 20,40,60	Weigh loss [%]: 4.5–10.3 (T = 220C); 34.6–42.1 (T = 220–300). HHV[MJ kg-1]: 22.9–32.2	[53]
	Fast pyrolysis	T[C]: 429-550 t[s]:23-42	Bio-oil yield[%]:61.8 biochar yield[%]:20.6	[146]
	HTC	T[C]: 180-250 t[h]: 3	Yield[%]: 61.7–87.2(SY); 9.7–22.6(LY); 3.1–15.8(GY) HHV[MJ kg-1]:23.64–31.15	[110]

t-residence time; T-temperature; SY-solid yield; EY-energy yield; ΔG0-Biochar standard Gibbs free energy of formation; T_X_{99}-time to achieve 99% conversion; T_X_{50}-time to achieve 50% conversion; R_{50}-Reactivity corresponding 50% conversion.

220–280 °C temperature in eucalyptus [107], and over 32 $MJ \cdot kg^{-1}$ for SCG at conditions described in Refs. [53].

As the reactions of the two processes are somewhat similar, so are the reaction products, but their behaviors differ due to the presence of water in HTC. Dry torrefaction produces a gas-phase mixture consisting of significant fractions of H_2O and CO_2, and various condensable and non-condensable organic compounds of mostly low to moderate heating value [108]. The HTC yields similar products, but as the process takes place in liquid water, the organic compounds remain dissolved in the water [109]. Experimental research of treating coffee residues by dry torrefaction or HTC is currently limited; available data is shown in Tables 4 and 5 [53,110].

The suitability of a given residue feedstock for the conversion technologies described above depends on a number of qualities and parameters. Table 3 summarizes briefly the most important effects of some parameters in thermochemical conversion processes.

4. Evaluation of the potential of coffee residues as biofuel feedstock

Based on chemical and thermal characterization analysis explained in section 2, description of thermochemical conversion technologies in

Table 5
Experimental results from previous studies of thermochemical routes for coffee solid residues.

Feedstock	Operation parameters	Optimum obtained results	Ref.
Direct combustion			
Husk	**Biomass in [kg]:** 200 **Reactor type:** Pilot-scale fluidized bed (FBC) **Reactor bed material:** quartz sand (0.48 mm) **T [°C]:** 500-900 **Flue gas (O_2) concentration [vol%]:** 10-16	**Exhaust gas composition (mg·m^{-3}):** NOx = 450–525; N_2O = 3-27 **N concentration in volatiles [%]:** 54.2 (at 500 °C); 52 (at 600 °C); 53.2 (at 700 °C); 60.2 (at 800 °C); 67.6 (at 900 °C) **Ash concentration [wt%]:** SiO_2 = 16.6; FeO3 = 2.4; P2O5 = 3.4; Al2O3 = 4.5; CaO = 9.8; MgO = 3.7; Na2O = 0.5; K2O = 36.9 **Note:** over 700 °C sintering observed	[161]
Pulp	**Technique:** combustion under TGA curve analysis **Heating rate [°C·min^{-1}]:** 10	**T_{comb} [°C]:** 130 **T_m [°C]:** 73 (peak 1); 302 (peak 2); 437 (peak 3); 592 (peak 4, associated to its high lignin content) **Residue yield [wt%]:** 9.40 **Exhaust gas yield [°C·mg^{-1}]:** H_2O = 0.07; CO_2 = 0.08; CO = 0.02; COH = 0.0015; NO = 0.0027; C_2H_5O = 0.0009; CH_3 = 0.0002; NO_2 = 0.0001	[138]
PVA	**Technique:** combustion under TGA curve analysis **Heating rate [°K·min^{-1}]: 15** **Biomass in [kg]:** 20 mg Air flow rate [Ml min^{-1}]: 100 **T [°K]: 303.15 to 873.15**	**T_m [°K]: 572.1** (peak 1); 698.1 (peak 2) Intensity [mg sec^{-1}]: 0.05 (peak 1); 0.04 (peak 2) T_{ig} [°K]: 528 T_b [°K]: 725	[24]
SCG	**Biomass in [kg·h^{-1}]:** 1.17 wb (11.1% MC) **Biomass in [kcal·h^{-1}]:** 5577 **Test time [min]:** 146 **Flue gas (O_2) concentration [vol%]:** 17.8 **Capacity of the boiler [Kw]:** 6.5	**Euxhaust composition (ppm):** CO = 643; Nox = 163	[155]
Gasification			
Husk	**Reactor type:** Fluidized bed gasifier **T [°C]:** 790 **$Air_{rate}/Biomass_{admission}$ [kg.h^{-1}/Nm^3.h^{-1}]:** 0.48	**Syngas Composition (vol%):** H_2 = 12.4; CO = 11.4; CH_4 = 1.6; CO_2 = 18.7; N_2 = 52.3; C_2H_4 = ~4.36; C_2H_6 = ~1.01; C_2H_2 = ~3.86. **HHV (MJ·Nm^{-3}):** 3.34	[140]
Parchment	**Mathematical model** **T [°C]:** 850 **$Air_{rate}/Biomass_{admission}$ [kg.h^{-1}/Nm^3.h^{-1}]:** 0.5	**Syngas Composition (vol%):** H_2 = 50.2; CO = 44.8; CH_4 = 0.9; CO_2 = 4.1 **LHV (MJ·Nm^{-3}):** 12.41	[162]
Pulp	**Reactor type:** Downdraft gasifier **T [°C]:** 700 **$Air_{rate}/Biomass_{admission}$ [kg.h^{-1}/Nm^3.h^{-1}]:** 0.55	**Syngas Composition (vol%):** H_2 = 22.6; CO = 19.17; CH_4 = 1.28; CO_2 = 11.5; N_2 = 45.45 **HHV (MJ·Nm^{-3}):** 5.81	[44]
SCG	**Reactor type:** Fluidized bed gasifier **T [°C]:** 632 **$Air_{rate}/Biomass_{admission}$ [kg.h^{-1}/Nm^3.h^{-1}]:** 0.61	**Syngas Composition (vol%):** H_2 = 6.69; CO = 14.7; CH_4 = 3.86; CO_2 = 18.1; N_2 = 56.3 **HHV (MJ·Nm^{-3}):** 3.95	[60]
Pyrolysis			
SCG	**Slow pyrolysis** **Reactor specification:** Thermolyne 79400 tube furnace **Biomass in [g]:** 100 g **T [°C]:** 450 **Heating rate [°C/min]:** 50 **Residence time [hr]:** 2	**Yield [%]:** SY (28); NCGY (21); aqueous phase (23.8); bio-oil (27.2) **Proximate analysis biochar [wt%]:** MC (1.3); AC (3.5) **Biochar composition [%]:** C (76.2); H (5.6); N (3.9); S (0.05); P (0.48); K (1.94); Ca (0.56); Mg (0.60); Na (0.17) **Biochar composition [ppm]:** Zn (51); Fe (676); Mn (156); Cu (105); B (31) **HHV biochar [MJ.kg^{-1}]:** 31 **Surface area of biochar [m^2·g]:** 1.1-.12	[21]
PVA	**Slow pyrolysis** **PVA impregnated with phosphoric acid (85%) at 3:1 mass ratio.** **Equipment: muffle furnace** **Temperature [C]: 500** **Residence time [min]: 30** **Study aim to produce activate carbon**	**Yield [%]: SY (29.68)** **Proximate analysis activate carbon [wt%]:** AC (3.8) **Activate carbon composition [%]:** C (81.1); H (3.5); N (1.8); S(0.01); O(13.7) Specific surface area [m2g-1]: 341.01 Pore diameter [nm]:4.9 Mesopore volume [cm3g-1]:0.2 Micropore volume [cm3 g-1]:0.03	[163]
Silverskin	**Slow pyrolysis** **Reactor specification:** vertical electrical heating furnace containing a tubular fixed-bed quartz reactor Biomass in [g]:6.00 **Nitrogen flow rate [mL min-1]: 49** **T [°C]:** 560	**Organic phase yield [%]: 15.2** **Solid weight loss [%]: 70** **bio-oil composition:** 50 N-compounds (18.51%), 30 phenols (26.70%), 30 unsaturated aliphatic hydrocarbons (8.28%), 28 saturated hydrocarbons (6.69%), 21 aromatic hydrocarbons (7.77%), 19 ketones (6.44%), 19 esters (4.90%), 12 carboxylic acids (5.54%), 9 alcohols (2.05%), and 10 compounds classified as “others” (3.20%): 3 aldehydes, 5 furan(one)s, and 2 indan(one)s.	[164]
Husk	**Fast pyrolysis** **Biomass in [g]:** 100 g stirring rate [rpm]: 64 **Heating rate [°C/min]:** 20 **T [°C]:** 500	**Yield [%]:** SY (26.2–28.7); LY (47.5–56.5); NCGY (18.6–24.8) **Biochar composition [%db]:** C (73.75 ± 0.5); H (1.99 ± 0.1); N (1.90 ± 0.2); O (6.00 ± 0.3) **HHV biochar [MJ.kg^{-1}]:** 24.6 ± 0.28 **LHV biochar [MJ.kg^{-1}]:** 23.16 ± 0.26 **Proximate analysis biochar [wt% db]:** VM (9.5 ± 1.18); FC (73.5 ± 1.48); AC (17 ± 0.63) **MC [wt% wb]:** 1.89 ± 0.14 **Apparent density biochar [kg·m^3]:** 401 ± 6	[69]

(*continued on next page*)

Table 5 (*continued*)

		Specific density biochar [kg·m^3]: 770 ± 10 **porosity biochar [−]:** 0.48 **Moisture aqueous phase (at different temperature ranges) [%wb]:** 82.05 ± 0.24 (25–200 °C); 77.22 ± 0.22 (200–250 °C); 61.09 ± 0.29 (250–300 °C); 55.31 ± 0.37 (300–350 °C); 29.55 ± 0.23(350–400 °C); 22.76 ± 0.22 (400–500 °C) **HHV aqueous phase (at different temperature ranges) [MJ. kg^{-1}]:** 16.77 ± 0.45 (25–200 °C); 17.17 ± 0.40 (200–250 °C); 21.75 ± 0.33 (250–300 °C); 27.87 ± 0.38 (300–350 °C); 30.63 ± 0.42(350–400 °C); 33.51 ± 0.29 (400–500 °C) **Ph aqueous phase (at different temperature ranges) [−]:**3.63 ± 0.01 (25–200 °C); 4.12 ± 0.01 (200–250 °C); 4.74 ± 0.01 (250–300 °C); 6.44 ± 0.01 (300–350 °C); 7.87 ± 0.01 (350–400 °C); 8.19 ± 0.01 (400–500 °C)	
SCG	**Moderate fast pyrolysis** **Reactor specification:** 0,70 L stainless steel, mechanically shaken. Batch reactor. **Residence time [s]:** 23 **T [°C]:** 500	**Yield [%]:** SY (20.6); LY (61.8); NCGY (17.6) **Elemental and Proximate analysis biochar [wt%]:** C (75.30); H (3.52); O (0.11); N (4.40); S (0.12); Cl (24.00); AC (5.56); H:C (0.56). **Elemental and Proximate analysis bio-oil [wt%]:** C (44.97); H (12.03); O (42.07); N (0.80); S (0.12); Cl (14.00); AC (<0.1); H:C (3.21).	[154]
Silverskin	**Intermediate pyrolysis** **T [C]:280–500** **Residence time [min]:10**	**Bio-oil pH [-]:8.1 (T=500C); 8.5 (T=400C); 4.3 (T=280C)** **Bio-oil phenolic content [mg of gallic acid equivalents/g]: 2.92–6.09(Folin-Ciocalteu method); 1.7–3.02(DPPH assay)** **Bio-oil yield [% w/w]:<20** **Biochar yield [% w/w]: 80** **Biochar composition [%]: 55.01–56.68 (C); 2.39–4.76 (H); 35.71–36.63 (O); 2.65–3.49 (N); 0.13–017 (S)** **Biochar LHV [MJ kg-1]: 21.09–23.08**	[165]
Torrefaction			
Husk	**Residence Time [min]:** 30 **T [°C]:** 280	**Composição do biochar [wt%]:** MC = 0.38; VM = 38.99; AC = 38.62; FC = 22.39. **Yield [%]:** SY (76.78) **Heating value [MJ kg^{-1}]:** 24.43	[108]
SCG	**Technique:** Torrefaction under TGA curve analysis **Purge:** Nitrogen (N_2) **T [°C]:** 220-300 **Rate [°C/min]:** 5, 15, 25 **Residence time [min]:** 20, 40, 60	**Heating value [MJ kg^{-1}]:** 22.89–32.16 **Weight loss [%]:** 4.56–40.04 **Elemental analysis [wt%]:** C (52.9–69.6); H (7.1–9); N (2.4–3.6); O (19.6–35.8)	[53]
Silverskin	**Technique:** Torrefaction under TGA curve analysis **Purge:** Nitrogen (N_2) **T [°C]:** 220-300 **Rate [°C/min]:** 5, 15, 25 **Residence time [min]:** 20, 40, 60	**Heating value [MJ kg^{-1}]:** 20.6–25.5 **Weight loss [%]:**8.6–16.3 (T = 220C); 38.4–44.9 (T = 220–300) **Elemental analysis [wt%]:** C (49.7–60.2); H (5.7–7.7); N (4–2.5); O (30–40)	[53]
Hydrothermal carbonization			
Parchment	**Reactor specification:** 1 L stainless steel. Batch reactor **Biomass in [g]:** 50.9 wb (50 db) **Water in [g]:** 399.1 **Feedstock ratio W/B:** 8 **T [°C]:** 220 **Residence time [h]:** 3	**Yield [%]:** SY (46); LY (49); NCGY (5) **HHV hydrochar [MJ.kg^{-1}]:** 18.07 **LHV [MJ.kg^{-1}]:** 16.69 **Equilibrium moisture content [%]:** 1.12 **Proximate analysis [wt%]:** VM (60.76); FC (36.52); AC (1.59)	[110]
SCG	**Reactor specification:** 2 L stainless steel (AISI 316) batch reactor **Biomass in [g]:** 850 ± 0.11 wb (about 346 g on db) **Water in [g]:** 534.5 ± 0.1 of DI water **Feedstock ratio B/W:** 0.33 **Purge:** Nitrogen (N_2) **T [°C]:** 220 **Rate [°C/min]:** 10 **Residence time of reaction temperature [h]:** 1	**Yield [%]:** SY (72.5); LY (16.9); NCGY (10.6) **HHV [MJ.kg^{-1}]:** 28.28 **LHV [MJ.kg^{-1}]:** 26.82 **Equilibrium moisture content [%]:** 2.74 **Proximate analysis [wt%]:** VM (70.69); FC (27.83); AC (1.49) **Elemental analysis [wt%]:** C (67.26); H (6.7); N (3.09); O (21.46)	[166]
PVA	**Reactor specification:** 1 L stainless steel. Batch reactor **Feedstock ratio W/B:** 30 **T [°C]:** 120 **Residence time [h]:** 3	**Yield [%]:** SY (67.3) **HHV hydrochar [MJ.kg^{-1}]:** 21.64 **Equilibrium moisture content [%]:** 4.9 **Proximate analysis [wt%]:** VM (17.43); FC (75.84); AC (1.81)	[56]

T-Reaction temperature; T_{comb}-Temperature at which combustion started; T_m-Temperature at which peak in the DTG curve was observed; T_{ig}-Ignition temperature; T_b-burnout temperature HHV-High heating value; LHV-Low heating value; SY-Solid yield; LY- Liquid yield; NCGY- Non-condensable gases yield; VM-Volatile matter; FC-Fix carbon content; AC- Ash content; MC-Moisture content.; W-water; B-biomass; wb-wet basis; db-dry basis.

SY-Solid yield; LY- Liquid yield; NCGY- Non-condensable gases yield; VM-Volatile matter; FC- Fix carbon content; AC- Ash content; MC-Moisture content.; wb-wet basis; db-dry basis.

section 3, available data on coffee residues for energy generation presented in Tables 1 and 2, and different studies reported in literature showed in Tables 4 and 5, the routes appearing most promising for the residues from coffee harvest and processing are discussed in this section.

For coffee pulp the biochemical routes are generally the most viable alternative. The high moisture content of the pulp would be a drawback for most of the thermochemical conversion routes except for hydrothermal carbonization, since a large amount of energy would have to be spent on water evaporation. The high ash content is also a drawback and may cause sintering at high temperatures. On the other hand, the high fractions of cellulose, hemicellulose and phenolic compounds in the chemical composition of the pulp are a favorable for obtaining bioethanol, proteins, enzymes, vitamins, amino acids, lactic acid and acetic acid through hydrolysis and biodegradation according to several studies [25,147].

A relatively high fraction of volatile matter and a fixed carbon content similar to wood samples [148] was observed in the proximate analysis of the coffee cherry parchment (CCP). These characteristics are associated with susceptibility to thermal degradation and indicate that the feedstock is suitable for producing biochar. A drawback of the CCP as

biochar feedstock is the ash content. Ash not only reduces the heating value [23], but the alkali metals and chlorine can be problematic due to the formation of alkali chlorides. These can cause agglomeration, fouling, and corrosion in high-temperature processes such as gasification and combustion [149]. Research on the sintering properties of the CCP needs to be developed, since agglomeration and corrosion problems increase the costs of operation and maintenance of the combustion systems, particularly with fluidized bed technology [149].

Another possible route for CCP could be the hydrothermal carbonization process. HTC removes efficiently inorganic compounds from lignocellulosic biomass by dissolving them in the liquid phase [150]. The HTC can be an attractive solution to turn the raw CCP into a valuable product, for example as soil conditioner, activated carbon or an adsorbent agent. Further analysis of coffee cherry parchment HTC products has to be performed in order to investigate the potential of the material. Biochemical processes are also viable route for CCP: the high content of cellulose and hemicellulose facilitates the recovery of energy, similarly to how it is with coffee pulp. The parchment can also be densified through physical routes; the high lignin and low extractive contents facilitate the agglomeration of particles, resulting in a durable product.

The chemical compositions of coffee silverskin and parchment do not differ dramatically; both can be considered suitable for thermochemical, biochemical and physicochemical conversion. Likewise, the husk obtained in the dry treatment route is also suitable for all conversion routes. The high content of polysaccharides, proteins and minerals can make the husk also suitable for acting as a substrate support in fermentation processes for extraction of compounds for food and pharmaceutical industries [25], as well as material for composting application [151]. [152] reported some of the value-added applications of the coffee residues, mainly in the bioprocessing, detoxification and vermicomposting.

No literature reports were found on combustion of low quality PVA coffee beans for energy. This can be attributed to the inefficient process of defective beans separation in the farms and cooperatives leading to limited availability of PVA residue. However, the proximate analysis and lignocellulosic content indicated low levels of moisture and ashes, and high fixed carbon and volatile concentrations, implying thermal stability and suitability for dry thermochemical conversion processes.

The SCG composition includes large amounts of carbon and low AC, factors that contribute to the production of fuels with high calorific value through thermochemical conversions. Additional advantages of the SCG for energetic conversion are the high HHV and low sulfur and nitrogen content. The high content of VM found for SCG shows the large number of compounds that can be devolatilized, which increases the ignition speed of the feedstock. Moreover, high lignin and low extractive content indicate a potential application in physical processes such as the production of briquettes/pellets showed in Ref. [153]. Another approach concerns to the amount of phenolic and organic compounds in the chemical composition of the SCG, such as lipids. This improves extraction and hydrolysis processes [154], which is an advantage for biochemical and physical conversion routes. Among the applications, SCG is used as raw material for the production of bio-oil and biochar by slow pyrolysis [21], biogas production through anaerobic co-digestion, as solid fuel for direct combustion in boilers [155], bio-alcohol by fermentation, biodiesel production trough transesterification [79], biofuels, biopolymers, antioxidants and biocomposites [39]. Additionally SCG also has other applications such as fertilizer in the agroindustry [156,157], production of activated carbon [158], animal feed [159] and as an adsorbent [160].

4.1. Mass and energy balances of solid coffee residues

In order to utilize the coffee residues efficiently, process parameters must be selected appropriately for a each process and it's feedstock. Table 5 shows the selected experimental results from previous studies in order to carry out the mass and energy balance calculations.

Mass and energy balances are generally the first step in solving a chemical engineering problem. The mass balance, or material balance, is an application of the principle of mass conservation for the analysis of physical systems, by the measurement of input and output properties. The energy balance is a systematic expression of energy fluxes and transformations in a system, based on the first law of thermodynamics according to which energy cannot be created or destroyed, only modified [59]. Fig. 4 shows the input and output streams of the thermochemical routes considered in this study.

Table 6 shows the energy and mass balance equations used in the calculations to establish a comparative analysis between the conversion routes. With those technologies for which experimental results with some of the considered residues was not available, such hydrothermal carbonization and pyrolysis, balances were made considering the typical yields obtained from the literature.

The drying stage was the first fundamental procedure to study the energy potential of the coffee residues. Typically, this takes place before the conversion process, with the exception of hydrothermal carbonization where drying is the last stage, after the carbonization (Fig. 4). The drying can take place at a comparatively low temperature with correspondingly low-temperature heat sources. This has several advantages, from minimizing the need for more valuable high-exergy heat, to minimizing the fire hazard, and also minimizing the losses of volatile organic compounds (VOCs). VOC emissions begin at above 100 °C temperature and increase with increasing drying temperatures; a dryer can be designed to operate below this temperature.

Experimental heat and power consumption figures are not available for the specific case of coffee residues. Consequently, a specific heat consumption q_{spec} of 1.2 $kWh \cdot kg^{-1}_{H2Oevap}$, considered a typical or conservative estimate for solid biomass fuels dryer heat consumption without heat recovery [170], is considered here. Efficient heat recovery could improve the heat consumption at the expense of investment cost. The availability and cost of heat source would decide the economically optimal configuration. Power consumption e_{spec} is assumed at 200 $kJ \cdot kg^{-1}_{H2Oevap}$ based on [171].

It is assumed that no biomass dry matter is lost in the dryer, $\dot{m}_{d,in} = \dot{m}_{d,out}$.

Consumption of heat and power is determined from specific heat and power consumptions,

$$P_{el} = e_{spec}\left(\dot{m}_{in}MC_{in} - \dot{m}_{out}MC_{in}\right)$$

$$\Phi_{h} = q_{spec}\left(\dot{m}_{in}MC_{in} - \dot{m}_{out}MC_{in}\right)$$

Due to the low temperatures possible with drying, effect of volatile loss in drying is assumed negligible,

$$HHV_{daf,in} = HHV_{daf,out}$$

4.1.1. Mass and energy balances results

Based on the experimental results (Table 5) and equations reported in Table 6 results of the mass and energy balances are showed in Table 7. Values from Table 1 were also implemented to quantify mass feedstock in the input of the balances when the literature studies did not offer enough parameters, or information was absent. From the obtained results it was possible to observe that for almost all the technologies, coffee residues have to be previously dried, in order to undergo thermochemical treatment, except for hydrothermal carbonization [51].

For gasification, the mass and energy balances are according to Ref. [167,168]. The results demonstrate syngas generation above 91% (mass) relative to the initial feedstock, with the gas consisting mostly of CO and H_2. Parchment resulted in the best gasification performance with the highest energy conversion rate at 84%. According to Ref. [162] the gasification process for not only parchment but for agricultural residues

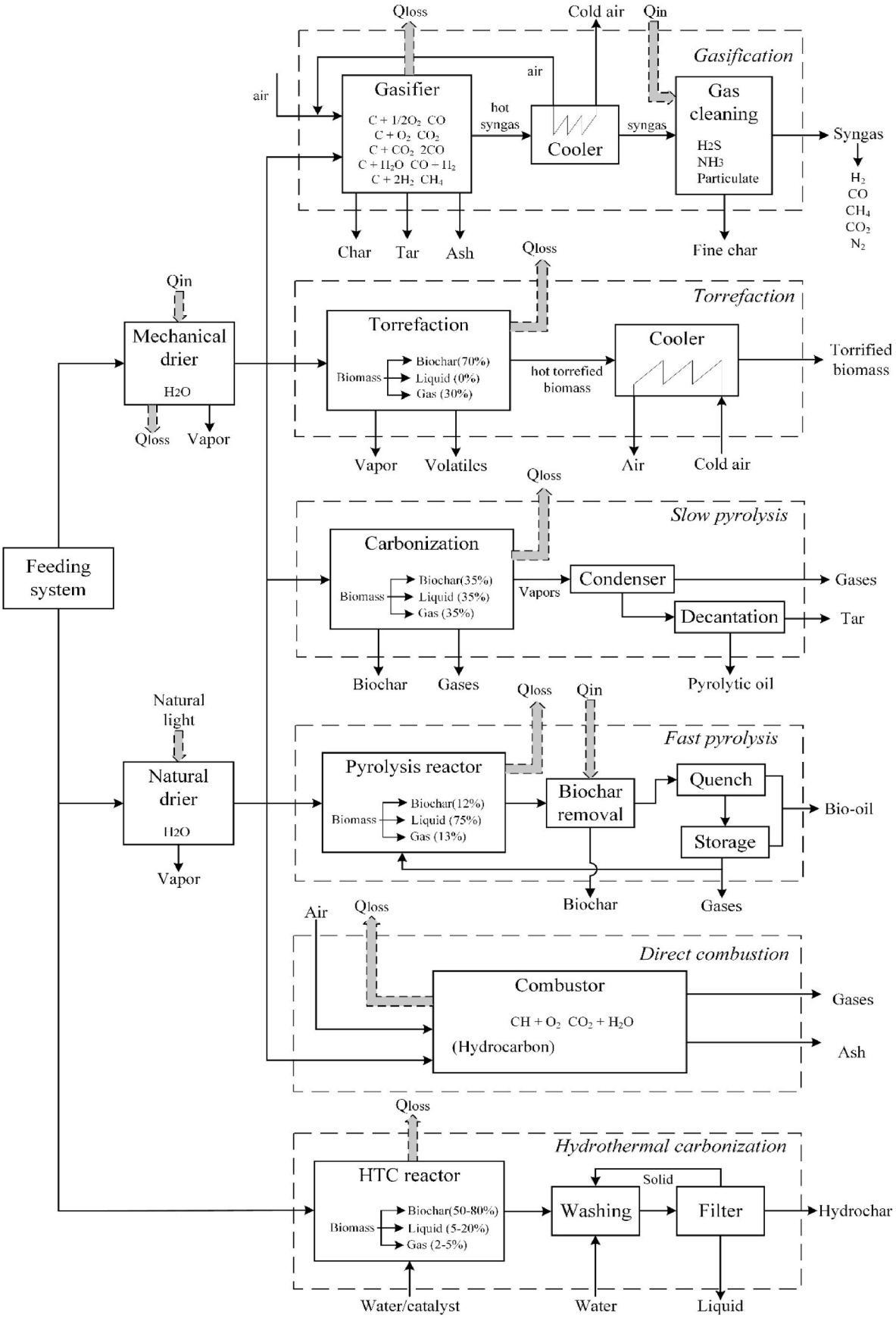


Fig. 4. Process diagram of different thermochemical conversion technologies.

Table 6
Mass and energy balances.

Routes	Mass balance	Energy balance
Gasification	$\sum_{in} m^{'} = \sum_{out} m^{'}$ $m^{'}_{biomass} + m^{'}_{air} = m^{'}_{syngas} + m^{'}_{tar} + m^{'}_{char} + m^{'}_{ash}$ $m^{'}_{air} = V^{'}_{air}\left[\frac{Nm^3}{h}\right]\cdot 1.303\left[\frac{kg}{Nm^3}\right]$ According to Ref. [167]: $m^{'}_{tar} = (6.411 - 0.203\cdot\sqrt{T_g})^2 + (0.248\cdot AF) - (0.024\cdot W)$ $m^{'}_{char} = (6.643 - 0.006\cdot T_g)^2 + (2.108\cdot AF) + (0.193\cdot W) + 0.487\cdot AC)$ According to Ref. [168]: $m^{'}_{ash} = m^{'}_{biomass}\cdot\left(\frac{AC}{100}\right)$	$LHV_{Syngas} = \sum_i y_i \cdot LHV_i$ $ECR = \frac{LHV_{Syngas}\cdot V_{Syngas}}{LHV_{Biomass}\cdot W_{Biomass}}\cdot 100$ $WR = \frac{\sum\int W_i\cdot Cp_i\cdot dT}{LHV_{Biomass}\cdot W_{Biomass}}$ $EC = 1 - ECR - WR$
Torrefaction	$m^{'}_{biomass} = m^{'}_{gas} + m^{'}_{vapor} + m^{'}_{torrified}$ $m^{'}_{vapor} = [m^{'}_{biomass} - m^{'}_{biomassa(db)}] - [m^{'}_{torrified} - m^{'}_{torrified(db)}]$ $m^{'}_{torrified} = \frac{RC\,.\,m^{'}_{biomass}}{100}$	$Q_{biomassa} = m^{'}_{biomassa}\,.\,LHV_{biomassa}$ $Q_{evaporação} = m^{'}_{vapor}.\,2,443$ $Q_{char} = m^{'}_{char}\,.\,LHV_{char}$ $Q_{gas} = \frac{Q_{biomassa} - Q_{char} + Q_{evaporação} + (\Delta H.m^{'}_{biomassa})}{m^{'}_{gas}}$
Hydrothermal carbonization Fast pyrolysis Slow pyrolysis	$SY = \frac{m^{'}_{char}}{m^{'}_{biomass}}*100$ $LY = \frac{m^{'}_{liquid}}{m^{'}_{biomass}}*100$ $NCGY = 100 - (m^{'}_{char} + m^{'}_{liquid})$	$Q_{biomass} = m^{'}_{biomass}.\,LHV_{biomass}$ $Q_{char} = m^{'}_{char}.\,LHV_{char}$ $Q_{liquid+gas} = \frac{Q_{biomass} - Q_{char} + (\cdot H.m^{'}_{biomassa})}{m^{'}_{liquid+gas}}$Energy recovery efficiency (ERE) as follows [169]: $ERE = \frac{LHV_{char}}{LHV_{biomass}\cdot SY}$

AF-air/biomass ratio; W-biomass moisture content [wt%]; T_g-gasifier temperature [°C]; AC-biomass ash content [wt%]; y_i-volumetric fraction of each component; LHV_i-low heating value of component; *ECR*-energy conversion rate; V_{Syngas}-volume of the syngas; $W_{Biomass}$-weight of the biomass; *WR*-waste heat energy rate; cp_{gas}-heat capacity; EC-energy consumed by the gasifier; $m^{'}_{biomassa}$-biomass mass in dry base; RC-charcoal yield [%]; SY-solid yield; LY-liquid; NCGY-non-condensable gases yield; $m^{'}_{hydrochar}$-hydrochar mass in dry base; $m^{'}_{liquid}$-liquid mass in dry base.

is an energy alternative potential route for communities located in areas not interconnected to the national electricity system. Regarding defective coffee beans and enough information for silverskin to develop the balances were not found in the available literature.

For the torrefaction of parchment, PVA beans and pulp, the data required for mass and energy balances as described in Table 5 were not found in the literature. In addition, the TGA analysis of SCG did not provide information about product yields. Thus, the mass quantification for these residues were obtained from torrefaction studies of biomass. A typical yield of solid biochar was estimated at 73% of the initial feedstock (db), condensable volatiles at 22%, and non-condensable gases at 5% [152].

In hydrothermal carbonization, typical yields commonly obtained for biomass were also used in mass balance for the pulp and husk residues, due to the absence of information for the performance of HTC with those residues. HTC yields of 80% solid, 15% liquid and 5% gas were estimated [172]. For pulp and husk feedstock-to-water ratio of 1:8 was considered, as used in the HTC treatment of parchment [110]; for the PVA beans, 1:20 was assumed [56]. The lowest gas yield and highest liquid yield were observed for coffee pulp, together with parchment and husk. Pyrolysis balances also follow the typical yields: 35% and 12% solid yield, 30% and 75% liquid yield, 35% and 13% gas yield, for slow and fast pyrolysis, respectively [172]. High bio-oil generation was found for pulp and parchment, whereas SCG and husk provided higher biochar and non-condensable gas yields, although in fast pyrolysis a significant amount of bio-oil was still produced. Intermediate pyrolysis was calculated for silverskin due to available literature data, the high solid yield reported produce high heat value for the biochar in the energy balance. Low gas yield was found for SCG; husk, parchment, PVA, silverskin and pulp had similar product values under slow pyrolysis conditions. In direct combustion, almost complete combustion usually takes place, with ash remaining as almost the only solid product, in addition to a typically very small amount of unburnt carbon. Almost all solid mass is converted to flue gas. Due to the lack of information in the literature, mass and energy balances were not developed for direct combustion.

From the results was possible to observe that thermochemical conversion routes can transform low grade biomass into high-value products. Coffee residues especially spent coffee grounds, can produce biochar with high market potential, especially as a fuel for heat and electricity generation, or as a soil amendment product. Another attractive output is bio-oil, obtained by pyrolysis conversion, which also can have a variety of uses including energy, chemical feedstock for industries, liquid fuel, carbon sequestration, bioremediation, and soil amendment. Biochar, bio-oil, hydrochar and syngas can add value to coffee production chain economy, and the need for external energy sources can be reduced or removed altogether. Overall, there is an opportunity to significantly reduce costs and create additional revenue in the process from the coffee shrub plantation to soluble coffee production. However, the initiatives of coffee residues treatments for sustainable development will require subsidies and technology transfer for a successful venture.

5. Practical implications of this study

Methods of coffee residues management are outlined to create awareness of the opportunities and constraints associated with the maximization of coffee residues utilization and the reduction of environmental pollution. Currently these residues are most often used as fertilizer, livestock feed, or compost. The substantial amounts of fermentable sugars makes the residues suitable for such purposes, but higher-value applications are also possible. To identify how the coffee production chain can help local and regional socioeconomic development, an evaluation of new technologies should be made. This article supports the Brazilian agricultural research and recommend systematizing the available knowledge about coffee residues through a study of viable thermochemical routes to improve the coffee production chain for both coffee growers and the coffee industry.

Brazil supports coffee production as well as local and regional development, including transportation, electricity, sanitation, and security. Within the coffee industry, the quality of the product is an important factor than needs to be addressed. The agricultural production and industry chain is constantly undergoing structural

Table 7
Mass and energy balance of coffee residues for different thermochemical processes.

Properties	Biomass					
	Husk	Parchment	Pulp	SCG	PVA	Silverskin
	Gasification					
V_{syngas} [Nm^3]	172.93	173.68	177.11	161.08	–	–
Y_{syngas} [%]	78.39	76.78	52.51	83.06	–	–
D_{syngas} [$kg.m^{-3}$]	1.21	1.25	1.27	1.45	–	–
Mass Balance[a] [kg·h^{-1}]						
*m'$_{biomass_in}$	128.85	133.35	93.00	133.80	–	–
m'$_{air_in}$	93.82	97.72	107.50	119.93	–	–
m'$_{syngas_out}$	208.51 (93.64%)	217.47 (94.11%)	184.43 (91.99%)	233.28 (91.94%)	–	–
m'$_{tar_out}$	0.87 (0.39%)	0.56 (0.24%)	1.26 (0.63%)	2.58 (1.02%)	–	–
m'$_{char_out}$	6.71 (3.01%)	5.3 (2.29%)	7.92 (3.95%)	13.45 (5.30%)	–	–
m'$_{ash_out}$	6.57 (2.95%)	7.73 (3.34%)	6.88 (3.43%)	4.42 (1.74%)	–	–
Energy Balance [%]						
ECR	18.67	84.81	46.84	23.50	–	–
WE	3.05	2.41	4.09	2.25	–	–
ECG	78.28	12.77	49.07	74.25	–	–
	Torrefaction					
Mass Balance[b] [kg·s^{-1}]						
m'$_{biomass}$	859	889	233	892	–	925
m'$_{condensate}$	137.93	195.58	51.26	196.24	–	183.22
m'$_{gas}$	94.27	53.34	13.98	53.52	–	88
m'$_{solid\ (torrefied\ biomass)}$	767.8	648.97	170.09	651.16	–	837
Energy Balance [kJ·h^{-1}]						
Q'$_{biomass}$	13361.068	15138.792	3849.501	20116.106	–	15709.35
Q'$_{condensate}$	336.960	–	–	-	-	-
Q'$_{gas}$	21.97	–	–	-	-	-
Q'$_{solid\ (torrefied\ biomass)}$	11627.33	–	–	-	-	19968.97
	Hydrothermal carbonization					
Mass Balance[b] [kg·s^{-1}]						
*m'$_{biomass_in}$	859	982	233	933.9	907	–
m'$_{water_in}$	6872	7856	1864	2830	3023	–
*m'$_{hydrochar_out}$	687.2 (8.7%)	451.72 (5.1%)	186.4(6.51%)	677.1 (17.68%)	610.4 (15.2%)	–
m'$_{liquid_out}$	7141.85 (90.72%)	8355.18 (94.34%)	2665.95 (93.08%)	3053.92 (79.73%)	3374.8 (83.9%)	–
m'$_{gas_out}$	42.95 (0.54%)	49.1 (0.55%)	11.65 (0.41%)	98.99 (2.58%)	38.15 (0.94%)	–
Energy Balance [kJ·h^{-1}]						
Q'$_{biomass}$	13134.74	16385.34	4515.74	19736.74	16514.63	–
Q'$_{hydrochar}$	–	7539.20	–	18154.95	12321.6	–
Q'$_{liquid+gas}$	–	16.75	–	6.16	27.47	–
ERE [%]	–	45.79	–	91.98	74.61	–
	Fast pyrolysis					**Intermediate pyrolysis**
Mass Balance[b] [kg·s^{-1}]						
*m'$_{biomass_in}$	899	881	887	907	–	925
*m'$_{char_out}$	235.54	105.72	106.44	186.84	–	740
m'$_{liquid_out}$	505.24	660.75	665.25	560.53	–	175.75
m'$_{gas_out}$	155.53	114.53	115.31	159.63	–	9.25
Energy Balance [kJ·h^{-1}]						
Q'$_{biomass}$	15582.59	14988.62	15006.45	19156.79	–	15192.5
Q'$_{char}$	5459.04	–	–	-	-	**17079.2**
Q'$_{liquid}$	11701.31	–	–	-	-	-
ERE [%]	35.03	–	–	-	-	-
	Slow pyrolysis					
Mass Balance[b] [kg·s^{-1}]						
*m'$_{biomass_in}$	899	881	887	907	907	925
*m'$_{char_out}$	314.65	308.35	310.45	253.96	269.19	277.5
m'$_{liquid_out}$	269.7	264.3	266.1	462.57	230.74	237.86
m'$_{gas_out}$	314.65	308.35	310.45	190.47	269.19	277.5
Energy Balance [kJ·h^{-1}]						
Q'$_{biomass}$	15582.59	14988.62	15006.45	19156.79	16514.63	15137.86
Q'$_{char}$	–	–	–	7512.13	–	–
Q'$_{liquid+gas}$	–	–	–	17.83	–	–
ERE [%]	–	–	–	39.21	–	–

*Dry basis.
[a] Calculation base: 150 kg h^{-1}.
[b] Calculation base: 1000 kg h^{-1}. V-Volume; Y-Yield; D-Density; m-Mass; Q-Heat content; ECR-Energy conversion rate; WE-Waste energy conversion rate; ECG-Energy consumed by the gasifier; ERE- Energy recovery efficiency.

transformations based on research and development efforts aiming at the development of new products. This and the necessary investment in new technologies and requires also improving the knowledge and skills of coffee farmers and process engineers in the coffee industry. This behavior was configured in what the specialists came to call the third wave of coffee, in which the search for quality, associated with technological development, has become key factor in competition, both domestic and international [173]. The coffee sector is searching new ways of adding value through the whole coffee production chain, from the production to the commercialization of the final product.

The main policy instruments included in the Brazilian current policy projections pathway are the energy efficiency national plans and the incentives for increasing the share of renewables in the energy sector [174]. This includes capacity auctions in the power sector, and the ethanol and biodiesel mandates in the transportation sector. Brazil is facing an increasing need to improve its environmental and energy policies. In 2018, Brazil recorded the world's highest loss of tropical primary rainforest of any country, reaching 1.3 million hectares, largely due to deforestation in the Amazon [174]. This breaking of records in deforestation and forest fires, despite weather conditions being milder than in previous years, point to an increase in anthropogenic causes, including illegal logging. This trend takes Brazil in the opposite direction of its Paris Agreement commitments [175]. Brazil still needs to develop sectoral plans to reduce emissions in also other sectors of the economy but most of those policies and instruments are still not part of the national development planning or regulation.

6. Conclusion

Brazil is one of the countries with the most advanced biomass energy recovery technologies. Conversion processes are a viable option to improve wastes and side streams into higher quality energy carriers, even in remote locations. Coffee is Brazil's chief agricultural export and is grown extensively throughout the country. The processing chain generates large amounts of waste materials. However, while significant progress has been made in converting coffee side streams into useful biofuels and bioproducts, there are still further research needs to fully take advantage of these opportunities and commercialize the products.

Fast pyrolysis for bio-oil, gasification for syngas, torrefaction and slow pyrolysis for biochar, and hydrothermal carbonization for hydrochar and HTC liquor production, were considered in the literature review and analyzed in the mass and energy balances. In general, the residual biomass of the coffee production chain can be considered suitable raw material for thermochemical conversion processes.

When moisture and ash contents are low, a number of technologies are often suitable; for high-moisture residues such as particularly coffee pulp (76.7 wt%) but also husk and parchment, hydrothermal carbonization (HTC), taking place in water, can be considered particularly suitable. Pulp and husk are further limited by the composition and high fraction of ash, up to 5–7 wt%, which can create fouling, agglomeration and corrosion problems in high-temperature and fluidized bed applications. Fast pyrolysis produced reasonable mass yields of bio-oil from all feedstocks for which data was available, but has the disadvantage of high oxygen content in the oil, which would require additional treatment; slow pyrolysis may thus be more appropriate. Gasification appears particularly suitable for parchment, with a clearly higher heating value of 12.4 $MJ{\cdot}Nm^{-3}$ than the syngases from other residues (less than 6 $MJ{\cdot}Nm^{-3}$). In addition to thermochemical conversion, those residues with high content of cellulose and hemicelluloses such as coffee pulp (63.5 wt% cellulose and 27 wt% hemicelluloses) can be considered suitable for biochemical processes, while those with high lignin content such as SCG (33.6 %wt lignin) can be expected to be suitable for physical processes such densification.

Overall, this study provides possible routes to obtain valuable biofuels and bioproducts as a source of energy. In addition, important information is collected that can be used to help minimize the negative impacts of residue disposal, such as long transportation distance, decontamination costs, and environmental impacts.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Hydrothermal carbonization of lignocellulosic agro-forest base biomass residues

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Hydrothermal carbonization of lignocellulosic agro-forest based biomass residues

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ABSTRACT

To increase the understanding of hydrothermal carbonization (HTC) of lignocellulosic biomass residues, four feedstocks: giant bamboo, coffee wood, eucalyptus, and coffee parchment, were studied. The effect of operating conditions on the products in terms of yield, composition and energy densification were quantified. Each feedstock was treated for 3 h at temperatures of 180, 200, 220 and 240 °C. For all samples, the higher heating value (HHV), fixed carbon content and energy density increased with increasing reaction severity, while volatile matter content and mass yield decreased. The HHV of hydrochar samples obtained at temperatures ≥220 °C were in the range of 24.6–29.2 MJ kg^{-1} and indicated the high potential of these materials for fuel applications. The mass yields varied in the range of 46.5–56.9%, with the exception for coffee parchment, where the lower values of 34.4–46.0% were obtained. The fixed carbon varied from 33.8% to 53.0%. The HTC liquor had pH values of 2.9–4.4 due to organic acids. The results were used to model and evaluate different industrial-scale HTC simulation cases. The overall efficiency was similar within all studied biomasses. The integration with a bio-fired power plant allows simplification of the process while also bringing efficiency gains. All studied biomasses appear to be suitable for energy and value-added products generation through HTC treatment. Coffee residues, which have received little research consideration previously, responded well.

1. Introduction

The growing importance of sustainability and climate change mitigation has vastly increased interest in biotechnology and the circular economy. Nevertheless, in many areas, the bioeconomy can be considered as being underdeveloped and not fully exploiting its considerable potential. To enable full yet sustainable development of an effective bioeconomy, new markets must be opened, and new materials produced from available feedstocks. An important issue related to development of the bioeconomy is the extensive volume of biomass waste from forestry and agriculture, which has been estimated to be as much as 140 Gt annually worldwide [1,2]. This waste holds significant potential for a variety of applications, although currently only a small percentage is used as a feedstock for industrial applications or as fuel, mainly due to legal restrictions and the cost of collection and further processing [3]. These underutilized residues not only represent unused potential, but landfilling or burning can have significant negative environmental impacts (e.g., emission of large quantities of volatile organic compounds in the case of combustion, and contamination of groundwater in the case of landfill) [3]. In this context of widespread availability, underutilization and economic potential, many studies have been conducted on the use of agro-forest solid residues for energy generation, for example [4–7].

Agroforest residues are mainly produced by wood-product industries (i.e. paper mills, furniture industry and sawmills) and crops. Bamboo and eucalyptus are two fast growing plants particularly common in tropical and subtropical regions. Bamboo is distributed across approximately 320 000 km^2 of all global forested area [8,9]. Its naturals composite materials have made bamboo a widely used material, as timber, for indoor carpentry, and as a raw material for the chemical industry [10–12]. Different studies reveal the potential of bamboo as a raw material to produce dissolving pulp, cellulosic fibers for paper and starch granules for saccharification and production of ethanol [13]. Eucalyptus is a widely grown commercial plantations, which covered over 200 000

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Nomenclature

AC	Ash content [wt%]
ACP	Aqueous co-product
BD	Belt Dryer
BFB	Bubbling Fluidized Bed
HTC	Hydrothermal carbonization
CW	Coffee wood
CP	Coffee parchment
CHP	Combined heat and power
CPP	Condensing Power Plant
ESR	Energy saving ratio [-]
EW	Eucalyptus wood
FC	Fixed carbon [wt%]
FCY	Fixed-carbon yield [%]
GB	Giant bamboo
HHV	Higher heating value [$MJ \cdot kg^{-1}$]
HP	High Pressure
IC	Inorganic carbon
LP	Low Pressure
LY	Liquid yield [%]
M	Mass [kg]
MC	Moisture content, wet basis [-]
MP	Medium Pressure
MY	Hydrochar mass yield [-]
NVR	Non-volatile residue [$g \cdot l^{-1}$]
P	Power [W], [MW]
RB	Recovery Boiler
RDD	Rotary Drum Dryer
SEM	Scanning electron microscope
SA	Stand-alone
SD	Standard deviation
T	Temperature [°C]
TOC	Total organic carbon
VM	Volatile matter [wt%]

Greek letters

Φ	Heat rate [W], [MW]
η	Efficiency [-]

Subscripts

b	solid feedstock
wb	wet basis
co-gen	co-generation
hc	hydrochar sample
l	liquor sample
db	dry basis
daf	dry ash free
el,in	electricity consumption of HTC plant
el,net	net electricity production
HC	hydrochar

km^2 in 2019 [14]. The short, relatively uniform and simple cell structure fiber and low degree of lignification are some of the properties that makes eucalyptus one of the largest source of market pulp [15], as well as for other uses such as building materials or charcoal production [16,17].

From the agricultural sector, coffee is an economically important commodity in producing countries, particularly Brazil, Vietnam, Colombia and Indonesia, which together account for more than half of global coffee production [18]. Coffee parchment is an agricultural residue from processing the coffee fruit and constitutes 12% (dry basis) of the coffee cherry. Coffee wood residue, on the other hand, is produced during pruning of the shrubs; typically, approximately 25% of the shrub becomes residue in pruning [18]. In Brazil alone, over 31 million tons of coffee wood and 0.6 million tons of parchment were generated in 2017 [18]. Coffee residues are considered suitable as feedstock for thermochemical conversion processes [18,19].

The significant use of species such as bamboo, eucalyptus and coffee, large quantities of residues are generated every year, which are typically either left in the land or burned [20]. Sustainable utilization of agro-forestry residues by converting these waste streams into valuable products offers considerable benefits, both environmental and economic. A typical use for biomass residues is as fuel, although in many respects raw solid biomass compares unfavorably to other solid fuels such as coal or peat; drawbacks include the low energy density of solid biomass, its hygroscopic nature, poor grindability, a tendency to degrade in storage, and a propensity for causing high-temperature corrosion and slagging. These drawbacks can, however, be mitigated by various pre-treatment processes [21].

1.1. Hydrothermal carbonization

Hydrothermal carbonization (HTC) is a relatively recent conversion process for upgrading various woody and agricultural feedstocks. The HTC process occurs in an aqueous environment at relatively low temperatures, usually in the range of 180–260 °C, in a closed system under autogenous pressures of 1–5 MPa and external heat supply [22]. The HTC process involves mainly hydrolysis, an endothermic reaction. At high temperatures (≥260 °C), however, the exothermic reactions of sugars such as monosaccharides will dominate the process [8]. The main product of HTC is an energy-dense solid, which is called hydrochar, biochar or HTC char; gases and liquids are also produced. The gaseous product consists mainly of CO_2, which can account for over 90% of the total non-condensable gases produced, as well as small amounts of CO, H_2 and light hydrocarbons such as CH_4 [23]. The liquid product includes both aqueous co-products (ACP) and reaction water [24].

HTC char typically holds 55–90% of the initial mass of the feedstock and 80–95% of its energy content. As a solid fuel, the properties of hydrochar are similar to those of lignite [23]. In addition to its ability to upgrade lignocellulosic biomass, HTC process removes alkali and alkaline metals from the biomass, unlike dry torrefaction, a currently popular low temperature pre-treatment process which requires dry and high-quality biomass as a feedstock. At present, HTC char is used as a solid fuel, an absorbent for water purification, for soil amendment, and in carbon sequestration [25,26].

Recent studies have mainly focused on the effect of HTC operational parameters on mass and energy yields and hydrochar characteristics. Differences in biomass composition result in significant variations in decomposition behavior during HTC treatment. In general, the carbonaceous structure of hydrochar becomes more stable and compact compared to the feedstock. Although aromatic functional groups and C–C and C–O bonds gradually increase during the thermal degradation [27], characteristics such as ignition energy, reactivity, heating value and morphological structure, and therefore potential uses of the final product, depend greatly on the composition of the feedstock material.

Hydrochar produced by hydrothermal treatment of bamboo has been shown as suitable for solid fuel use [28]. High concentrations of nutrients, especially nitrogen, phosphorus and potassium, have been found in the aqueous solution of HTC treatment of bamboo [28]. Hydrochar studies of eucalyptus bark have reported increased fixed carbon content compared to the raw material and a higher heating value of approximately 29.2 MJ kg^{-1} [29], indicating potential as a solid fuel. For residues from coffee production, no significant information on HTC experiments is available. Coffee residues, however, present different characteristics such as high values of average volatile matter content and heating value indicate high potential for energy applications. Coffee wood and the parchment of coffee cherry have high anhydrosugars content, increasing their thermal degradation at low temperatures [18].

Due to the relative novelty of the HTC process as a thermochemical biomass conversion technology, detailed reaction mechanisms for different feedstocks are not fully understood, and only a few comprehensive reports have been published. A number of studies [26,30] have investigated the properties of HTC liquor, which contains valuable substances utilized in various industrial applications, such as organic acids, furans and phenols. A few HTC pilot plants have already been studied, mainly for wastewater treatment. Currently, the world's first HTC full-scale facility based on green technology have been built to recycles wet pulp mill residual flows into useful energy and agricultural nutrients while stopping greenhouse gas emissions and environmental contamination [31].

This study aims to investigate the HTC conversion of residues from bamboo, eucalyptus, coffee wood and coffee parchment into valuable products and therefore find a potential solution for their management. A specific focus was examination of the potential of coffee residues as a fuel with enhanced properties after HTC processing, which remains an under-researched topic. The importance of the coffee industry for the local economies in producer countries leads to searching for a sustainable destination of the coffee residues generation. The amount of coffee residues can vary significantly depending on regions and climate conditions [19]. The discontinuity of coffee residues production would result in low capacity utilization in dedicated treatment plants. A more feasible solution would be industrial-scale treatment with other biomasses to complement the coffee residues, particularly with industries available in the regions to avoid high transport cost. Hence, industrial-scale HTC plants were simulated in order to analyze the potential of HTC treatment as a biorefinery process using biomass residues. In terms of circular economy, eucalyptus and bamboo side stream in the pulp mill sector may play a significant role contributing to the growing HTC plant additional unit operation into pulp mills. Integration of two processes utilizing the same feedstock can often bring advantages in terms of efficiency improvement, process simplification and cost savings. Additionally, coffee residues typically generated in the same regions as eucalyptus and bamboo were considered as a potential feedstock to be treated in the integrated HTC plant. Although other thermochemical conversion processes such as fast pyrolysis or torrefaction [32] have been studied as potential additional revenue streams for south American pulp mills, the potential of hydrochar production in a pulp mill has not yet been investigated.

2. Materials and methods

2.1. Materials

The samples were provided by the University of Viçosa, Minas Gerais state, Brazil. Coffee wood (CW) and parchment of coffee cherry (CP) from *coffea arabica* species were collected from a rural farm in the municipality of Paula Candido, Minas Gerais state, Brazil. *Eucalyptus sp.* wood (EW) and giant bamboo (GB) were collected from commercial cultivation sites of the experimental units of the Federal University of Viçosa, Minas Gerais state, Brazil. All samples were ground in an electric hammer mill, with a fixed speed of 3520 rpm, linked to a sieve with a mesh size of 1 cm. The grinding is required to ensure uniform size distribution of the feedstock particles. After grinding, the biomasses were stored in sealed polyethylene bags at room temperature.

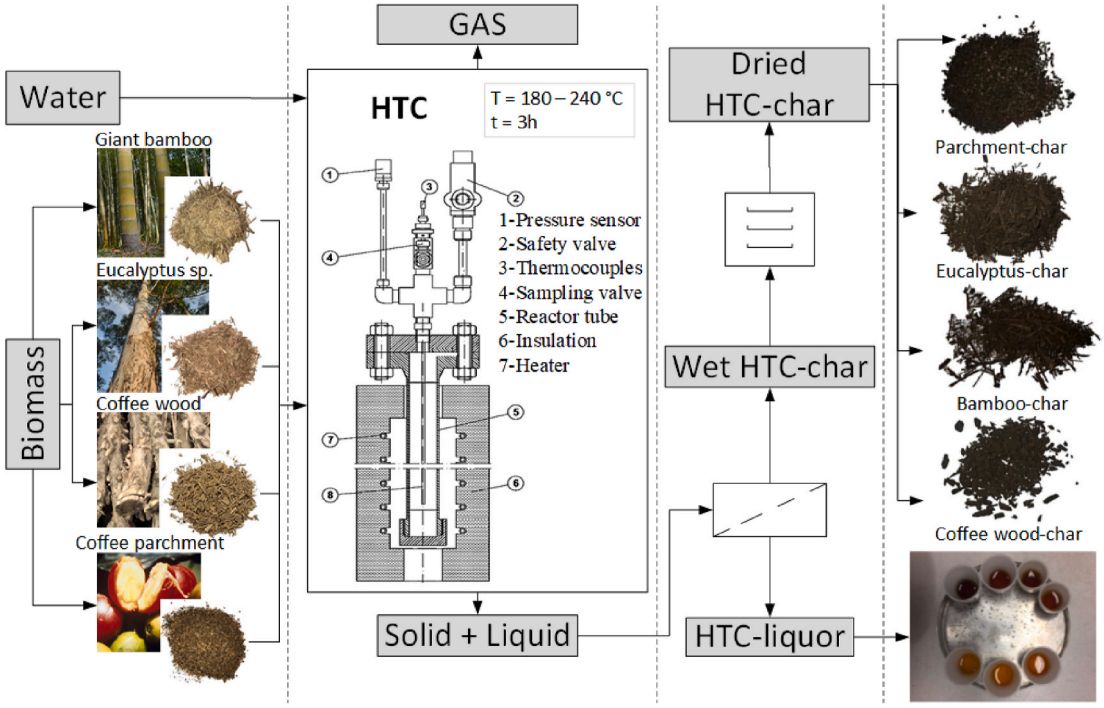


Fig. 1. HTC experimental unit.

2.2. Hydrothermal carbonization

Hydrothermal carbonization of selected lignocellulosic biomasses was performed in the laboratory facilities of Lappeenranta-Lahti University of Technology LUT, Finland, in four main stages: feedstock preparation and characterization, HTC treatment, liquid-solid separation, and product characterization. The experimental procedure is depicted in Fig. 1. For each experiment, a pre-weighed sample of the biomass was dispersed in water and stirred manually.

The characteristics of a hydrochar product depend on the process parameters selected: temperature, water-to-biomass ratio and residence time. Of these, temperature has by far the greatest impact on process severity [23,33,34]. The impact of water-to-biomass ratio is clearly less, and that of residence time less still [33]. Similar thermal degradation behavior, chemical structure and H/C and O/C ratios can be observed in hydrochar when residence time is varied at constant temperature [33]. Consequently, the temperature was varied in the tests, with four values considered: 180, 200, 220 and 240 °C. Water-to-biomass mass ratio was set at 8:1 (approximately 50 g of biomass dry matter and 400 ml of water), and residence time was 3 h, which were considered typical representative values.

The stainless-steel batch reactor used in the experiments had an inner volume of approximately 1 L (705 mm height and 42 mm inner diameter) with a flange connection at the top and screw closing at the bottom. The temperature inside the cylindrical reactor was monitored with two thermocouples; one at 245 mm and one at 645 mm from the top of the reactor. An additional thermocouple measured the temperature of the outer surface of the reactor. A pressure sensor and a pressure relief valve (set point pressure 40 bar, maximum temperature 300 °C) were installed for pressure measurements and safety purposes. The heat demand for the process was provided by a heating jacket. The heater consisted of electric resistance wire elements surrounded by a ceramic fiber insulation and an outer steel cover. National Instruments LabVIEW software was utilized for device control and measurement of the operating parameters. The required temperature level inside the reactor during the period studied was maintained with a proportional-integral-derivative (PID) controller.

At the end of each experiment, the hydrocarbonized biomass and liquid products were collected and then separated by vacuum filtration using a Büchner funnel with a Whatman glass microfiber filter paper of grade GF/A (pore size: 1.6 μm). Hydrochar was subsequently dried overnight in the oven at a temperature of 105 ± 2 °C. All tests were carried out at least in duplicate and average values were used. The retrieved HTC liquors were stored in 100 ml disposable plastic sample containers; 16 samples in total were taken for analysis.

2.3. Biomass characterization

Both feedstock and hydrocarbonized biomass samples were characterized by proximate analysis and heating value measurements in accordance with DIN EN 15148:2010–03 (2010), DIN EN 14775:2010–04 (2010) and DIN EN 14918:2014–08 (2014) standard procedures for volatile matter (VM), ash content (AC) and higher heating value (HHV), respectively. Fixed carbon (FC) was calculated by subtracting from 100% the sum of VM and AC. Additionally, microstructure pictures of the samples were analyzed using a scanning electron microscope (SEM) to examine the morphological structure of the hydrochar surface.

Non-volatile residue (NVR) content, pH and total organic carbon (TOC) were determined for the HTC liquid of the samples. The samples were filtered twice using a grade GF/F microfiber filter with a pore size of 0.7 μm in order to reduce the presence of hydrochar particles and to protect the analysis equipment from damage. In analysis of the NVR content, approximately 4 ml of the samples were introduced into a crucible. Once all the samples were weighed, the crucibles were placed in an oven and kept at a temperature of 105 ± 5 °C for 24 h in order to vaporize all water [26]. The pH analysis was performed with a digital pH meter; a triplicate was taken per sample and the average values used. For total organic carbon (TOC) analysis, a Shimadzu TOC-Lcph/cpn analyzer unit with a dilution function in the range of 10–100 mg L^{-1} was used according to EN 1484-H3 standard procedure.

2.4. Hydrochar quantification parameters

The variation of the mass yield (MY) of the solid product defined as the dry solid mass ratio of hydrochar to that of the initial biomass, together with fixed carbon yield (FCY), energy density factor (EDF) and energy yield (EY) were calculated for the hydrochar samples according to Eqs. (1)–(4) to evaluate the effectiveness of the hydrothermal carbonization process. The energy density factor indicates the elevation of HHV during the HTC process; it should be noted that this parameter does not indicate the economic value addition gained in the process since degradation of the samples is not considered in the equation, unlike in calculation of the energy yield [35].

$$Solid\ mass\ yield: MY = \frac{(M_{hc})_{db}}{(M_b)_{db}} \times 100\% \quad (1)$$

$$Fixed-carbon\ yield: FCY = MY \times (FC/100) \quad (2)$$

$$Energy\ density\ factor: EDF = \left(\frac{HHV_{hc}}{HHV_b}\right)_{daf} \quad (3)$$

$$Energy\ yield: EY = MY \times EDF \quad (4)$$

Mass and energy yield correlations were evaluated in order to describe the obtained yield results of all biomasses in a single equation. Different simple models of diverse forms were run on the data in order to select the best fit. First, the correlation curves were fitted by minimizing the residual sum of squares of the error term using $(X'X)^{-1}X'Y$. A comparison was then made on the basis of the R-squared values. A single equation Eq. (5) defined the selected model that explained the highest percentage of variation for all four feedstocks. The values of the coefficients a, b and c and R-squared values are shown in section 3.2.

$$Y = 100 - a(T-b)^c \quad (5)$$

Correlations proposed and/or applied for estimating the O/C and H/C atomic ratios from HHV were collected from the literature, which are summarized in Table 1. The correlations were carefully selected from several available in the literature for the estimation of biomass HHV using ultimate analysis approach. The accuracy of these correlation is statistically evaluated based on a database of a large quantity of biomass samples. In addition, the validation of the correlations through estimation errors were also considered in the selection of the equations, including the mean absolute error (MAE), average absolute error (AAE) and average biased error (ABE).

After each HTC treatment, the liquor was recovered for subsequent characterization, i.e. determination of the non-volatile residue (NVR) and liquid yield (LY). NVR and LY were defined as in Eqs. (8) and (9).

Table 1
Existing ultimate analysis-based correlations using the properties of low temperature conversion biomass.

Eq.	Ref.	Correlation (HHV, MJ•kg^{-1})	MAE	AAE	ABE	Specification
(6)	[36]	$HHV = 4.4804 + 0.3194 \cdot C$	1.25	5.66	0.64	Approximate heating value of biomass on a dry weigh ash free basis, applied in low temperature treatments.
(7)	[36]	$HHV = 32.7934 + 0.0053 \cdot C^2 - 0.5321 \cdot C - 2.8769 \cdot H + 0.0608 \cdot C \cdot H - 0.2401 \cdot N$	1.13	5.01	0.49	Empirical correlations study using multiple variables' linear or non-linear regression analysis of many data points of torrefaction biomass process.

$$NVR = \frac{(M_l)_{db}}{(M_l - (M_l)_{db}) \cdot 10^{-6} \left[mg \cdot L^{-1}\right]} \quad (8)$$

$$LY = \frac{(M_l)_{db}}{M_l} \quad (9)$$

The results obtained from the gravimetric NVR analysis and the liquid yields are summarized in Table 4.

2.5. HTC plant modelling

Flowsheet models of industrial-scale HTC plants were developed using commercial IPSEpro software in order to investigate the technical performance of possible HTC plant configurations, and to quantify the performance of the investigated cases. IPSEpro is a comprehensive equation-oriented steady-state process simulation software widely used as a decision support tool for complex plant designs [37]. In the IPSEpro environment, the overall plant flowsheet models are constructed with discrete modules representing individual components. The software model library covers many common components, while user-defined component models can be created for special tasks in a separate model development kit (MDK) supplied with the software. The calculation of a flowsheet model is based on the simultaneous solution of mass and energy balances together with specific equations describing the behaviour of each component, and the simulation result represents a steady-state operating point of a plant. The configurations of the simulated CHP plants will be presented in Section 3.5.

2.6. HTC plant performance indicators

LHV basis net efficiency, η_{LHV}, and energy saving ratio, ESR, were used as key performance indicators for the simulated HTC plants. Net efficiency is defined in Eq. (10) for the stand-alone HTC plant and in Eq. (11) for the integrated plant.

$$\eta_{LHV} = \frac{\Phi_{HC}}{\Phi_{b,boiler} + \Phi_{b,HTC} + P_{el,in}} \quad (10)$$

$$\eta_{LHV} = \frac{\Phi_{HC} + P_{el,net}}{\Phi_{b,boiler} + \Phi_{b,HTC}} \quad (11)$$

ESR is defined as:

$$ESR = \frac{\left(\Phi_{b,boiler} + \Phi_{b,HTC}\right)_{sep} - \left(\Phi_{b,boiler} + \Phi_{b,HTC}\right)_{co-gen}}{\left(\Phi_{b,boiler} + \Phi_{b,HTC}\right)_{co-gen}} \quad (12)$$

Table 2
Chemical analysis of feedstock and hydrochar samples.

Biomass	Properties	Units	Feedstock	Reaction Temperature [°C]			
				180	200	220	240
Eucalyptus	VM[a]	[wt%]	$84.9_{(0.2)}$	$79.1_{(0.4)}$	$65.6_{(1.5)}$	$56.5_{(0.7)}$	$47.9_{(0.4)}$
	AC[a]	[wt%]	$0.2_{(0.05)}$	$0.1_{(0.02)}$	$0.1_{(0.1)}$	$0.1_{(0.1)}$	$0.2_{(0.1)}$
	FC[a]	[wt%]	$14.8_{(0.2)}$	$20.8_{(0.5)}$	$34.3_{(1.8)}$	$43.4_{(1.0)}$	$51.9_{(1.0)}$
	HHV[a]	[MJ·kg^{-1}]	$20.0_{(0.1)}$	$21.7_{(0.1)}$	$24.6_{(0.1)}$	$25.4_{(0.1)}$	$25.5_{(0.1)}$
	LHV[a]	[MJ·kg^{-1}]	$18.5_{(0.1)}$	$20.4_{(0.1)}$	$23.3_{(0.1)}$	$24.1_{(0.1)}$	$24.2_{(0.1)}$
	MY	[%]	–	$72.3_{(0.6)}$	$64.2_{(0.4)}$	$56.9_{(0.4)}$	$51.6_{(0.4)}$
	EY	[%]	–	$78.8_{(0.7)}$	$79.1_{(0.6)}$	$72.1_{(0.5)}$	$65.9_{(0.5)}$
	EDF	[-]$_{(\times 10^2)}$	–	$1.1_{(0.6)}$	$1.2_{(0.7)}$	$1.3_{(0.1)}$	$1.3_{(1.1)}$
Giant bamboo	VM[a]	[wt%]	$83.5_{(0.5)}$	$73.9_{(2.7)}$	$66.5_{(4.3)}$	$56.6_{(1.6)}$	$44.6_{(3.2)}$
	AC[a]	[wt%]	$1.2_{(0.01)}$	$0.7_{(0.1)}$	$0.8_{(0.1)}$	$0.7_{(0.1)}$	$1.5_{(0.5)}$
	FC[a]	[wt%]	$15.3_{(0.5)}$	$25.4_{(2.8)}$	$32.6_{(4.0)}$	$42.6_{(1.8)}$	$53.9_{(3.0)}$
	HHV[a]	[MJ·kg^{-1}]	$19.9_{(0.1)}$	$22.5_{(0.1)}$	$23.7_{(0.1)}$	$24.6_{(0.1)}$	$27.0_{(0.1)}$
	LHV[a]	[MJ·kg^{-1}]	$18.7_{(0.1)}$	$21.1_{(0.1)}$	$22.4_{(0.1)}$	$23.2_{(0.1)}$	$25.7_{(0.1)}$
	MY	[%]	–	$63.9_{(0.8)}$	$59.3_{(1.0)}$	$54.3_{(1.7)}$	$52.5_{(0.8)}$
	EY	[%]	–	$73.0_{(0.9)}$	$71.3_{(0.8)}$	$67.9_{(1.4)}$	$69.4_{(1.4)}$
	EDF	[-]$_{(\times 10^2)}$	–	$1.1_{(0.4)}$	$1.2_{(0.8)}$	$1.2_{(1.5)}$	$1.3_{(0.5)}$
Coffee wood	VM[a]	[wt%]	$82.7_{(0.2)}$	$77.6_{(0.3)}$	$73.9_{(0.5)}$	$64.6_{(3.8)}$	$53.1_{(0.9)}$
	AC[a]	[wt%]	$1.8_{(0.1)}$	$1.1_{(0.1)}$	$0.9_{(0.1)}$	$0.9_{(0.1)}$	$0.8_{(0.1)}$
	FC[a]	[wt%]	$15.5_{(0.2)}$	$21.3_{(0.6)}$	$25.2_{(0.7)}$	$34.4_{(4.0)}$	$46.04_{(1.2)}$
	HHV[a]	[MJ·kg^{-1}]	$20.2_{(0.1)}$	$22.2_{(0.1)}$	$22.8_{(0.1)}$	$25.6_{(0.1)}$	$26.5_{(0.1)}$
	LHV[a]	[MJ·kg^{-1}]	$18.8_{(0.1)}$	$20.7_{(0.1)}$	$21.3_{(0.1)}$	$24.1_{(0.1)}$	$25.1_{(0.1)}$
	MY	[%]	–	$68.0_{(1.3)}$	$65.5_{(0.4)}$	$56.7_{(1.0)}$	$46.5_{(1.0)}$
	EY	[%]	–	$75.0_{(0.7)}$	$74.0_{(0.3)}$	$71.9_{(1.2)}$	$61.3_{(0.6)}$
	EDF	[-]$_{(\times 10^2)}$	–	$1.1_{(1.0)}$	$1.1_{(0.6)}$	$1.3_{(0.5)}$	$1.3_{(5.3)}$
Coffee parchment	VM[a]	[wt%]	$76.3_{(0.1)}$	$73.9_{(0.3)}$	$69_{(0.7)}$	$61.4_{(1.0)}$	$49.5_{(1.6)}$
	AC[a]	[wt%]	$6.8_{(0.1)}$	$1.4_{(0.3)}$	$1.4_{(0.4)}$	$1.6_{(0.3)}$	$1.7_{(0.1)}$
	FC[a]	[wt%]	$16.9_{(0.3)}$	$24.6_{(0.6)}$	$29.6_{(0.6)}$	$36.9_{(0.8)}$	$48.8_{(1.4)}$
	HHV[a]	[MJ·kg^{-1}]	$18.4_{(0.1)}$	$22.1_{(0.1)}$	$23.4_{(0.1)}$	$25.2_{(0.1)}$	$29.2_{(0.1)}$
	LHV[a]	[MJ·kg^{-1}]	$17_{(0.1)}$	$20.7_{(0.1)}$	$22_{(0.1)}$	$23.9_{(0.1)}$	$28_{(0.1)}$
	MY	[%]	–	$55.4_{(0.7)}$	$54.1_{(1.6)}$	$46.0_{(0.6)}$	$34.4_{(1.8)}$
	EY	[%]	–	$66.4_{(0.7)}$	$68.8_{(1.6)}$	$63.0_{(0.8)}$	$54.6_{(2.5)}$
	EDF	[-]$_{(\times 10^2)}$	–	$1.2_{(0.6)}$	$1.3_{(0.5)}$	$1.4_{(1.0)}$	$1.6_{(0.7)}$

[a] dry basis. $_{(...)}$ Standard deviation. VM-Volatile Matter. AC-Ash content. FC-Fixed carbon. HHV-High heating value. LHV-Low heating value. MY-Mass yield, EY-Energy yield. EDF-Energy density factor.

Table 3
Coefficients and R-squared for mass and energy yield equation adjustment.

Sample	Mass yield				Energy yield			
	a	b	c	R^2	A	b	c	R^2
HTC-CW	0.313	99.209	1.035	0.93	0.125	71.591	1.109	0.86
HTC-EW	3.516	143.315	0.575	0.99	0.116	85.982	1.123	0.87
HTC-GB	5.166	108.835	0.458	0.92	2.365	−1.239	0.473	0.89
HTC-CP	0.622	84.007	0.918	0.87	0.249	48.049	0.983	0.78

Hydrochar from CW-coffee wood, EW-eucalyptus wood, GB-giant bamboo, CP-coffee parchment.

Table 4
NVR and TOC of HTC liquor.

Biomass	T [°C]	NVR Gravimetric Analysis		TOC analysis [g·L^{-1}]		
		NVR [g·L^{-1}]	LY [%]	TOC	TC	IC [·10^{-3}]
Eucalyptus	180	14.74	1.45	20.00	20.02	15.14
	200	12.25	1.21	20.53	20.55	15.25
	220	9.88	0.98	17.78	17.80	19.61
	240	7.43	0.74	17.22	17.24	21.14
Giant bamboo	180	22.66	2.22	27.15	27.17	16.94
	200	19.64	1.93	24.96	24.98	16.67
	220	16.62	1.64	21.93	21.95	17.01
	240	13.61	1.35	19.46	19.48	16.94
Coffee wood	180	12.31	1.22	18.37	18.39	15.44
	200	11.76	1.16	20.83	20.85	20.66
	220	11.97	1.18	31.05	31.06	14.76
	240	11.67	1.15	36.09	36.11	16.27
Coffee parchment	180	31.82	3.08	24.80	24.82	17.37
	200	27.27	2.65	24.80	24.82	15.52
	220	27.34	2.66	25.52	25.54	17.53
	240	24.29	2.37	22.51	22.53	16.43

where subscripts *sep* and *co-gen* refer to the fuel and feed consumption of the separate stand-alone and integrated co-generation of hydrochar and electricity, respectively. Boiler fuel consumption for non-integrated production is defined as a sum of the boiler fuel consumption of the non-integrated HTC plant and separate power plant boiler for production of the same amount of electricity as the integrated plant, accounting for the consumption of the HTC plant.

3. Results and discussion

3.1. Properties of the biomass feedstock and hydrochar

Proximate and calorific analysis values of the biomass feedstocks are listed in Table 2, as well as the mass and energy yields, and the energy density factors. The last three indicators are explained in section 3.2. In general, all the tested carbonization temperatures successfully upgraded the quality of the raw material by increasing the heating value of the final product.

Higher heating value is one of the most important parameters in thermochemical conversion processes [18]. In addition to being an important indicator of energy density and thus quality of the product, the heating value in HTC typically tends to correlate with the severity of the hydrocarbonization process. In this study, a gradual increase of HHV with increasing temperature from feedstock to $HTC_{240°C}$ of 21.6, 26.3, 23.8 and 37% for EW, GB, CW and CP, respectively, was observed. The increase in higher heating value demonstrated the energetic improvement of the hydrochar due to dehydration and decarboxylation [38]. The HHV of the $HTC_{220°C}$ and $HTC_{240°C}$ samples (except for GB at $HTC_{220°C}$) exceeded the higher heating value of commercial lignite (25.0 MJ kg^{-1}) [39] and the HHV of CP at $HTC_{240°C}$ was slightly higher than that of sub-bituminous coal (28.7 MJ kg^{-1}) [40]. The results obtained for HHV were close to the values reported in the literature for earlier HTC experiments carried out with similar parameters for *eucalyptus sp*. (20.2–29.2 MJ kg^{-1}) [29] and bamboo (17.5–28.7 MJ kg^{-1}) [28,41]. No information on HTC treatment results could be found for coffee residues, i.e. coffee parchment and coffee wood. The HHV of the hydrochar samples can be compared to the HHV of dry torrefied coffee residues treated at 240 °C for 0.5 h (21.9 MJ kg^{-1}) [41], eucalyptus species treated at 160–230 °C for 5–15 h (19.5–21.3 MJ kg^{-1}) [42] and bamboo treated at 220–280 °C for 1 h (19.3–24 MJ kg^{-1}) [43]. The results indicate that the HTC process is more effective at upgrading the HHV than dry torrefaction and can convert lignocellulosic biomass into a more desirable value-added product for energy applications. Additionally, HTC process is not affected by the high moisture content of the feedstock, and therefore eliminates the pre-drying requirement, which consumes high amount of energy that results in a financial load. However, post-drying of hydrochar is required for energy applications. According to Ref. [44] hydrochar produced via HTC from grass biomass were found more hydrophobic compared to biochar sample produced from torrefaction, which may have an economical advantage in the post-drying stage.

The volatile matter content of the hydrochar decreased with increasing HTC temperature as a result of devolatilization/depolymerization taking place during HTC. The decrease of absolute volatile matter, VM, (fraction of VM multiplied by the mass yield, MY) in percentages from feedstock to $HTC_{240°C}$ were 43.3, 46.4, 36.0 and 34.9% for EW, GB, CW and CP, respectively. The FC values, on the other hand, indicate potential for hydrochar generation from the devolatilized biomass [18]. For all studied samples, the FC increased due to carbon concentration resulting from devolatilization; this conversion increases with increasing temperature. From feedstock to $HTC_{240°C}$, the total quantity of fixed carbon (FC multiplied by MY) increased by 82%, 85% and 38% for EW, GB, and CW, respectively. For CP, no change of total quantity of FC was observed, as mass loss and FC fraction increase almost exactly compensated for each other. The changes in the VM and FC contents were less pronounced with the coffee residues than with EW and GB, which indicates that eucalyptus and bamboo samples are more susceptible to thermal degradation, thus requiring less time for a thermochemical conversion, while coffee residues are more stable to HTC process conditions, probably due to differences in the chemical and structural composition.

Biomass degradation can also be explained by the structural composition of the samples [18], because low molecular weight products are released from the side chains of hemicelluloses and lignin, and slight disintegration of water extractives also takes place at low temperatures of approximately 250 °C [38,45]. Same coffee residues samples used in this study were characterized previously in Ref. [18]; 18.25 wt% and 20.65 wt% of lignin and 29.57 wt% and 26.59 wt% of hemicelluloses were obtained for CW and CP, respectively. For eucalyptus and bamboo structural composition data was obtained from diverse reports of samples collected in the same regions as the biomasses considered in this study, average values of 22.5 and 31.4 wt% for EW [46,47], and 21.5 and 23.4 wt% for GB [48] for lignin and hemicelluloses, respectively were found. The values demonstrate the high potential of these materials for hydrochar production, even though they may have different resistances to thermal degradation during the process. The higher the lignin content and the lower the hemicellulose content, the higher the resistance of the biomass to degradation at HTC process conditions. According to Yang et al. [49], lignin is the chemical constituent of biomass that contributes most to hydrochar yield.

Ash is an inorganic solid residue, mostly in the form of oxides, contained in biomass as a result of normal plant growth process. Ash represents a risk to biorefinery equipment due to its corrosive properties [50]. In this study, HTC treatment of EW resulted in a slight reduction of ash content in the hydrochar in comparison to the raw feedstock. Minor variation was observed in GB treatments: in most cases a slight reduction in ash content was found, but at $HTC_{240°C}$ there was a small increase compared to the raw biomass. The AC increase in the hydrochar is probably associated with the precipitation of minerals in the ash as the temperature increases [29]. Some inorganic compounds may become organically bound, form insoluble salts, adsorb on the hydrochar or dissolve in liquid but remain in the hydrochar during thermal drying. In general, removal of inorganics from the feedstock by the HTC process is efficient, due to the inorganics becoming partially dissolved in the liquid phase [51]. This phenomenon was more evident during the HTC conversion process of coffee residues, which showed a significant ash content reduction of 75% for CP and 56% for CW for $HTC_{240°C}$ in comparison to the raw feedstock. Section 3.3 shows that coffee hydrochar tends to exhibit higher porosity, which facilitates the circulation of solvents and consequently the removal of inorganics. Alkali and alkaline earth metals were likely removed from the samples, since the literature is consistent about the effectiveness of HTC in their removal, e.g. 95% of potassium was removed in all cases reported by Stirling et al. [52]. The ash content is also related to the reactivity of the samples due to the deposition of inorganic compounds on the sample surface, contributing to hydrochar from higher HTC temperature being more reactive than its lower HTC temperature counterpart.

Biomass is mainly composed of elements C, H, O, N and S, where the former three are the main ones, representing up to 97–99% of the biomass organic mass. Ultimate compositions of the biomasses studied were calculated using the heating value correlations of Table 1; Eq. 6 for C and Eq. 7 for H. Changes to N and S contents in HTC treatment of different biomasses have been reported as insignificant in different studies [53–55]. In this study, the feedstock N and S content of 0.05 and <0.01 for eucalyptus [53], 0.6 and < 0.01 for bamboo [54], 1.86 and 0.21 for coffee wood [56], and 0.82 and 0.2 for coffee parchment [56], respectively were used along the HTC process temperature variation. The calculated values for the feedstock were compared to data available in the literature for eucalyptus [53], bamboo [54] and coffee residues [56]. Fig. 2 shows the fuel characteristics of biomass through ultimate composition by means of a van-Krevelen diagram. Increasing HTC process temperature reduces the oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratios of the samples and makes them more comparable to lignite and coal. A strong trend of dehydration with increasing HTC temperature was observed, which indicates the hydrolysis reactions of hemicelluloses and cellulose, probably of xylose and glucose

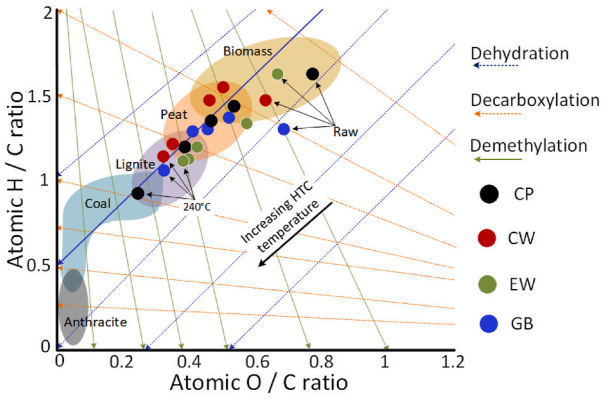


Fig. 2. van-Krevelen diagram of hydrochars produced at various HTC temperatures.
Hydrochar from CW-coffee wood, EW-eucalyptus wood, GB-giant bamboo, C P-coffee parchment.

degradation, respectively. The average carbon content was 60 wt% which can be considered as an indicator of successful biomass dehydration [57]. In general, the elemental carbon increased with higher HTC temperature from 43 to 49 wt% to 66–77 wt%. Similar results were observed for different biomasses under HTC treatments such as garden prunings that increase C content from 56.45 wt% to 65.83 wt% [57] or bamboo from 44.10 wt% to 66 wt% [54]. More carbon in the sample indicates the potential of carbon-base materials production, carbon sequestration, and soil amendment applications [58].

3.2. Mass and energy yields of hydrochar

Fig. 3 and Fig. 4 depict the mass and energy yields of hydrochar together with the correlation curves, described by Eq. (5). Table 3 shows the coefficients obtained from the regression analysis and the corresponding R-squared values of the mass and energy yield equations.

The mass yields obtained for the biomasses were considered satisfactory compared to previous findings. For example, the hydrochar yield obtained for *Eucalyptus sp.* did not exceed 46.4% (conditions of 220–300 °C for 0.5–10 h) [29], while MY values of approximately 50–71% have been found for wood samples [26], values supported by pine wood studies [23]. For agricultural residues e.g. sugarcane bagasse, corn stover and rice hulls, MY values of 36–72% at HTC temperatures of 200–300 °C have been reported [26]. Similar trends of MY decrease with increasing temperature were observed in this research.

For all four biomasses, increasing the temperature in the range of 180–240 °C increased the mass loss, from 45% to 66%, 32%–54%, 28%–48%, and 36%–48% for CP, CW, EW and GB, respectively. The mass yield (MY) reduction is connected to the deoxygenating reactions and VM conversion, as the hydrogen and oxygen contents become lower at higher temperatures [59]. The lowest MY values were observed for the agricultural residue (CP), and the lowest MY variation was found for GB samples, followed by EW, CP and CW, in that order.

Total organic carbon (TOC) in HTC liquid consists mostly of organic acids and sugars [60]. The higher anhydrosugar content of agricultural residues compared to woody biomasses leads to increased degradation of carbon compounds in the residues compared to wood. These accelerate the hydrolysis process, further catalyzing the hydrocarbonization, resulting in a lower MY for agricultural residues than woody biomass.

With the GB, the amount of TOC decreased at increasing temperature. This is also consistent with the lowest MY variation observed in GB, as the reducing catalytic effect could be expected to also reduce the increase of reaction severity from increasing temperature. The liquid from CP had the highest pH values, which led to increased hydrolysis and consequently lower MY. HTC liquor is discussed in more detail in section 3.4.

The energy yield, EY, of the process is a product of two factors: mass yield and energy densification (relative increase of heating value). As the HTC temperature increases, the mass yield decreases, and energy densification increases for all feedstocks (Table 2). The total EY within the studied HTC temperatures resulted in values ranging from 61 to 79% for woody biomass and 54–69% for CP. The energy yields indicate solid matter energy content reductions of 31%–45%, 25%–39%, 21%–34% and 27%–31% for CP, WC, EW, and GB samples, respectively. The results are consistent with literature reports for woody biomass (EY: 66–85%) [23,26,60] and agricultural residues (EY: 56–78%) [26].

The type of biomass influenced the yield distribution. As can be seen in Figs. 3 and 4, woody biomass produces more solid matter and, consequently, less tar, water and gas than agricultural residues. This finding is in qualitative agreement with previous studies, where higher energy and solid yields from wood residues were attributed to higher lignin content and lower amounts of anhydrosugars and inorganics [61,62].

Fixed carbon yield (FCY) is an indicator of the quality of the final hydrochar product [46]. Fig. 5 shows the FCY values obtained for the samples. FCY values of 13–18%, 13–23%, 14–27% and 15–29% were

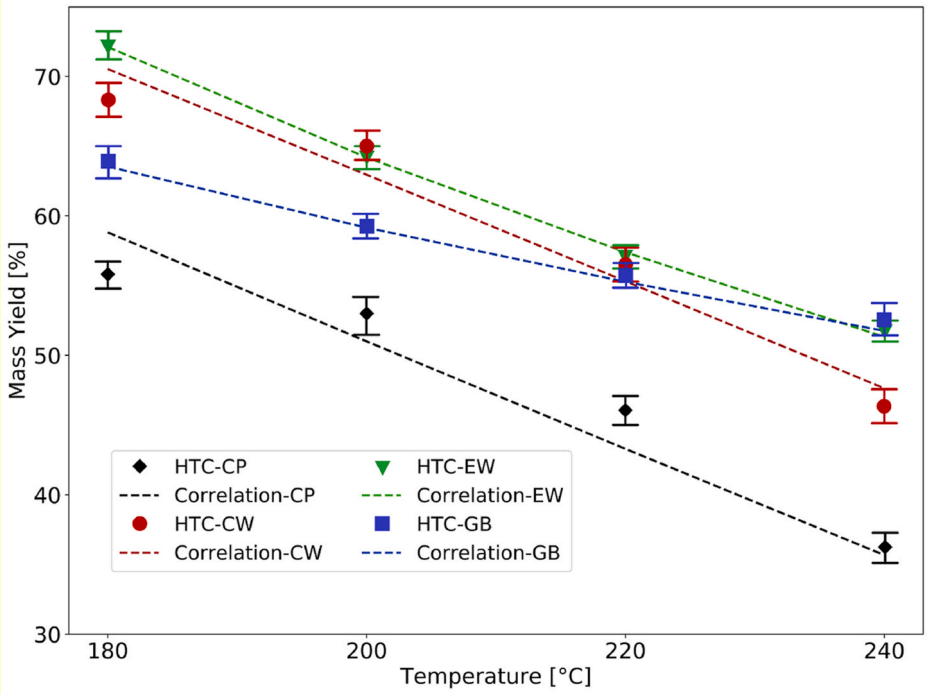


Fig. 3. Mass yield of hydrochar as a function of temperature at 8:1 water-to-biomass ratio. Hydrochar from CW-coffee wood, EW-eucalyptus wood, GB-giant bamboo, C P-coffee parchment. Bars represent standard deviation.

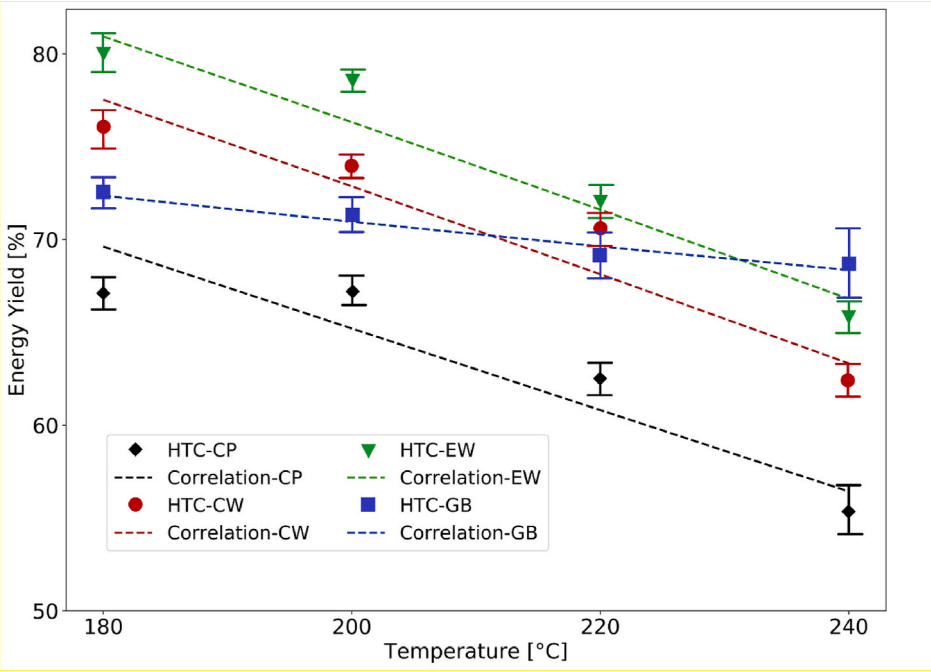


Fig. 4. Energy yield of hydrochar as a function of temperature at 8:1 water-to-biomass ratio. Hydrochar from CW-coffee wood, EW-eucalyptus wood, GB-giant bamboo, C P-coffee parchment. Bars represent standard deviation.

found for CP, CW, EW and GB, respectively. Fixed carbon yield has a positive correlation with lignin content [46], which explains the differences in behavior of the feedstocks, especially the difference between agricultural and woody biomasses. Wood biomass often has a higher carbon content than agricultural materials, which tends to result in more carbon assimilation during the conversion process, yielding a product with good characteristics for energy applications as a solid biofuel [18].

3.3. Morphological structure analysis

Morphological transitions of the biomasses under different HTC temperature conditions were studied with scanning electron microscopy

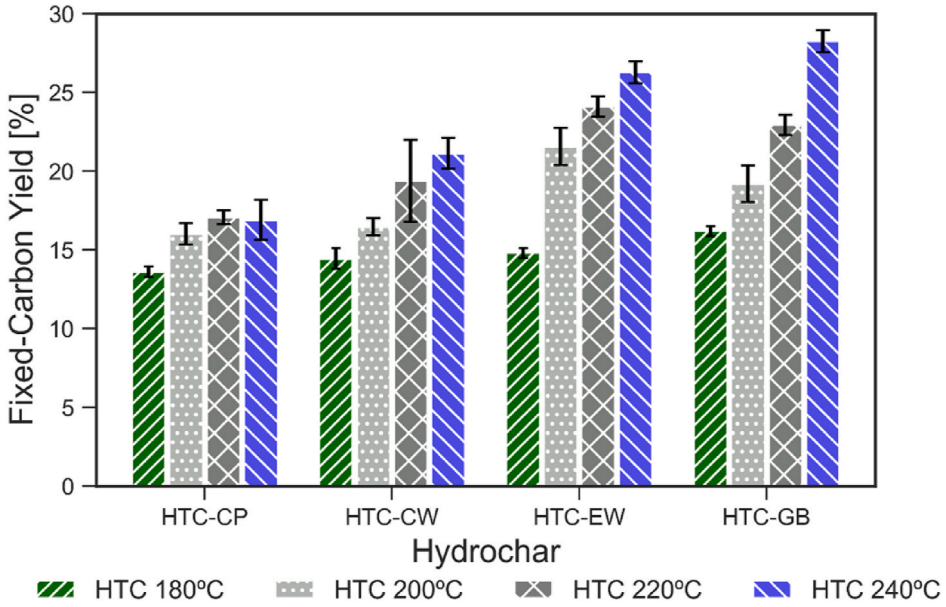


Fig. 5. Fixed carbon yield of hydrochar Hydrochar from CW-coffee wood, EW-eucalyptus wood, GB-giant bamboo, C P-coffee parchment. Standard deviation (bars).

(SEM). The surface morphology micrographs for the feedstocks and the hydrochars are shown in Fig. 6. As expected, the shapes, arrangement of the pores and their radii, and the fibres of the samples were all modified during the HTC treatment. Surface changes during HTC treatment are associated with the reduction in organic compounds and volatilization, which results in formation of the hydrochar matrix [63]. The feedstock samples displayed the typical cellular structure of lignocellulosic biomass with continuous smooth thick surfaces. As a consequence of the HTC treatment, the lignocellulosic structure ruptured into small fragments, due to the presence of easily decomposable polymers such as hemicelluloses in the samples. Protuberances in the hydrochar, which are likely cell wall changes caused by thermal degradation, can also be observed. Literature reports indicate that at high temperature dissolution of anhydrosugars followed by polymerization of monomers and fragments in the liquid phase can result in the formation of carbonaceous spheres on the hydrochar surface [64,65]. These are known as secondary hydrochar. The number of heterogeneous fragments increases as the temperature is increased, and for the same temperature, new microsphere structures and pores are formed on the hydrochar surface; this behaviour can be seen by observing the SEM images. When the cellulose and hemicellulose contents of the biomass are high, the hydrochar becomes more fragmented, and the presence of carbonaceous microspheres, esters and hydroxyl groups on the hydrochar surface increases [65]. The hydrochar from coffee residues, which have high contents of polymers that are decomposable at low temperatures, as noted in section 3.1, thus produce a higher density of carbon microspheres on the surface than bamboo or eucalyptus. The spheres from coffee residue also exhibit lower integrity, resulting in more irregular shapes. These characteristics also benefit the production of pores in the material. The pores in coffee parchment hydrochar were also found to be of lower diameter than in hydrochar from woody biomasses.

Porosity increases due to gas emissions from volatile matter, fragmentation of biomass composition [29] and reduction of the parenchyma cells. The parenchyma cells have thin primary walls and are easily degraded by temperature [66]. The CP hydrochar showed higher porosity than the hydrochar from the woody samples. Consequently, CP hydrochar has good potential for soil amendment usage, since the pores on the hydrochar can hold moisture and thereby increase the water holding capacity of the soil [67]. The higher porosity can be explained by the difficulty of dissolving and dispersing lignin and cellulose into the aqueous phase at low temperatures. In summary, the formation of hydrochar can be described as a conversion of non-dissolved lignin and/or cellulose and dissolved fragments through homogeneous hydrocarbonization [29].

It can be seen that the fibres were the most affected cells during the hydrocarbonization and changes in the cell walls were easily discernable. As temperature increased, the reduction in the cell wall thickness of the fibres increased. The fibres exhibited a glassy and brittle appearance after hydrocarbonization, which was also observed by Yildiz and Gümüşkaya [68].

3.4. HTC liquid-phase products

During the HTC process, the liquid phase acts as a heat transfer medium, solvent and reactant. This phase participates actively in the degradation of carbohydrates during hydrolysis. Due to dehydration reactions, the liquid content at the end of each HTC experiment is usually higher than the original water input. The appearance of the collected HTC liquor samples varies depending on the process parameters and the feedstock. In this study, the aqueous suspension had a yellow/brown tone. The HTC liquors consist mainly of sugars, organic acids, furfural and phenols, among other components [26,60]. Quantification of the HTC liquor compounds from HTC treatment of biomass should be considered for future research due to their importance as valued-added products. Nevertheless, pH values, non-volatile residue NVR, liquid yield LY and total organic carbon of HTC liquors were measured in this study.

The results of pH measurements are shown in Fig. 7 pH was found to vary from 2.9 to 4.4, due to organic acids production. The results are in agreement with earlier literature, which also reported slightly more acidic HTC liquors from woody biomass than from agro-based residue feedstocks, although the difference was not statistically significant [12]. Hoekman et al. [26] observed a minor reduction in pH levels with increased HTC process temperature, which was found in this study for EW and GB but not with the CW and CP samples. The different behavior of the CW and CP samples can be attributed to the lower amount of acid production in general and a smaller amount of formic acid in the case of CP [69]. Another reason may be the higher liquid alkali content of

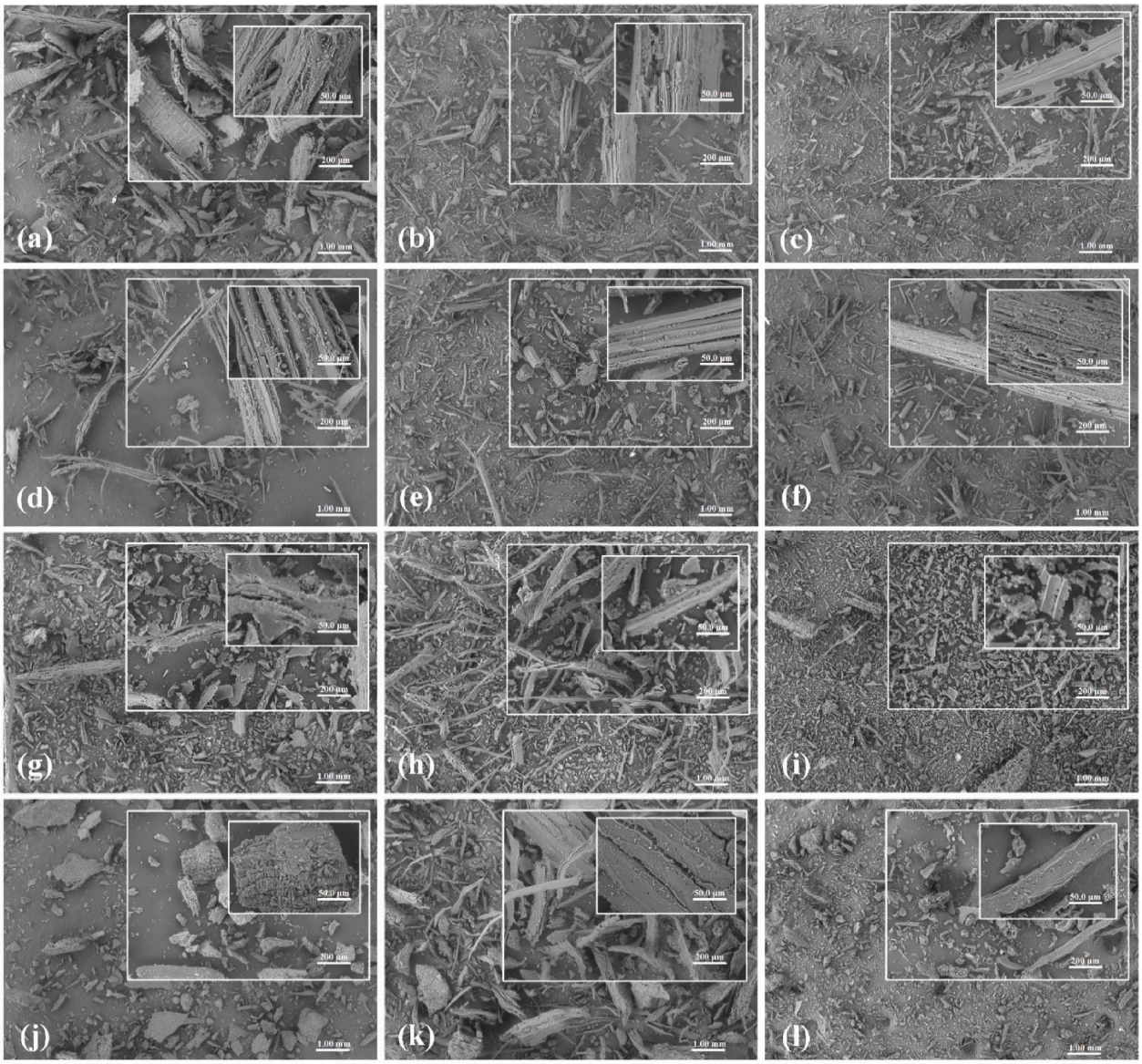


Fig. 6. SEM images: eucalyptus wood: (a) raw, (b) $HTC_{180°C}$ and (c) $HTC_{240°C}$; bamboo: (d) raw, (e) $HTC_{180°C}$ and (f) $HTC_{240°C}$; coffee wood: (g) raw, (h) $HTC_{180°C}$ and (i) $HTC_{240°C}$; coffee parchment: (j) raw, (k) $HTC_{180°C}$ and (l) $HTC_{240°C}$.

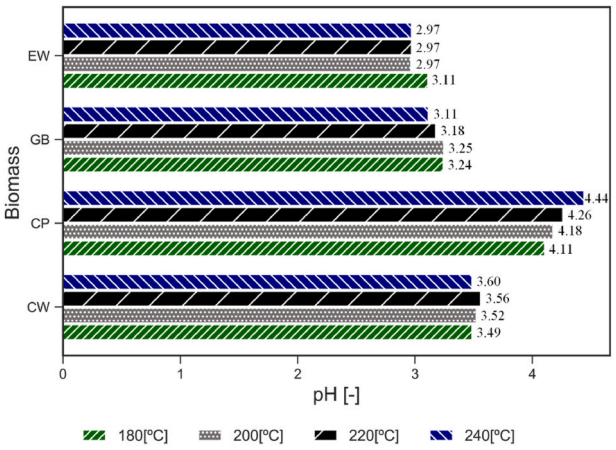


Fig. 7. pH levels of HTC liquors. pH values in front of the bars, standard deviation (SD) < 0.1.

agricultural residues compared to woody biomass [69]. The variation in the pH level throughout the range of treatment temperatures in this study can be considered relatively small: 3.1%, 4.6%, 4.2% and 7.5% for CW, EW, GB and CP, respectively.

As a general trend, the non-volatile residue NVR and liquid yield LY of HTC liquors decrease with increasing temperature. This happens as a result of non-volatile organic products, which would remain in the liquor at mild conditions, reacting further and breaking down into non-condensable gases at higher temperatures [26]. At $HTC_{180°C}$ to $HTC_{240°C}$, NVR content was between 7 and 31 $g \cdot L^{-1}$, with liquors from treatment of CP having higher values than those from woody biomasses or bamboo. The results are similar to those reported in Hoekman et al. [26] for woody and agricultural feedstock.

In addition to NVR and LY, Table 4 includes also the total organic carbon (TOC), inorganic carbon (IC) and total carbon (TC) concentrations in the HTC liquors. TOC values in the liquor samples ranged from 17 to 21 $g \cdot L^{-1}$, 19–27 $g \cdot L^{-1}$, 18–36 $g \cdot L^{-1}$ and 22–26 $g \cdot L^{-1}$ for EW, GB, CW and CP, respectively. As the reaction temperatures increased from 180 °C to 240 °C, the TOC concentrations decreased by 13.9% in the EW liquor and 28.3%, in the GB liquor. In the CP liquor samples, a smaller

TOC change of 11% was observed, i.e. process temperature did not have a strong influence on TOC. In the CW liquor, the temperature dependency of TOC was the opposite: a clear increase of TOC values with increasing temperature. Unlike the other feedstocks, the liquid yield of coffee wood also does not significantly reduce with temperature. It thus appears that the organic compounds in the CW liquor are less prone to thermally degrade into gaseous products than those of the other feedstocks. Further analysis of the compounds in the liquid and gas phases will be needed to fully explain this difference in liquor behavior. The TOC concentrations found in this research appear clearly higher than those found in the literature; the highest TOC concentration reported in Elyounssi et al. [35] was approximately 18 $g \cdot L^{-1}$ for liquors from HTC treatment of maize silage at 200 °C for 0.3 h, and Hoekman et al. [26] reported measured TOC levels for a selection of woody and herbaceous biomasses in a narrow range of 7–13% of the starting mass. The results indicate a high content of sugars (e.g. glucose or xylose) in the liquor.

3.5. Industrial-scale HTC plant simulation

In the second stage of the study, industrial-scale plants were simulated. Different plant configurations and operating schemes were considered, including stand-alone, and integration to the steam cycle of either a small biomass-fired condensing power plant, or the combined heat and power (CHP) plant of a large kraft pulp mill. The HTC process requires heating and pressurizing a large mass of water along with the feedstock. Recovering most of this heat is vital for a reasonably efficient process. Accomplishing this with a relatively simple plant configuration was the main goal of the process design part of the study.

All cases consider a continuously operating plant with a Kamyr feeder for feed slurry mixing, direct steam heated reactor, 1:8 dry-to-water ratio, 3 h residence time, and 50% of HTC liquor recirculated to the feed. Ambient temperatures of 20 °C (water) and 25 °C (air, biomass) were assumed. Initial design focused on a relatively small stand-alone plant, producing 2 t h^{-1} of 10% MC (*wb*) hydrochar pellets at rate at 200 °C temperature, amounting to approximately 4–6 t h^{-1} of 40% MC (*wb*) feedstock. Steam for final reactor heating to carbonization temperature was provided by a grate-fired boiler. Two variations, differing in the heat recovery and final product drying, are considered, shown in Fig. 8. SA-B represents the simpler case with a belt dryer at 1.2 kWh/kg_{evap} heat consumption [19] and heat recovered from the product slurry stream as flash vapour as the heat source, while case SA-D represents a more efficient but also more complex plant utilizing a rotary drum dryer at 0.9 kWh/kg_{evap} heat consumption [70], using boiler flue gas as a heat source. This SA-D scheme needs more depressurization stages to prevent boiling in the feed stream (with a 5 °C safety margin) while simultaneously maintaining a pressure gradient from flash tank towards the feed stream for vapour injection.

The boiler fuel is bamboo when bamboo is the HTC feedstock, eucalyptus for other HTC feedstocks. Coffee residues were not considered as boiler fuel due to inconsistent availability and, in case of coffee parchment, also corrosive ash properties. The biomass dry matter specific heat $c_{p,d}$ was estimated using correlations for woody biomass (coffee wood and eucalyptus) [71], giant bamboo [72] and coffee parchment [73]. For hydrothermal carbonization reaction enthalpy h_f available data is still sparse, but the net h_f appears likely to be small but exothermic. To obtain a conservative estimate for the energy needed, the heat gained from the small and difficult-to-estimate h_f was not considered in the reactor model. Results obtained for the two stand-alone plants with different feedstocks are presented in Table 5. Even with a high-end efficiency estimate assumed for the drum dryer, only a small boiler fuel saving could be achieved, and efficiency advantage is all but lost due to the higher power consumption. As the cost of electricity likely exceeds that of solid biomass fuel, the SA-D scheme is simpler, and the drum dryers with high-temperature heat supply introduce a fire hazard not present with belt driers, the SA-B case appears preferable as a stand-alone concept.

Integration with steam power plants was evaluated in different concepts. Two power plants were considered for integration: the steam cycle of a large South American pulp mill recovery boiler, labelled RB (Fig. 9), and a small-scale biomass-fired condensing power plant, CPP (Fig. 10). The boiler and steam cycle modelling was performed as described in Refs. [74,75].

The plant RB produces power and steam for the adjacent pulp mill. Steam is available as 4 bar low-pressure (LP) steam, medium-pressure levels of 16.5 bar MP1 and 10 bar MP2, and 28 bar high pressure (HP) for boiler sootblowing. Steam remaining after mill and deaerator demands is expanded through a condensing turbine. The condensing turbine flow is throttled to maintain required pressure and flow to steam

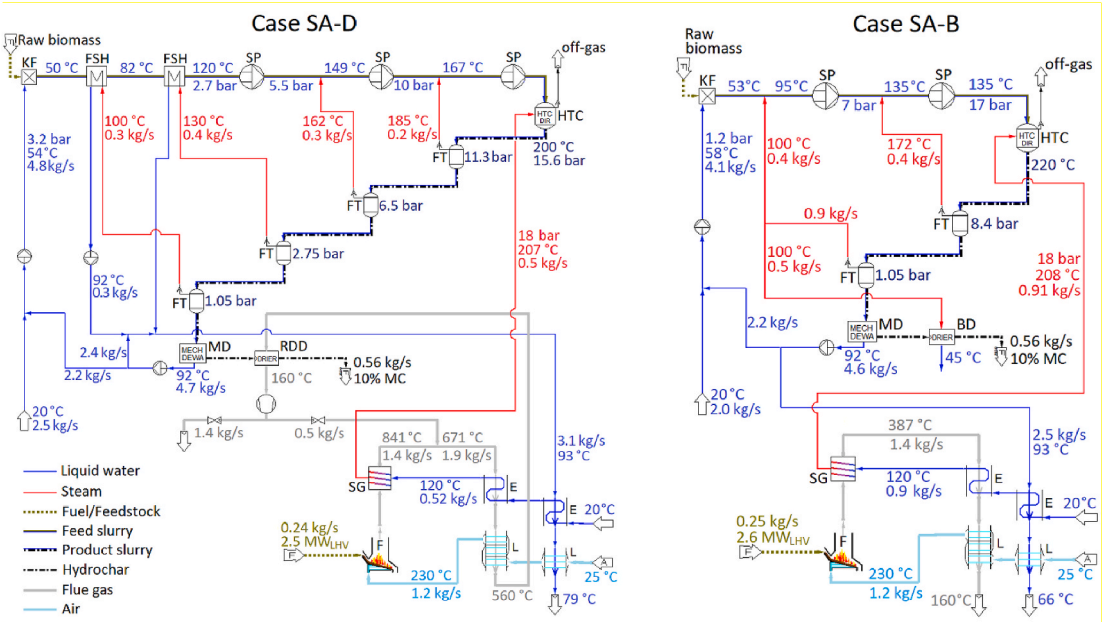


Fig. 8. Design model of the stand-alone HTC process schemes. KF - Kamyr feeder; FSH - feed slurry heater; SP - slurry pump; FT - flash tank; MD - mechanical dewatering; RDD - drum drier; BD - belt drier; SG - steam generator; E - economizer; L - air preheater; F - furnace.

Table 5
Energy inputs and outputs of stand-alone HTC plants SA-B and SA-D.

	Case SA-B				Case SA-D			
	EW	CW	CP	GB	EW	CW	CP	GB
Boiler fuel $\Phi_{b,boiler}$ [MW_{LHV}]	2.53	2.57	3.06	2.44	2.47	2.78	2.86	2.63
HTC feedstock $\Phi_{b,HTC}$ [MW_{LHV}]	13.31	13.84	15.22	14.61	13.31	13.84	15.22	14.61
Power consumption $P_{el,in}$ [MW_{el}]	0.39	0.39	0.40	0.39	0.45	0.45	0.46	0.46
Hydrochar output Φ_{HC} [MW_{LHV}]	11.51	10.51	10.87	10.43	11.51	10.51	10.87	10.43
Net energy efficiency η_{LHV} [%]	77.1	68.6	63.5	64.4	77.2	68.7	64.1	64.6

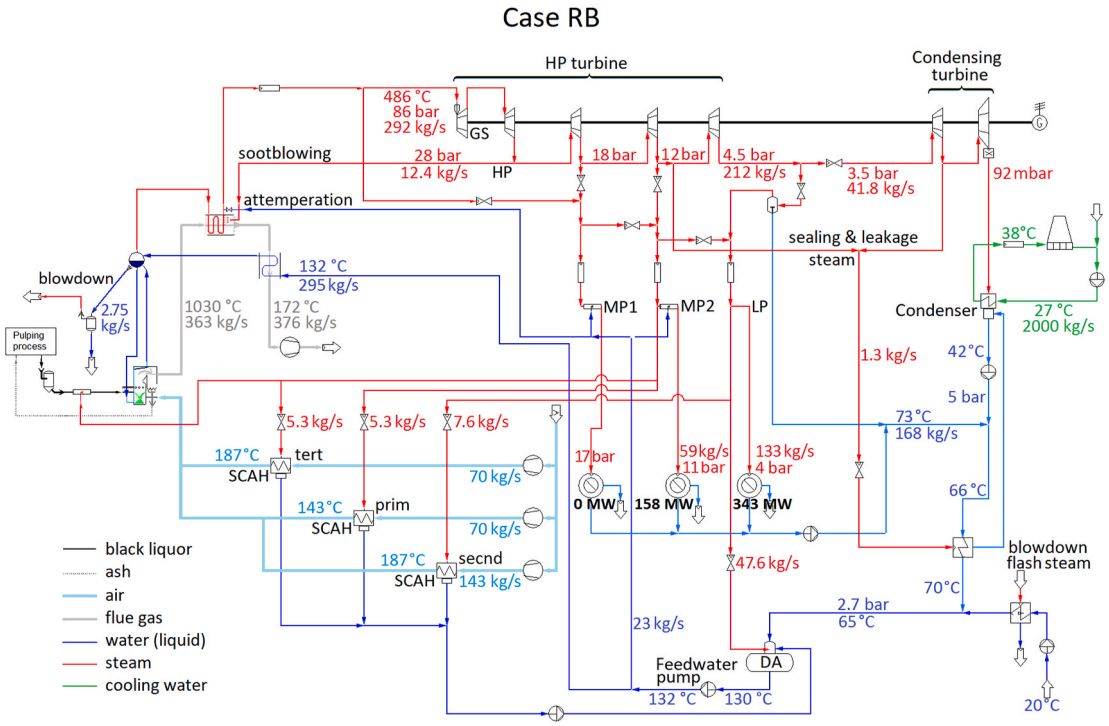


Fig. 9. Steam cycle of a large south american pulp mill recovery boiler, Case RB. BFB-bubbling fluidized bed furnace; SH-superheater; E-economizer; L-air preheater; SCAH - steam coil air heater; DA-deaerator; GS-governing stage.

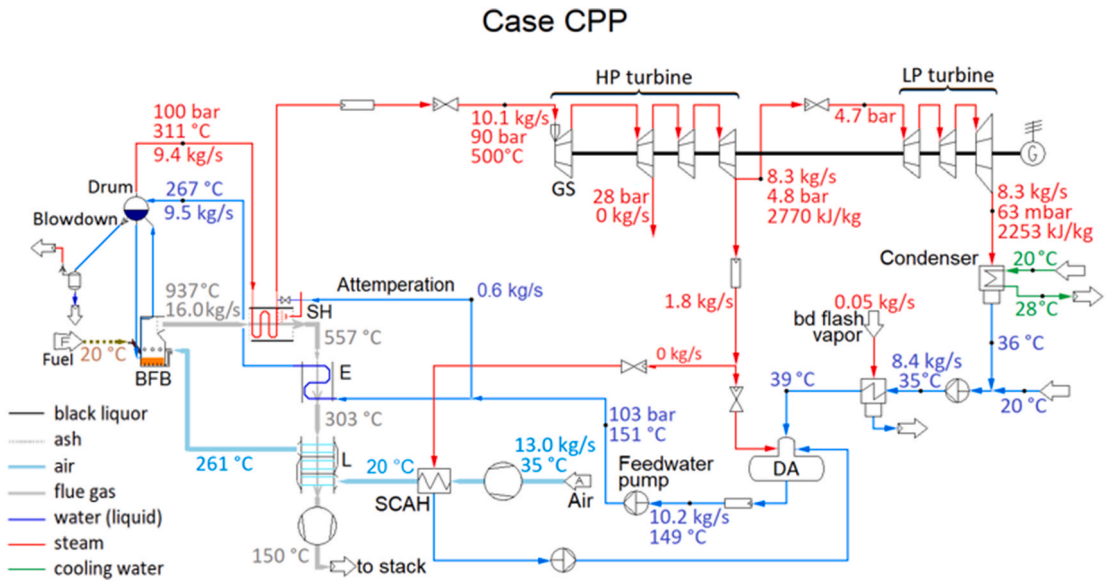


Fig. 10. Steam cycle of a small condensing power plant, Case CPP. BFB-bubbling fluidized bed furnace; SH-superheater; E-economizer; L-air preheater; SCAH - steam coil air heater; DA-deaerator; GS-governing stage.

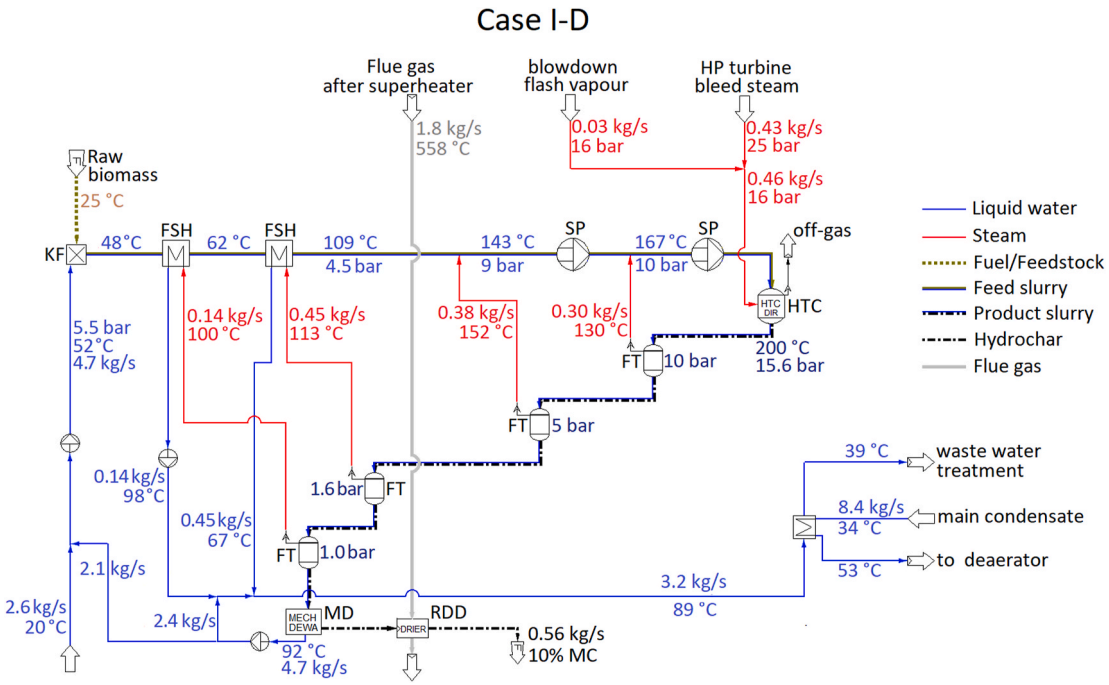


Fig. 11. Flowsheet model of the integrated HTC schemes case I-D. KF-Kamyr feeder; FSH–feed slurry heater; SP–slurry pump; FT-flash tank; MD-mechanical dewatering; RDD - rotary drum drier; BD – belt drier.

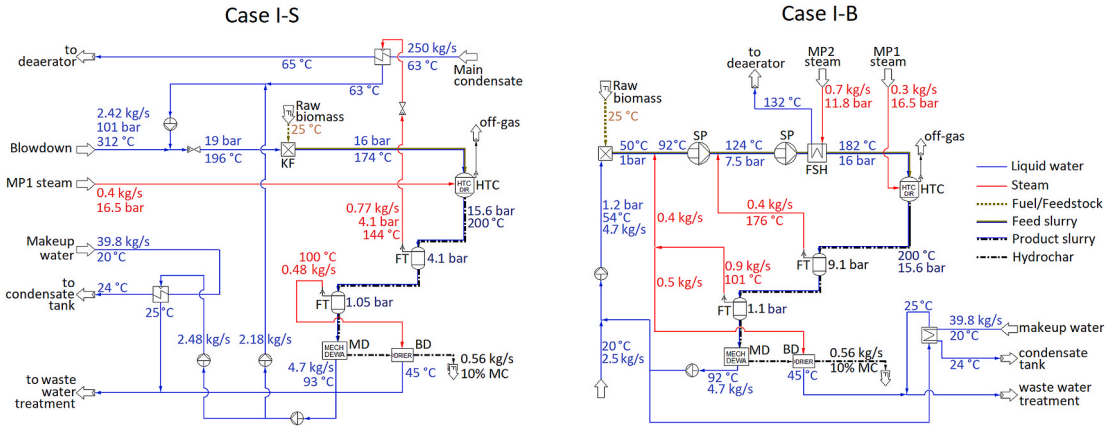


Fig. 12. Flowsheet models of the integrated HTC schemes cases I–S and I–B. KF-Kamyr feeder; FSH–feed slurry heater; SP–slurry pump; FT-flash tank; MD-mechanical dewatering; RDD - rotary drum drier; BD – belt drier.

consumers. Typically such plant produces considerable excess electricity that can be sold to the national grid. For the purposes of this work, the relative fractions of mill consumption and sold electricity are irrelevant, and only the net power available after the boiler and steam plant own auxiliary consumptions is considered.

The CPP plant is simpler and without process steam production; only two extractions are thus available. The LP turbine valve is maintained open, allowing LP bleed steam pressure to vary. The pressures are solved according to the ellipse law as described in Ref. [74].

In addition to steam heating, feedwater and blowdown are considered potential sources of hot water, and flue gas from CPP boiler backpass, after superheater, is used as heat source for the drum dryer. Recovery boiler flue gas, however, is fouling and corrosive due to high ash and SO_2 contents, and thus rejected as an option for dryer heating. The main condensate stream and makeup water were considered potential heat sinks for the flash vapours from HTC product slurry depressurization.

With the above heat source and sink options available, three basic configurations of integrated HTC plant were designed. Integration with the RB is depicted, except when flue gas drum dryer is used, which is only considered with the CPP. Of the three integration schemes, I-D (Fig. 11) and I–B (Fig. 12) represent variants of the stand-alone schemes SA-D and SA-B, using gas-heated rotary drum and vapour/water heated belt hydrochar driers, respectively. The I–S (Fig. 12) represents a simpler, more integrated scheme using drum blowdown and feedwater for feed slurry water, and makeup water or main condensate as product slurry heat recovery heat sinks, without multi-stage feed slurry heating or slurry pumps. 8:1 solids-to-water ratio, 200 °C temperature, 2 t/h hydrochar production, and 1:1 HTC liquor disposal-to-recirculation ratio were evaluated for all process schemes and feedstocks.

The HTC process of the I-D integration scheme is similar to the equivalent stand-alone SA-D. Aside from different heating steam parameters resulting in slightly changed flows and flash tank pressures, the main difference is in the heat recovery: the large flow of the CPP main condensate permits more efficient cooling of the hot waste water. In the RB cycle with it's large makeup water flow, the heat recovery is even

Table 6
Results of integration simulations with the recovery boiler cogeneration plant.

Scheme		no HTC	RB-I-S				RB-I-B			
Feedstock			EW	CW	CP	GB	EW	CW	CP	GB
RB	Φ_f [MW_{LHV}]	1036.3	1036.3	1036.3	1036.3	1036.3	1036.3	1036.3	1036.3	1036.3
	P_{el} [MW]	168.44	167.79	167.78	167.71	167.77	167.69	167.68	167.62	167.67
	ΔP_{el} [MW]	–	0.659	0.665	0.734	0.675	0.756	0.760	0.823	0.774
HTC	Φ_f [MW_{LHV}]	–	13.3	13.8	15.2	14.6	13.3	13.8	15.2	14.6
	$P_{el,HTC}$ [MW]	–	0.334	0.334	0.337	0.335	0.364	0.365	0.374	0.367
	Φ_{HC} [MW_{LHV}]	–	11.5	10.5	10.9	10.4	11.5	10.5	10.9	10.4
	ESR [-]	–	1.004	1.004	1.004	1.004	1.003	1.003	1.004	1.003
	η_{LHV} [%]	62.3	62.5	62.4	62.3	62.3	62.5	62.4	62.3	62.3

Table 7
Results of integration simulations with condensing power plant.

Scheme		no HTC		CPP-I-S				CPP-I-B				CPP-I-D			
Feedstock		EW	GB	EW	CW	CP	GB	EW	CW	CP	GB	EW	CW	CP	GB
CPP	Φ_f [MW_{LHV}]	30.59	30.59	30.59	30.59	30.59	30.59	30.59	30.59	30.59	30.59	30.59	30.59	30.59	30.59
	P_{el} [MW]	9.686	9.740	8.942	8.935	8.833	8.965	9.002	8.999	8.938	9.047	8.960	8.954	8.874	8.989
	ΔP_{el} [MW]	–	–	0.744	0.751	0.853	0.775	0.684	0.687	0.748	0.693	0.726	0.732	0.812	0.751
HTC	Φ_f [MW_{LHV}]	–	–	13.3	13.8	15.2	14.6	13.3	13.8	15.2	14.6	13.3	13.8	15.2	14.6
	$P_{el,HTC}$ [MW]	–	–	0.338	0.334	0.342	0.335	0.364	0.365	0.374	0.367	0.364	0.365	0.374	0.367
	Φ_{hc} [MW_{LHV}]	–	–	11.5	10.5	10.9	10.4	11.5	10.5	10.9	10.4	11.5	10.5	10.9	10.4
	ESR [-]	–	–	1.098	1.098	1.111	1.107	1.103	1.103	1.118	1.113	1.100	1.100	1.114	1.109
	η_{LHV} [%]	31.7	31.8	46.6	43.8	43.0	42.9	46.7	43.9	43.2	43.1	46.6	43.8	43.1	43.0

more effective, as seen in the case of I–B depicted in the context of RB plant integration. As this case is based on using much of the depressurization vapour for belt drier heat supply, the feed slurry enters the reactor considerably colder, needing more steam for final heating. Indirect feed slurry preheating with lower pressure steam is used to minimize the use of higher-pressure steam in reactor heating to minimize power generation loss.

The simplest scheme, labelled I–S in Fig. 12, uses drum blowdown water augmented with recirculated HTC liquor. In the RB plant, drum water is sufficient, while in the CPP, where the HTC plant water need far exceeds the blowdown, feedwater is also used. The pressurized water is mixed with HTC feedstock in the Kamyr feeder. No slurry pumps or feed slurry preheating are used. The product is depressurized in two stages so that the final depressurization produces enough flash vapour to supply the belt dryer, and all vapour from the preceding one is used to heat the main condensate stream of the steam power cycle. As in scheme I–B, the disposed liquid is cooled with the makeup water (RB) or main condensate (CPP).

The results of the baseline integration schemes are shown in Tables 6 and 7. The energy saving ratio ESR exceeds 1 for all cases, indicating an efficiency benefit over stand-alone plants. In efficiency terms, the main advantage shared by all integrated process schemes is the availability of large, relatively low-temperature heat sinks facilitating more effective cooling of the hot HTC liquor than what is possible with stand-alone processes, reducing heat lost with the effluents from 0.5 to 1.0 MW (stand-alone plants) to 0.1–0.3 MW (integrated plants).

The ESR is much higher for the CPP integration schemes than for the pulp RB plant. Rather than showing superior performance, this is mainly due to the HTC plant being relatively much larger in CPP integration and thus affecting the performance indicators more. The loss of power generation, ΔP_{el}, is only slightly more for the RB-I-B at 0.76–0.82 MW as opposed to the 0.68–0.75 MW for the CPP-I-B. For the simplified process scheme I–S, the RB-I-S in fact superior at ΔP_{el} of 0.66–0.73 MW, versus 0.74–0.85 MW of the CPP-I-S. Between the CPP-I-D and CPP-I-B, the flue gas heated rotary drum dryer concept proved to perform poorly, with very little advantage in generator power being completely lost through higher power consumption.

Several factors influence the different behaviours of the RB and CPP integration schemes. A drawback of the RB is that as a CHP plant, it must supply LP steam to the mill at constant pressure, which requires throttling the condensing turbine. Additional steam consumers, such as the HTC plant, will thus reduce not only the steam flow available, but also the specific work of all steam flowing through the turbine. In the CPP, pressure levels between turbine stages can be allowed to vary, and throttling avoided. An advantage of the RB plant is the variety of steam pressure levels available. This often permits a closer match of extraction pressure to minimum pressure needed for HTC reactor heating, allowing further expansion before extraction. This, and the large makeup water flow for efficient HTC effluent cooling, alleviates but fails to fully compensate for the effect of condensing turbine throttling in case I–B.

With the I–S scheme, the RB has an additional advantage due to being much larger. Using high-pressure, high-temperature water as in the I–S scheme is a fundamentally less efficient way of providing heat and water to the feed slurry than heating with lower-temperature heat sources over smaller temperature differences and pressurizing the only as needed; however, the RB plant is large enough that the drum blowdown that is removed in any case is sufficient for HTC feed slurry. The CPP variant uses mostly feedwater, thus needing significantly more steam. The RB variant, for which the blowdown is sufficient, is slightly more efficient.

The results indicate that the relative scale of the HTC process and the power plant plays a role in the efficiency of the integrated schemes. The availability of suitable extraction pressure levels is also a factor, and related to HTC temperature. Consequently, the sensitivity of performance to the scale and process temperature was evaluated, by simulating the integrated schemes at 180 °C and 220 °C, and 4–6 t/h hydrochar production rates. The results, obtained for EW feedstock, are shown in Fig. 13. The specific loss of power generation per hydrochar production can be seen to generally increase with increasing production rate and temperature, as could be expected. The RB curves are at slightly below and also increase at a slightly lower rate than those of CPP, as the larger plant remains less affected by an HTC plant that even at 6 t/h production is comparatively small relative to the RB steam cycle; RB-I-B in particular maintains a constant specific loss of power generation with increasing scale. The CPP-I-S, on the other hand, shows a particularly dramatic loss of performance when 6 t/h production or 220 °C is reached, in both cases due to the same reason, requiring 90 bar live steam for reactor heating. At 220 °C, this is due to the required pressure

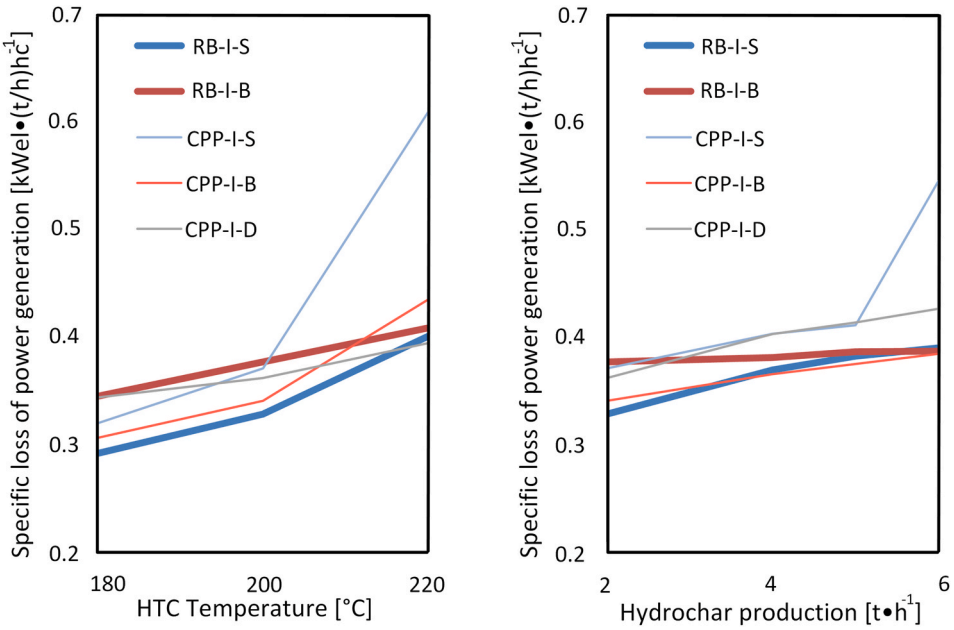


Fig. 13. Specific loss of power generation as a function of HTC temperature and hydrochar production.

level, while at 6 t/h the steam demand is high enough that at reduced flow, the HP bleed steam pressure falls below that required even for 200 °C HTC process. It becomes clear, that the performance of an integrated plant is heavily influenced by the combination of HTC process parameters, available steam pressure levels, and the scale of the process.

4. Conclusions and recommendations

The hydrothermal carbonization (HTC) properties of four types of globally important woody and non-woody residual biomasses were analyzed and compared in this study. The work analyzes the behavior of coffee residues in HTC treatment, which is a topic that has not previously been reported in the literature. The following findings and conclusions were drawn:

- HTC produces a hydrochar with improved energy carrier properties compared to the raw feedstock. As the HTC temperature increases, the higher heating value and fixed carbon increase, the volatile matter reduces, and the ashes become partially dissolved into the liquid phase; this all combines to improve the characteristics of the hydrochar as a solid biofuel.
- The type of biomass influences the characteristics of the product. Higher energy and solid yields were obtained from woody biomasses than from agricultural residues, which is likely attributable to the higher content of anhydrosugars and inorganics in agricultural residues, and the higher lignin content of woody biomasses.
- Integrating the hydrothermal carbonization process with a Rankine-cycle power plant can allow a simpler process design, and an efficiency benefit, provided that extraction steam is available at sufficient pressure levels. A pulp mill cogeneration plant can be a particularly advantageous candidate for HTC plant location for the combination of multiple steam pressure levels available, and large enough plant scale that operation is not excessively affected.
- Removing the need for the pre-treatment drying required by most thermochemical technologies is an advantage of HTC over other thermochemical conversion processes. Drying with a belt drier heated with flash vapour from product slurry depressurization showed good performance while permitting simpler process design than using a flue gas heated drier, even when the latter was assumed to be clearly more efficient in heat use.
- The aqueous phase characterization was considered insufficient to discuss possible HTC liquor application options. In contrast to the hydrochar, the liquid products require extraction and fractionation to identify the main compounds. However, the results obtained for the parameters analyzed (pH, TOC and NVR) were in a similar range to literature reports for the studied biomasses. Further analysis is recommended. The liquid is likely to contain a variety of both organic compounds and minerals, and these compounds may be potentially valuable for a variety of applications, such as fertilizer production or as adsorption agents.

In general, all the biomasses studied could be considered suitable feedstock for HTC treatment. Coffee wood and coffee parchment hydrochars exhibit suitable properties for use as adsorbent agents, activated carbon synthesis precursors or soil conditioners, while bamboo and eucalyptus appear suitable for use as solid fuels.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2021.106004.

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Publication IV

Mendoza, C.L.M., Sermyagina, E., Carneiro, A.C.O, Vakkilainen, E., & Cardoso, M.

Production and characterization of coffee-pine wood residue briquettes as an alternative fuel for local firing systems in Brazil

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Research paper

Production and characterization of coffee-pine wood residue briquettes as an alternative fuel for local firing systems in Brazil

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ABSTRACT

In this work, the production viability, physical, chemical and mechanical properties of briquettes produced from mixtures of coffee shrub residues and pinewood, were evaluated. The densification was carried out under constant operating conditions (temperature of 120 °C, pressure of 8.27 MPa) in a piston-press type laboratory-scale briquetting machine. Coffee shrub residues were mixed with pinewood in ratios of 25%, 50% and 75%. In addition, reference briquettes of pure pinewood and of each type of coffee shrub residue were produced. To characterize the raw material, ash content, volatile matter, fixed carbon together with the calorific value of produced samples, were measured. To characterize the suitability of the briquettes produced: apparent density, energy density, tensile strength, and equilibrium moisture content were determined. The highest values of energy density (19133–19899 MJ m^{-3}), tensile strength (415–569 kgf), apparent density (1107–1163 kg m^{-3}) and favorable values of equilibrium moisture content (9–11 wt %) were obtained from a mixing ratio of 75% of pinewood. The novel contribution of this research was to develop briquettes with appropriate physical and mechanical parameters from new raw materials that could serve as sustainable fuel sources for local firing systems.

1. Introduction

In brazil, utilization of biomass from agriculture, agroindustry and forestry are advantageous as their availability is not hindered by a requirement for arable land for food and feed production [1]. It is estimated that more than 200 million tons from agroindustry residues are not utilized energetically, mainly due to their poor energy characteristics: e.g. low density, low heating value and high moisture content [2]. In order for biomass to be considered for implementation as a viable fuel, it must be transformed into a readily useable and high energy resource.

Technologies that can transform firewood, agroforestry and industrial residues into a final product with high potential properties are attractive for the Brazilian energy matrix. One alternative to conventional energy sources is the utilization of pressed residues in the form of briquettes or pellets. Thus, the proper densification contributes to high volumetric concentration of energy, improving the handling and reducing the volume and resulting storage and transport costs [3].

1.1. Biomass briquetting in Brazil

Briquettes have long been used by residences, industries and commercial establishments, substituting for considerable quantities of firewood that would otherwise be extracted from the forest, thereby reducing negative environmental impacts. Briquettes in Brazil are used as substitutes for firewood in bakeries, food establishments, pizza restaurants, as well as factories with fuelwood-burning furnaces, like red brick factories [4,5]. Briquetting activities in Brazil are limited to those few regions with high wood residues concentrations, such as the states of Sao Paulo, Santa Catarina and Mato Grosso [5]. Nevertheless, the quest for sustainability and the so-called green economy has contributed to expanding consumption, and consequently, the production of briquettes. This expansion primarily depends on three factors: residue availability, adequate technologies and a growing market for briquettes [5].

Briquetting presents an efficient densification process that produces a uniform fuel, increases the energy density and reduces the transport and handling costs of the biomass residues [6,7]. The briquettes are

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generally produced in a piston (mechanical or hydraulic) press by applying load on a die with biomass particles. Additional binder and heat treatments can be applied depending on the properties of the feedstock [5]. To evaluate the final product, resistance to compression, energy density, compaction rate and equilibrium moisture, among others properties, should be measured [8].

Several studies have evaluated the possibility of utilizing different agricultural wastes and by-products for briquetting. A number of authors have investigated rice residue potential: analyzing the briquettes from rice straw and rice bran [10–12]; briquetting of rice and coffee husks for domestic cooking applications [13]; production of activated carbon briquettes from rice husks and eucalyptus wood [14]. Very positive results were obtained from blends of rice husks with corn cobs [15,16] and other residues of corn [17,18]. This rational use of biomass tends to promote the development of less economically favored regions, through the creation of jobs and reduction of external energy dependence, based on their local availability. The advantage of briquettes being manufactured from industrial and agroforestry residues is that their resulting price is lower compared to a large variety of fuels: e.g. charcoal [3,9].

1.2. Coffee residual biomass potential

The coffee production chain generates a large quantity of residues from both the berries (beans) themselves and the shrub. It is estimated that over ten million tons of residues yearly (solid and liquid) are produced [19]. In addition, there are residues from cultivation (pruning), which are difficult to estimate due to the differences in agronomic management practices. Brazil is the largest producer and exporter of coffee in the world. About 2.78 million tons of coffee beans were produced in 2016–2017. From this production, approximately 2.3 million tons of solid residues are generated each year [20]. Currently, these residues; coffee pulp, parchment, coffee wood and effluents, are not utilized efficiently and can result in severe environmental impacts due to inappropriate disposal [21]. The disposal of coffee wastes remains a challenge due to the presence of caffeine, free phenols and tannins (polyphenols), which are even toxic to many forms of life [22]. Currently, only a small fraction of available coffee pulp and parchment is utilized; as fertilizers, livestock feed, etc. The possibility of improving the properties and converting the waste streams into a competitive fuel in the energy market (production of solid fuels [briquettes, pellets and charcoal], biogas, liquid fuels) or extraction of the valuable chemicals from them may result in not only environmental but economic benefits as well. For this reason, it is necessary to develop the pretreatment technologies to improve the biomass feedstock characteristics and make it more suitable for energy or chemical applications.

As for coffee by-products themselves, there is still very little information about the energy potential and specific characteristics of the treatments for the residues from the coffee production chain. Only a few works present some results on the possible utilization pathways for these materials. One study [23] analyzed a process of anaerobic co-digestion of coffee husks and microalgal biomass after thermal hydrolysis pretreatment. In another work, high temperature air-steam gasification of coffee husks was studied experimentally [24]. Another group of researchers provided the results of their two-dimensional CFD simulation of the coffee husks' gasification in a fluidized bed reactor [25]. In addition to the residues typically associated with coffee production, the coffee chain provides another potentially abundant energy source, coffee wood [26]. Ethanol fermentation and gasification of coffee wood were evaluated by Ref. [27]. Additionally, it was proven that gasification represents a promising way to convert coffee wood into energy with high energy yields and resultingly low environmental impacts.

According to Ref. [26], the energy potential of coffee residues - coffee husk and coffee wood - in Brazil is highly significant with annual available energy of 11.3 PJ and 49.5 PJ, correspondingly. More information is needed to choose the most optimum treatment technology for these residues. Use of coffee residues along with traditional biomasses already utilized in the production of briquettes, such as pinewood, may considerably improve the potential of coffee residue utilization. Pine cultivation areas occupy a rather significant landmass in Brazil with $1.58{\cdot}10^6$ ha planted in 2015, so the availability of feedstock would not be a limiting factor [28]. Additionally, pinewood is rich in natural resins that increase its calorific value [29]. It also has a high lignin and silica content in its composition. Briquettes production would not require any additional binders since lignin acts as a natural binding material during the pressing process. The present work analyses the viability of a briquetting process for the mixture of residues from the coffee production chain and pinewood to produce a solid fuel of regular shape and high energy density and resistance, for use in local firing systems.

2. Materials and methods

2.1. Materials

Three biomass materials were studied: coffee wood, the coffee berry parchment layer (this covers the coffee beans and represents about 12 wt % of the berry on a dry basis) and pinewood. The coffee (*Coffea Arabica* L.) residues were provided by a rural farm in the municipality of Paula Cândido, Minas Gerais state, Brazil (20°49′50.0″ S 42°55′03.3″ W). The plant cultivation was established in 1986, and due to low productivity, stumping of new plant formation was required. The wood collected was 11 years old (from subsequent to the last stumping period). The coffee wood samples were separated into (I) stems, (II) primary branches and (III) secondary branches according to their diameter, 10 ± 2 cm, 2 ± 1 cm and 1 ± 0.5 cm, respectively. The three components were considered separately mainly due to coffee shrub aerial morphology, which is related to two types of burgeon: orthotropics (coffee beans grown on the stem) and plagiotropic (coffee beans grown on the branches). In addition, previous analysis had reveales chemical differences between coffee stem, primary and secondary branches [30]. The pinewood residues were collected at the commercial cultivation sites of the experimental units of the Federal University of Viçosa, Minas Gerais State, Brazil (20°45′14″ S 42°52′55″). The wood collected was 7 years old (from subsequent to the last stumping period).

The research from the experiments presented in this work was composed of two stages:

i) Classification, physical and chemical characterization of biomasses;
ii) Production of briquettes and their physical, mechanical and chemical characterization.

2.2. Classification and characterization of biomass feedstock

All biomasses were initially ground in a Weg® electric hammer mill at a fixed speed of 368.6 rad s^{-1}, which was coupled with a 2 mm opening sieve. For the samples intended for proximate analysis, the particle size was further reduced using a Thomas model 4 Wiley® knife mill with a fixed speed of 83.7 rad s^{-1} at 60 Hz. The biomasses were finally classified into superposed sieves with openings of 40 mesh (0.47 mm) and 60 mesh (0.31 mm) according to German Institute for Standardization (DIN) EN 14780, 2017 routine procedure [31].

The moisture content (MC) was determined according to DIN EN 14774–1, 2010 standard procedure [32], by keeping the sample in an oven at 105 ± 2 °C until the constant mass was obtained. The ash content (AC) was determined according to DIN EN 14775, 2012 standard [33], as the residue after complete combustion by the gradual heating of the sample in the muffle oven with the maximum temperature of 550 °C. The volatile matter (VM) was measured as mass loss after devolatilization of the samples in the oven at 900 °C according to DIN EN 15148, 2010 standard [34]. The fixed carbon (FC) was calculated as

the difference between 100 and the sum of all measured components.

The bulk density was measured with the standard procedure presented in DIN EN 15103, 2010 [35]. The higher heating value (HHV) was obtained using an adiabatic calorimetric pump IKA300 according to DIN EN 14918, 2014 procedure [36].

2.3. Production and characterization of briquettes

The recommended moisture range of the feedstock materials before the briquetting process varies from 8 wt % to 15 wt % on a wet basis (wb). In this work, the biomass samples were dried in an oven at 25 °C, until reaching 8 ± 0.5 wt % (wb) of moisture content. The initial moisture of the samples was 20 wt %, 17 ± 5 wt % and 12 wt % (wb) for pinewood, shrub coffee woody parts and parchment, respectively. The briquettes were produced in a piston-press type of the laboratory-scale briquetting machine from Lippel®, model LB 32. The briquetting conditions were defined experimentally from preliminary tests carried out in the laboratory. The materials were compressed for 4 min at a temperature of 120 °C and pressure of 8.27 MPa with a subsequent cooling for 8 min. Pinewood was mixed in ratios of 25%, 50% and 75% with stem, primary branch, secondary branch and a mixture of all woody parts of coffee shrub, and coffee berry parchment. The presence of stems, and primary & secondary branches were proportional in the mixture of all woody parts. At the end of the homogenization of the biomasses, 20 g of mixture was weighed and placed in a steel capsule (10 cm long and 3 cm in diameter) in the briquetting machine. 10 briquettes per treatment were manufactured.

After cooling, the briquettes were kept in an air-conditioned chamber at a temperature of 23 ± 1 °C and a relative humidity of 60 ± 10% until equilibrium moisture content was reached. Visual analysis was taken both before and after conditioning in the climatic chamber to verify the visual appearance of the briquettes.

The equilibrium moisture content (EMC) was determined by mass difference. Equilibrium was considered as having been reached when the sample mass difference between two successive days was less than the balance accuracy. Apparent density was measured in triplicates by the mercury immersion method according to Ref. [37]. The relation between the apparent density of the briquette, and the bulk density of the ground biomass calculated compact rate. The net heating value (NHV), was determined using equation (1), according to DIN EN 14918 [36]:

$$NHV = [(HHV - 54 \cdot H) \cdot (1 - EMC)] - (600 \cdot EMC) \quad (1)$$

Where,

HHV = High heating value ($MJ \cdot kg^{-1}$); H = Hydrogen content (wt %); EMC = Equilibrium moisture content (wt %)

The energy density was obtained by the multiplication of the apparent density and the NHV.

The tensile strength by diametrical compression for briquettes was measured in triplicates according to the guidelines of NBR 7222 standard with adaptations presented in Ref. [38]. The tests were carried out in a universal test machine, Contenco brand, UMC-300 model. The result of maximum load was obtained by the Pavitest software 2.7.0.7.

2.4. Experimental design

The tests were carried out for the briquettes' composition in a completely randomized factorial design (5 × 5), considering five mixing ratios of residues (0%, 25%, 50%, 75% and 100%), five mixing biomasses (stem, primary branch, secondary branch, mixture of wood parts and parchment) and ten replicates, yielding a total of 250 sampling units.

The influence of the pine share in the blend with coffee residues was evaluated and subjected to analysis of variance (ANOVA). The combinations with the significant differences were compared with Tukey's test at a 5% probability level. Statistical analyzes were performed with the help of the Statistica 8.0 program [39].

For the results on equilibrium moisture content (wt%), maximum load (kgf), apparent density ($kg\,m^{-3}$) and energy density ($MJ\,m^{-3}$) properties, models were defined with the aid of R program for explaining the data distribution. The comparison between the treatments was done by the identity model test [40], according to equation (2)

$$Property = \beta_0 \cdot Pinewood^2 \pm \beta_1 \cdot Pinewood \pm \beta_2 \quad (2)$$

Where,

$Pinewood$ = Pinewood ratio in the mixture (0, 25, 50, 75, 100%)
β_0, β_1, β_2 = Regression coefficients

3. Results and discussion

3.1. Characterization of the feedstock

The biomass particle size distribution is one of the most important initial characteristics of the raw material with respect to any densification process. Table 1 shows the particles size distribution of the biomasses used for the briquettes production in this study.

The particle size distribution of the coffee wood residues was relatively similar. The samples had a high percentage (45.1–51.2%) of particles with diameters of less than 0.31 mm, which passed through both 40 and 60 mesh sieves. Between 16.6% and 22.2% of particles were retained in the 60 mesh sieve (corresponding diameter range between 0.31 mm and 0.47 mm). The bigger particles with diameter between 0.47 mm and 2 mm had a share from 26.6 to 38.3%. The coffee parchment had the lowest presence of fines among the studied materials (21.9%) and the highest share of particles with diameters between 0.47 mm and 2 mm (42.8%). Most probably, the rounded shape of the parchment particles caused the higher resistance to the trituration process and resulted in higher share of larger fractions. Such behavior may be responsible for a decrease in the material homogeneity, strength, durability and resistance of resulting briquettes [41,42]. The pine sawdust contained the highest presence of fine particles (60.3%). According to Refs. [43,44], the quality and volumetric density of briquettes is inversely proportional to the particle size because smaller particles in the feedstock correspond to a larger surface area for bonding during densification. The increased compacting pressure result in the biomass particles being closely packed due to a reduction of void ratio and plastic deformation of the sawdust particles, therefore resulting in higher density of the briquettes [45]. However, very small particles can lead to jamming of the briquetting machine and affect the production capacity [46].

3.1.1. Chemical characterization

As the objective of this study was the production of solid biofuels, it is desirable for the feedstock materials and consequently the final products to have low ash content, high energy as well as fixed carbon

Table 1
Particle size distribution of the lignocellulosic residues used in the production of briquettes.

Biomass material	Designation	Particle size [mm]		
		Ø < 0.31	0.31 ≤ Ø < 0.47	0.47 ≤ Ø ≤ 2
Pine	Wood	60.3%	19.0%	20.7%
Coffee	Stem	51.2%	22.2%	26.6%
	Primary Branch	47.5%	21.4%	31.1%
	Secondary Branch	45.1%	16.6%	38.3%
	Parchment	21.9%	35.3%	42.8%

Table 2
Chemical characterization of the lignocellulosic residues.

Parameter	Unit	Biomasses					
		PW	CS	PB	SB	MIX	CCP
MC	wt%	12.23 a	10.96 a	8.70 c	9.28 b	9.65 b	11.09 a
VM[a]	wt%	82.46 a	79.76 ab	80.67 a	76.50 bc	79.57 ab	73.80 c
FC[a]	wt%	16.79 b	18.09 ab	17.05 ab	19.36 ab	14.62 d	20.09 ab
AC[a]	wt%	0.75 d	2.15 c	2.27 c	4.14 b	2.63 c	5.91 a
HHV	MJ/kg	20.71 a	20.12 b	19.75 bc	19.72 c	19.86 bc	18.92 d

Averages along the rows followed by the same letter among biomasses do not differ by Tukey test at 5% of significance.
[a] Dry basis; MC-moisture content; VM-volatile matter; FC-fixed carbon content; AC-ash content; HHV-higher heating value; PW-pinewood; CS-coffee stem; PB-primary branch; SB-secondary branch; MIX = CS + PB + SB; CCP-Coffee Cherry Parchment.

content and low volatile matter. The main combustion properties of the studied lignocellulosic residues are presented in Table 2.

The feedstock moisture plays an important role in the densification process, considering that water acts as both a binder and a lubricant. Material that is too dry makes the bonding between the particles difficult due to the elevated frictional forces in the compression channel. Excess moisture can cause explosions inside the briquette due to the formation of steam [47]. observed that the moisture in the biomass increases during densification through the van der Waals forces by increasing the contact area between the particles. They also concluded that low moisture content (5–10 wt%) results in more stable, resistant and denser briquettes compared to higher moisture biomasses (15 wt %). Several studies recommended that the feedstock for the briquettes' production should contain a moisture content between 8 and 15 wt % (wb) [48–51] suggested low feed moisture content in the range of 8–12 wt % (wb) to produce strong briquettes that are free of cracks. Levels above or below this would lead to densified material of lower quality [52]. studied the compaction of platanus tree chips at different initial moistures (5.7–23.9 wt%) and found that for the briquetting production it is better to use lower moisture content material (up to about 12 wt%) because at higher moisture levels a sharp decrease in rupture force and density occurs. The moisture content of the studied biomasses was in a relatively narrow range from 8.7 wt % to 12.23 wt %, characteristic of the particulate material that influenced in the absence of surface cracks and significant axial expansions in the briquettes.

Volatile matter is the portion of the fuel that is released in form of gases when the material is heated. The more volatile a fuel is, the faster it burns, and the more reactive and more easily it is ignited [53]. In many domestic uses, a slow rate of burning is preferred. The typical volatile matter range for general biomass is 65–85 wt % and 76–86 wt % for woody biomass [54]. In the current work, the woody residues had a higher share of the volatile matter than the parchment. Pine sawdust followed by the primary branches had the highest VM values of 82.5 wt % and 80.7 wt %, respectively. Many other materials used in the production of briquettes, such as rice husk (65.5 wt %), sugarcane bagasse (73.8 wt %) [55], shea meal (66.3 wt %) [56], paper sludge (48.7 wt %) and coal (33.1 wt %) [57], reveal values of volatile matter lower than the values found for the raw material used in this study, and due to this, the coffee residues and pine wood are attractive for burning processes.

The fixed carbon content is inversely proportional to the volatile matter. The FC for parchment was 20.1 wt % and for wood residues 14.6 wt % - 19.4 wt%. According to Ref. [58], high FC indicates that the materials tend to burn more slowly, requiring longer residence time compared to fuels with a low FC. This suggests that briquettes containing parchment in their composition may demonstrate a slower burning rate when compared to briquettes manufactured with coffee wood residues.

The ash content implies the presence of inorganic components, mostly in the form of oxides [59]. Due to this, the results indicated the highest inorganic composition of the parchment (5.9 wt % db) followed by the secondary coffee wood branches (4.1 wt % db). Other studied materials had a relatively low ash content with the minimum value being for pinewood (0.8 w t%). According to Ref. [60], the ash content in the feedstock does not influence the densification process itself. However, an ash content greater than 10 wt % will cause wear on the equipment matrix.

The elevated heating values were relatively high for all biomasses: from 18.9 MJ kg^{-1} for parchment to 20.7 MJ kg^{-1} for pinewood. In comparison with other feedstocks generally used in the briquettes' manufacturing, such as rice husk (16.4 MJ kg^{-1}) [61], wheat straw (16.4 MJ kg^{-1}), timothy grass (16.3 MJ kg^{-1}) [62], sugarcane bagasse (17.3 MJ kg^{-1}) [55] and eucalyptus wood (19.0 MJ kg^{-1}) [63], the studied samples present rather attractive materials for briquetting. Higher energy content increases the efficiency of the subsequent utilization of the briquettes and reduces the process costs.

3.1.2. Bulk density

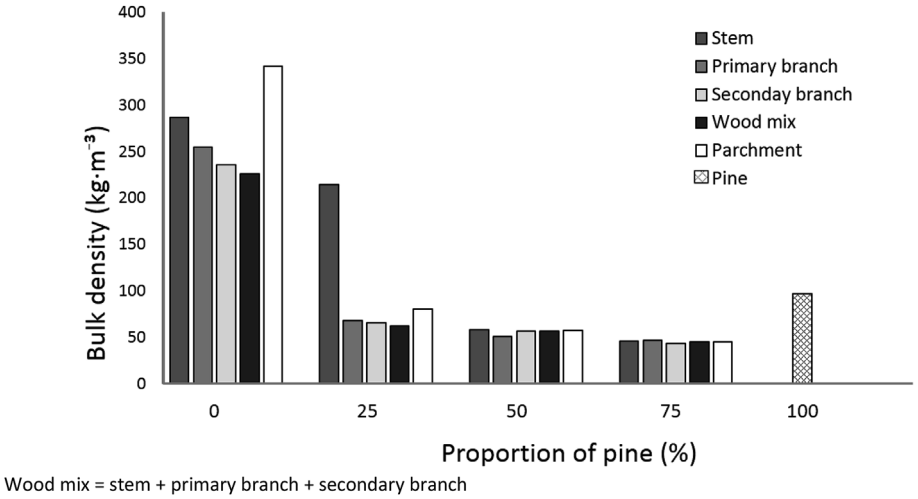
Bulk density is an essential factor influencing the economic viability of biomass materials utilization, since it affects the transport costs and the energy density of biomass. For this reason, the lignocellulosic residues with higher bulk density values are more desirable for the production of briquettes. The average values of the bulk density of the investigated biomasses are presented in Fig. 1.

The 0% proportion of pine feedstock had notably higher bulk densities than the other mixtures. The 100% parchment feedstock showed the highest bulk density (341.5 kg m^{-3}) due to high basic density of the material and flat-shaped particles. The addition of pinewood sawdust significantly decreases the density levels of all studied materials. The lowest density was obtained in the case of the mixtures with 75% of pine: 45 kg m^{-3} on average. The bulk density of the studied biomasses (raw material) used in the production of briquettes is analogous to unprocessed wood residues (250 kg m^{-3}) [64], ground switchgrass (181.6 kg m^{-3}) [41], wheat straw (97.4–121.3 kg m^{-3}), corn stover (131.4–157.7 kg m^{-3}) and barley straw (81–112.1 kg m^{-3}) [41]. The decrease in bulk density when mixing residual biomasses from the coffee production chain with pine results in such mixtures requiring compaction such as briquetting.

3.2. Characterization of the briquettes

The briquettes produced from coffee residues and pinewood in ratios of 25%, 50%, 75% as well as the briquettes from each individual biomass sample showed satisfactory visual appearance: good uniformity, absence of cracks, with smooth and shiny surfaces. The produced briquettes are presented in Fig. 2.

One way of evaluating the briquetting process is by measuring the compaction rate, which represents the ratio between the apparent density of the briquette (Fig. 3B) and the bulk density of the feedstock. Higher compaction rates indicate a higher reduction of the briquette's volume during the densification process, which likely results in a density gain. Table 3 shows the average values obtained for the compaction



Wood mix = stem + primary branch + secondary branch

Fig. 1. Bulk density of studied biomasses (raw material).

rate in relation to the proportion of pine.

It was observed that the pinewood briquettes have a compaction rate nearly three times higher than the ones produced from the residues without pine addition. This is due to the significant difference between the bulk densities of the materials: lower bulk density increases the likelihood of compressing the material. As a result, the compaction rate of the mixtures with 75% of pinewood and 25% of coffee residues showed the highest values in volume reduction. The residues with higher initial density would require higher energy to produce the briquette since these materials present greater resistance to densification. In this sense, the addition of pinewood in briquettes, mostly at 50% and 75% can contribute to increasing the density without the need of spending additional energy to increase the pressure in the compaction stage.

3.2.1. *Physical – chemical characterization*

The average values of equilibrium moisture content, compressive strength, apparent density and energy density of briquettes are illustrated in Fig. 3.

Equilibrium moisture content is a notably important parameter for



CS-coffee stem; PB-primary branch; SB-secondary branch; MIX=CS+PB+SB; CCP-Coffee Cherry Parchment.

Fig. 2. Briquettes produced from coffee residues mixed with pinewood in different ratios.

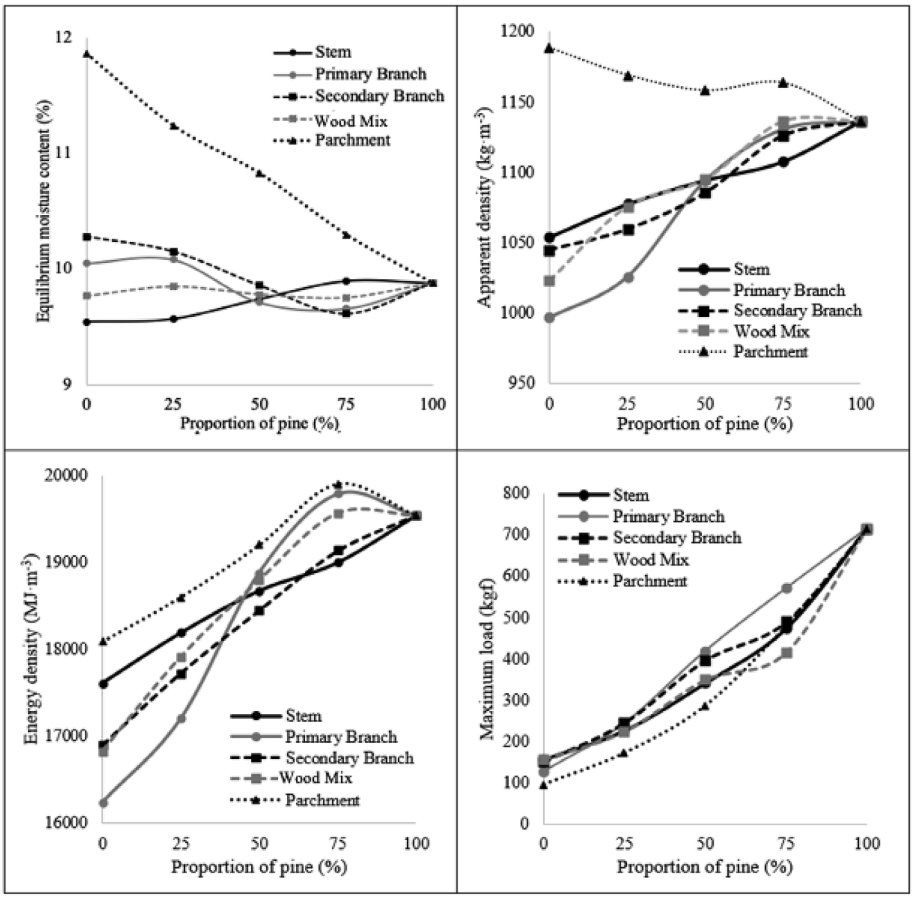


Fig. 3. Properties of briquettes produced with the studied biomasses: equilibrium moisture content (upper-left), apparent density (upper-right), energy density (lower-left) and compressive strength (lower-right).

Table 3
Compaction rate of the briquettes produced with studied biomasses.

PW (%)	Biomasses				
	CS	PB	SB	MIX	CCP
0	3.67	3.92	4.43	4.53	3.48
25	5.02	15.16	16.25	17.23	14.58
50	18.81	21.64	19.30	19.52	20.13
75	24.12	24.29	25.86	25.41	25.88
100	11.78	11.78	11.78	11.78	11.78

PW-pinewood; CS-coffee stem; PB-primary branch; SB-secondary branch; MIX = CS + PB + SB; CCP-Coffee Cherry Parchment.

evaluating the possible changes in physical conditions of biomass briquettes during storage and transportation. The briquettes with low equilibrium moisture content (5–12 wt%) are better suited for transportation not only with respect to the lower concentrations of water carried in the biomass material but also due to increased physical and mechanical resistances of such low-moisture briquettes [46,65]. Additionally, a higher EMC level complicates the ignition of the fuel and leads to lower energy density values due to the inverse relationship between the EMC and the net heating value [46]. The equilibrium moisture content for the majority of the produced briquettes was observed to be in a relatively narrow range between 9 and 10.3 wt % with little effect from the pine addition (Fig. 3A). Consequently, these briquettes can be handled more efficiently during storage and transportation. As for the parchment, the increase of pine proportion decreased the briquettes EMC: from 11.9 wt % in the case of purely parchment briquettes to 10.3 wt % in the case of 75% of pine in the blend.

The measurement of apparent density after densification is essential for the evaluation of the biomass potential: lower density raises the costs of transportation and decreases the energy density. The apparent density of the briquettes increases with the share of pine in the mixture for stem, primary branch, secondary branch and wood mix (Fig. 3b) from 996.7 kg m^{-3} - 1054 kg m^{-3} to 1136.1 kg m^{-3} which represents a nearly 10% increase in density. This is due to higher compaction rate of the briquettes with greater percentage of fines. In case of the briquettes with parchment in their composition, the addition of pine only slightly decreases the apparent density of the samples, likely due to the high basic density of the parchment. The values observed in this work are similar to briquettes produced with eucalypt sawdust (1060 kg m^{-3}), corn residues (1159 kg m^{-3}) and coffee husk (1248 kg m^{-3}) [38].

The energy density indicates the energy content per volume unit and affects the efficiency of subsequent use of the briquettes [66]. The energy density of all produced briquettes increased with the addition of pinewood to the coffee residuals due to the higher heating value of the pine (Fig. 3c). The energy density of briquettes with parchment in their composition presented the highest average values for high bulk density, with increments of up to 700 MJ m^{-3} corresponding to every 25% addition of pinewood. However, the residue that showed the greatest variation in this property was that of primary branches with an increase of 3551 MJ m^{-3} from the absence of pine to 75% of pine in the mixture; the increments were of approximately 1184 MJ m^{-3} for every 25% of pinewood addition.

The tensile strength of diametric compression and maximum force is related to the ability of briquettes to withstand mechanical impacts during storage and transport. The briquettes with low resistance tend to disintegrate more quickly, which can cause problems during their combustion [42]. concluded that the size of particles, chemical

Table 4
Covariance analysis for the properties measured in the briquettes.

VS	DF	SQ	MQ	F	P (> F)
Equilibrium moisture content					
IM	4	4	1	8.15	0.62E-04
Residual	18	2.21	0.12		
Energy density					
IM	4	1771328	442832	3.04	0.043
Residual	18	259174	143984		
Apparent density					
IM	4	23151	5788	6.60	1.88E-03
Residual	18	15784	877		
Maximum load					
IM	4	12001	3000	2.7035	0.06
Residual	18	19976	1110		

VS-Variation sources; DF-*Degrees* of freedom; SQ-Sum square; MQ-Mean square; F-F calculated statistics; p-statistical probability F tabulated; IM-Identity model.

Table 5
Adjusted equation for the physical – chemical properties of briquettes.

Property	Treatment	Adjusted Equation			R^2
		β_0	β_1	β_2	
Equilibrium moisture	CS-MIX model	2E-06	2.1E-03	9.65	0.99
	PB-SB model	9E-05	−1.3E-02	10.23	0.76
	CCP model	3E-05	−2.3E-02	11.84	0.99
Energy density	General model[a]	−1.9E-01	46.60	16835	0.99
	CCP model	- 1.8E-01	35.34	17995	0.93
Apparent density	General model[a]	−4.3E-03	1.5	1027	0.99
	CCP model	1E-05	- 4.4E-01	1185	0.85
Maximum load	General model	3.2E-02	2.5	139	0.99

[a] Adjusted equation for briquettes without presence of CCP in its composition; CS - Coffee Stem; PB - Primary Branch; SB - Secondary Branch; Mix = CS + PB + SB; CCP - Coffee Cherry Parchment. R^2 – Coefficient of determination. β_0, β_1, β_2 – Regression coefficients.

composition, lignin content, compaction rate and equilibrium moisture content influence the tensile strength of the briquettes. In this study, it was observed that the resistance to diametric compression and maximum force increased in conjunction with the increase of the pine briquette content for all studied materials (Fig. 3D). The highest values were found for the briquettes produced from pine alone. This result is probably due to the low volumetric expansion after the densification of the mixtures because of the presence of fines, low EMC and high lignin content of the pine.

3.3. Identity model test for the physical-chemical properties measured in the briquettes

The obtained results confirm the similarity of the biomasses' behavior in the majority of the cases and likely explain the dependencies of the studied properties with the general equations. However, this is only possible for the maximum resistance property due to the covariance analysis (Table 4), which reveals a higher p-value than the level of significance $\alpha = 0.05$, contrary to EMC, energy density and apparent density properties.

As a result, the data were regrouped without the presence of the coffee berry parchment for the energy density and apparent density properties. The analysis of covariance showed that the equations present similar estimates in relation to the behavior of the briquettes with the pinewood addition. Model identity tests for the equilibrium moisture property indicated that it is not advisable to apply a single equation adjusted for the data set. Meanwhile, for stem – wood and primary branch - secondary branch mixtures, a single adjusted equation can be used to represent the data set of these biomasses.

Table 5 shows the parameters of the models for the measured properties as a function of the proportion of pine wood (Eq. (2)), according to the adjustments made by the model identity test. These results have a significant importance, once the adjusted models could be used to estimate the value of the physical–chemical properties of briquettes by varying the proportion of pinewood in the mixture.

4. Conclusion

In this study, it was demonstrated that the residues from the coffee production chain such as stems, primary branches and secondary branches of coffee shrubs and the parchment of coffee berries can be used to produce briquettes for combustion processes when mixed with pine wood, creating a new source for the utilization of undervalued residual biomasses. The mechanical strength obtained from coffee residues alone was quite low. However, when blended with pine wood, strong and high-quality briquettes can be produced. The resulting briquettes present a regular format and homogeneous constitution, characteristics that are indicative of better quality and durable products after handling, transportation and storage. additionally, the high energy density of the briquettes produced presents an attractive advantage for increasing the Brazilian energy production matrix using densified material.

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Publication V

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NEGATIVE CARBON DIOXIDE EMISSIONS FROM EUCALYPTUS PULP MILL INCLUDING BIOSLUDGE HTC TREATMENT

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ABSTRACT

Kraft pulp mills produce CO_2 for the most part in combustion processes. The recovery boiler, the biomass boiler, and the lime kiln are the largest sources of CO_2. As these CO_2 emissions originate almost entirely from burning biomass (bioenergy), the pulp mill can be considered already nearly carbon neutral as long as the wood feedstock is obtained from sustainable sources. By applying to this bioenergy use carbon capture and storage (BECCS) or use (BECCU) to permanently remove some of the carbon from circulation, pulp mills can therefore provide some of the negative emissions needed for climate change mitigation. An alternative way of creating negative emissions in a pulp mill is converting process residues that are currently disposed of by landfilling or incineration to material that can serve as a stable permanent carbon storage; ideally the residues could also be converted in additional products resulting in additional revenue for the plant. In BECCS technology, the CO_2 is captured, transported, and permanently stored in an appropriate geological formation, resulting in negative net carbon dioxide emissions. In BECCU, the captured biogenic CO_2 can be used as a raw material for bioproducts. Potential processes for CO_2 utilization in pulp mill include tall oil manufacturing, lignin extraction, and production of precipitated calcium carbonate (PCC), depending on mill specificities and local conditions. CO_2 can be captured from a stream of flue gases by absorption in an aqueous solvent. Chemical absorption by alkanolamines (amine scrubbing) appears to offer an attractive alternative for CO_2 separation from combustion flue gases at pulp mill. In addition to BECCS/BECCU technologies, carbon can also be removed from circulation permanently by applying conversion technologies other than combustion on some of the biomass streams containing carbon. In case of lignin extraction, by removing lignin from the black liquor before combustion in the recovery boiler, some of the CO_2 emission can also be avoided altogether. Hydrothermal carbonization of the bio-sludge generated during primary (chemical) and secondary (biological) wastewater treatment processes is another possibility of removing carbon in a pulp mill. The produced hydrochar is an inert substance and resistant to biological degradation. It has potential use for example as adsorbents for environmental applications. When mixed in soil, it can improve its carbon organic matter, reduce N_2O emissions, as well as forming a permanent carbon storage. In this paper the potential of the before mentioned technologies – post-combustion amine scrubbing for BECCU, and hydrothermal carbonization of bio-sludge – are evaluated.

Keywords: *Bioenergy with carbon capture and storage BECCS; Bioenergy with carbon capture and utilization BECCU; Kraft pulp mill; Climate change mitigation; Negative CO_2; Hydrothermal carbonization.*

1. INTRODUCTION

Anthropocene refers to the period when human activities have influenced the geological and environmental aspects at global levels [1]. The term was adopted by the Intergovernmental Panel on Climate Change (IPCC), emphasizing the negative human impact to the ecosystems [2]. One of the main concerns is climate change, with a global temperature increase of 0.85 ºC reported so far over the period of 1880 to 2012. According to IPCC, the atmospheric CO_2 concentration has increased by over 100 ppm (36%) in the last 250 years, from 280 ppm in the pre-industrial era to a current figure of 410 ppm [2]. Therefore, several countries signed in 2015 the Paris Agreement to reduce anthropogenic emissions in order to mitigate the climate change. Maintaining the global warming well below 2 ºC and pursuing efforts to limit the temperature increase to 1.5 °C above pre-industrial levels are the main objectives of the agreement [3].

Pulp and paper industry is one of the largest energy users in the world at an estimated 5.9 EJ, while producing approximately 195 $MtCO_2$/year [4]. Over 80% of CO_2 emissions come from combustion of residual biomass [5]. The pulp industry has established several measures to reduce its CO_2 emissions. These include replacing fossil fuels with alternative fuels, increasing

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the energy efficiency of the process by e.g. waste heat recovery, among others. Although effective, these measures alone are not sufficient to achieve the established CO_2 emission reduction rates targets. Bioenergy with carbon capture and storage (BECCS) or utilization (BECCU) technologies have been identified as some of the most promising and potentially cost-effective negative emission technologies (NETs) to mitigate carbon emissions. After being captured, the concentrated CO_2 can be pressurized and stored in underground deposits, or used for the production of fuels, chemicals, tall oil manufacturing, lignin extraction, or production of precipitated calcium carbonate (PCC).

In the chemical pulp industry, sulphate (kraft) pulping is the most common method, accounting for up to 80% of the global pulp production. Like in many industries, significant amounts of byproducts and waste are also produced. Some of these can be used profitably, i.e. transport fuel from tall oil or energy production from bark and sawdust. However, all end products cannot be reused or disposed easily. The biosludge produced in the pulp industry is an example of a challenging side stream that is neither valuable raw material nor easy to dispose of. Biosludge has accounted for over 50% of overall wastewater treatment costs in some mills. It is typically disposed in landfills, composting, or burning in the recovery or biomass boiler, all of which can be in some ways problematic. Environmental legislation also sets requirements for industries to achieve environmental targets, prompting a search for alternative solutions to comply with laws while maintaining or improving the competitiveness of the products in the market. One way of reaching negative CO_2 emissions in a pulp mill and reduce the cost in the residual management, is treating the residues that are currently disposed of by landfilling or incineration to material that can serve as a stable permanent carbon storage. In this paper the potential of the technologies, BECCS/BECCU and hydrothermal carbonization (HTC) as a possible route for sludge generated during primary (chemical) and secondary (biological) wastewater treatment processes, are evaluated.

1.2. CO_2 emission sources in pulp mills

Kuparinen *et al*. (2019) identified two main CO_2 sources in a pulp mill: the recovery boiler and the lime kiln [5]. When a biomass boiler is present, it is also a significant source of CO_2. Of these, the lime kiln is the main emission source originating from fossil fuels. In the lime kiln, calcination process takes place: calcium carbonate ($CaCO_3$) is heated to approximately 900 °C generating CO_2 and lime (CaO) [6]. The CO_2 generated in the lime kiln thus originates both from the calcination process and fossil fuel combustion.

The role of the recovery boiler is recovering the pulping chemicals in the black liquor while simultaneously burning the organic wood residues remaining in the liquor after pulping. Typically, fossil fuels used during startup and shutdown produce 10–20 kg CO_2/ADt [5]. Additionally, process upsets or equipment failures occasionally require burning fossil oil or gas. Some mills have a biomass boiler for burning organic residues generated in the wood processing stage such as bark or fines, which also use fossil fuels during startup and shutdown [5].

2. METHODS

In the IPCC (2018) report, future scenarios are created in order to evaluate the greenhouse gas (GHG) emissions mitigation and, among the technologies presented, BECCS/CCU is one of the most attractive [7]. According to the Global CCS Institute (2019), there are currently 19 large-scale carbon capture facilities in operation, 4 in construction and 28 in various stages of development around the globe. The total capture capacity of all large-scale carbon capture facilities at all stages of development has risen by 51% since 2017, and these technologies have recently received increased attention [8].

CO_2 capture technologies for fossil and biomass fuels are often divided in four basic categories: capture from industrial process streams, pre-combustion, oxy-combustion, and post-combustion [9]. In addition to these, chemical looping combustion is a promising technology with potentially very low parasitic losses [10]. Few detailed studies have been applied to pulp mills, however.

In pre-combustion carbon capture, oxygen is used in the gasification of fuels to produce syngas consisting mainly of H_2 and CO. The syngas is sent to a reactor where the gas-water displacement

reaction takes place, forming CO_2 and H_2. After the product is desulfurized and passed through carbon dioxide separator unit, CO_2 can be captured and H_2 used in an energy generation processes [11]. The CO_2 concentration at the inlet of the separator is generally in the range of 15 to 60% dry basis. The total pressure is typically 2 - 7 MPa [9]. Several techniques can be used to separate the CO_2, including cryogenic separation, absorption, adsorption and membrane separation. In the pulp industry, pre-combustion systems based on black liquor gasification have been studied, but not yet demonstrated in operating plants.

In oxy-combustion the combustion air is replaced by a mixture of oxygen (O_2) and recirculated exhaust gas (mainly CO_2 and H_2O), in which combustion temperature is controlled by the flue gas recirculation rate. The exclusion of nitrogen in the process creates a stream of highly concentrated CO_2 (> 80%), allowing more efficient capture. The oxy-combustion can be applied to recovery boiler, bark boiler, or lime kiln, but modifications to the flue gas passages may be required. Implications on heat transfer, reactions and additional cost and auxiliary power consumption due to extra demand of oxygen should be taken into account.

Post-combustion carbon capture is a commercially available technology based on CO_2 absorption by chemical solvents. The absorption processes make use of the reversible nature of the chemical reaction of an aqueous alkaline solvent, usually an amine-base. Various solvents have been tested, including monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) [11,12]. This solution is inserted in an absorption column which comes in contact with the CO_2 containing gas stream. In this column, at temperatures typically between 40 and 60 °C, CO_2 is bound by the solvent. The 'rich' solvent containing the chemically bound CO_2 is then pumped to the top of a stripper (or regeneration vessel), via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at higher temperatures of 100–140 °C. The 'lean' solvent, containing far less CO_2, is then pumped back to the absorber via the same heat exchanger, closing the loop [9]. Separation processes using solvents have some disadvantages due to the degradation of amine by SO_2, high corrosion rate of equipment and high consumption of energy during solvent regeneration. In practice, typical CO_2 recoveries are between 80% and 95%, but the exact recovery choice is an economic trade-off, since a higher recovery will lead to a taller absorption column, higher energy penalties and hence increased costs [9].

Several reports of post-combustion capture process based on absorption with alkanolamines have been found. Studies involving simulations [13–17], process optimization [18], reaction mechanisms [19], process implications [20] and pilot plant studies [21]. In addition to studies linking post-combustion capture process with pulp mills. Onarheim *et al*. evaluated the performance and the economic feasibility of retrofitting post-combustion CO_2 capture to a pulp mill and an integrated pulp and board mill [22,23]. Also, Kuparinen *et al*. investigated the use of CC technologies integrated to pulp mills [5]. In general, the results show the potential of the application of BECCS/CCU technology on the plants, but the cost depends heavily on policy frameworks, regulations and incentives for negative emissions.

2.1 HTC as alternative liquid effluents treatment for CO_2 emission reduction

Currently the average water consumption in kraft pulp mills is approximately 60 m^3/adt (air dried ton). This value tends to increase in older mills or those where there is little concern about the availability of fresh water, and tends to decrease down to 25 m^3/adt in the most modern plants or those with limitations in capturing and treating water. However, it is unanimous in the industry that there is a strong environmental pressure to reduce water consumption in the production of cellulose and paper. The effluents of pulp mills are rich in suspended solids, dissolved organics, color and, above all, organochlorine compounds (in factories that use chlorine lap and derivatives in bleaching), giving them a high polluting potential. Liquid effluents are generated at different points in the process, woodhandling, digester, fiber line, bleaching, drying, evaporation, recovery boiler, causticization and calcination. The treatment of those liquid effluents, typically called sludge, is composed of a sequence of four distinct stages with different objectives: removal of coarse solids, removal of suspension solids, removal of biodegradable organic matter and toxicity, and color removal. Incineration in a recovery boiler is a potential way to dispose the sludge. Recovery boilers are designed for challenging fuels and have advanced monitoring and control systems, which is an advantage for sludge combustion. Sludge incineration results in some additional costs due to the moisture content, however: moisture vaporization requires a significant

amount of energy, flue gas flow rate increases, boiler losses are increased, and ash transportation and treatment costs, and maintenance needs are increased. The exact costs depend on energy prices [24].

The potential to reduce the CO_2 emissions and manage residual streams of a modern eucalyptus (*Eucalyptus globulus*) kraft pulp mill located in South America has been analyzed via case studies. Simplified block diagram is showed in Figure 1.

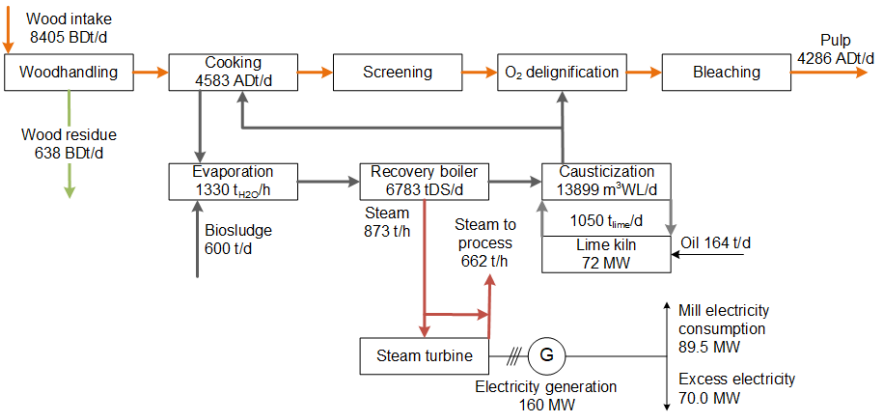


Figure 1: Flow diagram of the southern mill process in case 0.

The considered mill is a large, modern stand-alone kraft pulp mill producing bleached pulp from eucalyptus. Annual pulp production is 1.5 million ADt. The sole energy source is the recovery boiler; there is no biomass boiler. The recovery boiler is able to cover the energy demand of the mill, which is typical for a modern stand-alone mill. In the base case 0, CCS is assumed to be implemented via MEA scrubbing in the recovery boiler and lime kiln as in Kuparinen *et al.* [5].

Biosludge is dried mechanically and mixed with weak black liquor at the evaporator plant, and combusted in the recovery boiler. Biosludge production is 11.2 BDkg/ADt. Steam from the recovery boiler is used in the mill processes and for power generation in a turbogenerator. Low temperature heat flows are abundantly available to, for example, drying purposes. The electricity generation exceeds the mill power requirements, and thus the sale of excess electricity is possible. The main operational parameters are collected in Table 1. A detailed description of the mill can be found in [25].

Table 1. Operation parameters and main process flows of southern mill.

Operational parameters		Unit	Mill
Production	Operating hours	h/a	8400
	Pulp production	ADt/d	4286
	Paper production	t/d	-
Wood handling	Wood input	BDt/d	8405
	Wood type		eucalyptus
	Residue	BDt/d	638
	Wood moisture	-	45%
Recovery boiler	Dry solids to boiler	tDS/d	6783
	Net steam flow	t/h	873
Biomass boiler	Biomass fuel use	BDt/d	-
	Net steam flow	t/h	-
Biosludge	Production	BDkg/ADt	11.2
	Production	tDS/d	48
Energy	Steam use, pulp mill	t/h	662
	Steam use, paper mill	t/h	-
	Power generation	MW	160
	Power use, pulp mill	kWh/ADt	501
	Power use, paper mill	kWh/t	-

In this study, hydrothermal carbonization (HTC) of the sludge was considered instead of the traditional combustion. HTC is a mild thermochemical conversion process for biomass, taking place in a closed system at temperatures of 180–250°C and under autogenous pressure. Residence time is typically several hours. HTC offers a low emission and low waste toxicity technology for treating and upgrading diverse feedstocks. HTC treatment is suitable for high moisture content feedstock such as sludges, as no energy-intensive pre-drying is needed [26]. The process results in a hydrochar with heating value increased over that of raw sludge solids [27], while destroying any organic pollutants. The sterile end product is suitable not only for use as an energy carrier, but also as e.g. soil conditioner, absorbent or in carbon sequestration [28,29]. HTC process is also effective in removing alkali metals and other inorganic substances from the feedstock. Typically, the hydrochar holds 55-90% of the feedstock initial dry mass and 80- 95% of its energy content. As a solid fuel, the hydrochar properties are similar to lignite [30].

The effect of biosludge HTC treatment on the energy balance of the South America kraft pulp mill is studied. The implementation of HTC is compared with traditional biosludge disposal processes (case 0), where the biosludge is combusted in the recovery boiler after introducing the sludge into black liquor in the evaporator. Two different HTC plant configurations are considered. In both, the sludge is first mechanically dewatered to 8% moisture content prior to being fed to the HTC plant. Unlike in HTC processes using solid feedstocks, no water other than the flash vapour from product slurry is added to the feed slurry; even then, the final water-to-dry ratio in the HTC reactor becomes relatively high at approximately 16:1. The HTC reactor operates at conditions of 200°C temperature and 16 bar pressure, with a 3 hour slurry residence time. Mechanical dewatering to 35 % wet-basis dry solids content (case A) and thermal drying to 90 % dry solids (case B) was considered.

The calculations are made based on the literature review, the results of laboratory-scale HTC trials conducted at LUT, and HTC process modelling. IPSEpro software was used to model the HTC unit. The HTC plant model is based on a previous study that evaluated HTC treatment of forest biomass [31]. The pulp mill balances are calculated using an updated Millflow program that includes the detailed mass and energy balances of a kraft pulp mill. Millflow has been developed at LUT and presented in more detail in earlier studies [25]. During this study, an HTC unit based on the modelling was added to calculate its effect on the balances.

3. RESULTS AND DISSCUSION

In the southern reference mill, biosludge production is 11.2 BDkg/ADt, corresponding to 48 tds/d; in Case 0, the 600 t/d sludge flow is mixed with black liquor in the evaporation plant, and burnt in the recovery boiler. Table 2 shows the reference mill operations and the main process flows. The recovery boiler steam production of 873 t/h yields a total of 159.5 MW power generation, of which the mill consumption amounts to 89.5 MW, leaving a net excess of 70.0 MW to be sold. The mill also consumes 662 t/h extraction steam from the turbine.

Table 2. Energy production and consumption data of different sludge treatment cases southern mill.

		Unit	Case 0	Case A	Case B
Sludge	Total	t/d	600	600	600
	Dry solids	t/d	48	48	48
Hydrochar	Total	t/d	-	37	96
	Dry solids	t/d	-	34	34
	Dry solids		-	90%	35%
Steam	Live steam production	t/h	873	880	880
	Mill total consumption*	t/h	662	664	663
	HTC plant consumption	t/h	-	2.68	2.06
Electricity	Gross production	MW	159.5	161.1	161.2
	Mill total consumption*	MW	89.5	89.7	89.6
	HTC plant consumption	MW	-	0.28	0.14
	Net production	MW	70.0	71.4	71.7
	Net production change	MW	0	1.39	1.68

* includes HTC plant consumption

When the HTC process is integrated in the mill process, the sludge is no longer sent to the evaporator plant or the recovery boiler. Figure 2 shows the main process flows in case A and case B. HTC treatment of the sludge by Case A type plant produces low moisture char at a rate of 37 t/d. Not sending the sludge to the evaporator plant allows drying the black liquor to a significantly higher dry solids content. The net result is a clearly increased steam production of 880 t/h in the boiler, while electricity generation increases to 161.1 MW. After the 0.28 MW auxiliary power consumption of the HTC plant itself, the net electricity production of the mill increases by 1.39 MW.

The Case B HTC plant lacking the thermal drier produces a 96 t/d stream of 35 % dry solids content char. While the moisture content is clearly higher than that of the char from Case A HTC plant, the evaporator capacity is similarly freed for producing higher dry solids content firing liquor, and steam generation is the same as with the Case A at 880 t/h. Although steam consumption is slightly reduced, the gross power generation is almost identical at 161.1 MW, but the slightly lower power consumption of the Case B HTC plant results in very slightly greater net generation. Table 2 summarizes the main consumption and production of the southern pulp mill.

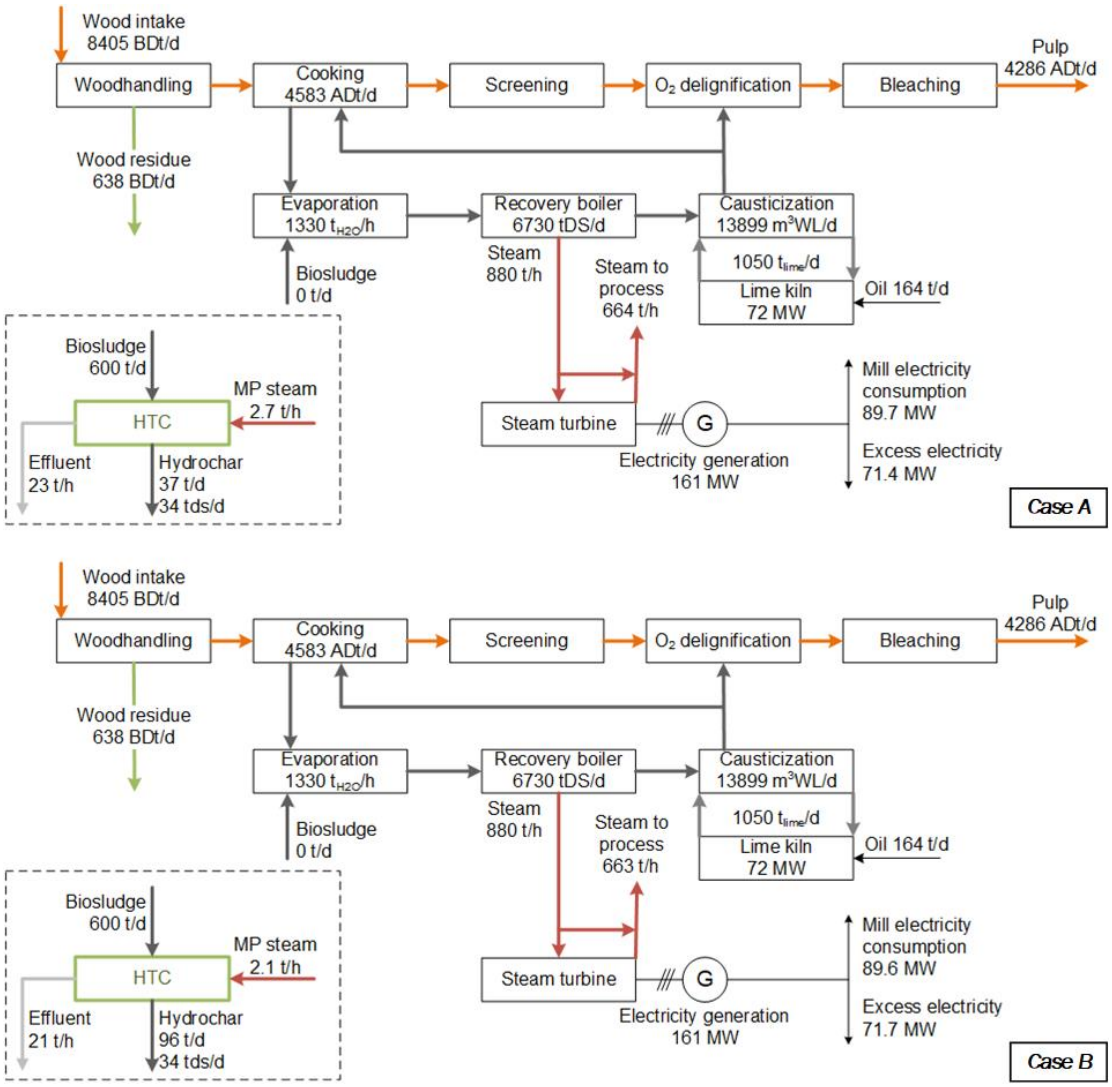


Figure 2: Flow diagram of the southern mill process in case A and case B.

Not feeding high-moisture biosludge to the evaporator plant results in a positive net change in electricity generation over the case 0 in both cases. If the intended end use of the hydrochar does not require thermal drying to a very low moisture content, Case B is clearly superior as it yields a 0.3 MW net power generation benefit in addition to having a simpler process without the dryer.

In general, the impact of the moisture of the biosludge on the operation of the recovery boiler is clear; this was demonstrated earlier in [32] by calculating the steam production of the boiler. When the share of biosludge is 1% total fuel mass flow rate, the steam production would change for moisture contents of 75%, 85%, and 95% are 0.16%, 0.31%, and 0.47%, respectively. The effect on the recovery boiler's operation may appear small, but in the long run the amount of lost steam is notable. The calculations also showed that the CO_2 emissions of the recovery boiler was 7524 t/d and 1099 t/d for the lime kiln [5]. The effect of carbon capture process in the energy balances, when MEA based post-combustion process is used to capture CO_2 from recovery boiler flue gas, was 2378 t/d for case 0. In the HTC integration, when biosludge is combusted in the recovery boiler it increases the boiler load. If the recovery boiler is the bottleneck of the pulping process, biosludge disposal using other methods enable pulp production increase, HTC treatment offers, however, also other utilization possibilities for biosludge in addition to combustion. HTC has previously been presented as a method to produce for example activated carbon, and HTC-treated biomass can be used as soil conditioner, unlike untreated biosludge. Biosludge typically includes e.g. nitrogen and phosphorous that are needed in fertilizers [33,34].

4. CONCLUSIONS

The growing concern with the environmental impacts generated in the pulp mills, has been inducing the development of new methods that help to understand, control and, or reduce these impacts. The analysis of the life cycle of products, processes and activities have proved to be an important tool in helping studies of this nature, considering the environmental impact throughout the product's life cycle: from the extraction of the raw materials used to the production, use and final disposal of the product. BECCS/CCU is an attractive technology for climate change mitigation and can be a source of reach negative CO_2 emissions in kraft pulp mills. In the case of a modern pulp mill, relatively small amount of carbon capture and storage could make a pulp mill a carbon sink instead of a carbon source. If HTC-treated biomass is used as soil conditioner, the carbon in the biosludge is then stored and not released in the atmosphere. For a pulp mill, this can offer a way to get closer to negative emissions.

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Bioenergy technology solutions in Brazil

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Bioenergy Technology Solutions in Brazil

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ABSTRACT Governments and society are concerned about the climate change that has been increasing over the years. It is known that the main cause is the emission of greenhouse gases, due to the burning of non-renewable fuels that are mainly used in the generation of energy both in companies and in the transport industry. At this moment a great opportunity opens up for the diffusion and the stimulus of the use of renewable energies, in order to make the energy matrix more sustainable. This article presents an overview of the Brazilian energy matrix, background, challenges and degree of sustainability in the production of energy, based on economic and environmental aspects of its production. Due to hydroelectricity and bioethanol, Brazil is still in a privileged position compared to many other countries in the South American. The country is self-sufficient in oil and complements its generation of energy with "modern" resources, i.e. wind, solar and biomass plants. However, future will largely depend on how the government will be able to shape its renewable energy policies as the country faces challenges regarding regulations for innovation and foreign investment.
Keywords: Energy matrix; renewable source; megatrends.

Soluções Tecnológicas em Bioenergia no Brasil

RESUMO Nos últimos anos, a sociedade e as autoridades públicas têm demonstrado maior interesse sobre as mudanças climáticas, as quais são mais significativas ao longo dos anos. Sabe-se que o principal fator de agravamento desse processo é a emissão de gases de efeito estufa, em razão da queima de combustíveis não renováveis, utilizados principalmente por empresas e pelo setor de transportes para a geração de energia. Neste momento, tem-se uma grande oportunidade para a difusão e o estímulo ao uso de energias renováveis, com o objetivo de uma matriz energética mais sustentável. Este artigo apresenta uma visão geral da matriz energética brasileira, e o histórico, os problemas e as questões sobre a sustentabilidade do setor energético no país, com base em aspectos econômicos, sociais e ambientais. Em razão do potencial hidroelétrico e da presença do bio-etanol na matriz energética brasileira, o país está em posição privilegiada em relação a maioria dos países da América do Sul. O país é autossuficiente em petróleo e complementa sua geração de energia com recursos "modernos", tais quais, usinas eólica, solar e de biomassa. No entanto, o futuro depende, em grande parte, de como o governo conduzirá as políticas de energia renovável, uma vez que o país enfrenta desafios relativos às regulamentações sobre inovação e investimento estrangeiro.
Palavras-chave: Matriz energética; energia renovável; megatendências.

Introduction

Brazil is going through considerable transformations in the political, social, environmental and economic fields. Several key trends act together and influence the development stages and living standards of societies. Successful countries will be those that adapt to these trends and discover how to turn them into opportunities. Energy consumption is one of the main indicators of the country performance. Brazil is facing this energy challenge with two strategies: (i) maintaining the renewable energy matrix, and (ii) promoting energy efficiency and energy conservation through various

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government programs (OLIVEIRA; TRINDADE, 2018). The government opted to use its state-owned companies - Eletrobras and Petrobras - to execute the energy programs in a collaborative action between Ministry of Mines and Energy - Ministério de Minas e Energia (MME), National Agency of Electrical Energy – Agência Nacional de Energia Elétrica (ANEEL), National Petroleum, Natural Gas and Biofuels Agency – Agência Nacional do Petróleo, Gás Natural e Biocombustiveis (ANP), National Institute of Metrology, Normalization and Industrial Quality – Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO). All programs are conducted by the National Council of Energy Policy – Conselho Nacional de Política Energética (CNPE) - through a National Program on Energy Efficiency – Plano Nacional de Eficiência Energética (MME).

In 2017, the largest share of the Brazilian energy came from petroleum and oil products (36%), followed by sugarcane by-products use (17%), hydroelectricity (12%), and natural gas (13%) (EPE, 2018). At the same time, the electricity generation mix was predominantly renewable, with domestic hydroelectricity production accounts for 68% of the supply (EPE, 2018). Hydropower presented a relatively advantageous source of renewable electricity; and with one of the largest hydroelectric potentials in the world, Brazil will continue to expand the hydroelectric generation (SILVA et al., 2016). However, the country's strong dependency on a single energy source threatens the security of electricity supply considering the predicted growth of the power demand in the near future. Within the present expansion rates, Brazil will reach the maximum obtainable capacity of hydroelectric generation in the next decades (SILVA et al., 2016; BRADSHAW, 2017). In addition, the vulnerability of the systems is increased in case of the droughts, which were already experienced in the last years (SILVA, 2016). Under these circumstances, the country energy supply system has to be modified to be more balanced within other renewable sources. Figure 1 shows the structure of the internal supply of electricity in Brazil according to the national energy balance in 2018 - base year 2017 (EPE, 2018) and the energetic projection for 2030 (TOLMASQUIM et al., 2007).

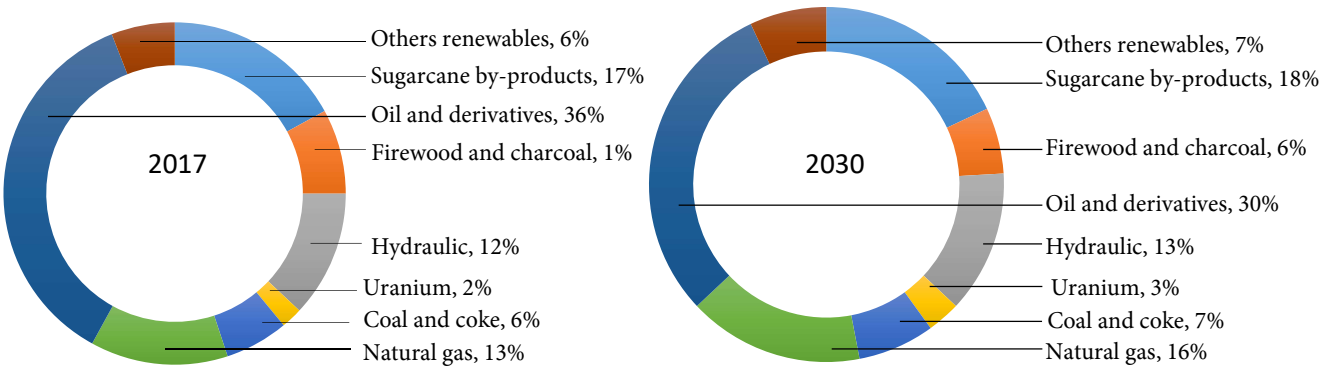


Figure 1. Domestic electricity supply by source in 2017 and 2030.
Figura 1. Fornecimento de energia elétrica por fonte em 2017 e 2030.

The Figure 1 shows that the participation of non-renewable sources will be important in 2030 and the application of renewables will still continue growing. The energy policies implemented in Brazil are mainly aimed on

supporting the use and production of liquid biofuels (FELFLI et al., 2011). At the same time, use of residual biomass for energy generation is not promoted in the sufficient way. According to the Brazilian energy balance (2017), the share of bioenergy (incl. sugarcane, forest residues and black liquor from pulp and paper industry) in the domestic power supply was about 9% in 2016 with 14 GW of installed capacity (almost 80% is by sugarcane bagasse utilization facilities). Recent incentives (Brazil's 'National Climate Change Plan', '2030 National Energy Plan' and 'Decennial Plan') determine certain targets for the reduction of the greenhouse gas emissions and increasing renewable energy generation - with particular focus on bioenergy and hydropower in large scale. Brazil has a significant bioenergy potential that can be successfully used for both, the domestic energy demand and the exports targets (WELFLE, 2017).

The production of electricity in Brazil has a variety of technologies that use fuels, wind energy, agricultural waste, biogas, solar energy, among others. Studies show a high participation of fossil fuel power plants in the energy matrix, as can be seen in the current energy balances, where the national oil production grew 3% in 2016 (LIMA et al., 2015). The main reason was the strong growth of production in the Lula and the Sapinhoá oil fields (EPE, 2018). However, Brazilian energy policies prioritize the use of domestic liquid biofuels to increase energy production. At the same time, recurring international concerns about the need to promote the development of nations by improving the quality levels of life, education, culture and health request alternative solutions against the usual limited funds.

In this direction, the increased implementation of renewable energies can be a vector to induce further sustainable development in Brazil. In particular, the continued implementation of energy crops and challenges related to the possible impacts that can be caused by the country's current energy consumption patterns (LORA; ANDRADE, 2009). It will also highlight the importance of hydroelectricity and bioethanol, which put Brazil in an important position in relation to the other countries around the world. The replacement of gasoline by ethanol, diesel by biodiesel and fuel oil by sugarcane bagasse, are important to reduce the external dependence on oil, which is the reality of Brazil and of many other South American countries.

The objective of this work is to show an overview of the Brazilian energy matrix, background, challenges and degree of sustainability in the production of energy, based on economic and environmental aspects, in order to analyze the bioenergy technologies as a solution to expand the Brazilian energy matrix. Trends that affect the Brazilian energy sector was also included, as well as an assessment of the main ongoing projects.

Megatrends that affect Brazil in the energy sector

The demographic growth rate (Fig. 2) of the population in majority of the countries has contributed significantly to changes in all social areas, from the economic to political and environmental power (DEAN et al., 2015; EEA, 2015). Some of the societies face declining growth, which affects their respective work forces in relation to population. On the other hand, societies that keep a constant growth rate benefits from more standardized work forces and markets, results in greater growth prospects (SAMANS et al., 2017). These societies have the challenge of feeding, educating and employing their new members in order to achieve high productive potential.

According to reports from the United Nations (UN, 2014), Brazil is the fifth largest country in terms of population in the world, after China, India, United States and Indonesia. Its population represents approximately 2.76% of the world population, and it has been gradually increasing. The last

demographic censuses showed an increment of approximately 0.75% from 2017 to 2018, which is considerable high when compared to China (0.39%), that presents the largest population of the world (18.58%) (WORLSDOMETERS, 2018).

With the growth of the population, the demand of energy also gradually increases, since it is necessary for industrial, agricultural and transport developments. The population, that is, families or individuals, consume energy through the market or domestic production. According to the Brazilian energy balance (EPE, 2018), in 2016, the highest energy consumption was found in the service sector (39.5%), more specifically in trade and transport, followed by the industrial sector (35%). The greater contributions to the industrial transformation is granted to the ferrous and non-ferrous plants, foods and beverages companies, and paper and pulp mills (EPE, 2018).

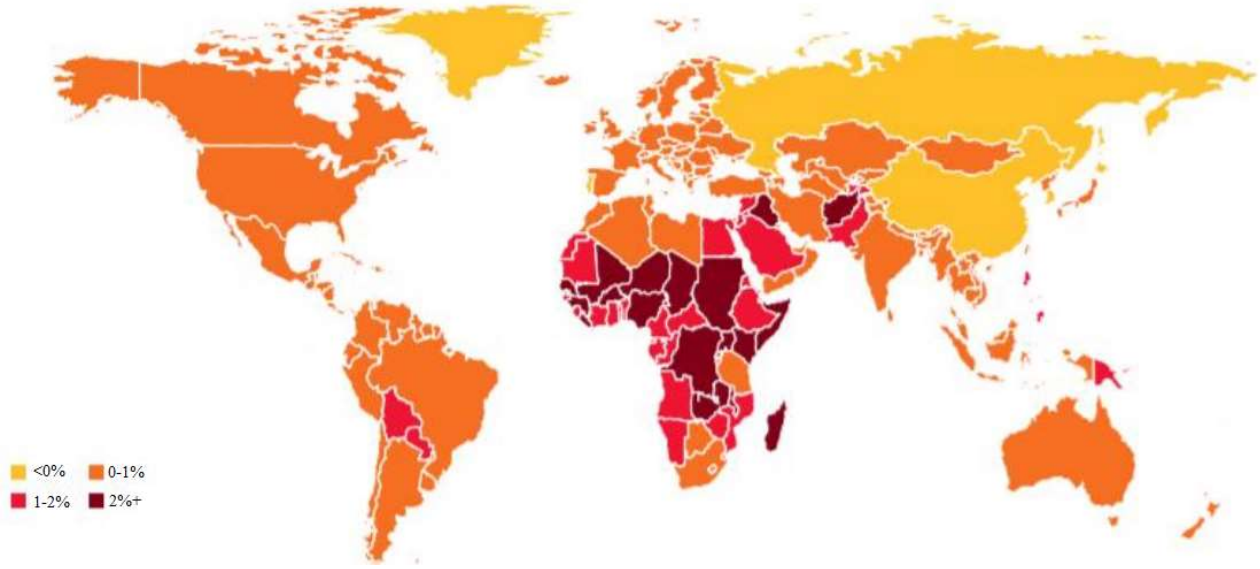


Figure 2. Annual population growth rate, 2010 – 2050 (MODLY, 2016)
Figure 2. Taxa de crescimento anual da população, 2010 – 2050 (MODLY, 2016)

The domestic production directly generates environmental impacts at the end of consumption, whereas goods and services obtained through the market represent indirect or external impacts due to the use of materials and energy during production, transport and marketing (SAWYER, 2015). In addition, the education, health and transportation facilities, who are major consumers of the energy production chain must be taken into account for the sustainable development analysis of a country.

Besides the development of the markets, it is important to recognize the commercial networks and the investments among them. Innovation plays a very important role in the growth and structural change of the economy. Brazil faces the transition from the agrarian economy to industrialization. Increasing the productivity of developing regions such as the Amazon and of already emerging regions such as Minas Gerais (EEA, 2015). One of the possible implications of the change of economic power is the increasingly multipolar world, due to the change of the competitive environment of the companies due to variations in the organizations led (MODLY 2016). This type of economy opens space for new global references of sectoral businesses that in a certain way

can create and support regions that want to develop. However, established and mature markets may lose influence and cease to be attractive for the business (BONASSA et al., 2018).

Brazil makes part of the group of countries known as BRICS (Brazil, Russia, India, China and South Africa). This group is composed of emerging countries, which in the next 50 years could become the main strength of the global economy, becoming even greater than the current G7 (Canada, France, Germany, Italy, Japan, United Kingdom and United States) (VIEIR; VERÍSSIMO 2009). These nations have in common a dense population and a large territory, which gives them a strategic continental dimension and availability of natural resources. These factors attract a lot of foreign direct investment, low labor costs and high Gross Domestic Product (GDP) growth rates. In this context, Brazil is the most prosperous market in Latin America, with innumerable projects regarding industrialization, urbanization, technological innovations and international cooperation, which improves the level of education and employment opportunities, environment and climate changes (AL-MULALI et al., 2016).

Koengkan et al. (2017) studied the impact of wind energy production on the market. They demonstrated that renewable energy public policies not only results in clean energy also generating jobs and economic development in some particular regions. On the other hand, Del Rio and Burguillo (2008), concluded that renewable energy projects have positive effects on the municipal budget since these projects involve granting of subsidies for companies and local communities with government funds, in addition to financial transfers for environmental compensation.

The scarcity of resources and the impact of climate changes are a growing economic concern as well. Energy demand is expected to increase by more than 50% by 2030 and water withdrawals by 40% (ANDRADE et al., 2015). The need for sustainable solutions may be in conflict with the need of resources to boost growth and feed populations. The most consecrated traditions will be challenged by changes in the physical environment (VIEIRA; VERÍSSIMO, 2009; MARGULIS; SCHMIDT, 2010).

The impact of the climate variations because of the increasing global temperatures could reduce the country GDP and slight increase poverty. The region most vulnerable to this physical phenomenon in Brazil will be the Amazon and the Northeast, with a reduction of approximately 40% in floral coverage (VIOLA; FRANCHINI, 2017). In the rest of the country, expressive losses in agriculture will be evident, with the exception of cooler regions in the south and southeast that will keep more pleasant temperatures (MARGULIS; SCHMIDT, 2010). However, the country is preparing with some mitigation actions, for example, the replacement of fossil fuels, which will avoid domestic emissions of 92 to 203 million tons of CO2 equivalent until 2035 (LIMA, 2017). The growth of planted areas would avoid both the substitution of areas originally destined to subsistence cultures and the deforestation of the Amazonian region (MARGULIS; SCHMIDT, 2010).

The Brazilian National Policy on Climate Change goal, is to reduce emissions between 36.1% to 38.9% by 2020. In addition, considering the size of its territory, the country contribution to global greenhouse gases emissions (GHG) is relatively small, 3.4% of the world total (SEEG, 2016). In that sense, the use of renewable energies has a great implication in the country energy policies. The estimated potential for reducing emissions would be 1.8 billion tons of CO2 in the 2010-2030 period. With a discount tax of 8% per year, the estimated cost would be negative meaning a benefit of US$ 34 billion until 2030, which is equivalent to US$ 13 per ton of CO2 (MARGULIS; SCHMIDT, 2010).

Technology solutions

A wide range of technologies are available now and in constant development for optimization with the aim of satisfying the global energy demand. The energy scenario is mainly focused on energy savings and renewable sources potential, primarily in the heat and power generation sectors (GREENPEACE et al., 2015). The technologies implemented for the generation of energy depend mainly on the type of fuel that is being used.

Oil, coal and natural gas combustion are the main fossil fuel technologies, commonly used for power generation. Oil is still used in areas where other fuels are not readily available, such as islands or remote sites. In that sense, technologies have been introduced to improve the environmental performance of conventional fossil fuel combustion (GREENPEACE et al., 2015). These include fuel cleaning technologies, to reduce emissions of particulates, Sulphur dioxide (SO2) and nitrogen oxide (NO) and combined cycle gas turbine (CCGT), where the gas turbine generator produced electricity and the exhaust gases from the turbine are used to make steam to generate additional electricity (RODRIGUES et al., 2003; GREENPEACE et al., 2015). Several studies about the implementation of new technologies and the main issues and uncertainties affecting electricity demand and supply in Brazil have been carried out, Rodrigues et al. (2003) evaluate the co-firing of gas derived from biomass and natural gas combined system to increase the energetic efficiency and Gomes et al. (2013) analyzed the use of the Brazilian coal and biomass through a cleaner production in order to reduce atmospheric emissions and ashes.

The use of renewable power and heating technologies are atractive solutions for the Brazilian energy matrix expansion. Renewable energy includes sources such as biomass, solar energy, geothermal heat, hydropower, ocean thermal and wind energy. Currently, the country has a large contribution from renewable sources, approximately 42% of the Brazilian total primary energy supply come from renewables (EPE, 2018). The decennial plane of Brazilian energy expansion 2024, offers a promising perspective for the energy industry in Brazil, based on an integrated view of the various energy sources, providing a market with better investment decisions (EPE, 2015). Photovoltaic, wind energy and biomass technologies are currently being improved the most in the country.

Photovoltaic (PV) technology involves the generation of electricity of light. According to Greenpeace et al. (2015), each square meter of land is exposed to enough sunlight to produce 1,700 kWh of power every year. European countries have been developed specific regulatory mechanisms to encourage the PV systems either by government programs or by financial and tax incentives. In Brazil, the encouragement to technology is still incipient, despite the large existing solar potential (FERREIRA et al., 2018). However, the International Renewable Energy Agency revealed that Brazil had installed 1GW of solar generation in 2017 and several projects are in progress (BARROS, 2018).

Wind energy has grown faster than all other electricity sources in the last 20 years worldwide (GREENPEACE et al., 2015), in Brazil over the last decade the wind energy increased from 19Â MW to 2.2Â GW (PES et al., 2017). Nowadays, modern wind technology is available for low and high wind speeds, and in a variety of climates (GREENPEACE et al., 2015). Brazil implemented industrial policies in the wind energy sector in some regions of the country, motivated by national programs to stimulate the development of this source (ADAMI et al., 2017). According to Jong et al. (2017), wind powerin the Brazilian Northeast (NE) is expected to generate 57% of the NE electricity supply by 2020.

Programs, projects and technologies related to the use of biofuels in Brazil have an important participation in the energy matrix, the availability of biomass and electricity generation potential for different industrial and agricultural sector is increasing. Several studies have been carried out, Martinez et al. (2019) present selected agroindustry solid residues from Brazilian coffee production chain for energy purposes, Walter et al. (2011) and Bordonal et al. (2018) reported the high efficiency of sugar cane for ethanol production.

Challenges and opportunities to increase biomass usage in Brazil

Handling solid biomass (branches, animal carcasses, leaves, barks, among others) is not economical feasible for the purpose of generating energy. The concentration of energy is low and there is no regularity of physical properties such as dimension, density, humidity, stiffness, which are crucial factors for transportation, handling and storage (LUBWAMA; YIGA, 2018). One of the solutions found is the conversion of biomass into liquid and gaseous biofuels with higher energy density and more viable characteristics. There are several processes of biomass conversion to produce heat, electricity and/or fuels. They can be grouped into three categories, namely physical-chemical, biochemical and thermochemical, as presented below.

- Physical-chemical: They involve physical transformations in the biomass that do not result in molecular modifications. Among the most common operations are: (i) densification, (ii) granulometric reduction, and (iii) mechanical pressing (TURKENBURG et al., 2000).
- Biochemical: Biomass molecules are broken down into smaller molecules by the action of living organisms, namely bacteria or enzymes. The three main conversion routes are (i) digestion, (ii) fermentation, and (iii) hydrolysis (BASU, 2013).
- Thermo-chemical: All the biomass is either directly burned or converted into gases that are used to synthesize biofuel for power generation. Among the conversion options are the routes of (i) combustion, (ii) pyrolysis, (iii) gasification, and (iv) liquefaction (BASU, 2013).

Traditionally, the main technologies for thermochemical conversion of biomass studied in Brazil are: combustion, pyrolysis, torrefaction and gasification. In each one, a series of reactions occurs with the hydrocarbons, cellulose, hemicelluloses and lignin, compounds generally present in the biomass (YANG et al., 2007). Modern biomass is used in several sectors of the economy in Brazil. The industrial sector have the pulp and paper mills that uses wood and bleach residues as fuel in gasification processes (JOELSSON; GUSTAVSSON, 2008); the cogeneration systems with sugarcane bagasse in the sugar and alcohol sector and in the beverage sector, especially in the fruit juice processing industries; and also the sawmills that use wood residues in the production of heat for plant operations and electricity generation (JUNIOR, 2004).

The implementation of a program for the production and use of ethanol from sugarcane would certainly not have to go through all the steps that Brazil has already successfully overcome. By replicating this initiative, it is possible to take a technological leap and produce ethanol at competitive prices. Another important point concerns the reforestation policy of the Brazilian paper and pulp industry. This sector, that is frequently breaking records, produces 10.357 million metric tons of paper per year (FARINHA et al., 2016). For instance, a factory in the state of Mato Grosso do Sul, known to be the largest single-line factory in the world, uses eucalyptus plantations to obtain kraft pulp for paper raw material. Três Lagoas is another example of a mega factory in Brazil that

often break its own world records regarding daily pulp production.

The pulp and paper industry is energy intensive, with significant amounts of carbon dioxide (CO_2) emissions. The sector is making increasing efforts to reduce fossil fuel use, and consequently emission levels in all parts of the world (FRACARO et al., 2012). A large share of energy use in the pulp industry is already based on biomass (IEA, 2017). Under normal operations, modern kraft pulp mills are generally self-sufficient in energy making the carbon neutral if the biomass used by the industry is cultivated and harvested in a sustainable way. If the CO_2 emissions from the pulp and paper industry are captured and stored permanently, this can make the pulp industry a potential carbon sink.

To increase the use of biomass and to develop the technology needed for this, different aspects must be taken into account: (i) Investments in agricultural and industrial development, (ii) Training of human resources, (iii) Adequate legislation (environmental protection, transportation sector (regulation, fuel quality, percentage of biofuel, inspection) and electrical sector (authorization for the production and sale of bioelectricity, market rules), and (iv) Infra-structure for the production, distribution and exportation.

Among the environmental aspects, the challenges for the production of biofuels in Brazil from biomass concern the reduction of greenhouse gases, since it is necessary to assess the life cycle of the region and the development of a standardized accounting methodology (BLOTTNITZ; CURRAN, 2007). On the other hand, poor planning may cause soil erosion, water pollution, evaporative air emissions and possible loss of biodiversity (DEMIRBAS, 2009). However, the opportunity to overcome these barriers can maximize synergy in many areas at the national level.

With respect to economic aspects, the challenges are: the scale of production; the availability of the energy market as well as the obtaining of raw material; the local and international subsidies of the raw material; the high material costs, conversion and transportation; the availability of financing internal and external and the import rates (DEMIRBAS, 2009). The thrill of these barriers creates the opportunities for an economic and national market uplift and the identification of viable businesses.

Finally, regarding social aspects, the challenges for the production of energy are the distribution of benefits, existing monopolies, food security and resistance to changes. However, overcoming these challenges generates the opportunity to increase the commitment of the public administration and also creates strategies for poverty reduction (GUI; MACGILL, 2018).

Final Considerations

Brazil has the largest renewable energy market in Latin America and half of its energy is generated by natural inputs (78%); this is more than three times the world average. The diversity of energy sources (hydroelectric, wind, biomass, solar) is the key issue of the Brazilian energy matrix relevance, once in addition to a mixture of alternatives, it also contributes to the dilution of geopolitical risks. According to the Brazilian Ministry of the Environment, the country, despite having a renewable energy matrix, it still needs new investments to improve the energy production chain to make it sustainable, to encourage research and to develop new technologies.

On the other hand, the main obstacle the country is facing in the energy sector is precisely the absence of public policies that would ensure the establishment of public actions to encourage the development of the energy industry. Although Brazil is considered a world leader in renewable energy, which

guarantees the credibility to negotiate international proposals, agreements and protocols, linked to the following topics: greenhouse gas reduction, climate change and low carbon production. These are the main issues addressed today, related to economic, social and environmental sustainability.

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