JONAS ZEFANIAS MASSUQUE

MEETING THE INDUSTRIAL DEMAND OF BIOENERGY IN BRAZIL: THE POTENTIAL OF NON-COMMERCIAL *Eucalyptus* and *Corymbia* WOODS

LAVRAS-MG
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Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência e Tecnologia da Madeira, área de concentração em Ciência e Tecnologia da Madeira, para obtenção do título de Doutor.

Orientador: Prof. Dr. Paulo Fernando Trugilho

Coorientador: Prof. Dr. Paulo Ricardo Gherardi Hein

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ATENDENDO À DEMANDA INDUSTRIAL DE BIOENERGIA NO BRASIL: O POTENCIAL DAS MADEIRAS NÃO COMERCIAIS DE *Eucalyptus* and *Corymbia*

Tese apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação em Ciência e Tecnologia da Madeira, área de concentração em Ciência e Tecnologia da Madeira, para obtenção do título de Doutor.

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LAVRAS-MG
2023

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RESUMO GERAL

A madeira é matéria-prima relevante para a bio-economia, especialmente aquela oriunda de plantios energéticos, pois a sua utilização na cogeração de energia e produção de carvão vegetal, usado na siderurgia, tem elevado potencial de substituir os combustíveis fósseis, contribuindo com a redução da emissão de gases de efeito estufa. No Brasil as plantações de *Eucalyptus* são amplamente utilizadas para produção de lenha, cavacos e carvão vegetal para atender ao setor siderúrgico. Diante do exposto, o presente estudo tem como objetivo avaliar a qualidade da madeira de *Eucalyptus* e *Corymbia*, sem tradição comercial no Brasil, tendo em vista o seu uso energético. Após seis anos de plantio, as propriedades químicas, físicas, energéticas, térmicas da madeira, rendimentos gravimétricos e desempenho do carvão, oriundo de *Corymbia citriodora*, *C. variegata*, *C. henryi*, *C. torelliana*, *Eucalyptus amplifolia*, *E. longirostrata*, *E. major* e *E. urophylla*, foram analisadas. O *E. major, E. amplifolia* e *C. torelliana* se destacaram por apresentarem as características que favorecem a produção de carvão vegetal de qualidade superior para uso siderúrgico quando comparadas com o *E. urophylla*, espécie mais utilizada no Brasil para esta finalidade. As espécies *C. citriodora, C. variegata, C. henri* e *E. longirostrata* são mais potenciais para uso em sistemas de cogeração de energia.

Palavras Chaves: Propriedades energéticas; Pirólise, Combustão; Cogeração e Siderurgia sustentável

GENERAL ABSTRACT

Wood energy plantations are important sources of feedstock for bioeconomy, given their potential to replace fossil fuels, which would ultimately result in the reduction of greenhouse gas emissions. *Eucalyptus* and *Corymbia* woods have been widely used for the production of firewood, wood chips, and charcoal for the steel industry in Brazil. The present study aims to assess the properties of non-commercial *Eucalyptus* and *Corymbia* woods for energy purpose in Brazil. Six years after planting, the chemical, physical, energy, thermal properties, gravimetric yeilds and combustion performance of charcoal from *Corymbia citriodora*, *C. variegata*, *C. henryi*, *C. torelliana*, *Eucalyptus amplifolia*, *E. longirostrata*, *E. major*, and *E. urophylla* were analysed. Compared to *E. urophylla*'s wood, the most used species in the steel industry in Brazil, the wood from *E. major*, *E. amplifolia*, and *C. torelliana* had properties that favoured the production of high-quality charcoal for use in steel industry. *C. citriodora, C. variegata*, *C. henryi*, and *E. longirostrata* presented a high potential for use in energy cogeneration systems.

Keywords: Energy properties, Pyrolysis, Combustion, Cogeneration and Sustainable steelmaking

SUMÁRIO

PRIMEIRA PARTE

1. INTRODUÇÃO

O Brasil está entre os 15 maiores emissores de gases de efeito estufa (GEE) do mundo. Neste sentido, o país precisa atender os novos compromissos definidos pelo Acordo de Paris visando à redução das emissões de carbono. Para alcançar as emissões previstas na Convenção das Nações Unidas para Mudanças Climáticas, o Brasil deve reduzir 0,16 Gt de CO_2 entre 2015 e 2030 em emissões líquidas (MACHADO et al., 2020).

A bioeconomia tem potencial para evitar a emissão de até 2,5 bilhões de toneladas de CO_2 por ano (IBA, 2020). O Brasil é o único país no mundo onde o uso de carvão vegetal para redução de ferro é competitivo (PINTO et al., 2018). Sem a bioenergia ou captura e fixação de carbono, as emissões de CO_2 por ciclo de produção de aço seria de 1,3 a 2,4 t CO_2/t de aço. O uso do carvão vegetal na siderurgia diminuiu as emissões de CO_2 líquido numa ordem de -0,5 a 0,1 t CO_2/t de aço produzido (TANZER et al., 2020). A madeira é matéria prima relevante para a bioeconomia, especialmente aquela oriunda de plantios energéticos, pois podem substituir parte do carvão de origem fóssil usado na siderurgia e em centrais termoelétricas, contribuindo com a redução da emissão de GEEs.

Nesse cenário, o Brasil se destaca por produzir carvão vegetal majoritariamente de espécies e híbridos de *Eucalyptus*. O gênero *Eucalyptus* se destaca na produção de bioenergia devido ao seu rápido crescimento, alta produtividade volumétrica de madeira e qualidade adequada do carvão vegetal para finalidade siderúrgica (PEREIRA et al., 2016; PROTÁSIO et al., 2019, 2020, 2021; DIAS JUNIOR et al., 2020). Estudos recentes também demonstraram que as madeiras de *Corymbia* podem ser adequadas para a produção de carvão vegetal de uso siderúrgico (Ignacio et al., 2019; Loureiro et al., 2019)

As espécies mais estudadas e difundidas no Brasil para uso energético são o *Eucalyptus urophylla* e *E. grandis*. A literatura demonstra variação de 450 a 500 $kg.m^{-3}$ para a densidade básica dessas espécies (PEREIRA et al., 2016; PROTÁSIO et al., 2019, 2020, 2021; DIAS JUNIOR et al., 2020). Entretanto, madeiras de eucalipto que apresentam, simultaneamente, em média diâmetro a altura do peito (DAP) $\geq$15,1 cm e densidade básica $\geq$ 560 $kg.m^{-3}$, são mais adequados produção de carvão vegetal, visando abastecer de forma eficiente a indústria siderúrgica (PROTÁSIO et al., 2021). Dessa forma, o estudo das características de crescimento e de qualidade da madeira de novos materiais genéticos é necessário visando compor as florestas energéticas com propriedades superiores para a produção de madeira para cogeração e carvão vegetal de uso industrial.

Atualmente, o gargalo das florestas de *Eucalyptus* destinadas ao suprimento de matéria prima, consiste no uso de clones ou espécies que apresentam rápido crescimento (IMA ~ 40 m^3/ha.ano), mas com densidade da madeira variando de baixa a média (~500 kg/m^3)(COSTA et al. 2020). Pesquisas recentes têm demonstrado as intensas variações nas propriedades da madeira e na produtividade de clones de *Eucalyptus* cultivados em ambientes contrastantes (ALMEIDA et al. 2020; COSTA et al. 2020). No entanto, essas pesquisas se concentram na avaliação de clones comerciais utilizados no país, sendo fundamentais novas informações de genótipos não comerciais que se encontram em fases iniciais de melhoramento genético.

Plantios de *Eucalyptus* e *Corymbia* têm expandido para várias regiões do Brasil que, por sua vez, apresentam condições edafoclimáticas muito distintas, como ampla variação de temperatura, precipitação e distintos atributos de solo. Portanto, torna-se fundamental a seleção e classificação de novos genótipos que apresentam elevada plasticidade fenotípica, além da adaptação às condições de determinado sítio, para atender à crescente demanda por florestas energéticas. Com isso, novas espécies sem utilização em escala comercial estão sendo introduzidos no Brasil pelo projeto ‘Espécies Potenciais’ por meio do Programa Coorporativo de Melhoramento Florestal do Instituto de Pesquisa e Estudos Florestais (IPEF), sendo quatro espécies do gênero *Corymbia* (*C. citriodora* subesp. *citriodora, C. citriodora* subesp. *variegata, C. henryi* e *C. torelliana*) e 15 do gênero *Eucalyptus* (*E. amplifolia, E. argophloia, E. brassiana, E. brookeriana, E. camaldulensis, E. cladocalyx, E. crebra, E. denticulata, E. longirostrata, E. macarthurii, E. major, E. moluccana, E. occidentalis, E. thozetiana* e *E. urophylla*).

Destaca-se que o uso de novas espécies para uso energético amplia e diversifica a base genética no país e pode melhorar o desempenho para esta finalidade, melhorando o balanço de massa da carbonização, além de reduzir as emissões dos gases intensificadores do efeito estufa nas siderurgias nacionais. Genótipos adaptados de bom crescimento volumétrico e com madeira de elevada densidade básica, teores de lignina, extrativos e cinzas favoráveis ao uso energético direto ou indireto são necessários, pois vão impactar favoravelmente os custos de produção.

1.1. Objetivos

1.1.1. Geral

- Avaliar a potencial de genótipos sem tradição comercial de *Corymbia* e *Eucalyptus* visando o uso energético no Brasil.

1.1.2. Específicos

- Avaliar a qualidade da madeira de genótipos de *Eucalyptus* e *Corymbia* para uso geração de progênies adaptadas às demandas energéticas em escala industrial no pais
- Avaliar a qualidade e o comportamento da combustão de carvão vegetal produzido por espécies com boa produtividade volumétrica que ainda não são plantadas comercialmente para setor siderúrgico

2. REVISÃO DE LITERATURA

2.1. Propriedades da madeira para uso energético

2.1.1. Propriedades físicas

A umidade e a densidade são índices de qualidade da madeira para produção de carvão vegetal e cogeração de energia. Quanto menor a umidade da madeira menor será o custo com transporte e mais matéria seca será movimentada. A umidade não pode ser considerada apenas como parâmetro essencial para diminuir os custos com o transporte, mas também como de qualidade para o uso energético. Quanto maior a umidade da madeira maior será o gasto de energia na etapa da secagem e, consequentemente, menor será o seu poder calorífico útil (ZANUNCIO et al., 2013).

A densidade da madeira também influencia no custo de transporte, quanto maior a densidade da madeira menor será o seu custo. Do ponto de vista energético a densidade da madeira é a propriedade que afeta diretamente a sua densidade de energia, ou seja, maior a quantidade de energia que será liberada durante a combustão por unidade de volume do combustível da madeira (PROTÁSIO et al., 2021).

2.1.2. Componentes químicos majoritários da madeira

A composição química estrutural da madeira é constituída geralmente majoritariamente por celulose, hemiceluloses e lignina, e em menor proporção por substâncias químicas de baixa massa molecular como, extrativos e minerais, sendo que estes constituintes variam de acordo com as espécies vegetais.

Estes constituintes estruturais da madeira apresentam grande influência na sua decomposição térmica (YANG et al., 2006, 2007; WANG et al., 2017). A quantificação dos constituintes da madeira é fundamental na classificação e seleção de madeira para produção de carvão vegetal para uso siderúrgico e cogeração de energia.

As hemiceluloses e a celulose são os constituintes com menor estabilidade térmica. A menor estabilidade térmica das hemiceluloses está associada a sua fração mais reativa que se degradar em baixas temperaturas, uma vez que se trata de componentes amorfos, facilmente hidrolisáveis (Yang et al., 2006, 2007). Porém, a decomposição térmica das hemiceluloses e celulose ocorre quase que simultaneamente (Magdziarz and Werle, 2014). A lignina é o constituinte estrutural da madeira com maior estabilidade térmica, devido a força das ligações carbono-carbono na macromolécula e elevada massa molecular (Yang et al., 2006). A lignina apresenta-se mais estável do que a celulose e as hemiceluloses, degradando lentamente, devido as suas propriedades físicas e químicas, decompondo-se na faixa de 280 a 500°C, formando principalmente o produto sólido da pirólise (LI et al., 2016)

A lignina é constituída por monômeros de guacilpropano (G), siringilpropano (S) e phidroxifenilpropano (H), originados da polimerização desidrogenativa de três álcoois precursores, trans-coniferílico, trans-sinapílico e trans-para-cumárico, respectivamente (LIN e DENCE, 1992). Espera se que madeiras com elevadas proporções do monômero guaiacil em relação ao siringil na macromolécula da lignina proporcionem maior resistência à degradação térmica, durante a pirólise da madeira. O monômero guaiacil possui uma posição aromática, no C5, disponível para ocorrência de ligações carbono-carbono e estas ligações apresentam maior estabilidade e, consequentemente, mais energia será necessária para quebrá-las, o que confere maior resistência à degradação térmica (WANG et al., 2017). Assim sendo, além de qualificar os constituintes da madeira é importante estudar a relação entre os monômeros siringil e guaiacil da lignina e verificar a sua influência sobre a decomposição térmica.

Os extrativos influenciam as produtividades energéticas das madeiras, por ocuparem parte dos espaços vazios existentes na parede celular, que seriam normalmente ocupados pela água (MASSUQUE et al., 2020), também por estes elevarem o poder calorifico (SOARES et al., 2014). Os extrativos apresentam relação com a densidade básica e com a densidade energética da madeira (LIMA et al., 2021). No entanto, quanto maior a densidade energética, mais propício o combustível será para uso energético.

2.1.3. Composição química imediata

Para utilização da madeira, para geração de energia térmica é indispensável a quantificação dos teores de materiais voláteis, cinzas e carbono fixo. A quantificação destes constituintes da biomassa por meio da decomposição térmica é denominada de composição química imediata.

Quanto maior o teor de cinzas na madeira maiores serão as perdas energéticas pelo aquecimento dos óxidos minerais durante a sua degradação térmica (PROTÁSIO et al., 2019). Elevado teor de cinzas tende a reduzir o poder calorifico da madeira (GARCÍA et al., 2014), além de causar incrustações e corrosão nos equipamentos de queima (SHEN et al., 2010).

Os materiais voláteis são gases oriundos da decomposição térmica dos constituintes da madeira. Em mistura com o oxigênio estes gases reagem e promovem a combustão da biomassa (SHEN et al., 2010), consequentemente, quanto maior o teor de materiais voláteis menor será a temperatura de ignição e tempo necessário para ignição da madeira (PROTÁSIO et al., 2019).

De maneira geral, a madeira apresenta teor de materiais voláteis entre 70% a 87% e teor de carbono fixo entre 15% a 30% (SHEN et al., 2010).O carbono fixo é o produto sólido formado após a desvolatilização da biomassa. Combustíveis com maiores teores de carbono fixo queimam mais lentamente (CUVILAS et al., 2014).

2.1.4. Propriedades energéticas

O poder calorífico é considerado a propriedade energética mais importante para conversão da madeira em energia. O poder calorífico é definido como a medida da quantidade de calor liberado após a combustão completa de um determinado combustível (HUANG et al., 2009), levando-se em consideração o calor latente do vapor d’água. Para efeitos práticos é calculado o poder calorífico inferior (PCI) que, ao contrário do poder calorífico superior (PCS), é a quantidade de energia disponível quando se desconsidera o calor latente de vapor d’água presente no combustível. No entanto, o PCI somente pode ser utilizado diretamente se o combustível não apresentar umidade. Quando o combustível tiver umidade deve-se utilizar o poder calorífico líquido (BRAND, 2010), poder calorífico líquido ou útil desconta a energia necessária para evaporar a água presente na madeira.

2.2. Pirólise da madeira

2.2.1. Produtos da pirólise da madeira

A pirólise é um processo extremamente complexo, que envolve uma série de reações que ocorrem paralelamente e em série, abrangendo a desidratação, despolimerização, isomeração, aromatização e descarboxilação (COLLARD; BLIN, 2014). Os produtos podem ser divididos em três frações: fração líquida, fração sólida e fração gasosa.

Geralmente é usada a faixa de temperatura entre 380 a 500 ºC no processo de pirólise lenta. Em temperaturas até 400 ºC o carvão vegetal representa a fração mais elevada (DIAS

JUNIOR et al., 2020). A maior quantidade de bioóleo é produzida entre 500 e 550 ºC durante a pirólise flash (CHEN et al., 2016). Entre 700 a 1000 ºC o gás não condensável representa o maior produto gerado e independente da temperatura final usada no processo de pirólise o bioóleo e carvão vegetal representam até aproximadamente 80% dos produtos gerados (DIAS JUNIOR et al., 2020).

2.2.2. Parâmetros de pirólise

O estudo de parâmetros cinéticos da madeira é essencial para o entendimento e eficiência do processo de conversão da madeira em carvão vegetal, além de contribuir para melhorar a qualidade do produto final. A cinética da pirólise é importante pois estuda as reações e os fatores que podem influenciar o processo termoquímico.

A temperatura é o fator mais importante para a distribuição dos produtos finais da pirólise. O aumento da temperatura reduz o rendimento em carvão vegetal (ZENG et al., 2015; DIAS JUNIOR et al., 2020). A taxa de aquecimento é outro fator importante na pirólise da biomassa, uma vez que a taxa de mudança de calor influencia a composição do produto final. Elevadas taxas de aquecimento favorecem a rápida desvolatilização produzindo pressão interna e causando rachaduras no carvão (ZENG et al., 2015). O tempo de residência no reator influencia a ocorrência de reações de pirólise primária e/ou secundária durante a decomposição térmica. Curtos tempos de residência minimizam as reações secundárias (AYSU; KÜÇÜK, 2014).

A análise termogravimétrica (TGA) endotérmica é a tecnologia que têm sido empregada recentemente para determinar as propriedades termoquímicas e estimar os parâmetros cinéticos das reações de modo a compreender o mecanismo de degradação térmica da biomassa e seus derivados (BRILLARD et al., 2017).

Duas constantes são usadas para estimar experimentalmente os parâmetros cinéticos sendo elas o fator pré-exponencial e a energia de ativação. A energia de ativação (Ea) pode ser considerada como o limiar de energia que deve ser superada antes que as moléculas cheguem perto o suficiente para reagir e formar produtos. Apenas as moléculas com energia suficiente para superar essa barreira de energia irão reagir. O fator pré-exponencial (*A*) fornece a medida de frequência com que ocorrem todas as colisões moleculares independentemente do seu nível de energia (OZAWA, 1965; FLYNN; WALL, 1966; AKAHIRA e SUNOSE, 1971; YAO et al., 2008)

Vários métodos podem ser empregados para estimar os parâmetros cinéticos do processo termoquímico, considerando os modelos cinéticos não isotérmicos, com destaque para os método de Friedman (YAO et al., 2008), KAS (AKAHIRA e SUNOSE, 1971) e FWO (FLYNN e WALL, 1966). Dentre os diferentes modelos empregados para estimar a energia de ativação, o modelo de Friedman é o mais preciso (YUAN et al., 2017) e apresenta valores superiores em relação ao FWO (SETTER et al., 2020).

2.3. Propriedade do carvão para uso siderúrgico

A utilização do carvão no setor siderúrgico, como agente biorredutor, depende de algumas propriedades com destaque para a densidade relativa aparente, poder calorifico, reatividade e composição química imediata e elementar.

A densidade do carvão vegetal representa a quantidade de material seco disponível em dado volume. Quanto maior a densidade relativa aparente maior será a densidade energética (LIMA et al., 2021), o estoque de carbono fixo por volume (PROTÁSIO et al., 2021), a resistência a compreensão (Assis et al., 2016) e a rigidez (NETO et al., 2018)

O Poder calorifico representa a medida da quantidade de calor liberado por determinada massa de carvão durante a sua combustão completa. Quanto maior a quantidade de energia térmica liberada durante a combustão do carvão melhor é o seu desempenho nos sistemas de conversão de energia (HUANG et al., 2009).

A percentagem dos elementos químicos constituintes do carvão vegetal é designada de composição química elementar. O calor gerado durante a combustão do carvão vegetal está inteiramente relacionado aos teores de carbono e hidrogênio, pois esses são os principais elementos químicos combustíveis. Proporções elevadas de oxigênio, nitrogênio e minerais resultam em diminuição do valor calórico (PROTÁSIO et al., 2021). Alguns minerais podem provocar o fenômeno da segregação, o que prejudica a qualidade do ferro gusa reduzido nos altos fornos siderúrgicos.

A baixa presença de enxofre no carvão vegetal representa um diferencial em relação ao carvão mineral, este elemento apesar de ser combustível, durante a combustão causa corrosão dos equipamentos utilizados, além de gerar problemas ambientais (DEMIRBAS, 2004).

A combustão do carvão vegetal também depende da composição imediata, que é representada pelos teores de matérias voláteis e carbono fixo. O carbono fixo expressa a fração combustível que queima na forma sólida, enquanto que os materiais voláteis são os componentes que representam a fração combustível que queima na forma gasosa e geram a chama. A maior relação materiais voláteis/carbono fixo está diretamente relaciona a maior intensidade da combustão (GARCÍA et al., 2013), gerando maior energia térmica dentro do biotermorredutor na indústria siderúrgica ou calor para aquecimento ou na cocção de alimentos.

A reatividade expressa a taxa de conversão do carvão vegetal em monóxido de carbono (CO), gás necessário à redução do minério de ferro. Carvão muito reativo fornece gases de redução em taxas elevadas desperdiçando parte do gás que devia ser aproveitado no processo, enquanto que materiais pouco reativos tornam o processo de produção mais prolongado (MACHADO et al., 2010).

2.4. Combustão do carvão vegetal

A análise termogravimétrica pode ser empregada para determinar o desempenho de combustão e reatividade do carvão vegetal ou biotermorredutor na indústria siderúrgica. Para avaliar a combustibilidade de materiais combustíveis, por meio de termogravimetria, são considerados os seguintes parâmetros: a temperatura de ignição (Ti), a temperatura final da combustão (Tf), o índice característico da combustão (S), o índice de ignição (Di), o tempo correspondente à máxima taxa de combustão (tp), o tempo de ignição (tig), a taxa máxima de combustão e a taxa média de combustão.

A temperatura de ignição, determinada por meio da curva da derivada termogravimétrica, é definida como sendo aquela em que a taxa de combustão aumenta a 1% min^{-1}, iniciando-se a maior intensidade do processo de combustão. A temperatura final da combustão (burnout temperature) pode ser definida como sendo aquela em que a taxa de combustão diminui 1% min^{-1} e refere-se ao final do processo de combustão (WANG et al., 2011).

O índice de ignição (Di) é a medida usada para determinar a energia necessária para o início desse processo de oxidação. O índice característico da combustão (S) pode ser utilizados para determinar o desempenho de combustão e a geração de energia térmica, pois se relacionam com a reatividade do material combustível (WANG et al., 2011; MOON et al. 2013). Quanto maiores forem os valores obtidos para esses índices de ignição e de combustão melhor será o desempenho durante a ignição e o processo de combustão da biomassa, respectivamente.

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SEGUNDA PARTE

ARTIGO 1 (VERSÃO PUBLICADA): EVALUATING THE POTENTIAL OF NON-COMMERCIAL *Eucalyptus* spp. AND *Corymbia* spp. FOR BIOENERGY IN BRAZIL

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ABSTRACT

Wood energy plantations are important sources of feedstock for bioeconomy, given their potential to replace fossil fuels, which would ultimately result in the reduction of greenhouse gas emissions. *Eucalyptus* and *Corymbia* woods have been widely used for the production of firewood, wood chips, and charcoal for the steel industry in Brazil. The present study aims to assess the properties of non-commercial *Eucalyptus* and *Corymbia* woods for energy purpose in Brazil. Six years after planting, the chemical, physical, energy, and thermal properties of *Corymbia citriodora*, *C. variegata*, *C. henryi*, *C. torelliana*, *Eucalyptus amplifolia*, *E. longirostrata*, *E. major*, and *E. urophylla* were analysed. The results showed significant variations in basic density (480-662 kg·m^{-3}), total extractives (1.03–4.56% db), lignin (28.33-34.25% db), holocellulose (61.54-69.07% db), higher heating value (19.22-20.33 MJ·kg^{-1}), syringyl/guaiacyl ratio (2.20-3.36), energy density (9.45-12.51 GJ·m^{-3}), ash content (<1% db), and pyrolysis activation energy (247-468 kJ·mol^{-1}). Compared to *E. urophylla*'s wood, the most used species in the steel industry in Brazil, the wood from *E. major*, *E. amplifolia*, and *C. torelliana* had properties that favoured the production of high-quality charcoal for use in steel industry. *C. citriodora*, *C. variegata*, *C. henryi*, and *E. longirostrata* presented a high potential for use in energy cogeneration systems.

Keywords: Energy properties, Activation energy, Chemical composition, Cogeneration and Sustainable steelmaking

1. INTRODUCTION

Brazil is fifteenth largest contributor of greenhouse gases (GHG) emissions in the world. Thus, as part of the Paris Agreement, and in line with the United Nations Convention on Climate Change, the country must cut 0.16 Gt of carbon dioxide (CO_2) emissions by 2030 [1]. The development and intensification of bioeconomy has been promoted as a prominent solution to tackle this challenge. It can potentially prevent up to 2.5 billion tons of CO_2 emission per year [2]. Wood, especially that derived from energetic plantations, is an important raw material for bioeconomy, and can be a suitable alternative to fossil fuels in the steel industry and thermoelectric power plants, thereby helping to reduce GHG emissions.

Eucalyptus urophylla, *Eucalyptus grandis* are the most studied and planted species for energy purposes in Brazil. Their hybrids represent more than 85% of the plantations in Brazil due to *E. grandis* rapid growth and the hardiness of *E. urophylla* [3, 4]. The wood basic density of these species varies from 450 to 500 kg/m^3 [5–10]. However, according to Protásio et al. [10], it is recommended to use eucalyptus with diameter at breast height (DBH) of > 15.1 cm and basic density > 560 kg/m^3, as they result in denser charcoal and suitable physical quality for steel industries. Thus, it has become essential to study the growth characteristics and wood quality of new genetic materials to find species with suitable properties for energy cogeneration and charcoal production.

Currently, the supply of feedstock mainly consists of eucalypts clones or species that show rapid growth but with wood density ranging from low to medium (450 to 500 kg.m^{-3}) [6, 10, 11]. Recent studies have assessed wood properties and productivity of eucalypts clones grown in different environments [11–13]. However, these studies only focused on the evaluation of widely used commercial clones. Non-commercial species are in the early stages of genetic improvement and studies on their wood properties and productivity are rather scant, despite being essential for the selection and establishment of high- performance energy plantations.

Eucalyptus and *Corymbia* plantations have expanded to several regions of Brazil, which have very distinct edaphoclimatic conditions, such as in their temperature, rainfall, and different soil attributes [14]. Thus, it is crucial to select and classify new genotypes with high phenotypic plasticity that are adapted to the conditions of a given region, to meet the growing demand for energy forests. Thus, new and non-commercial species, namely, *Corymbia citriodora*, *Corymbia variegata*, *Corymbia henryi*, *Corymbia torelliana*, *Eucalyptus amplifolia*, *Eucalyptus argophloia*, *Eucalyptus brassiana*, *Eucalyptus brookeriana*, *Eucalyptus camaldulensis*, *Eucalyptus cladocalyx*, *Eucalyptus crebra*, *Eucalyptus denticulata*, *Eucalyptus longirostrata*, *Eucalyptus macarthurii*, *Eucalyptus major*, *Eucalyptus moluccana*, *Eucalyptus occidentalis*, *Eucalyptus thozetiana*, and *Eucalyptus urophylla* are being introduced in Brazil within the scope of the Potential Species Project by the Corporate Forest Improvement Program of the Forest Research and Studies Institute (Instituto de Pesquisa e Estudos Florestais - IPEF) [14, 15].

It is noteworthy that the use of new species for energy use expands and diversifies the genetic base in the country and can improve energy performance, the carbonization mass balance, in addition to reducing greenhouse gas emissions in national steel mills. The present study aimed to evaluate the wood properties of *Eucalyptus* and *Corymbia* species that had no traditional commercial use in sustainable steel industries in Brazil.

2. MATERIALS AND METHODS

2.1. Biological material and sampling

The genetic materials were collected in a six years old *Eucalyptus* and *Corymbia* experimental plantations located in the municipality of Borebi, São Paulo state, Brazil (28° 48′ S latitude, 48° 54′ W longitude, and 711 m altitude). According to the Köppen classification, the climate of the region is humid tropical with hot, rainy summers and dry, cold winters. The mean annual rainfall is 1350 mm, and the mean temperature is 21 °C. The experiment was conducted at the company Bracell, which belongs to a network comprising the Potential Species Project.

The Potential Species Project consists of an experiment established in January 2014, in rectangular plots of 7 × 7 plants, with four species of the genus *Corymbia* and 15 species of the genus *Eucalyptus.* The plants were spaced 3.0 × 2.6 m (7.8 m^2). Only the eight species that showed high adaptability were selected for the present study (Table 1). The adaptability analysis was performed based on the survival and initial growth data [14, 15]. The trees were collected six years after plantation, in January 2020, and seven trees were selected per species, from which 2.5-cm-thick discs were removed at the 0% (base), breast-height (1.30 m), 25%, 50%, 75%, and 100% longitudinal positions of the commercial height of the trees, considered at diameters of at least 4 cm.

Table 1. Species selected for the study and their dendrometric characteristics

Species	DBH (cm)	CH (m)	CVb (m^3 per tree)
Corymbia citriodora	19.1	19.1	0.277
Corymbia variegata	23.2	22.2	0.498
Corymbia henryi	23.2	22.7	0.502
Corymbia torelliana	17.9	15.8	0.222
Eucalyptus amplifolia	18.4	16.8	0.249
Eucalyptus longirostrata	18.0	20.2	0.281
Eucalyptus major	18.7	16.3	0.252
Eucalyptus urophylla	22.7	24.6	0.543

DBH: Diameter at breast height; CH: commercial height; CVb: commercial volume with bark.

The management practices applied to the different experiments were those adopted by the company Bracell for commercial species, as shown in Table 2.

Table 2. Management practices adopted in the experimental plantations of Eucalyptus and Corymbia, implanted in the city of Borebi, State of São Paulo, Brazil.

Practice	Description
Soil preparation	Subsoiling depth >0.45 m.
Ant control	Use of ant bait.
Weed control	Use of pre- and post-planting herbicide until canopy closure.
Mineral fertilization	Liming with dolomitic limestone.
Pre- and after- planting fertilization	Amount determined after soil chemical analysis.
Gel application or irrigation	Use of 2 to 4 liters of water per plant after planting

2.2. Physicochemical wood characterization

Two opposite wedges were used to determine the basic density of the wood according to the procedure of the Brazilian Standard NBR 11941 [16], in which the volume was measured by the water immersion method. To calculate the basic density, the arithmetic mean of all sampling positions was determined, according to the procedure used by [7].

The chemical and energy properties of the wood were determined in samples from all longitudinal sampling positions. The wood samples were transformed into sawdust using a Willey knife mill according to the TAPPI 257 om-52 standard [17]. Proximate chemical analysis of the wood was performed to determine the ash content based on the E1755-01 standard [18], volatile matter content according to the E872-82 standard [19], and the fixed carbon content was calculated using Equation 1. The same procedure was adopted by [7, 20, 21].

$$FC = 100 - (VM + ASH) \qquad (1)$$

Where FC = fixed carbon content of wood (% db); VM = wood volatile matter content (% db); and ASH = ash content of wood (% db).

The content of acetone-soluble extractives was determined based on the T280 pm-99 standard [17]. The insoluble lignin content was determined by the Klason method as recommended by [22]. The soluble lignin content was determined by UV spectroscopy as proposed by [23]. The total lignin content represents the sum of the soluble lignin content and the insoluble lignin content. The holocellulose content was calculated via Equation 2, procedure adopted by [7, 8]:

$$Holocelulose = 100 - (Lignin + \text{Extratives} + Ash) \qquad (2)$$

Lignin degradation, for subsequent determination of the syringyl/guaiacyl (S/G) ratio, was performed by the alkaline oxidation of the wood with nitrobenzene, followed by high-performance liquid chromatography for quantification of its derivatives, according to the method described by Lin and Dance [24] and adapted by Araujo et al. [25].

The higher heating value (HHV) of the wood was determined according to the E711-87 standard (ASTM 2004) using an adiabatic calorimetric pump, procedure used by [27]. Energy density was calculated using Equation 4, as recommended by [7]:

$$ED = \frac{(\text{BD } x \text{ HHV})}{1000} \qquad (4)$$

where ED is the energy density (GJ·m^{-3}), HHV is the higher heat value (MJ·kg^{-1}), and BD is the basic density (kg·m^{-3}).

2.3. Thermal analysis and kinetic parameters

The thermal analysis of the wood was performed on 4 mg of ground wood per sample, with a particle size smaller than 200 mesh to minimize problems related to heat transfer in the sample, in an inert atmosphere of high-purity nitrogen gas (N_2) (99.99%) at a flow rate of 60 mL·min^{-1}, and at final temperature of 600 °C. Heating rates of 10, 15, and 20 °C·min^{-1} were used. Data for mass loss and temperature up to 100 °C were disregarded when calculating the kinetic parameters, to reduce the influence of moisture on the activation energy, according to Setter et al. [28].

The activation energy was determined with Friedman's global reaction model (Equation 5) using mass loss, time, and temperature data. The Friedman model is more accurate than other global reaction models [29]. This method is the most direct way to evaluate the activation energy as a function of the conversion value (α), and it is assumed that the conversion function f(α) remains constant, which implies that biomass degradation is independent of temperature and depends only on the rate of mass loss [30]:

$$ln\frac{d\alpha}{dT} = \ln[f(\alpha)] + lnA - (\frac{E_a}{R})(\frac{1}{T}) \quad (5)$$

where dα/dt = reaction rate; α is the mass of volatiles released at time t; A = pre-exponential factor (min^{-1}); E_a = activation energy (kJ/mol); T = temperature (K); R = universal gas constant ($kJ \cdot mol \cdot K^{-1}$); and f(α) = reaction model

2.4 Data analysis

The experimental design used for the statistical analyses was a completely randomized design with eight treatments (species) and seven replicates (sample trees). The data were subjected to the Shapiro-Wilk ($p < 0.05$) and Bartlett tests ($p < 0.05$) to test the normality of the residuals and homogeneity of variances, respectively. The data showed normality, homogeneity of variance, and absence of residual autocorrelation.

Analysis of variance was performed at a significance level of 5% and was used to test the effect of species on the physical, chemical, energy, and thermal properties of wood. When there was a significant difference between species, the Scott–Knott univariate grouping test ($p \leq 0.05$) was applied. Subsequently, the species were grouped by principal component analysis (PCA). The PCA scores allowed us to group similar species according to their wood properties. For this multivariate analysis, the data were standardized into a correlation matrix to obtain the principal components (PCs). Variables with the greatest contributions to the PCs were identified based on their eigenvectors. Statistical analyses were performed in R® version 3.4.3 [31]

3. Results and Discussion

3.1 Wood basic density

It was observed differences among species on the basic density of wood, with the formation of four groups of species, each represented by a specific color (Fig. 1). *C. citriodora* and *C. henryi* (≥650 kg·m^{-3}) belong to group 1, *C. variegata*, *E. longirostrata*, and *E. major* (≥600 kg·m^{-3}) to group 2, *E. amplifolia* and *C. torelliana* (≥500 kg·m^{-3}) to group 3, and *E. urophylla* (<500 kg·m^{-3}) belongs to group 4. Species of the genus *Corymbia* had the highest mean wood basic density values except for *Corymbia torelliana.*

According to [32], wood is classified as having very low (200-300 kg·m^{-3}), low (300-500 kg m^{-3}), medium (500-750 kg·m^{-3}), high (750-1000 kg·m^{-3}), and very high density (>1000 kg m^{-3}). Traditionally, in Brazil *E. urophylla* is the main species used for energy and other purposes [4]. It had a low density when compared to the other species in this study, which had medium density.

To produce charcoal production used in the steel industry, the use of wood with basic density greater than 500 kg·m^{-3} is recommended due to its low specific consumption of wood during carbonization and results in denser charcoal [10]. In practice, a process with low specific wood consumption results in high productivity and volumetric yield of masonry ovens [33]. The carbonization of wood with high basic density results in denser charcoal and higher mechanical strength [34].Wood with high density ensures lower utilization of the useful volume and higher productivity of the burning equipment, gasifiers, and carbonization furnaces. Hence, the introduction of these species in the market would benefit the production of charcoal and energy cogeneration. In addition, these genetic materials may have less wood moisture content at the time of carbonization [35]. The carbonization of wood with lower moisture content results in higher gravimetric yield in charcoal [36].

The wood form *C. citriodora* (662 kg m^{-3}) and *C. henryi* (635 kg m^{-3}) and *C. variegata* (615 kg m^{-3}), *E. longirostrata* (605 kg m^{-3}), and *E. major* (608 kg m^{-3}) had higher wood density values as compared to commercial clones and hybrids of the same age assessed in different studied [6, 9, 10, 13, 37] ranging from 400 to 530 kg m^{-3}. In addition, *C. henryi* had an individual volume of 0.502 m^3.tree^{-1} (see Table 1). Due to its high basic density, the dry mass production would be higher than that of *E. urophylla.* The study of new species can generate changes in the production system, ensuring a better yield and quality of the final product.

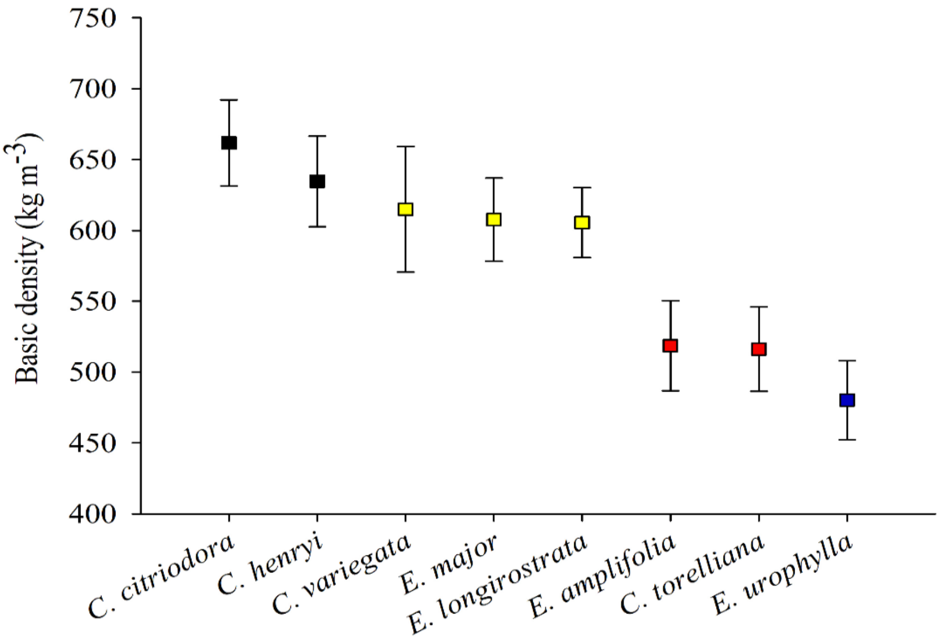

Figure 1. Classification of the genetic materials of *Eucalyptus* and *Corymbia* according to wood basic density. Different colors represent the groups of means according to the Scott-Knott test ($p \leq 0.05$) and error bars, the standard deviation.

3.2 Wood molecular chemistry and lignin monomeric composition

The mean total extractives, total lignin, holocellulose, syringyl unit (S), and guaiacyl unit (G) contents, and the S/G ratio were influenced by the species, according to the analysis of variance at 5% probability (Table 3). The extractives, total lignin, and holocellulose contents ranged from 1.03% (*E. urophylla*) to 4.56% (*C. torelliana*), 28.33% (*C. variegata*) to 34.25% (*E. major*), and 61.54% (*E. major*) to 69.07% (*C. henryi*), respectively.

As for the lignin composition and the S/G ratio, the variation in S units ranged from 1.38 mmol·L^{-1} (*C. torelliana*) to 1.71 mmol·L^{-1} (*E. urophylla*), and in G units from 0.47 mmol·L^{-1} (*C. henryi*) to 0.75 mmol·L^{-1} (*E. major*). The S/G ratio ranged from 2.20 (*E. major*) to 3.36 (*C. variegata*).

E. major stands out in almost all important quality characteristics to charcoal production for steel industry, especially when compared to *E. urophylla*, which is traditionally used in Brazil for this purpose. *E. major* showed high levels of extractives and total lignin, as well as low holocellulose content and S/G ratio. Wood with high lignin and extractive content, low S/G ratio, and a higher proportion of G units is prone to promote a high gravimetric yield in charcoal, in addition to better carbon and hydrogen balance during pyrolysis[7]. *C. torelliana* and *E. amplifolia* also have characteristics suitable for charcoal production, while the other species have low lignin content and high S, high holocellulose, and a high S/G ratio, characteristics that favour its use for energy cogeneration or for heating due to their high reactivity during combustion, which ensures lower specific consumption of firewood during heating.

Table 3. Mean molecular chemistry parameters and lignin monomeric composition values of the wood species evaluated.

Species	Molecular chemistry (% db)			Lignin monomeric composition		
	Extractives	Total Lignin	Holocellulose	S	G	S/G
C. citriodora	$3.22^{\pm0.77}$c	$29.64^{\pm1.09}$a	$66.57^{\pm1.79}$c	$1.67^{\pm0.09}$b	$0.54^{\pm0.04}$b	$3.12^{\pm0.30}$c
C. variegata	$2.51^{\pm0.92}$b	$28.56^{\pm1.61}$a	$68.24^{\pm1.64}$d	$1.61^{\pm0.13}$b	$0.48^{\pm0.05}$a	$3.36^{\pm0.35}$c
C. henryi	$2.04^{\pm0.68}$b	$28.33^{\pm1.35}$a	$69.07^{\pm1.87}$d	$1.47^{\pm0.09}$a	$0.47^{\pm0.03}$a	$3.12^{\pm0.34}$c
C. torelliana	$4.56^{\pm1.06}$d	$29.01^{\pm1.62}$a	$65.58^{\pm2.36}$c	$1.38^{\pm0.05}$a	$0.59^{\pm0.02}$b	$2.36^{\pm0.13}$a
E. amplifolia	$2.60^{\pm0.58}$b	$32.96^{\pm1.57}$c	$64.03^{\pm1.64}$b	$1.41^{\pm0.11}$a	$0.51^{\pm0.05}$a	$2.79^{\pm0.22}$b
E. longirostrata	$4.25^{\pm0.73}$d	$30.89^{\pm1.21}$b	$64.59^{\pm1.28}$b	$1.54^{\pm0.17}$b	$0.47^{\pm0.06}$a	$3.33^{\pm0.37}$c
E. major	$3.83^{\pm0.93}$c	$34.25^{\pm0.87}$d	$61.54^{\pm0.61}$a	$1.64^{\pm0.20}$b	$0.75^{\pm0.11}$c	$2.20^{\pm0.20}$a
E. urophylla	$1.03^{\pm0.52}$a	$32.12^{\pm1.30}$c	$66.66^{\pm1.17}$c	$1.71^{\pm0.12}$b	$0.54^{\pm0.05}$b	$3.16^{\pm0.19}$c

S: syringyl and G: guaiacyl. Different lowercase letters in the columns indicate significant differences according to the Scott-Knott test ($p \leq 0.05$). Means ± Standard deviation.

3.3. Proximate composition and energy productivity

In general, the species used in this study had a low ash content (<1%), with average ranging from 0.19% (*E. urophylla*) to 0.85% (*C. torelliana*). However, the species of the genus *Corymbia* had more than 0.50% of mean ash content and thus lower mean HHV (~19 MJ·kg^{-1}), while the *Eucalyptus* species had higher HHV (~20 MJ·kg^{-1}) (Table 4).

Considering the genetic materials studied, *E. amplifolia*, *E. major*, and *C. torelliana* had, on one hand, the lowest volatile contents (≤85%) and consequently the highest fixed carbon contents (>13%), associated with their lower S/G ratios (< 3.00), therefore, they show potential for charcoal production. On the other hand, *C. citriodora*, *C. variegata*, *C. henryi*, *E. longirostrata*, and *E. urophylla* had a higher volatile contents and S/G ratios, thus, the wood of these species would be appropriate for the production of firewood and chips for the generation of heat and electricity (cogeneration).

Despite the significant difference observed in the HHV, *C. citriodora*, *C. variegata*, *C. henryi*, *E. longirostrata*, and *E. major*, species with high basic density (≥600 kg·m^{-3}), showed similar energy densities, while *E. urophylla*, with a lower basic density, had the lowest energy density (9.45 GJ·m^{-3}). These results are in line with [38] findings, who showed that the basic density is the characteristic that most affects the energy density of wood.

Table 4. Mean immediate chemistry and energy productivity parameter values of species of the genera *Eucalyptus* and *Corymbia*.

Species	Proximate composition (%)			Energy productivity	
	Ashes	Volatile materials	Fixed carbon	HHV (MJ·kg^{-1})	ED (GJ·m^{-3})
C. citriodora	$0.57^{\pm0.12}$c	$88.01^{\pm0.88}$d	$11.42^{\pm0.82}$a	$19.22^{\pm0.11}$a	$12.51^{\pm0.65}$c
C. variegata	$0.68^{\pm0.13}$c	$87.87^{\pm0.81}$d	$11.45^{\pm0.77}$a	$19.54^{\pm0.09}$b	$12.12^{\pm0.60}$c
C. henryi	$0.56^{\pm0.16}$c	$87.14^{\pm0.73}$c	$12.30^{\pm0.86}$ b	$19.28^{\pm0.20}$a	$12.05^{\pm0.95}$c
C. torelliana	$0.85^{\pm0.24}$d	$85.32^{\pm0.77}$b	$13.83^{\pm0.94}$ c	$19.57^{\pm0.21}$b	$10.11^{\pm0.58}$b
E. amplifolia	$0.41^{\pm0.10}$b	$84.44^{\pm1.01}$a	$15.15^{\pm0.80}$d	$20.03^{\pm0.17}$c	$10.39^{\pm0.65}$b
E. longirostrata	$0.27^{\pm0.08}$a	$87.09^{\pm0.87}$c	$12.64^{\pm1.02}$ b	$19.65^{\pm0.23}$b	$11.81^{\pm0.50}$c
E. major	$0.38^{\pm0.09}$b	$85.52^{\pm0.97}$b	$14.10^{\pm0.36}$ c	$20.33^{\pm0.12}$d	$12.25^{\pm0.63}$c
E. urophylla	$0.19^{\pm0.05}$ a	$87.97^{\pm0.34}$d	$11.84^{\pm0.96}$a	$19.68^{\pm0.53}$b	$9.45^{\pm0.57}$a

HHV: higher heat value; ED: energy density; Different lowercase letters in the columns indicate significant differences according to the Scott-Knott test ($p \leq 0.05$). Means ± Standard deviation.

3.4. Thermal decomposition and activation energy

The derivative thermogravimetric (DTG) curves at each heating rate in an inert atmosphere are shown in Figures 2 and 3, respectively, for *Corymbia* and *Eucalyptus* genus. The active stage of pyrolysis, i.e., the main degradation stage for both biomass samples, occurred similarly through the depolymerization reaction, which was responsible for approximately 70-73% of the mass loss. The temperature range in which the main pyrolysis stage occurred was between ~170 °C and 400 °C, which corroborates the temperature range of thermal degradation of the structural chemical constituents of lignocellulosic material, mainly hemicelluloses and cellulose. Among the chemical components, hemicelluloses are the least thermally stable (220-315 °C), followed by cellulose (315-400 °C) and lignin. The latter, despite starting to degrade near 160 °C, decomposes slowly up to ~900 °C [39].

The DTG curves for the intermediate heating rate (15 °C/min) and the lowest heating rate (10 °C/min) showed an medium peak at temperatures close to 280 °C (Fig. 2, arrow) and 270 °C (Fig. 2, arrow), possibly indicating the degradation of hemicelluloses. Kumar Mishra and Mohanty[40] evaluated the thermal behavior of different lignocellulosic biomasses and observed small peaks at temperatures ranging from 219 °C to 278 °C, which they attributed to the degradation of hemicelluloses.

The DTG profiles also demonstrated the influence of the heating rate on the shift of the curves to higher temperatures. For example, for *C. variegata*, the maximum mass loss rates were reached at temperatures close to 272 °C, 335 °C, and 327 °C for the heating rates of 10 °C/min, 15 °C/min, and 20 °C/min, respectively. The same behaviour was observed for the genus *Eucalyptus*. For example, the maximum mass loss rates for *E. major* were close to 277 °C, 313 °C, and 336 °C at the heating rates of 10 °C/min, 15 °C/min, and 20 °C/min, respectively. This shift of the DTG curves to higher temperatures as the heating rate increases is known as thermal lag [41]. At lower heating rates, the heat transfer between the biomass particles tends to be more effective. In contrast, at higher heating rates, there is usually a temperature gradient between the inner and outer part of the particles. Therefore, it is likely that there are differences in the degradation profile between a sample subjected to a high heating rate and one subjected to a low heating rate, since the degradation kinetics do not allow the completion of reactions at higher heating rates [42].

The rate of thermal decomposition increased with the heating rate, and the DTG peaks became broader and greater in magnitude. High heating rates favour rapid matter devolatilization [43], which contributes to the release of gases. In contrast, low heating rates prolong the residence time, which contributes to the medium release of volatile matter, so that secondary reactions can occur, contributing to the formation of charcoal [42]. Thus, at low heating rates, it was possible to specifically detect the degradation of hemicelluloses, while at higher heating rates, there was overlap of the thermal decomposition of the cell wall structural carbohydrates, intensely and with greater reactivity, resulting in greater devolatilization.

It was not possible to specifically detect the medium peak of the degradation of hemicelluloses in *C. torelliana* or *E. major*. This may have been associated with the high extractive contents and low S/G ratios observed in these species. Most likely, the hemicelluloses and the S units of lignin were degraded simultaneously, which did not allow the detection of this stage. At low temperatures, β-O-4 bonds in lignin break [44], and wood with high proportions of S units in the lignin macromolecule shows intense degradation in the temperature range between 150 and 300 °C during pyrolysis [45].

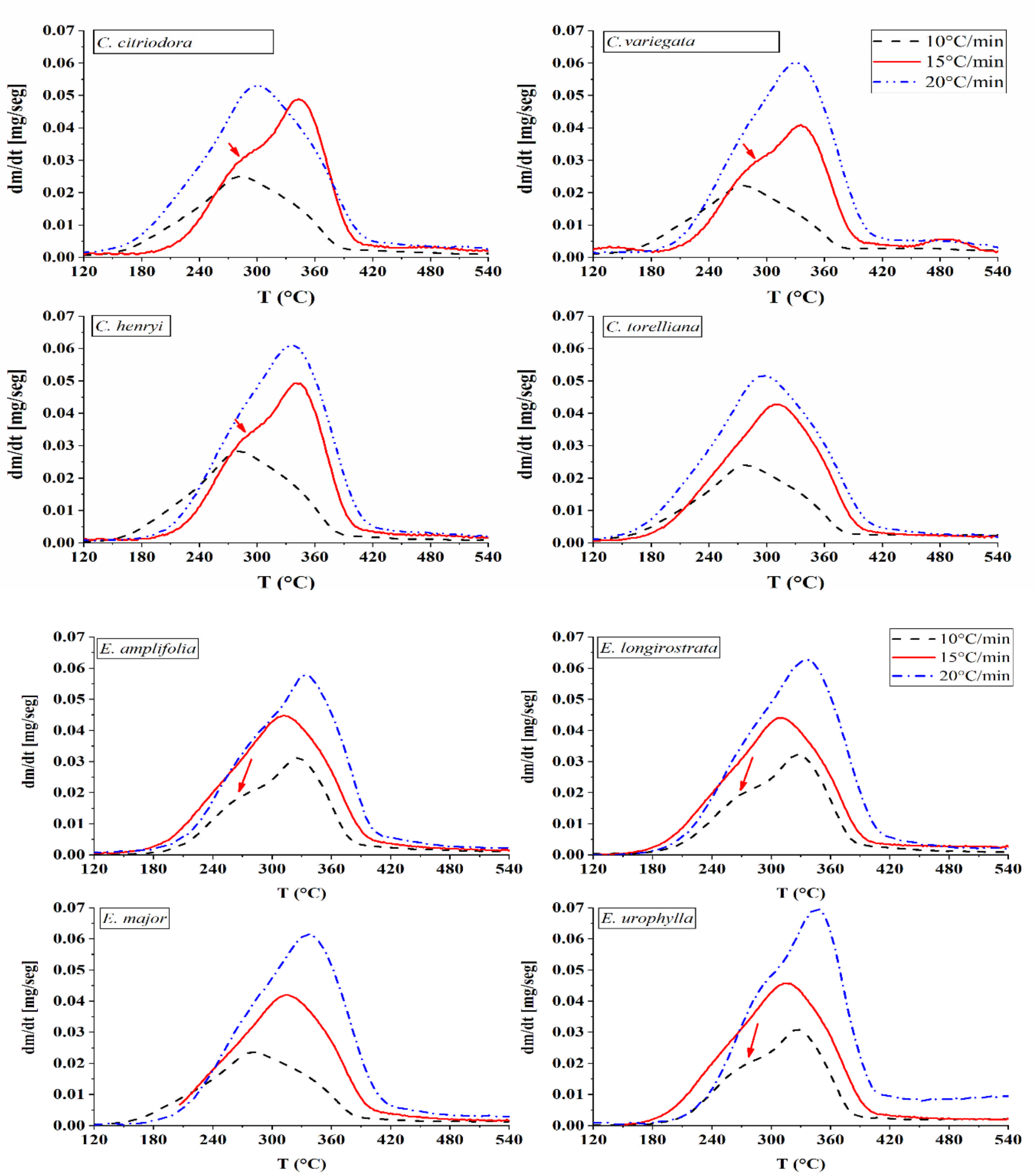

Figure 2. Mass fraction derivatives as a function of temperature for the pyrolysis at heating rates of 10, 15 and 20 °C/min

The activation energy was calculated from the linear regressions obtained by Friedman's global reaction model, with a conversion interval of 0.05 to 0.60 for the different species studied. The Friedman method showed a correlation coefficient (R^2) varying between 0.85 and 1.00 (see R^2 and the linearizations in the supplementary material), so it can be inferred that the model was reliable in its calculation of the activation energy (Fig. 3).

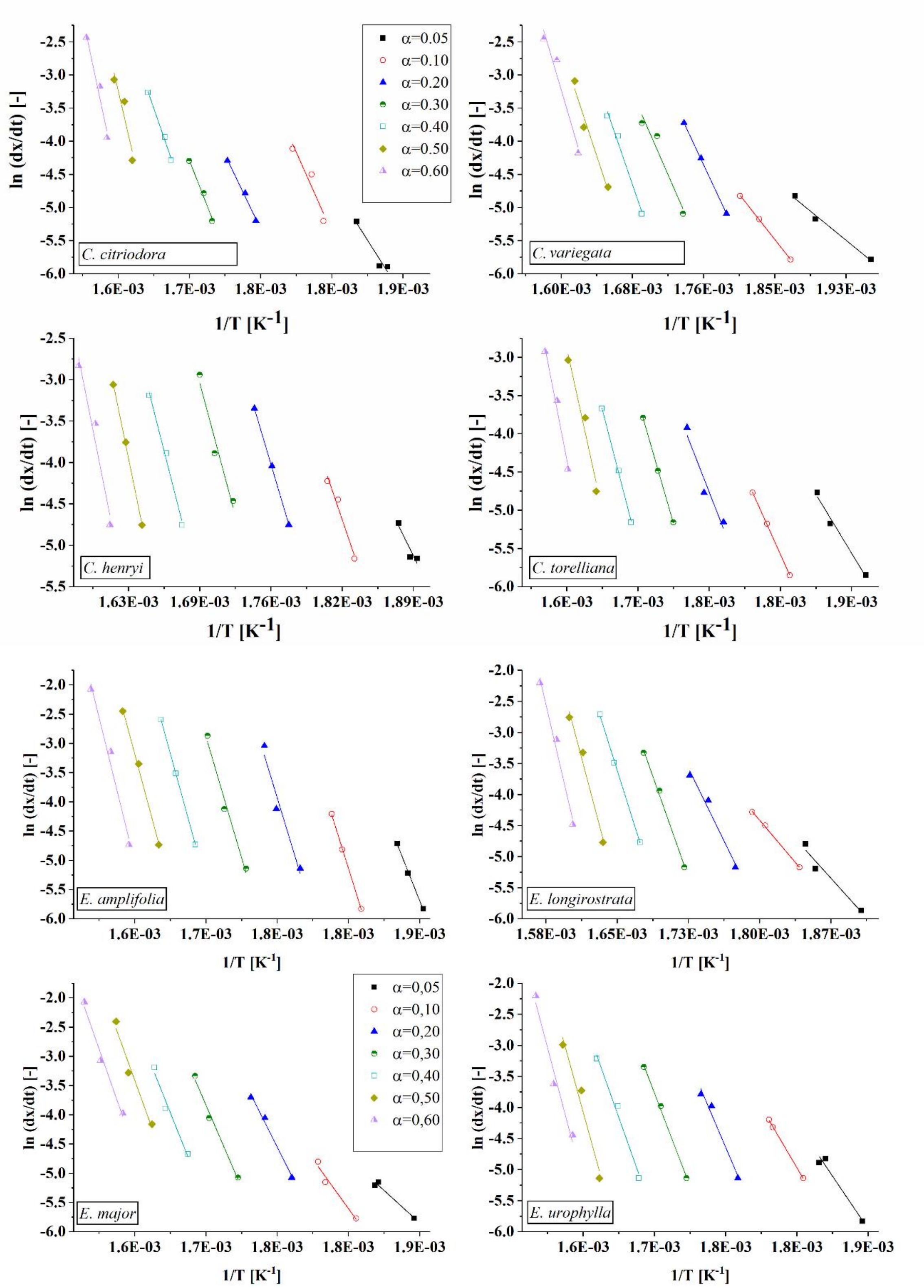

Figure 3. Linear regression for the estimation of the kinetic parameters of wood pyrolysis.

The results showed that the activation energy increased as a function of the degree of conversion for all studied woods (Table 5). At the beginning of the biomass conversion process, the activation energy values are lower due to the breaking of weaker hemicelluloses [28].

Weaker bonds are generally broken at lower temperatures, whereas stronger bonds are broken at higher temperatures, which requires more energy [46].

The lowest mean activation energy value was 247 $kJ \cdot mol^{-1}$ (*C. variegata*), while the mean highest value was 468 $kJ \cdot mol^{-1}$ (*E. amplifolia*). Woods with a high extractive content, high holocelulose content and low S/G ratio tended to have lower activation energy, but with a small variation with the degree of conversion. Woods with a higher S/G ratio, which thus have lignin with a less condensed structure, will result in greater reactivity and require less energy for conversion into charcoal. Lignocellulosic biomass is a heterogeneous material; therefore, each chemical component has a given degradation temperature range, which affects the activation energy variation and heating rates [40].

It is difficult to compare the activation energy values with other data from the literature, since substantial variations in the kinetic data for the same type of biomass were found [30]. These variations in activation energy may be attributed to the physical and chemical heterogeneity of the biomass [47]. Despite the variations, the values found in this study are consistent with the range of values reported in the literature for different lignocellulosic biomasses, such as wood [48], coffee husk [28], and *pequi* peel [49].

Table 5. Activation energy calculated by the Friedman global reaction model in conversion intervals from 0.05 to 0.60.

Species	Conversion (α)							Mean Ea
	0.05	0.10	0.20	0.30	0.40	0.50	0.60	
	Ea ($kj.mol^{-1}$)							
C. citriodora	$196^{\pm 98}$	$256^{\pm 101}$	$301^{\pm 95}$	$337^{\pm 88}$	$363^{\pm 91}$	$446^{\pm 76}$	$507^{\pm 92}$	$344^{\pm 92}$
C. variegate	$88^{\pm 3}$	$144^{\pm 19}$	$221^{\pm 21}$	$256^{\pm 24}$	$299^{\pm 27}$	$327^{\pm 11}$	$396^{\pm 43}$	$247^{\pm 21}$
C. henryi	$217^{\pm 16}$	$283^{\pm 37}$	$332^{\pm 36}$	$390^{\pm 23}$	$413^{\pm 35}$	$497^{\pm 72}$	$551^{\pm 34}$	$383^{\pm 36}$
C. torelliana	$214^{\pm 47}$	$268^{\pm 52}$	$325^{\pm 66}$	$395^{\pm 54}$	$466^{\pm 81}$	$514^{\pm 63}$	$569^{\pm 62}$	$393^{\pm 61}$
E. amplifolia	$321^{\pm 77}$	$394^{\pm 120}$	$425^{\pm 78}$	$478^{\pm 59}$	$511^{\pm 89}$	$547^{\pm 79}$	$599^{\pm 100}$	$468^{\pm 86}$
E. longirostrata	$178^{\pm 64}$	$240^{\pm 86}$	$287^{\pm 40}$	$337^{\pm 45}$	$379^{\pm 62}$	$412^{\pm 79}$	$460^{\pm 112}$	$328^{\pm 70}$
E. major	$143^{\pm 12}$	$231^{\pm 27}$	$297^{\pm 27}$	$337^{\pm 25}$	$359^{\pm 24}$	$410^{\pm 38}$	$448^{\pm 43}$	$318^{\pm 28}$
E. urophylla	$240^{\pm 46}$	$275^{\pm 66}$	$354^{\pm 37}$	$398^{\pm 63}$	$428^{\pm 71}$	$498^{\pm 69}$	$520^{\pm 22}$	$388^{\pm 53}$

Ea: activation energy. Means ± Standard deviation.

3.5. Multivariate clustering of species

The PCA revealed that three components explained 84.30% of the variability in the data (Table 6). The variables that most influenced the formation of the principal components (PC) were 1 – holocellulose and total lignin contents, HHV, S/G ratio, fixed carbon content, and volatile matter content; 2 – basic density, energy density, S and G monomers; and 3 – basic density, energy density, extractives content in acetone, S monomer, ash content, and volatile matter content. The basic density and total lignin content influenced the three principal components, which reinforced the finding that these were the best indices for wood quality for energy purpose. These characteristics influence the selection of genetic materials that have higher rate of CO_2 conversion into biomass, and this certainly will help yield a favourable carbon balance in the conversion of lignocellulosic feedstock into energy.

Table 6. Eigenvectors associated with the first three principal components.

Property	PC1	PC2	PC3
Basic density	-0.193	**-0.338**	**-0.341**
Energy density	-0.131	**-0.395**	**-0.333**
Activation energy	0.202	**0.424**	0.137
Extractives	0.156	-0.123	**-0.450**
Guaiacyl Monomer	0.285	**-0.313**	-0.050
Holocellulose	**-0.363**	0.258	-0.003
Total lignin	**0.321**	-0.236	0.296
Higher heating value	**0.359**	-0.204	0.121
S/G ratio	**-0.351**	0.036	0.194
Syringyl monomer	-0.142	**-0.433**	**0.336**
Fixed carbon content	**0.386**	0.135	-0.110
Ash content	-0.071	0.194	**-0.499**
Volatile matter content	**-0.371**	-0.165	0.187

PCA resulted in a formation of four groups, and the dispersion of the genotypes evaluated as a function of the scores obtained in the PCA (Fig. 4). Group 1 was composed only by *E. urophylla*; group 2: *C. citriodora citriodora*, *C. citriodora variegata*, *C. henryi*, and *E. longirostrata*, group 3: *E. major*, and group 4: *C. torelliana* and *E. amplifolia*. The species were grouped according to the physical, chemical, and energy properties of their wood to differentiate their quality and end use.

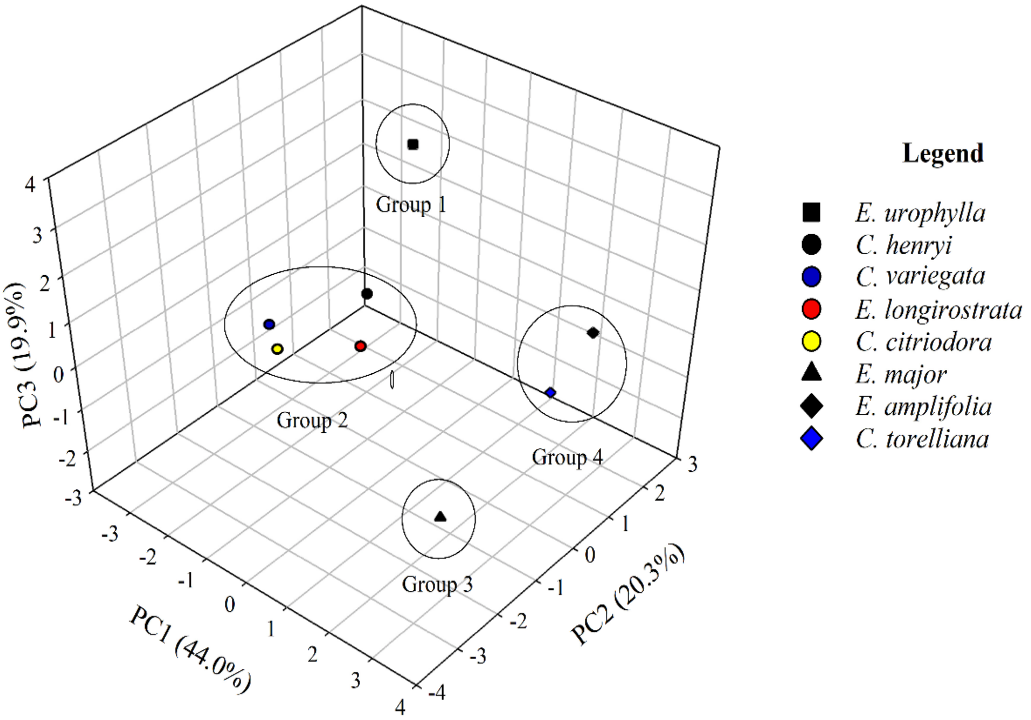

Figure 4. Graph of the scores of the principal component analysis of the properties of the genetic materials.

Group 3, composed only of *E. major*, had high basic density, energy density, extractive content, fixed carbon content, and HHV. In contrast, it had a low S/G ratio, activation energy, and volatile matter content values. This wood properties are considered as major economic characteristics affecting the forest stand productivity and subsequently the management profitability [50]. Harvesting wood with high basic density maximize fuel economy and harvesting rate [51]. The high wood basic verified on the species can reduce the cost of transport on to same volume of wood. The use of this genetic material in manufacturing plants producing charcoal, due to its high basic and energy densities, can result in high charcoal volumetric yield per oven and high energy productivity. Its high lignin content and low S/G ratio stand out as characteristics that ensure a high gravimetric yield in charcoal [25, 45], and its low activation energy ensures energy savings during carbonization [28]. This species should be used in the production of charcoal on an industrial scale because of the yield and energy savings it will bring, directly affecting the revenues of the charcoal production unit. Contrasting results were observed for group 1, where *E. urophylla* belongs. In Brazil, this species is already commercially used for energy purposes. Thus, the selected species have the potential to be competitive in the charcoal market for the steel sector, of which *E. major* is the most suitable for this purpose and for future hybridization projects aimed at improving the energy quality of forest biomass and ensuring economic benefits.

Group 2 showed interesting wood properties for use in direct combustion, cogeneration or charcoal production for domestic use due to the high density, holocellulose content, volatile matter content, and S/G ratio. The high volatile matter content and S/G ratio suggest high reactivity for these species, which is an important characteristic for the direct combustion [6, 7]. Group 4 could be used in charcoal production due to its low S/G ratio, high lignin content, and high extractive content. However, these species have lower volumetric growth, low basic density, and high activation energy.

This grouping can also benefit future hybridization projects of these species to improve energy quality. Crossbreeding between *C. torelliana*, and other *Coymbia species* (*C. citriodora*, *C. variegata*, and *C. henryi)*, and crossbreeding of *E. urophylla* (the main species of actual clones) with *E. longirostrata*, and *E. major*, all high-density species, may lead to superior-quality clones for use in a sustainable steel industry.

4. CONCLUSIONS

All study species have the potential to be competitive in the charcoal market. The *E. major* is the most suitable for sustainable use in the steel industry, with properties that favour the production of high quality charcoal, high gravimetric yield, and energy savings during the carbonization process. The other evaluated species present satisfactory performance for the production of biomass suitable for combustion, cogeneration and production of charcoal for domestic use. Nevertheless, these species can undergo an improvement program aiming at the generation of progenies adapted to the energy demands on an industrial scale. Future studies are needed under different agroecological conditions to understand the phenotypic plasticity of the species at different cutting ages. Moreover, there is a need for studies with new genetic materials still in the improvement phase for the generation of new progenies adapted to industrial-scale bioenergy demands.

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5. DECLARATIONS

Authors' contributions

Jonas Massuque: conceptualization, method, research, formal analysis, writing of the original draft. **José Yony Sima Cricel Sanchez and Breno Assis Loureiro:** research, writing and editing. **Carine Setter and Michael Douglas Roque Lima:** formal analysis, writing and editing. **Paulo Henrique Müller da Silva:** acquisition of funds and resources, writing and editing. **Thiago de Paula Protásio**: writing and editing. **Paulo Ricardo Gherardi Hein:** supervision, validation, writing and editing. **Paulo Fernando Trugilho:** conceptualization, method, supervision, validation, writing, acquisition of funds and resources.

Availability of data and materials

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

Ethics approval and consent to participate

Compliance with ethical standards

Consent for publication

All authors have consent for publication

Competing interests

The authors declare that they have no conflict of interest

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ARTIGO 2 (VERSÃO PRELIMINAR): POTENTIAL OF CHARCOAL FROM NON-COMMERCIAL *Corymbia* AND *Eucalyptus* WOOD FOR USE IN THE STEEL INDUSTRY

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ABSTRACT

The search for species that produce high-quality charcoal is necessary to reduce the use of non-renewable sources of energy in the steel industry. Therefore, the present study aimed to evaluate the charcoal quality of new and non-commercial species in Brazil. Eight species of *Corymbia and Eucalyptus* were sampled and analysed. The gravimetric yields of the carbonization, proximate and ultimate analysis, apparent density (AD) and energy density (ED), higher heating value (HHV), ignition (Di), and combustion (Si) indexes were determined. Non-commercial species, especially *C. variegata, E. longirostrata, E. major, C. henryi,* and *C. citriodora*, have a great potential for use and dissemination on an industrial scale. These species are competitively promising for producing charcoal for the steel industry when compared to the commercial species, for example *E. urophylla*, since they produce low reactivity charcoal (Si ~3 x10^7 $\%^2$ min^{-2} °C^{-3}), high energy (>13 MJ m^{-3}) and apparent density (>400 kg m^{-3}).

Keywords: Bioenergy, steel bioreducer, charcoal combustibility, energy productivity

1. Introduction

Brazil is the only country in the world where the use of charcoal for iron reduction is competitive [1]. It is estimated that the use of charcoal in the steel industry reduced net CO_2 emissions by 0.5t to 0.1t of CO_2/t of steel produced [2], which corresponds to 65% of the total Brazilian steel industry emissions [3].

Unlike fossil fuels, charcoal is an environmentally friendly resource, as it has a neutral balance in carbon emissions and has lower CO_2, NO_X, and SO_2 emissions, which makes it beneficial for the environment [4]. In addition to mitigating climate change, the use of charcoal in the steel industry has latent potential for the circular economy [3].

However, the steel industry in Brazil is mostly dominated by the use of coke. Charcoal accounts for approximately 20% of the production [5]. Quality differences with regards to density, porosity, reactivity, and combustibility are determining characteristics for the prevalence of fossil fuels. Coke has low reactivity, high density, and mechanical strength when compared to charcoal [6].

Brazil stands out for producing charcoal mainly from energetic plantations with *Eucalyptus grandis* and *E. urophylla* clones and their low-density hybrids. Currently, the major challenge is to find genetic materials with high basic density wood that produce high quality charcoal for steel industry [7,8]. The higher the charcoal apparent density, the higher the energy density [9], the fixed carbon content by volume, the compressive strength [10], and the rigidity [11]. Recently[12], found that *Eucalyptus* clones with DBH ≥15.1 cm, wood basic density ≥560 kg m^{-3}, and gravimetric yield ≥35% dry basis provided low specific consumption (<5.1 m^3 t^{-1}), increased brick kilns productivity, and resulted in denser charcoals (380 kg m^{-3}). Thus, the genus *Corymbia* has a great potential to produce charcoal for the steel industry due to its high density and high volumetric productivity [8,13].

The search for species that produce high quality charcoal is necessary to increase the competitiveness of charcoal and reduce the use of non-renewable sources in the steel industry. As a result, new and non-commercial species are being introduced in Brazil by the project *'Espécies Potenciais'* under the Corporate Forest Improvement Program from the Research and Forestry Studies Institute (IPEF) [14,15]. In line with this program, the present research aims to evaluate the quality and combustion behaviour of the charcoal produced from wood species with high volume productivity. These species are not yet commercially planted, but have the potential to be used in the steel industry.

2. Material and Methods

2.1. Genetic material and sampling

The genetic materials are 6-year age *Eucalyptus* and *Corymbia* experimental plantation under *Corporate Forest Improvement Program ('Espécies Potenciais' project)* from the Research and Forestry Studies Institute (IPEF), installed at 3.0 m x 2.6 m spacing, located in the municipality of Borebi, state of São Paulo, at latitude 28º 48' and longitude 48º 54' and altitude of 711 m. The Project *'Espécies Potenciais'*, consists of an experiment established in rectangular plots of 7 x 7 plants, with 4 species of the genus *Corymbia* and 15 species of the genus *Eucalyptus.* However, eight species that presented better adaptability were selected, namely: *Corymbia citriodora* var. *citriodora, Corymbia citriodora* var. *variegata, C. henryi, C. torelliana*, *Eucalyptus amplifolia*, *E. longirostrata*, *E. major,* and *E. urophylla.* Seven trees per species were selected, and 2.5cm-thick discs were removed in the longitudinal positions of 0% (Base), DBH (1.30m), 25%, 50%, 75%, and 100% of the commercial height of the trees, considered up to the minimum diameter of 4 cm including the bark.

2.2. Wood carbonization

The carbonizations in the laboratory were carried out in an electric muffle furnace (model Q318S25T, Quimis, São Paulo, Brazil), using a metal carbonization capsule connected to the water-cooled condenser, which is coupled to the condensable gas collection flask. Opposite wedges were used from all longitudinal positions of the tree sample, previously kiln-dried at 103±2 ºC. The initial and final carbonization temperatures were 100 °C and 450 °C, respectively. The heating rate used was 1.67 $^{\circ}C.min^{-1}$ ($100^{\circ}C.h^{-1}$) with a residence time of 30 minutes at maximum temperature. The same procedure has been reported in the literature by [12,16,17].

2.3. Charcoal quality and yield evaluation

After the carbonization, the gravimetric yields of charcoal, condensed pyroligneous liquid, non-condensable gases, and fixed carbon were calculated, based on equations 1, 2, 3, and 4.

$$CGY = \frac{DMC}{DMW} \text{ x } 100 \quad (1)$$

$$PLY = \frac{MPL}{DMW} \text{ x } 100 \quad (2)$$

$$NCGY = 100 - (CGY + PLY) \quad (3)$$

$$FCY = \frac{CGY \text{ x } FCC}{100} \quad (4)$$

where: CGY is the charcoal gravimetric yield (%, dry basis); DMC is the dry mass of charcoal (g); DMW is the dry mass of wood; PLY is the pyroligneous liquid yield (%, dry basis); MPL is the mass of pyroligneous liquid (g); NCGY is the non-condensable gases yield (%, dry basis); FCY is the fixed carbon yield (%, dry basis); and FCC is the fixed carbon content of the charcoal (%, dry basis).

The energy efficiency of transforming wood into charcoal was obtained based on Equation 5.

$$EE = \frac{HHVc}{HHVw} \text{ x } \frac{CGY}{100} \tag{5}$$

Where EE is the energy efficiency (%); HHVc is the higher heating value of charcoal (MJ kg^{-1}); GCY is the gravimetric charcoal yield (%); HHVw is the higher heating value of wood (MJ kg^{-1});

The charcoal apparent density (CAD) produced in the laboratory was determined according to the NBR 11941 standard [18]. Adaptations were made with regards to the time the charcoal sample remained in immersion (30 min), charcoal drying time (24 h) at room temperature (± 28 °C) after immersion, and the oven drying time (103 ± 2 ◦C for 2 h). Same procedure was used by [16,19]

The proximate analysis was performed in duplicate based on the D1762−84 standard [20], for volatile materials and ash determination. The fixed carbon content was calculated as shown by Equation 6.

$$FCC = 100 - (VMC + AC) \tag{6}$$

Where FCC is the fixed carbon content (% dry basis), VMC is the volatile matter content (% dry basis), and AC is the Ash content (% dry basis).

The charcoal higher heating value (HHVc) was determined according to the E711-87 standard (ASTM 2004) and energy density according to Equation 7.

$$ED = \frac{CAD \text{ x } HHVc}{1000} \tag{7}$$

Where ED is the energy density (GJ m^{-3}), CAD is apparent density of charcoal (kg m^{-3}), and HHVc is the higher heating value of charcoal (MJ kg^{-1}).

The ultimate composition, performed on an Elementar universal analyzer (Vario Micro Cube model), allowed the quantification, based on dry wood mass, of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents. The samples were ground and sieved, and the fraction that was retained between the 60 mesh and 200 mesh sieves was used for the analysis. The samples were previously dried in an oven set at 103±2°C. The oxygen value was quantified according to Equation 8. The H/C and O/C ratios were calculated using Equations 9 and 10, respectively.

$$O = 100 - (C + H + N + S + AC) \tag{8}$$

$$H/C = {}^{(H/1)}\!\big/_{(C/12)} \tag{9}$$

$$O/C = {}^{(O/16)}\!\big/_{(C/12)} \tag{10}$$

where H is the hydrogen (%); C is the carbon (%); N is the nitrogen (%); S is the sulfur (%); O is the oxygen (%); AC is the Ash content (% dry basis)1, 12, 14, and 16 correspond to the atomic mass of H, C, N, and O, respectively.

2.4 Charcoal combustion using thermogravimetry

For thermal analysis of charcoal, the heating rate was 10 ºC.min^{-1}, initial ambient temperature to the final temperature of 800 °C, in synthetic air (20±5% of oxygen and 80±5 % nitrogen), with a flow rate of 100 mL.min^{-1}, using mass of 4 mg per sample with granulometry less than 200 mesh. This same procedure was adopted by [22].

As suggested by [23],the ignition temperature (Ti), ignition time (tig), and final combustion temperature (Tb) were determined through the first derivative of thermogravimetric curve (DTG). The ignition temperature (Ti) and ignition time (tig) are defined as the temperature and time at which the combustion rate rises to 1 wt %. min^{-1} at the start combustion, respectively, and burnout temperature (Tb) is defined as the temperature at which the combustion rate diminishes to 1 wt %. min^{-1} at the end of combustion process. In addition, the ignition index (Di) and the combustion characteristic index (Si) were used to evaluate the combustion performance and the reactivity of charcoal, according to Equations 11 and 12.

$$Di = (dm/dt)max\ /(tp \text{ x } tig) \tag{11}$$

$$\text{Si} = ((dm/dt)max \text{ x } (dm/dt)av\ )/(Ti \text{ x } Tb) \tag{12}$$

where (dm/dt)max is the maximum combustion rate (% min^{-1}); (dm/dt)av is the average rate of combustion; tig is the ignition time; Ti is the ignition temperature (°C), tp is the time corresponding to the maximum combustion rate; and Tb is the final combustion temperature (°C).

2.5 Lignin quantification

Insoluble lignin content was determined by the Klason method, according to the procedure recommended by [24]. The soluble lignin content was determined by UV spectroscopy, according to the procedure proposed by [25]. The total lignin content represents the sum of the soluble and insoluble lignin contents. The degradation of lignin, for later determination of the S/G ratio, was carried out by the method of alkaline oxidation of wood with nitrobenzene, followed by high performance liquid chromatography (HPLC) to quantify its derivatives, according to the methodology described in [26].

2.6 Data analysis

A completely randomized design was used for the statistical analysis, with eight treatments (species) and seven replications (sampled trees). Data were submitted to Shapiro-Wilk, Durbin-Watson, and Bartlett tests to verify the residual normality, residual autocorrelation, and homogeneity of variances, respectively, and these three assumptions were met ($p < 0.05$). The Scott-Knott univariate cluster test ($p \leq 0.05$) was applied to test the effect of species on charcoal properties. Subsequently, the species were grouped through the principal components analysis (PCA). PCA scores allow to assess the similarity between species and to discriminate which variables are most important in the identification of groups. Variables with the highest contributions to the principal components (PC) were identified based on the eigenvectors.

3. Results and Discussion

3.1. Mass balance and energy efficiency

The species significantly influenced the charcoal gravimetric yield (CGY), pyroligneous liquid gravimetric yield (PLY), non-condensable gases gravimetric yield (NCGY), and fixed carbon yield (FCY) (Table 1). The highest mean values of CGY were observed in *E. amplifolia* (36.42%) and *E. major* (35.49%) (Table 1). This yield is higher than that of commercial *Eucalyptus* clones studied by [12,27]. The lowest PLY was from *E. amplifolia* (43.79%). The species that had the lowest NCGY averages were *E. urophylla* (17.64%), *C. torelliana* (17.70%), *E. longirostrata* (18.23%), *C. citriodora* (18.39%) and *E. major* (18.66%), while *E. amplifolia* (26.77%) and *E. major* (26.49%) had the highest FCY.

Table 1. Mass balance of the carbonization process

Species	CGY(%db)	PLY(%db)	NCGY(%db)	FCY(%db)
C. citriodora	$33.50^{\pm1.16}$b	$48.11^{\pm1.54}$b	$18.39^{\pm.0.85}$a	$24.73^{\pm1.04}$a
C. henryi	$32.40^{\pm0.58}$a	$48.02^{\pm1.20}$b	$19.58^{\pm1.46}$b	$24.29^{\pm0.48}$a
C. torelliana	$34.68^{\pm0.39}$c	$47.62^{\pm0.77}$b	$17.70^{\pm0.73}$a	$25.60^{\pm0.38}$b
C. variegata	$32.74^{\pm0.91}$a	$47.97^{\pm1.21}$b	$19.29^{\pm1.13}$b	$24.05^{\pm0.54}$a
E. amplifolia	$36.42^{\pm0.59}$d	$43.79^{\pm1.66}$a	$19.79^{\pm1.60}$b	$26.77^{\pm0.37}$c
E. longirostrata	$33.33^{\pm0.32}$b	$48.44^{\pm0.93}$b	$18.23^{\pm0.76}$a	$25.07^{\pm0.49}$b
E. major	$35.49^{\pm0.60}$d	$45.84^{\pm1.75}$b	$18.66^{\pm2.04}$a	$26.49^{\pm0.32}$c
E. urophylla	$34.94^{\pm0.79}$c	$47.42^{\pm1.10}$b	$17.64^{\pm1.30}$a	$25.66^{\pm0.59}$b

CGY: charcoal gravimetric yield; PLY: pyroligneous liquid yield; NCGY: non-condensable gases yield, FCY: fixed carbon yield. According to the Scott-Knott test, averages followed by the same letter in a column do not differ statistically ($p > 0.05$). Mean ± standard deviation

High CGY and FCY values express higher efficiency of the pyrolysis process [12,17]. Low NCGY yields result in a carbonization process with reduced greenhouse gas emissions [28]. However, higher PLY is advantageous when the production of bio-oil is desired. *E. major and E. longirostrata* stands out for charcoal production because it also has a lower yield in non-condensable gases, which results in a production process with lower emission of gases when compared to the species traditionally used (*E. urophylla*) in the Brazilian steel industry. This means that in addition to high productivity, high energy efficiency, it is environmentally sustainable.

The CGY found in the present study was positively influenced by the total lignin content in the wood and low S/G ratio (Figure 1). Pearson's correlation coefficient for CGY with total lignin content and the S/G ratio of wood was 0.48 and 0.41, respectively. Recent studies report a positive influence of total lignin content in wood and a low S/G ratio in CGY [16,27,29,30]. In addition lower S/G ratios lead to better carbon and hydrogen balance during pyrolysis [31]. Lignin has lower oxygen content than polysaccharides and, thus, the carbon and hydrogen content should increase. The HHV of lignin is higher than that of polysaccharides (Lignin>cellulose>hemicelluloses), which has an impact in its fixed carbon and charcoal HHV. Compared to *C. henryi*, *E. amplifolia* presented lower S/G ratio, implying higher C-C bonds and a more condensed lignin, which tends to result in more energy and charcoal gravimetric yield.

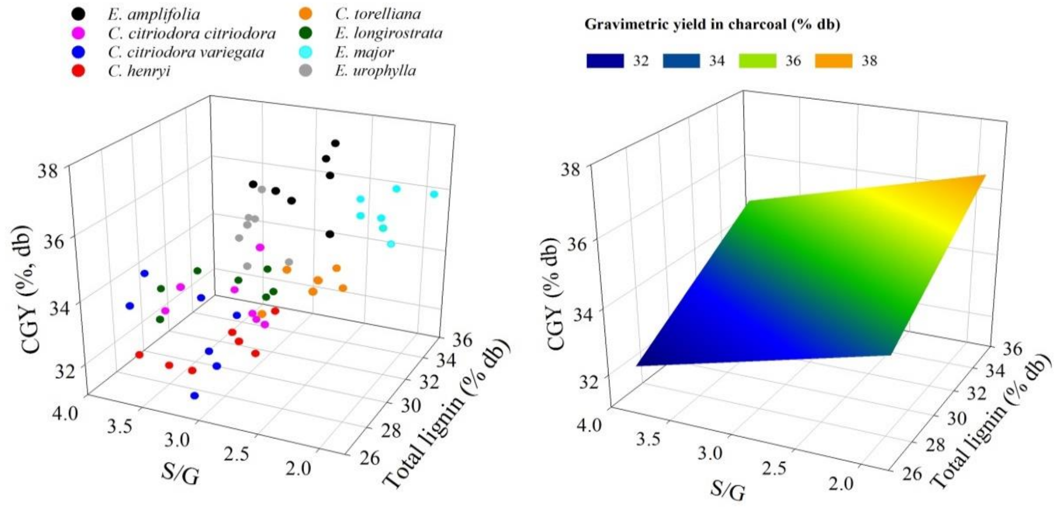

Figure 1. Relationship between the gravimetric yield of charcoal with the total lignin content and S/G ratio of wood. Where, CGY= 27.08800+0.31979*TL-0.92905*S/G, $R^2 = 0.48$, Syx = 3.21%, Fc = 23.33, *p*-value = 0.0001.

3.2. Charcoal apparent density

The Scott-Knott mean multiple comparison test ($p<0.05$) allowed the classification of species and the formation of four groups (Figure 2). Considering the decreasing order of density values, the species *C. citriodora* (>500 kg m^{-3}) belonged to group 1; *C. henryi*, *C. variegata*, *E. longirostrata,* and *E. major* (>400 kg m^{-3}) to group 2; *E. amplifolia* and *C. torelliana* (>350 kg m^{-3}) to group 3 and *E. urophylla* (~300 kg m^{-3}) was categorized into group 4. The species of the genus *Corymbia* presented mean values >400 kg m^{-3}, except *C. torelliana.* Charcoal with an apparent density higher than 380 kg.m^{-3} is preferable for the steel industry, since it increases the charcoal energy productivity [12].

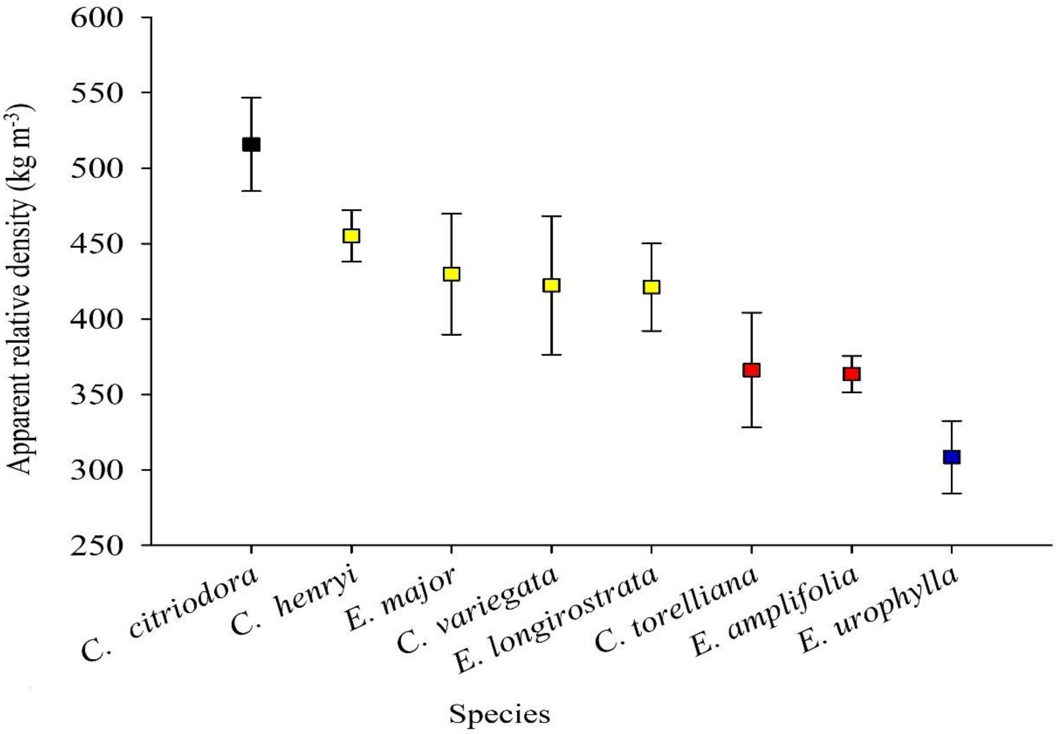

Figure 2. Classification of charcoal produced from *Eucalyptus* and *Corymbia* woods through apparent density. Different colors in the squares indicate a significant difference according to the Scott-Knott test at the 5% significance level. Error bars represent the standard deviation of each mean value.

Charcoal with high apparent density presents higher energy release per volume [10], high compressive strength [10,32], and is more rigid [11]. As a result, denser charcoal has high mechanical strength and contributes to the reduction of friability, improving the permeability of the bed inside the blast furnace [32]. *E. urophylla,* a species traditionally used in the Brazilian steel industry, has lower physical characteristics than the other evaluated species, demonstrating that non-commercial species are potentially competitive when compared to commercial cultivars that are already established in the market.

3.3. Ultimate composition and energy productivity

With regards to the elemental chemical analysis, there was only a significant effect of species for nitrogen content, in which the highest quantity was observed in *C. variegata* (2.17%) and the lowest in *C. citriodora* (1.71%). The charcoal produced with *Corymbia* species wood did not present sulfur content, while for eucalyptus charcoal it varied from 0.01% (*E. longirostrata*) to 0.13% (*E. major*).

Table 2. Ultimate chemical composition of charcoal

Species	N	C	H	S	O	H/C	O/C
C. citriodora	1.71$^{\pm0.07}$a	76.21$^{\pm1.19}$a	3.23$^{\pm0.26}$a	-	18.16$^{\pm1.47}$b	0.51$^{\pm0.04}$a	0.18$^{\pm0.02}$b
C. henryi	2.13$^{\pm0.05}$b	80.60$^{\pm2.12}$b	3.23$^{\pm0.27}$a	-	13.50$^{\pm2.13}$a	0.48$^{\pm0.04}$a	0.13$^{\pm0.02}$a
C. torelliana	1.91$^{\pm0.10}$a	76.84$^{\pm2.85}$a	3.12$^{\pm0.16}$a	-	16.50$^{\pm3.12}$b	0.49$^{\pm0.02}$a	0.16$^{\pm0.04}$b
C. variegata	2.17$^{\pm0.31}$b	78.02$^{\pm2.71}$a	3.28$^{\pm0.16}$a	-	16.03$^{\pm2.82}$b	0.51$^{\pm0.03}$a	0.16$^{\pm0.03}$b
E. amplifolia	1.87$^{\pm0.09}$a	76.44$^{\pm1.31}$a	3.18$^{\pm0.24}$a	-	17.49$^{\pm1.47}$b	0.50$^{\pm0.03}$a	0.18$^{\pm0.02}$b
E. longirostrata	1.81$^{\pm0.09}$a	78.72$^{\pm1.84}$b	3.38$^{\pm0.24}$a	0.01	15.13$^{\pm1.73}$a	0.52$^{\pm0.04}$a	0.14$^{\pm0.02}$a
E. major	2.06$^{\pm0.15}$b	79.42$^{\pm2.29}$b	3.46$^{\pm0.70}$a	0.13	13.95$^{\pm2.61}$a	0.52$^{\pm0.01}$a	0.13$^{\pm0.03}$a
E. urophylla	1.77$^{\pm0.09}$a	77.53$^{\pm0.77}$a	3.22$^{\pm0.25}$a	-	16.50$^{\pm0.89}$b	0.50$^{\pm0.04}$a	0.16$^{\pm0.01}$b

H: hydrogen (%); C: carbon (%); N: nitrogen (%); S: sulfur (%); O: oxygen. According to the Scott-Knott test, averages followed by the same letter in a column do not differ statistically (p >0.05). Mean ± standard deviation.

In general, eucalyptus species had higher levels of elemental carbon, except for *E. amplifolia*, which had lower levels of nitrogen and oxygen. These characteristics show that this genus has superior quality for use as a steel bioreducer. Charcoals with a high content of C and H and low levels of S and N are preferable for use as a bioreducer, as they release more energy in direct burning and reduce emissions of polluting gases into the atmosphere [17]. Despite that coal has high hydrogen (5%) and elementary carbon content (88.00%) when compared to charcoal analyzed in the present study, it usually has higher Sulphur content (>1%) [33]. The use of charcoal due to low S content can slow down the degradation of blast furnaces and high hydrogen and carbon content positively affects the blast furnace operation [34]. Carbon content of charcoal could be increased with use of high carbonization temperature than that used in this study.

Higher calorific value (HHV), volatile materials content (VMC), ash content (AC), fixed carbon content (FCC), energy density (ED), and energy efficiency (EE) were influenced by the species (Table 3). HHV ranged from 30.97 MJ kg^{-1} (*C. torelliana*) to 31.63 MJ kg^{-1} (*E. amplifolia*). The AC varied from 0.50% (*E. urophylla*) to 1.63% (*C. torelliana*). The lowest levels of VMC were observed in *C. henryi* (24.08%), *E. longirostrata* (24.25%), *C. torelliana* (24.55%), and *E. major* (24.66%%). The highest FCC values were found in *E. longirostrata, C. henryi*, and *E. major*, with approximately 75%. The highest ED was found in *C. citriodora* (16.00 GJ m^{-3}) and the lowest in *E. urophylla* (9.63 GJ.m^{-3}), while *E. amplifolia* presented better transformation EE (57.57%).

C. torelliana presented the highest AC (1.63%) and, consequently, the lowest HHV (30.97 MJ kg^{-1}) while the other species had AC lower than 1.5% and HHV > 31 MJ kg^{-1}. AC greater than 1.5% reduces the charcoal HHV [35]. Moreover, it can cause the accumulation of oxide minerals in the center of the metallic parts, impairing the mechanical properties of the crude iron or iron alloy [12]. However, the ash content present in charcoal is much lower than that reported in the literature for coal (up to 12%) [35]. The ash content and volatile matter of coal is significantly higher than that of charcoal [33]. The low ash content of the charcoal positively affects the blast furnace operation and high volatiles content implying high reactivity of charcoal and enriching the combustion process [36]

C. citriodora, C. henryi, E. longirostrata, and *E. major* stand out for use as a bioreducer in the steel industry since they have low VMC, high FCC and ED, which indicates high quality when compared to *E. urophylla*, a species that is traditionally used for this purpose. Charcoal with high FCC and high ED increases the productivity of blast furnaces, considering the same specific consumption of charcoal [12]. Charcoal has low FCC content than coal (81.50%) [33], however, the FCC of charcoal could be increased using high final carbonization temperature than that used in this study.

Table 3. Energy productivity and proximate analysis of charcoal

Species	HHVc (MJ kg^{-1})	VMC (%db)	AC (%db)	FCC (%db)	ED (GJ.m$^{-3)}$	EE **(%)**
C. citriodora	31.01$^{\pm 0.39}$a	25.20$^{\pm 0.89}$b	0.98$^{\pm 0.43}$b	73.82$^{\pm 1.16}$a	16.00$^{\pm 0.98}$d	52.83$^{\pm 1.66}$a
C. henryi	31.40$^{\pm 0.32}$b	24.08$^{\pm 1.23}$a	0.96$^{\pm 0.09}$b	74.96$^{\pm 1.23}$b	14.29$^{\pm 0.45}$c	52.64$^{\pm 1.16}$a
C. torelliana	30.97$^{\pm 0.23}$a	24.55$^{\pm 0.75}$a	1.63$^{\pm 0.37}$c	73.82$^{\pm 0.98}$a	11.34$^{\pm 1.20}$b	54.14$^{\pm 1.23}$b
C. variegata	31.02$^{\pm 0.46}$a	25.43$^{\pm 1.01}$b	1.11$^{\pm 0.16}$b	73.46$^{\pm 0.96}$a	13.10$^{\pm 1.46}$c	51.68$^{\pm 1.35}$a
E. amplifolia	31.63$^{\pm 0.59}$b	25.47$^{\pm 0.85}$b	1.03$^{\pm 0.13}$b	73.51$^{\pm 0.91}$a	11.50$^{\pm 0.86}$b	57.57$^{\pm 1.95}$c
E. longirostrata	31.05$^{\pm 0.13}$a	24.25$^{\pm 1.29}$a	0.53$^{\pm 0.09}$a	75.22$^{\pm 1.21}$b	13.07$^{\pm 0.90}$c	52.75$^{\pm 0.61}$a
E. major	31.17$^{\pm 0.13}$a	24.66$^{\pm 0.73}$a	0.69$^{\pm 0.19}$a	74.65$^{\pm 0.66}$b	13.39$^{\pm 1.20}$c	54.11$^{\pm 0.87}$b
E. urophylla	31.21$^{\pm 0.25}$a	26.05$^{\pm 0.53}$b	0.50$^{\pm 0.11}$a	73.45$^{\pm 0.56}$a	9.63$^{\pm 0.76}$a	54.27$^{\pm 0.81}$b

HHVc: higher heating value of charcoal; VMC: volatile matter content; AC: Ash content; FCC: fixed carbon content; ED: Energy density; EE: Energy efficiency. According to the Scott-Knott test, averages followed by the same letter in a column do not differ statistically ($p > 0.05$). Mean ± standard deviation

3.4. Parameters and combustion indexes of charcoal

Figure 3 shows the combustion behavior of charcoal resulting from the simulation through thermogravimetric analysis in synthetic air in the different species studied. Based on the thermogravimetric curve, it is possible to observe that the decreasing order of the species with greater thermal stability during combustion was: *E. longirostrata, E. urophylla, C. citriodora, E. major, E. amplifolia, C. torelliana C. henryi* and *C. variegata.* It is noteworthy that *E. longirostrata* burns more slowly than *C. variegata*. This behavior may be associated with the higher and lower fixed carbon content observed in these species, respectively.

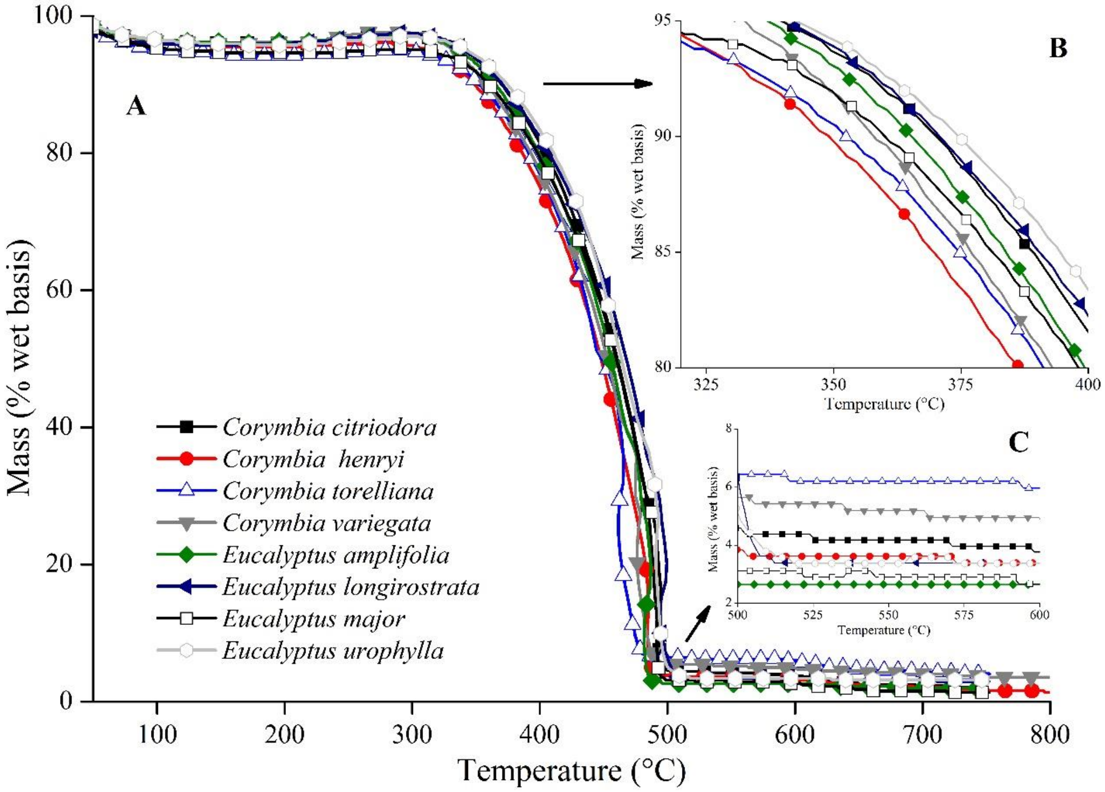

Figure 3. A: Thermogravimetric curves typical of the charcoals of the studied species, B: mass loss during ignition, C: Residual mass

Figure 4 shows the DTG curve (first derivative of the TGA curve), in which the stages involved in the combustion process of charcoal can be visualized. The first mass loss peak is associated with the charcoal drying process, which occurs up to 200°C. With increasing temperature, between 330 and 340°C, the curve becomes steep as a function of the ignition and combustion of volatile materials. Between 470-490°C, the highest peak of combustion occurs due to the burning of fixed carbon. This behavior is similar to that found in *E. grandis* charcoal [22].

The temperature required for the ignition of charcoal ranged from 330°C (*C. variegata* e *C. torelliana*) to 341°C (*E. urophylla*), while the shortest time required for ignition was observed in *C. henryi* (28.0 min) and the longest in *C. citriodora* (29. 8 min) (Table 4). In general, the *Corymbia* charcoal presented easier ignition since it required lower temperatures and time to start the combustion reaction, except *C. citriodora* which needed more time to start the ignition. The charcoal from *C. citriodora* presented higher oxygen content and lower carbon and hydrogen content, requiring a longer time to start the ignition.

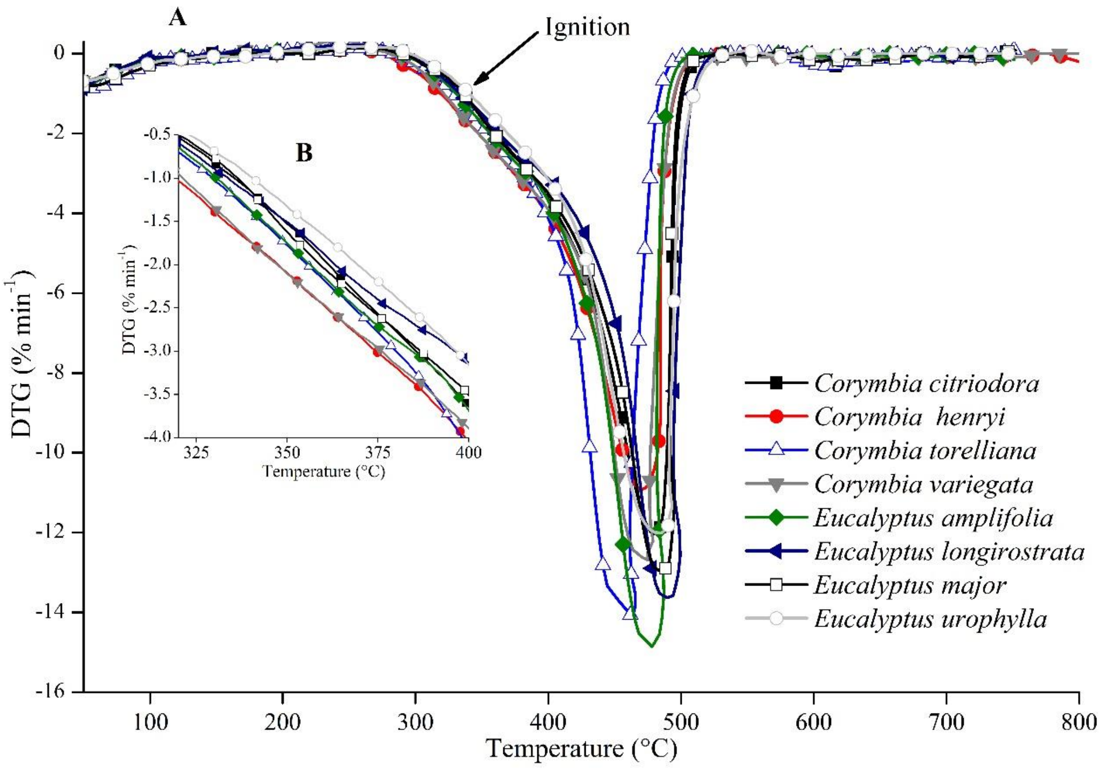

Figure 4. Thermogravimetric derivative of charcoal from the species studied (A), Ignition of charcoal (B)

The highest burnout temperature (Tb) and peak thermal degradation (dm/dt_{max}) were observed in *E. urophylla* at 516°C and 489°C, respectively, while *C. torelliana* had the lowest values at 485°C and 469°C, respectively. This behavior is associated with the higher and lower ash content observed in the charcoals of these species. Charcoal with low ash content has a high mass available for burning, a higher burnout temperature and, consequently, a longer burning time [22] which may result in longer residence time inside the steel blast furnace.

C. citriodora, *C. henryi*, and *E. urophylla* had lower rates of combustion (S) and ignition (Di) according to the multiple comparisons of means test, this behavior may be associated with the lower H/C ratio observed in these species. The combustion index represents, respectively, the indicative of charcoal reactivity, the higher the value obtained for this index, the greater its reactivity during the combustion process [37]. Very reactive carbon provides reduction gases at high rates, wasting part of the gas that should be used in the process, while less reactive materials make the production process longer [33]. Charcoal with a high combustion index is desirable for domestic use because it has better performance and reduced time for heating or cooking food [22]. *C. citriodora*, *C. henryi*, *E. urophylla*, and *E. major* had lower combustion rates, thus producing less reactive charcoal and are suitable for steelmaking. Higher ignition rates and combustion characteristics were observed in *E. amplifolia*, *E. longirostrata*, *C. torreliana*, and *C. variegata*, producing more reactive carbon with easy ignition, which is desirable for domestic use.

Table 4. Parameters and combustion indexes of charcoal

Species	Ti (°C)	Tb (°C)	Tmáx(°C)	$(dm/dt)_{max}$	tig (min)	Si x 10^7 ($\%^2 min^{-2}$ $°C^{-3}$)	Di x 10^3 (% min^{-3})
C. citriodora	$336^{\pm1}$b	$500^{\pm1}$d	$484^{\pm3}$c	$12.13^{\pm0.57}$a	$29.78^{\pm0.28}$c	$2.68^{\pm0.15}$a	$9.41^{\pm0.43}$a
C. henryi	$331^{\pm5}$a	$496^{\pm3}$c	$476^{\pm3}$b	$11.97^{\pm0.72}$a	$28.01^{\pm0.65}$a	$2.77^{\pm0.20}$a	$10.41^{\pm0.67}$a
C. torelliana	$330^{\pm1}$a	$485^{\pm5}$a	$469^{\pm5}$a	$15.41^{\pm1.33}$d	$28.67^{\pm0.26}$b	$3.62^{\pm0.32}$c	$13.27^{\pm1.52}$c
C. variegata	$330^{\pm5}$a	$489^{\pm2}$b	$472^{\pm5}$b	$14.42^{\pm0.31}$c	$28.42^{\pm0.66}$b	$3.44^{\pm0.11}$c	$12.63^{\pm0.47}$c
E. amplifolia	$332^{\pm2}$a	$488^{\pm1}$b	$474^{\pm5}$b	$16.07^{\pm0.99}$d	$28.52^{\pm0.44}$b	$3.73^{\pm0.35}$c	$13.86^{\pm1.04}$c
E. longirostrata	$338^{\pm4}$b	$503^{\pm4}$d	$488^{\pm4}$c	$15.74^{\pm0.79}$d	$28.62^{\pm0.35}$b	$3.47^{\pm0.27}$c	$13.17^{\pm0.83}$c
E. major	$337^{\pm2}$b	$501^{\pm4}$d	$485^{\pm4}$c	$13.76^{\pm0.87}$b	$28.91^{\pm0.30}$b	$3.10^{\pm0.20}$b	$11.33^{\pm0.60}$b
E. urophylla	$341^{\pm1}$c	$516^{\pm3}$e	$489^{\pm3}$c	$12.24^{\pm0.35}$a	$28.97^{\pm0.18}$b	$2.69^{\pm0.18}$a	$9.97^{\pm0.27}$a

Ti: ignition temperature, Tb: burnout temperature (°C); (dm/dt)max: maximum combustion rate; tig: ignition time; Si: combustion index; Di: ignition index. According to the Scott-Knott test, averages followed by the same letter in a column do not differ statistically ($p > 0.05$). Mean ± standard deviation

3.5. Multivariate grouping of charcoal

Principal component analysis (PCA) revealed that three components were sufficient to explain 84.30% of the data variability (Table 5). The variables that most influenced the formation of the main components were: 1 – the combustion and ignition indices, the gravimetric yield of charcoal, the charcoal apparent density and energetic densities, the yield in fixed carbon, and the H/C ratio; 2 – The contents of ash and volatile materials; the final combustion temperature, the combustion and ignition rates, 3 – The contents of volatile materials, ash and fixed carbon, the H/C and O/C ratios.

Table 5. Eigenvectors associated with the first three principal components.

Property	PC1	PC2	PC3
Volatile Matter content (VMC)	0.1235	**-0.4383**	**-0.3508**
Ash content (AC)	0.0992	**0.3475**	**-0.4123**
Fixed carbon content (FCC)	-0.1661	0.2386	**0.5410**
Higher heating value (HHV)	0.1571	-0.1207	0.0447
Burnout temperature (Tb)	-0.1368	**-0.4337**	0.3656
Combustion index (Si)	**0.3380**	**0.3263**	-0.1095
Ignition index (Di)	**0.3417**	**0.3250**	-0.0314
Charcoal gravimetric yield (CGY)	**0.3550**	-0.2164	-0.0525
Energy density (ED)	**-0.3860**	0.1925	-0.1230
Charcoal Apparent density (CRD)	**-0.3886**	0.1948	-0.1245
Fixed carbon yield (FCY)	**0.3358**	-0.1706	0.0770
H/C	**0.3286**	0.1465	**0.3186**
O/C	-0.1616	-0.2076	**-0.3532**

By means of PCA, it was possible to categorize the species into 4 groups. The dispersion of the evaluated species according to the scores obtained in the analysis of principal components can be observed in Figure 5. The charcoal produced by different species was grouped according to apparent and energetic density, combustibility, carbonization yields, proximate, and elemental chemical composition, to differentiate their appropriateness for the steel industry.

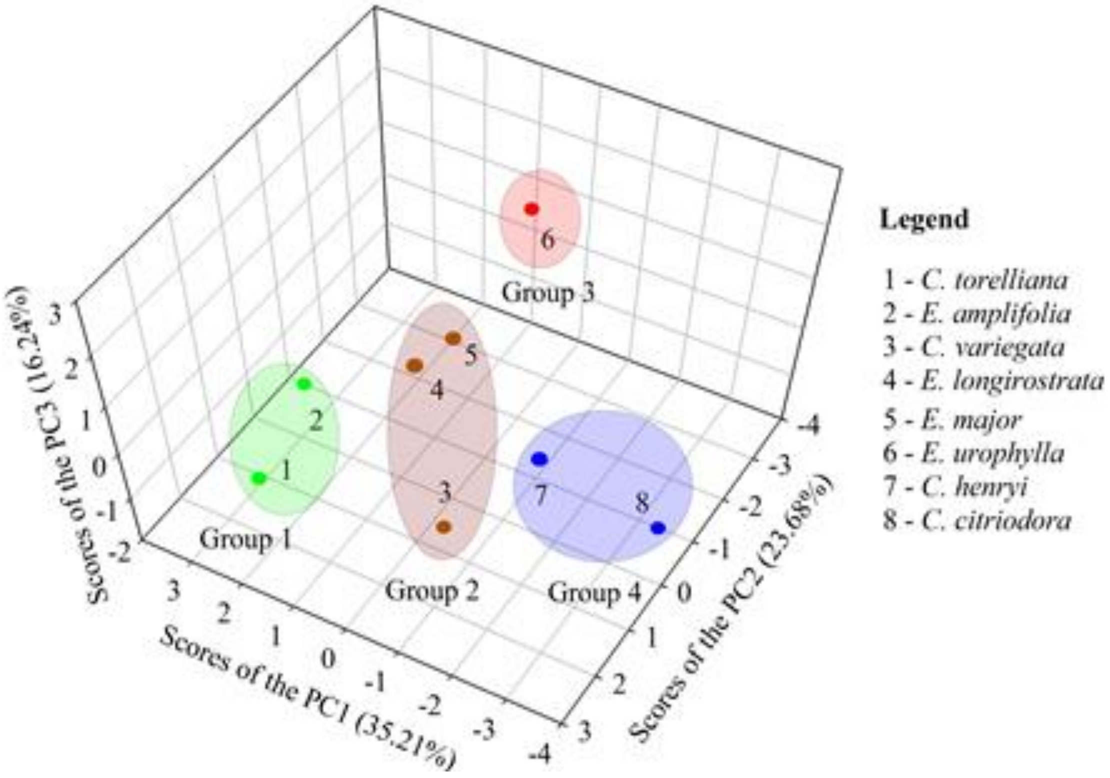

Fig. 5. Multivariate grouping of species of the genera *Corymbia* and *Eucalyptus*.

Group 1 (*C. torelliana* and *E. amplifolia*) produce charcoal with quality for domestic use due to its low density, high gravimetric yield, easy ignition, and high reactivity. Groups 2 (*C. variegata*, *E. longirostrata* and *E. major*) and 4 (*C. henryi* and *C. citriodora*), composed of non-commercial species, are promising for charcoal production for use in the steel industry, despite having lower gravimetric yield when compared to group 3, high ignition index, fixed carbon yield, apparent and energetic density. Group 3, composed only of *E. urophylla,* a species traditionally used in the steel industry in Brazil, presents appropriate characteristics for the steel industry, with emphasis on the high burnout temperature, gravimetric yield of charcoal, fixed carbon yield, H/C ratio, low ash content, combustion index, and O/C ratio. Characteristics that provide high energy productivity and low reactivity. However, this species has some undesirable characteristics such as low values for the ignition index, apparent density and energy, which makes the non-commercial species competitive.

4. Conclusions

Non-commercial species have the potential for use and dissemination on an industrial scale due to high charcoal apparent density, energy density, gravimetric and fixed carbon yield, easy ignition and high combustion performance. *C. variegata*, *E. longirostrata*, *E. major*, *C. henryi*, and *C. citriodora* are competitively promising species for charcoal production for steel industry as compared to commercial species and fossil fuels, since they produce low reactivity charcoal, with high ignition index, fixed carbon yield, apparent and energetic density. The quality of charcoal produced from *C. torelliana* and *E. amplifolia* is appropriate for domestic use due to its low density, high gravimetric yield, easy ignition, and high reactivity.

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Data availability

Dataset related to this article can be found at http:dx.doiorg/ 10.17632/xm6xwysstv.1, an open-source online data repository hosted at Mendeley data

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FINAL CONSIDERATIONS AND FUTURE PERSPECTIVE

Non-commercial species have the potential for use and dissemination on an industrial scale, where the *E. major* is the most suitable for sustainable use in the steel industry. Non-commercial species, especially *C. variegata, E. longirostrata, E. major, C. henryi,* and *C. citriodora*, have a great potential for use and dissemination on an industrial scale. These species are competitively promising for producing charcoal for the steel industry when compared to the commercial species (*E. urophylla*), since they produce low reactivity charcoal, with high ignition index, fixed carbon yield, apparent and energetic density. The quality of charcoal produced from *C. torelliana* and *E. amplifolia* is appropriate for domestic use due to its low density, high gravimetric yield, easy ignition, and high reactivity. For future hybridization projects of these species to improve energy quality, crossbreeding between *C. torelliana,* and other *Coymbia species* (*C. citriodora*, *C. variegata*, and *C. henryi),* and crossbreeding of *E. urophylla* (the main species of actual clones) with *E. longirostrata,* and *E. major,* all high-density species, may lead to superior-quality clones for use in a sustainable steel industry.

It is intended to evaluate the combustibility and energy performance of wood in order to simulate its use in energy cogeneration systems. Make relationships between wood properties, charcoal combustibility and carbonization mass balances. The evaluation and comparison of productivity, wood and charcoal quality of the different species planted in contrasting environments will also be carried out.