MARCELA RIBEIRO COURA

POTENCIAL DO PERGAMINHO DE CAFÉ PARA OBTENÇÃO DE BIOPRODUTOS

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Agroquímica, para obtenção do título de *Doctor Scientiae*.

Orientador: Antonio Jacinto Demuner

Coorientadores: Ana Márcia M. Ladeira Carvalho
Fernando José Borges Gomes

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RESUMO

COURA, Marcela Ribeiro, D.Sc., Universidade Federal de Viçosa, março de 2023. **Potencial do pergaminho de café para obtenção de bioprodutos.** Orientador: Antonio Jacinto Demuner. Coorientadores: Ana Márcia Macedo Ladeira Carvalho e Fernando José Borges Gomes.

A biomassa lignocelulósica encontra-se em abundância na natureza e atualmente é considerada o maior recurso renovável do planeta. A utilização de resíduos agroindustriais, como fonte de biomassa lignocelulósica reduz o uso de recursos florestais enquanto agrega valor de mercado a subprodutos que antes eram descartados, como por exemplo o pergaminho, resíduo de um importante produto agrícola, o café. A produção de café gera grandes volumes de resíduos, chegando a 32 milhões de toneladas por ano apenas no Brasil. Nesse contexto, este trabalho teve como objetivo avaliar o pergaminho do café quanto à sua composição química, física e morfológica, bem como seu potencial para produção de polpa kraft e demais produtos de alto valor agregado, como nanocelulose e lignina. A análise da densidade e propriedades químicas do resíduo da indústria cafeeira permite concluir que este material tem potencial para ser utilizado como matéria-prima para a produção de celulose. O pergaminho apresentou o conteúdo de extrativos (4,5%), cinzas (0,9%) e lignina (25,9%) semelhantes às matérias-primas mais utilizadas para a produção de celulose, como o eucalipto. Apesar de possuir baixo teor de celulose (36,4%), possui alto teor de hemiceluloses (30,8%), em relação à madeira de pinus e eucalipto, o que contribuiu para um ganho de rendimento na polpação kraft, esse estudo obteve 42,1 e 46,8% para polpa kappa 25 e 60, respectivamente. O branqueamento “Livre de cloro elementar” da polpa celulósica kappa 25 com a sequência $OQD_{HT}(EP)DP$ mostrou-se adequado para a produção de pasta branqueada 90%ISO, apesar do alto consumo de cloro ativo total, igual à 71,0 kg/odt. O licor negro proveniente do cozimento do pergaminho do café foi usado para isolar a lignina kraft, pelo método Lignoboost. As extrações resultaram em lignina de alta pureza (92,35% para a lignina K#60 e 93,96% para a lignina K#25), com poder calorífico de 23,8 e 25,4 MJ/Kg para as ligninas K#25 e K#60, respectivamente. Com a análise do infravermelho por transformada de Fourier (FTIR) foi possível observar picos característicos de lignina, e através da análise Pirólise-Cromatografia Gasosa-Espectrometria de massa (Py-GC-MS) foi possível observar leve predominância de lignina do tipo guaiacil, o que pode ser uma vantagem dependendo da aplicação. As fibras celulósicas obtidas com a polpação kraft do pergaminho e o processo de branqueamento, foram submetidas a uma desfibrilação mecânica, e mostraram-se uma alternativa viável para produção de celulose microfibrilada, apresentando em geral propriedades comparativas com as nanocelulose produzidas através de madeira. As nanocelulose, Lignocelulose microfibrilada-K#60, Lignocelulose microfibrilada-K#25 e Celulose microfibrilada-branqueada, apresentaram índice de cristalinidade de 52,5, 58,8 e 65,1%, respectivamente, e mostraram-se termicamente estáveis. Os espectros de FTIR foram similares para todas as nanocelulose, mostrando picos característicos dos polímeros celulósicos. Já através da microscopia eletrônica de varredura (MEV) foi possível confirmar que as fibras foram desfibriladas pelo processo mecânico. As polpas não branqueadas (kappa 25 e 60) e a branqueada também foram caracterizadas morfologicamente, não apresentando diferença significativa entre si, em geral são constituídas de fibras curtas e com alta espessura de parede. De acordo com os resultados apresentados referentes à análise morfológica e das relações entre as dimensões das fibras, e confirmado pelos resultados dos testes físicos, as fibras de pergaminho não são adequadas para a produção de papel de imprimir e escrever (P&W), no entanto podem ser testadas na produção de papéis especiais, como filtro de cigarro, ou misturadas com fibras de outras matérias-primas.

Palavras-chave: Resíduos cafeeiros. Celulose kraft. Celulose microfibrilada. Lignina.

ABSTRACT

COURA, Marcela Ribeiro, D.Sc., Universidade Federal de Viçosa, March 2023. **Potential of coffee parchment to obtain bioproducts.** Adviser: Antonio Jacinto Demuner. Co-advisers: Ana Márcia Macedo Ladeira Carvalho and Fernando José Borges Gomes.

Lignocellulosic biomass is found in abundance in nature and is currently considered the largest renewable resource on the planet. The use of agro-industrial waste as a source of lignocellulosic biomass reduces the use of forest resources while adding market value to by-products that were previously discarded, such as parchment, the residue of an important agricultural product, coffee. Coffee production generates large volumes of waste, reaching 32 million tons per year in Brazil alone. In this context, this work aimed to evaluate coffee parchment in terms of its chemical, physical and morphological composition, as well as its potential to produce kraft pulp and other products with high added value, such as nanocellulose and lignin. The analysis of the density and chemical properties of the residue from the coffee industry leads to the conclusion that this material has the potential to be used as a raw material to produce cellulose. The parchment showed a content of extractives (4.5%), ash (0.9%) and lignin (25.9%) similar to the raw materials most used for pulp production, such as eucalyptus. Despite having a low cellulose content (36.4%), it has a high hemicelluloses content (30.8%), compared to pine and eucalyptus wood, which contributed to a gain in yield in kraft pulping, this study obtained 42.1 and 46.8% for 25 and 60 kappa pulp, respectively. The "Elemental chlorine free" bleaching of kappa 25 cellulosic pulp with the OQDHT(EP)DP sequence proved to be suitable to produce 90%ISO bleached pulp, despite the high consumption of total active chlorine, equal to 71.0 kg /odt. Black liquor from coffee parchment cooking was used to isolate kraft lignin using the Lignoboost method. The extractions resulted in high purity lignin (92.35% for K#60 lignin and 93.96% for K#25 lignin), with calorific value of 23.8 and 25.4 MJ/Kg for K lignins #25 and K#60, respectively. With the Fourier transform infrared analysis (FTIR) it was possible to observe characteristic peaks of lignin, and through the Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS) analysis it was possible to observe a slight predominance of guaiacyl-type lignin, which can be an advantage depending on the application. The cellulosic fibers obtained with the kraft pulping of the parchment and the bleaching process, were submitted to a mechanical defibrillation, and proved to be a viable alternative to produce microfibrillated cellulose, presenting in general comparative properties with the nanocellulose produced from wood. The nanocellulose, microfibrillated lignocellulose-K#60, microfibrillated lignocellulose-K#25 and bleached microfibrillated cellulose, presented a crystallinity index of 52.5, 58.8 and 65.1%, respectively, and were thermally stable. FTIR spectra were similar for all nanocelluloses, showing characteristic peaks for cellulosic polymers. By scanning electron microscopy (SEM) it was possible to confirm that the fibers were defibrillated by the mechanical process. The unbleached pulps (kappa 25 and 60) and the bleached pulp were also morphologically characterized, with no significant difference between them, in general they are made up of short fibers with high wall thickness. According to the results presented regarding the morphological analysis and the relationships between the dimensions of the fibers, and confirmed by the results of the physical tests, parchment fibers are not suitable to produce printing and writing paper (P&W), however they can be tested in the production of special papers, such as cigarette filters, or mixed with fibers from other raw materials.

Keywords: Coffee residue. Kraft pulp. Microfibrillated cellulose. Lignin.

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LISTA DE ABREVIATURAS E SIGLAS

I_{002} – A intensidade máxima de difração
I_{AM} – A intensidade mínima
RPA – Air resistance
BL-KN 25 – Amostra de licor negro da polpação kraft visando número kappa 25
BL-KN 60 – Amostra de licor negro da polpação kraft visando número kappa 60
LCMF-K#25 – Amostra de lignocelulose microfibrilada obtida a partir de polpa celulósica kappa 25
LCMF-K#60 – Amostra de lignocelulose microfibrilada obtida a partir de polpa celulósica kappa 60
B – Brightness of O_2-pulp
B_b – Brightness of the brown pulp
C-C – Carbono-carbono
C3 – Carbono na posição 3
C5 – Carbono na posição 5
Ca – Cathecol type lignin
CHNS-O – Carbono, hidrogênio, nitrogênio, enxofre e oxigênio
BC – Celulose bacteriana
CMF – Celulose Microfibrilada
CNC – Celulose Nanocristalina
CNF – Celulose Nanofibrilada
COVID – Corona virus disease
TG – Curvas termogravimétricas
DTG – Curvas da derivada primeira do TG
DTPA – Dietilenotriaminopentaacetato
D – Dióxido de cloro
D_{HT} – Dióxido de Cloro em alta temperature
EA – Effective alkali
ECF – Elemental Chlorine Free (Livre de cloro elementar)
FTIR – Espectroscopia no Infravermelho por Transformada de Fourier
ES – Espírito Santo
EP – Extração alcalina com peróxido de hidrogênio
GC – Gas chromatography
G – Guaiacyl-type lignin
Hexa – Hexenuronic acids
HHV – Higher heating values
HMF – 5-hydroxymethylfurfural
H – Hydroxyphenyl-type lignin
I_C – Índice de cristalinidade
IRA – Índice de retenção de água
ISO – International Organization for Standardization (Organização Internacional de Normalização)

KN 25 – Kappa number 25
KN 60 – Kappa number 60
K#25 – Kappa number 25
K#60 – Kappa number 60
K – Kappa number of O_2-pulp
K_b – Kappa number of the brown pulp
K_f – Kappa number of the bleached pulp
LCP – Laboratório de Celulose e Papel
L – Length
LG – Levoglucosan
LCC – Lignin-carbohydrate complex
LCMF – Lignocelulose microfibrilada
LHV – Lower heating values
D – Lumen diameter
MS – Mass spectrometry
MEV – Microscopia eletrônica de varredura
MET – Microscopia eletrônica de transmissão
$P_{úmido}$ – Peso da amostra após a centrifugação
P_{seco} – Peso seco absoluto da amostra
P – Peróxido de hidrogênio
pH – Potencial hidrogeniônico
O – Pré-Deslignificação com oxigênio
PY-GC-MS – Pyrolysis gas chromatography mass spectrometry
Q – Quelante
S/G – Ratio lignin syringyl-type/guaiacyl-type
REA – Residual effective alkali
ºSR – Schopper-Riegler
MOE – Specific modulus
S – Syringyl-type lignin
IR – Tear index
IT – Tensile index
TAC – Total active chlorine
UFV – Universidade Federal de Viçosa
USA – United States of America
V – Viscosity of O_2-pulp
V_b – Viscosity of the brown pulp
T – Wall thickness
W – Width

APRESENTAÇÃO

Esta tese apresenta quatro capítulos intitulados:

Capítulo 1: COFFEE BIOMASS RESIDUE AS RAW MATERIAL FOR CELLULOSE PRODUCTION AND PY-GC-MS ANALYSIS

Capítulo 2: TECHNICAL KRAFT LIGNIN FROM COFFEE PARCHMENT

Capítulo 3: ESTUDO DA CELULOSE MICROFIBRILADA PRODUZIDA A PARTIR DA POLPA KRAFT DE PERGAMINHO DE CAFÉ

Capítulo 4: MORPHOLOGICAL AND PHYSICAL-MECHANICAL CHARACTERIZATION OF COFFEE PARCHMENT FIBERS FOR PAPER PRODUCTION

O primeiro deles teve como objetivo avaliar o resíduo da indústria cafeeira, pergaminho, como matéria-prima para a produção de celulose através de sua completa caracterização química e morfológica e o estudo do seu desempenho da produção de celulose kraft não-branqueada e branqueada.

O segundo teve como objetivo realizar a extração da lignina do licor negro kraft – obtido no primeiro artigo –, pelo processo Lignoboost, e fazer sua completa caracterização, comparando as ligninas kraft do pergaminho de café com as ligninas kraft de madeira.

O terceiro artigo teve como objetivo obter celulose microfibrilada (MFC) utilizando o processo de desintegração mecânica nas polpas kraft branqueada e não-branqueada obtidas no primeiro artigo, como também realizar uma completa caracterização das MFCs para um melhor entendimento de suas propriedades físicas e químicas, o que pode ser útil para orientar suas futuras aplicações.

E por fim o quarto artigo faz uma caracterização morfológica das fibras do pergaminho individualizadas através do processo kraft, seguida ou não do processo de branqueamento, do primeiro artigo, e estudar o potencial dessas polpas na produção de papel.

SUMÁRIO

INTRODUÇÃO GERAL

O movimento de conscientização ambiental tem motivado a busca pelo uso de recursos renováveis alternativos. O modelo recente do desenvolvimento sustentável resultou em uma grande quantidade de pesquisas sobre tecnologias de produção socialmente benéficas, economicamente viáveis e ambientalmente benignas (DADI *et al.*, 2018).

A produção de café representa uma parcela significativa da economia brasileira, sendo essencial no desenvolvimento da economia, gerando empregos diretos e indiretos (FERREIRA *et al.*, 2021). Principalmente nos países em desenvolvimento, cerca de 25 milhões de pequenos produtores contam com o setor cafeeiro para seus meios de subsistência (ICO, 2019). Os países produtores dominantes em 2018/2019 foram Brasil, Vietnã, Colômbia, Indonésia, Honduras, México, Guatemala e Costa do Marfim (ICO, 2019).

A produção mundial de café na safra 2021/22 está estimada em cerca de 167,5 milhões de sacas de 60 kg, sendo que o Brasil é o maior exportador mundial, exportando 42,4 milhões de sacas em 2021 (CONAB, 2022). Considerado uma das bebidas mais populares do mundo, e tendo aproximadamente metade do seu peso descartado durante o processamento do fruto, o café é apontado como uma fonte reutilizável de resíduos agrícolas (GONÇALVES *et al.*, 2021).

A produção, processamento e consumo de café geram uma enorme quantidade de resíduos, ricos em carboidratos (celulose, hemiceluloses), proteínas, pectinas e compostos bioativos como polifenóis, cafeína e taninos que podem ser possivelmente tóxicos para o meio ambiente (FAN *et al.*, 2003; MURTHY & NAIDU, 2010; REIS *et al.*, 2020).

Estudos sobre a reutilização desses resíduos são relevantes, tanto por razões ambientais, como também pelos possíveis destino desta enorme quantidade de biomassa lignocelulósica. Esses mostram que os resíduos da indústria cafeeira podem ser úteis em diversas aplicações, como biocombustíveis (DADI *et al.*, 2018), fibras (ELBA *et al.*, 2017; BENITEZ *et al.*, 2019) ou produtos químicos industriais, como xilitol, etanol, furfural, entre outros. (ARISTIZÁBAL-MARULANDA *et al.*, 2017; RAO *et al.*, 2023).

A biomassa lignocelulósica refere-se à matéria vegetal, que é composta principalmente de celulose, hemiceluloses e lignina, sendo as provenientes de resíduos agrícolas e florestais as mais promissoras devido a sua abundância e custo relativamente baixo (CAI *et al.*, 2017). A celulose é um biopolímero natural renovável, que consiste em um homopolissacarídeo linear composto de unidades β-D-glicopiranose ligadas entre si por ligações β-1-4 (Khalil *et al.*, 2014). A hemiceluloses, outro componente renovável abundante na biomassa lignocelulósica, é composto pelas unidades de açúcar D-xilose, D-manose, D-glicose, D-galactose, L-arabinose, ácido galacturônico e ácido glucurônico, formando em sua maioria cadeias curtas (RAO *et al.*, 2023). Já a lignina é formada por unidades fenilpropanóides, dentre elas unidades siringil (S), guaiacil (G) e p-hidroxifenil (H), conectadas por meio de várias ligações C-O e C-C (Wang *et al.*, 2023).

Uma caracterização profunda das propriedades físico-químicas e morfológica da biomassa lignocelulósica é essencial para o projeto e operação de processamento de conversão da biomassa.

Para sua desconstrução e aplicação em um produto de alto valor agregado, é normalmente necessária uma etapa de pré-tratamento. Atualmente a polpação kraft é o pré-tratamento dominante, nas indústrias, na produção de polpa celulósica, devido à boa recuperação química dos reagentes utilizados e da alta resistência das fibras das polpas resultantes (BI *et al.*, 2021). No processo kraft, a desconstrução da biomassa ocorre em condições de altas temperaturas (160-170 °C) e pressões, por meio de uma solução aquosa de NaOH e Na_2S (POTTHAST, 2006). O objetivo do processo é clivar e solubilizar a lignina e, como resultado, obter uma polpa composta basicamente por celulose e hemiceluloses.

Nos últimos anos, tem havido um interesse crescente em nanopartículas à base de celulose, por suas excelentes propriedades químicas, mecânicas e ópticas, além de se tratar de um material biocompatível, que apresenta excelente desempenho mecânico com baixo peso e altamente reativo devido aos grupos hidroxilas presente na superfície, o que torna a nanocelulose um biopolímero altamente atrativo para aplicações diversas (ALBORNOZ-PALMA *et al.*, 2020; M'BAREK *et al.*, 2022; WANG *et al.*, 2022).

As nanocelulose são obtidas por processamento de biomassas lignocelulósica. Dependendo do método de extração, a nanocelulose pode ser categorizada em três: nanofibrilas de celulose (CNF), nanocristais de celulose (CNC) e celulose bacteriana (BC) (OWOLABI *et al.*, 2020). A celulose microfibrilada (CMF) é considerada por alguns autores como nanofibrilas de celulose (CNF), e pode ser denominada como material celulósico, degradado moderadamente expandindo assim sua área de superfície, obtido através de um processo de desintegração mecânica sem uso de hidrólise (HERRICK *et al.*, 1983; ALBORNOZ-PALMA *et al.*, 2020).

No processo kraft é gerado além da polpa de celulose um licor residual, denominado licor negro. Este licor é rico em componentes inorgânicos e orgânicos, principalmente lignina e hemiceluloses clivadas durante o processo (KROTSCHECK & SIXTA, 2006). O licor negro é encaminhado para o ciclo de recuperação kraft do licor de cozimento. Neste ciclo, os reagentes de cozimento são recuperados e vapor/energia é gerado pela queima do licor na caldeira de recuperação. A geração de energia é importante para suprir as necessidades da própria fábrica kraft. Porém, parte da lignina presente no licor negro pode ser aproveitada para produzir produtos de alto valor agregado, sem prejudicar a geração de energia e inserindo a indústria kraft no atual conceito de biorrefinaria.

Dentre as diversas tecnologias para extração de lignina kraft do licor negro, as mais consideradas são os processos LignoBoost™, LignoForce™, eletroquímico assistido por membrana e líquidos iônicos (JIN *et al.* 2013; DESSBESELL *et al.* 2020; BAGH *et al.* 2021; DIAZ-BACA & FATEHI 2021; KALLIOLA *et al.* 2022). Esses processos possibilitam seu melhor aproveitamento e aumentam a rentabilidade e sustentabilidade das fábricas kraft. Nos processos LignoBoost™ e LignoForce™, que são os mais utilizados em escala piloto ou operação industrial, a lignina é extraída a partir da acidificação do licor negro (HUBBE *et al.* 2019).

A lignina Kraft tem as características de ser ambientalmente amigável, biodegradável e sustentável. Além disso, é um material versátil aplicado em biomateriais (GIL-CHÁVEZ *et al.*, 2021). Dentre as diversas oportunidades, a lignina tem sido estudada para a produção de adesivos, lignosulfonatos, fibras de carbono, bioplásticos, biocombustíveis e produtos químicos, como vanilina (CHENG & BREWER, 2017; THÉBAULT *et al.*, 2017; BAJWA *et al.*, 2019; DEMUNER *et al.*, 2019; MONGKHONSIRI *et al.*, 2021).

Nesse contexto, este trabalho teve como objetivo avaliar o pergaminho do fruto do café quanto à sua composição química, física e morfológica, bem como seu potencial para produção de polpa kraft e demais produtos de alto valor agregado, como nanocelulose e lignina.

Figura 1 – Fluxograma do Capítulo 1 e 2

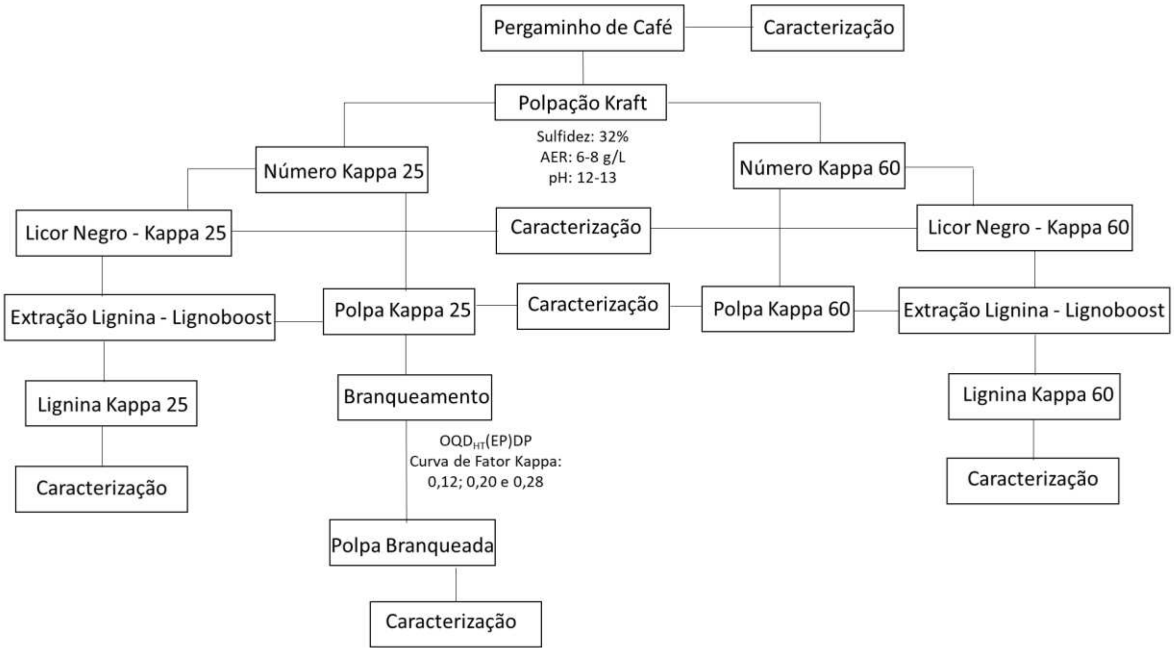
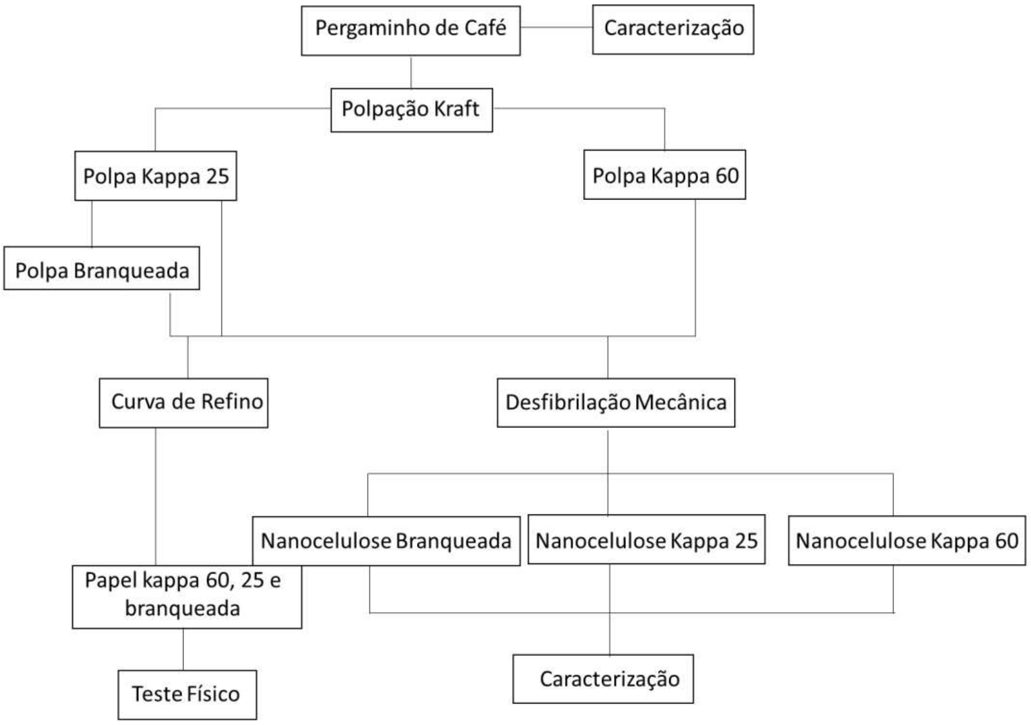


Figura 2 – Fluxograma do Capítulo 3 e 4



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CAPÍTULO 1: COFFEE BIOMASS RESIDUE AS RAW MATERIAL FOR CELLULOSE PRODUCTION AND PY-GC-MS ANALYSIS

ABSTRACT

The coffee production generates large volumes of residues, reaching 32 million of tons per year only in Brazil. This work aimed to evaluate the parchment of coffee fruit, a residue from the coffee industry, regarding its chemical composition as well as its potential for kraft pulp production. The parchment was characterized regarding the carbohydrates, lignin, extractives, and minerals content. The material was submitted to the kraft pulping process aiming kappa number 25. The main findings of this work were: glycans (38.5%), xylans (21.6%) and lignin (27.1%) as the main components of the raw material. The extractives content was 4.5%, quite similar to those found to hardwood species used for pulp production and the pulping yield was 42.6%. The lignins from the residual were extracted and characterized by their chemical composition, elemental analysis, and Py-GC-MS to evaluate the components of this biomass. The Py-GC-MS analysis provided the identification of 26 compounds, which were categorized into six different groups, such as acids, aldehydes, amines, furans, ketones, others and aromatics from the decomposition of lignin. Based on chemical biomass characteristics, the pulping performance was similar to those observed for softwood raw materials and with similar pulp bleachability. These results are indicative that the waste biomass evaluated has a good potential for the pulp production.

Keywords: Coffee industry. Kraft pulp. Pyrolysis.

1 INTRODUCTION

Wood is the main raw material for pulp production worldwide (BALKISSOON *et al.*, 2022). However, pulp can also be obtained from other lignocellulosic biomasses, such as bamboo, sugar cane bagasse, sisal as well as agricultural residues among others (IBA, 2021). Still concerning the pulp production, it is increasing strongly due to the society demand, e.g., Brazil jumped from the fourth to the second position as the largest pulp producer in the last years (IBA, 2021). All the large mills in the sector are fully consolidating their strategy, showing the market that there is room for growth in industrial production in the country (FUNCHAL, 2018).

Currently the country produces 21 million of tons per year, only behind the USA, which produces 42 million of tons per year (IBA, 2021). Pulp world production was 173 million tons in 2017 (FUNCHAL, 2018). It is also interesting to observe that during the COVID pandemic, the pulp and paper consumption is increasing, based on their collaboration to the society sustainability when compared to plastic materials (OLIVEIRA, 2021).

When considering that the wood price trends is to increase (IBA, 2021), and aiming to improve the Pulp & Paper mill competitiveness to find alternative raw materials is a necessary strategy; also, this collaborates to the society requirements regarding the sustainable production. Considering that the use of agricultural residues as raw material in pulp production has been highlighted due to its quantity, availability and the higher cost of wood-based feedstock, especially in developing countries with large agricultural production (BIAN *et al.*, 2019; CHERIF *et al.*, 2020; HARONI *et al.*, 2021) this strategy still needs to be strongly investigated by researchers from the industry and academic sectors. Pulp is a sustainable alternative to petrochemicals and considered a low cost and a rich source of chemicals, fuels, biopolymers and sugars (CHERIF *et al.*, 2020).

Coffee is one of the most important agricultural commodities in the world. Brazil is the largest producer and exporter of green coffee beans, followed by Vietnam, Colombia, Indonesia and Ethiopia. Brazilian production is around 3.5 million of tons of green coffee beans per year (EMBRAPA, 2020; MARTINEZ *et al.*, 2021). In 2019-2020, world coffee production was estimated at 10.1 million of tons. It is estimated that Brazil, which is responsible for around 35% of world production, which represents almost 3.6 million of tons per year (EMBRAPA, 2020).

Coffee refers to the seeds of a small fruit (coffee cherry) that is composed of the epicarp (red or yellowish peel that surrounds the fruit), mesocarp (thin sugary pulp, also called mucilage), endocarp (cartilaginous membrane that surrounds each seed, known as parchment), spermoderm (membrane highly adhered to the endosperm, better known as silver film or silver skin) and embryo (HALL *et al.*, 2022). Figure 1 illustrates the morphology of the coffee cherry.

Figure 1 - Morphology of coffee cherry indicating its layers

Industrial processing of coffee cherry can be done dry or wet, generating different residues, such as peel, pulp, parchment, silver film and wastewater (MARTINEZ *et al.*, 2021; LOPES *et al.*, 2022). In the processing of coffee beans, about 50% by weight of dried fruit are waste (HALL *et al.*, 2022). In producing countries, coffee residues are a source of severe contamination and making it a serious environmental problem (SERMYAGINA *et al.*, 2021; LOPES *et al.*, 2022).

Lignocellulosic biorefinery aims at greater sustainability through environmentally friendly process, bio-based materials, coproduction of chemicals and self-sufficient generation of energy (BHOWMICK *et al.*, 2018; NARESH *et al.*, 2019; MONGKHONSIRI *et al.*, 2021). Coffee processing residues can be also used as a raw material in the production of high-added value materials (BIAN *et al.*, 2019; CORRÊA *et al.*, 2021), because it consists mainly of cellulose, hemicelluloses and lignin. These residues can be converted into highly attractive substrates such as fuels, biogas and chemical products, for example, through the rapid pyrolysis of biomass, bio-oil is obtained, which is a source of value-added products and used in the production of hydrocarbons and hydrogen by through catalytic processes (ALVAREZ *et al.*, 2019; SAINI *et al.*, 2022).

Parchment is the fibrous endocarp that covers the two hemispheres of the coffee beans and separates them from each other. This basically consists of cellulose (40-49%), hemicelluloses (25-35%), lignin (22-35%) and ash (0.5-1%) (BRUM, 2007). The main component of the cell wall of plant fibers, cellulose is an attractive natural polymer due to its abundance and biodegradability. The use of cellulose has increased in polymers area due to its wide applicability.

As a benefit to the coffee producer, they may minimize the generation of waste and environmental impact, and the coffee biomass can be used as a raw material to another chain, being now a valuable material. Besides, the pulp mills may use this material in the pulp production, as raw material for the nanofibers production, paper for biodegradable packaging production or encapsulation of controlled drugs, among others (ARISTIZÁBAL-MARULANDA *et al.*, 2017; ELBA *et al.*, 2017; DADI *et al.*, 2018; REIS *et al.*, 2020; MBOOWA, 2021).

Chemical pulp production is strongly based on alkaline processes, being the kraft process the most used today (ZANÃO *et al.*, 2019). In kraft pulping, biomass is treated with sodium hydroxide (NaOH) and sodium sulfide (Na_2S) at high temperatures (140-170 °C) and pH above 12. This chemical process aims to dissolve the lignin, preserving the strength of the fibers. The kraft pulp production process can be used with several lignocellulosic species, uses proven production technology and efficient recovery of black liquor (DEMUNER *et al.*, 2021a).

As previously described, wood cost has grown largely in the last decades, the use of alternative biomasses for pulp production is important. The objective of this study was to evaluate the coffee industry residue as a raw material for the pulp production through its complete chemical and morphological characterization, and the bleached kraft pulp production performance.

2 MATERIAL AND METHODS

Coffee residues (parchment) from Santa Teresa, ES, Brazil were used. The residues were ground in a Wiley® Mill type knife mill and classified according to TAPPI T257cm-85 standard. The sawdust that passed through the 40 Mesh screen and was retained in the 60 Mesh screen was selected. The sieved biomass was air-dried in a conditioning room (23.0 ± 1.0 °C and 50.0 ± 2.0% humidity) for uniformity of moisture and stored in polyethylene bags.

2.1 Chemical composition of biomass

For the chemical composition characterization of parchment, the moisture content, total extractive content, silica content, ash content, metals content and chloride charge were determined in the sawdust according to the standards TAPPI T264 om-88, TAPPI T264 cm-97, TAPPI T245 cm-98, TAPPI T211 om-08, TAPPI T266 om-02 and TAPPI T256 cm-07, respectively. Elemental analysis was performed using CHNS-O model LECO equipment. For the analysis of the higher and lower heating value of the biomass, the TAPPI T684 om-15 standard was used.

The content of uronic acids, acetyl groups and sugars content (glucan, mannan, galactan, xylan and arabinan) were determined according to (SCOT, 1979), (SOLAR *et al.*, 1987) and SCAN-CM 71:09, respectively. Total lignin was measured by the sum of acid-soluble lignin (TAPPI UM250) and acid-insoluble lignin (TAPPI T222om-02). The lignin syringyl/guaiacyl ratio (lignin S/G ratio) was determined by oxidation with nitrobenzene (LIN, 1992).

2.2 Basic Density

Basic density is defined as the relationship between the dry weight of the sample and its saturated volume of water. The determination of the basic density of the parchment followed the methodology of the hydrostatic balance, described in the standard ABNT-NBR 11941.

2.3 Pulping process

The baking of the parchment was carried out, at first, in the form of tests, to analyze the behavior of the biomass and direct the ideal kappa values to work with.

Kraft pulping was carried out with 400 grams of dry biomass, in a MK digester. Table 1 shows the operating conditions of the pulping process.

Cooking was performed to obtain a delignification curve, varying the effective alkali and using the same H-factor (492) for the kappa number 60 curve and H-factor (1140) for kappa number 25 curve. The residual effective alkali values were set between 6 to 8 g/L. The maximum cooking temperatures for kappa numbers 60 and 25 were 158 °C and 168 °C, respectively. For both kappa number, the time to temperature was 60 minutes and time in temperature was 80 minutes.

The operational conditions of the pulping process obtained a direction, from preliminary tests to analyze the behavior of the biomass during kraft pulping and values practiced in the market for pulp production.

Table 1 - Operational conditions for kraft process targeting kappa 25 and 60

Parameters	**Conditions**
Liquor/Biomass ratio	5/1
Effective alkali, % NaOH	Variable*
Sulfidity, %	32
Residual effective alkali, g/L	6-8
H-factor	1140/492**

* Effective alkali charge was varied in order to meet the delignification curve at a controlled residual effective alkali of 6-8 g/L NaOH

** H-factor used in the kraft kappa process 25 and 60, respectively

The pulps were washed with water at room temperature to remove residual liquor after cooking. The individualization of the fibers was carried out in a laboratory hydrapulper, with a capacity of 25 liters. Pulp screening was performed in a Voith laboratory debugger with plates openings of 0.2 mm and the rejects were collected. The pulps were dewatered in a centrifuge and stored in plastic polyethylene bags. The parchment pulp and black liquor resulting from kraft process were characterized according to the parameters described in Table 2.

Table 2 - Parameters determined in kraft pulp and kraft black liquor

	Parameters	**Standard**
Kraft pulp	Hexenuronic acids	TAPPI T282 pm-07
	Brightness	TAPPI T452 om-08
	Sugars	SCAN – CM 71:09
	Total yield	Gravimetry
	Screen yield	Gravimetry
	Rejects content	Gravimetry
	Kappa number	TAPPI T236 cm-85
	Viscosity	TAPPI T230 om-08
Kraft black liquor	Residual effective alkali	SCAN N2 :88
	Elemental analysis	LCP Standard
	Heating value	TAPPI T684 om-15
	Total solids	Gravimetry

2.4 Bleaching process

Parchment kraft pulp was submitted to ECF bleaching, using the sequence OQD_{HT}(EP)DP in order to obtain brightness 90% ISO. Three bleaching curves were performed, varying the kappa factor of the D_{HT} stage. Then, it was determined the best reagent dosage adjustment to minimize the consumption of total active chlorine. The conditions for each stage of the bleaching sequence are shown in Table 3.

The conditions of the bleaching process obtained a direction, from preliminary tests to analyze the behavior of the biomass and values practiced in the market for the production of bleached pulp.

Table 3 - Bleaching conditions

Conditions	**O**	**Q**	**D_{HT}**	**EP**	**D**	**P**
Consistency, %	10	10	10	10	10	10
Temperature, °C	90	80	90	90	80	80
Time, min	60	30	120	60	120	60
Pressure, kPa	350	-	-	-	-	-
O_2, kg/odt	18	-	-	-	-	-
NaOH, kg/odt	15	-	*	14.5	*	6.5
$MgSO_4.7H_2O$, kg/odt	3	-	-	3	-	-
DTPA, kg/odt	-	2	-	-	-	-
Kappa factor	-	-	0.28; 0.20; 0.12	-	-	-
H_2SO_4, kg/odt	-	5.2	*	-	*	-
H_2O_2, kg/odt	-	-	-	7.8	-	3.0
ClO_2, kg/odt	-	-	-	-	**	-
Final pH	10-11	4-7	3.0	10-11	4.5-5.5	10-11

* H_2SO_4 or NaOH to pH adjustment
** Varied load for optimization of 90% ISO brightness

Oxygen delignification (O_2) was performed in a Quantum-Mark reactor under the conditions shown in Table 3. At the end of the reaction time, a sample of the residual filtrate was collected for pH analysis. The pulps were washed with distilled water in the proportion of 9 m^3/ton of pulp. O_2 pulps were characterized for brightness (TAPPI T452 om-08), kappa number (TAPPI T236 cm-85) and viscosity (TAPPI T230 om-08). From these parameters, the delignification efficiency, selectivity and brightness gain of O_2-stage were calculated according to the equations (1), (2) and (3). K_b, V_b and B_b represents the kappa number, viscosity and brightness of the brown pulp, respectively. K, V and B represents the kappa number, viscosity and brightness of O_2-pulp, respectively.

$$\text{Delignification efficiency} = \left[\frac{(K_b - K)}{K_b}\right] * 100 \tag{1}$$

$$\text{Selectivity} = \left\{\left[\frac{(K_b - K)}{K_b}\right] \div \left[\frac{(V_b - V)}{V_b}\right]\right\} \tag{2}$$

$$\text{Brightness gain} = B - B_b \tag{3}$$

For the chelating (Q), chlorine dioxide (D_{HT} and D), and alkaline extractions with hydrogen peroxide (EP and P) stages, the pulps were mixed with the reagents from each stage and H_2SO_4 or NaOH for pH adjustment in polyethylene bags. The treatments were carried out in a water bath with controlled temperature, and kept in it for the pre-established times, as shown in Table 3. At the end of each step, samples of the filtrate were collected to determine pH and residual. The pulps were washed with distilled water in the proportion of 9 m^3/ton of pulp, except in Q-stage, that the proportion of 50 m^3/ton of pulp was used.

To achieve the brightness of 90% ISO, in the D-stage a chlorine dioxide (ClO_2) dosage curve was performed. Three different loads of ClO_2 were used, adjusting the final pH in the range of 4.5 to 5.5 with H_2SO_4 and NaOH. Then, the ideal reagent dosage was obtained for each treatment. The parameters evaluated in the stages were: brightness, kappa number, viscosity and brightness reversion (TAPPI UM200 - 4h, 105 °C, 0% RH).

The parameters evaluated in the stages were: brightness (TAPPI T452 om-08), kappa number (TAPPI T236 cm-85), viscosity (TAPPI T230 om-08) and brightness reversion (TAPPI UM200 - 4h, 105 °C, 0% RH). The total active chlorine (TAC) and bleachability were calculated according to equations 4 and 5, respectively. K represents the kappa number of O_2-pulp and K_f the kappa number of the bleached pulp.

$$\text{TAC}\left(\frac{\text{kg}}{\text{odt}}\right) = \text{Total}\, ClO_2 \left(\frac{\text{kg}}{\text{odt}}\right) * 2{,}63 + \text{Total}\, H_2O_2 \left(\frac{\text{kg}}{\text{odt}}\right) * 2{,}09 \tag{4}$$

$$\text{Bleachability} = \frac{(K - Kf)}{TAC} \tag{5}$$

2.5 Py-GC-MS

Sawdust from parchment coffee (about 0.1 mg) was subjected to rapid pyrolysis in a Py-GC-MS using a micro-furnace pyrolyzer (Frontier Laboratories Ltd., Fukushima, Japan) connected to a GC-system MS (Shimadzu, model QP2020). Pyrolysis was carried out at a temperature of 550 °C and the interface at 290 °C. The GC operating parameters were: injector temperature (280 °C); Ultra-ALLOY$^{®}$ capillary column (UA5, 30 m x 0.25 mm ID, 0.25 µm film thickness); oven initial temperature (45 °C for 4 min), heated at 4 °C/min to 240 °C and held for 10 min; and helium carrier gas (1 mL/min) in splitless mode at 20:1 ratio. The mass spectrometer was operated in electron impact ionization mode at 70 eV and mass with a range of 50-350. The compounds were identified by comparing their mass spectra with the GC-MS spectral library (Willey and Nist) and with literature (BARBOSA *et al.*, 2008; FERNANDEZ-RODRÍGUEZ *et al.*, 2020; SILVA *et al.*, 2020; DEMUNER *et al.*, 2021b). The experiment was carried out in duplicate, and the 60 peaks with the largest area were analyzed. The S/G ratio was calculated by dividing the sum of the percentage of the syringyl-type lignin area (S) by the sum of the percentage of the guaiacyl-type area (G).

2.6 Fiber morphology

Analysis of the morphology of the parchment fibers was performed. For the individualization of the fibers, the samples were placed in a test tube, with a solution of hydrogen peroxide and glacial acetic acid, according to the method recommended by (DADSWELL, 1972). Subsequently, temporary blades were mounted to obtain the length (L), width (W), lumen diameter (D) and wall thickness (T) of the fibers. An optical microscope with a camera attached, an image acquisition system, and the Axio-Vision software were used.

3. RESULTS AND DISCUSSION

3.1 Parchment chemical composition

An advantage of kraft process is the versatility in terms of the raw material used. Knowledge of chemical composition of the wood or biomass is important due to it influences the efficiency of the process, yield, reagents consumption and pulp quality (XU *et al.*, 2020). The chemical composition of the coffee parchment is shown in Table 4. Zanão *et al.* (2019) reported chemical composition data for eucalyptus and pine wood (Table 4), and they were used for comparison with parchment as they are widespread raw materials in pulp production.

Uronic acids represented a fraction of 4.3% of the dry weight of the parchment. It is mainly made up of 4-*O*-methylglycuronic acid and galacturonic acid and, the former predominates in xylans, while the latter are constituents of pectin (EVANGELISTA, 2017). The content of uronic acids found for the parchment was higher than those obtained for eucalyptus and pine. This fact can be explained by the difference between the xylan content of coffee parchment (20.6%) and, eucalypt wood (10.2%) and pine (5.9%) found by (ZANÃO *et al.*, 2019).

The acid groups are related to the consumption of alkali in pulping, with its consequent hydrolysis and dissolution, and to the formation of hexenuronic acids (LI *et al.*, 2016; ZHANG *et al.*, 2019). Hexenuronic acids protects the xylans against terminal depolymerization reactions, preserving the pulping yield (BACARIN *et al.*, 2017; ZANÃO *et al.*, 2019), but negatively affect the pulp bleaching (LI *et al.*, 2016).

Table 4 - Chemical composition of dry wood-based coffee parchment, compared with eucalyptus and pine woods

Parameters, %	Coffee parchment	Eucalypt*	Pine**
Uronic acids	4.3	3.5 – 5.0	2.7
Acetyl groups	4.4	1.6 – 3.0	1.4
Total extractives	4.5	1.9 – 4.9	2.0
Acid-insoluble lignin	23.8	25.0 – 29.2	28.6
Acid-soluble lignin	2.1	2.9 – 4.2	0.6
Total lignin	25.9	27.1 – 31.3	29.2
Ash	0.865	0.1 – 0.32	-
Arabinan	0.2	0.2 – 0.3	1.3
Galactan	0.5	0.8 – 1.6	2.1
Glucan	36.8	42.3 – 49.4	42.7
Xylan	20.6	9.7 – 14.1	5.9
Mannan	0.4	0.7 – 1.4	9.7
S/G	0.78	2.50 – 3.12	-

* (NUNES *et al.*, 2010; ZANUNCIO *et al.*, 2013; JARDIM *et al.*, 2017; ZANÃO *et al.*, 2019)
** (ZANÃO *et al.*, 2019)

The content of acetyl groups found for the parchment was 4.4%, higher than the content found in wood-based materials. In the same way as the acid uronic groups, it followed the same trend of the xylan content. Acetyl groups are structural components of the hemicelluloses and connected to the xylan chain (QASEEM & WU, 2020). Acetyl groups negatively affect pulp production as they are easily removed during cooking, causing loss of yield and consuming alkali (ALVES *et al.*, 2011).

Extractives and lignin are considered undesirable to the pulping process and their contents directly affect the process yield and the consumption of reagents. The parchment presented extractives content (4.5%) similar to eucalypt wood (3.9%) found by (ZANÃO *et al.*, 2019).

Total lignin is determined by the sum of two fractions: acid-soluble and acid-insoluble. The parchment presented 25.9% of total lignin, represented by 23.8% of insoluble lignin and 2.1% of soluble lignin. In addition to the amount of lignin, it is important to measure the quality of lignin, that is, the relationship between the number of units derived from sinapyl alcohols (syringyl lignin) and coniferyl alcohols (guaiacyl lignin), called the lignin S/G ratio.

Lignin S/G ratio of 0.78 was found for the parchment. Nunes *et al.* (2010) reported higher S/G ratio values (2.50 to 3.12) for eucalyptus wood. On the other hand, pine wood has predominantly lignin of the guaiacyl type. Sequeiros and Labidi (2017) reported that the speed of wood delignification is influenced by the lignin structure, being directly proportional to the lignin S/G ratio. The S-type lignin is more reactive and, therefore, easier to be removed during the process of kraft pulping due to the G-type lignin containing higher amounts of C-C bonds at the C5 position (SJÖSTRÖM, 1993).

Gomes *et al.* (2008), studying commercial eucalyptus clones, found good correlations between the S/G ratio and the screen yield. Then, the desirable wood for the production of kraft pulp must have a low lignin content associated with a high lignin S/G ratio.

Among the various chemical components of biomass, the most significant fraction of its weight is represented by carbohydrates, mainly cellulose and hemicelluloses. Cellulose is composed exclusively of glucans and its content on the parchment was 36.4%. This content was lower than that found by Zanão *et al.* (2019) for eucalyptus and pine, which can be a disadvantage due to the cellulose content being directly associated with pulping yield.

Parchment presented xylan as the dominant fraction of hemicelluloses, similar to hardwoods. The other sugars (arabinan, mannan and galactan) presented content below 1%. In general, eucalyptus has higher levels of glucans and xylans when compared to pine wood. In pine, a predominance of glucans and mannans is observed (COLODETTE *et al.*, 2015; ZANÃO *et al.*, 2019).

The ash content, measured by the complete combustion of the raw material, is the parameter that represents the amount of non-combustible material in the biomass.

The ash content of 0.865% was found on the parchment, slightly higher than that commonly found in the literature for species of eucalyptus. Gomes *et al.* (2013) studying several eucalyptus clones for pulp production, found an average ash content in the range of 0.1 to 0.24%. However, the parchment showed a low value when compared with others lignocellulosic materials, as agricultural crops (5 to 10%) and agricultural residues (above 30%), such as rice husks (QUAAK *et al.*, 1999).

The ash content has an influence on the pulp production and mill operation, since they cause corrosion and deposits in the equipment, decrease mill throughput, reduce biomass heating value and problems vary from the clogging caused by the deposition of the residual combustion material to more severe damages in fluidized bed systems (QUAAK *et al.*, 1999). Main elements involved in scale and slag formation are the alkali metals present in the ashes, such as potassium and sodium (JENKINS *et al.*, 1998).

Table 5 - Characterization of coffee parchment regarding higher and lower heating values, and ultimate analysis

Parameters		Coffee parchment
HHV, MJ/Kg		20.2
LHV, MJ/Kg		18.8
Silica, %		0.015
Ultimate analysis	C, %	50.6
	H, %	6.3
	N, %	0.3
	S, %	0.3
	O, %	41.6
	Cu mg/Kg	3.8
	Mn mg/Kg	10.7
	Fe mg/Kg	125.2
	Mg mg/Kg	432.8
	Ca mg/Kg	595.9
	Na mg/Kg	700.3
	K mg/Kg	3175.9

Calcium, magnesium and silica are undesirable in most industrial processes because of their ability to cause deposits in the equipment during the liquid evaporation and solid combustion (TOMELERI, 2019). However, potassium is particularly dangerous due to its ability to decrease the melting temperature of ash during combustion. This causes sticky ash problems in recovery boiler systems (MU *et al.*, 2021).

The quantification of transition metals is a particularly important analysis in operating systems where oxygen derivatives chemicals are used in biomass bleaching. These metals are aggressive in relation to the oxygen-oxygen bonds, thus degrading any form of peroxide. Subsequently, highly reactive free radical intermediates are formed, that negatively affect the integrity of the carbohydrate chains (GOMES *et al.*, 2013).

The energy potential produced by a fuel can be expressed by its heating value, in terms of the energy ratio contained in the material to the amount of mass (TOMELERI, 2019). Table 5 shows the results of the higher heating value (HHV) and lower heating value (LHV) of the parchment.

HHV measure is used to refer to the amount of heat available in the fuel, while the LHV indicates the usable energy. For this reason, the HHV values are generally higher than LHV for the same material (HUGOT, 1986). For the parchment, the values found for HHV and LHW were 20.2 and 18.8 MJ/Kg, respectively.

The heating values for lignocellulosic biomass can vary with respect to their origin, species, harvest conditions, storage, chemical composition, and other environmental factors. Telmo and Lousada (2011) reports HHV varying between 17.6 and 20.8 MJ/Kg for hardwoods and for conifers, varying between 19.6 and 20.3 MJ/Kg. The parchment presented a similar result for wood-based materials.

The parchment presented 50.6% of carbon, 41.6% of oxygen, 6.3% of hydrogen and 0.3% of nitrogen (Table 5). These values are close to those found by Oasmaa *et al.* (2010) for eucalyptus wood (50.1% C, 44.0% O, 6.0% H and 0.1% N). Elemental analysis of wood varies little by species, and it can be assumed that it contains about 50% of carbon, 6% of hydrogen, 44% of oxygen and 0.1-0.5% of nitrogen (BRITO & BARRICHELO, 1981).

Hasan *et al.* (2018) reports that there are significant and positive correlations between the levels of carbon and hydrogen and the HHV. High levels of oxygen and ash reduce the heating value (HUANG *et al.*, 2009). The similar elemental analysis between parchment and eucalyptus justifying similar HHV values between these materials.

3.2 Basic density

The basic density is directly related to the performance of pulping process, as well as to the quality of the final product (SOUZA *et al.*, 2017). The result of the basic density of coffee parchment is shown in Table 6. Zhang *et al.* (2019) reported density values for eucalypt and pine wood and they are also shown in Table 6.

Table 6 - Basic density of parchment, compared to eucalypt and pine woods

Biomass	Basic density (kg/m^3)
Parchment	522.7
Eucalypt*	488.7
Pine*	346.7

*(ZANÃO *et al.*, 2019).

The basic density of the parchment was 522.7 kg/m^3, higher than that of wood-based materials commonly used for pulp production. A high density is favorable in the pulp production because it increases the pulp mill production, decreasing the biomass specific consumption, which is one of the most important parameters for the biomass quality for the pulp production (GALLO *et al.*, 2018). However, it may be unfavorable in relation to the penetration of white liquor when the conditions are not properly optimized (GALLO *et al.*, 2018; BATALHA *et al.*, 2012).

3.3 Parchment fiber morphology and histology

The study of anatomy is fundamental to the evaluation of the potential of a biomass for the pulp production. The morphological characteristics fibers can vary between species, between trees of the same species and even within the same tree (METCALFE, 1989). These variations affect fiber dimensions, which are important indicators of the potential of a biomass for the pulp and paper manufacture (GONÇALEZ, 2014).

The results of the fiber dimensions of parchment is presented in Table 7.

Table 7 - Average values of fiber dimensions, compared to eucalypt and pine woods

Parameters	Preachment	Eucalypt*	Pine**
Length, mm	0.53	0.86	3.50
Width, µm	23.59	17.39	40.55
Lumen diameter, µm	12.84	10.92	27.73
Wall thickness, µm	5.37	3.23	6.41

*MENEGAZZO, 2012
**VIVIAN *et al.*, 2015.

3.4 Py-GC-MS

Py-GC-MS analysis of biomass was performed and the mass spectra obtained were combined with the NIST library and the specific peak area values for each compound were listed in Table 7. The parchment pyrogram is shown in Figure 2 and the compounds equivalent to the peak number are also listed in Table 8.

Thermochemical transformations of lignocellulosic biomasses via pyrolysis result in charcoal, non-condensable gases and bio-oil, which contains a complex mixture of phenolic compounds, organic acids, ketones, aldehydes and furans (SILVEIRA JUNIOR *et al.*, 2021).

Figure 2 - Pyrogram of coffee parchment

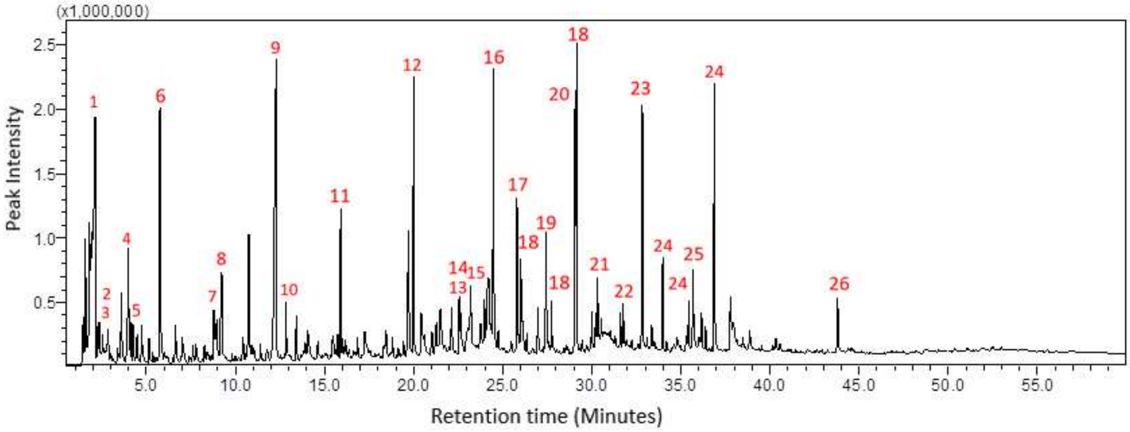


Table 8 - Py-GC-MS results and S/G ratios

Peak		Compounds	Origen	Mass fragments	Area
1	Acids	Acetic Acid	C	60	7.01
26		Hexadecanoic acid	C	129/73/60	0.82
2	Aldehydes	2-Butenal	C	70/55	0.65
4		2-Methyl-2-butenal	C	84/69/55	0.54
3	Amines	*N*-Nitrosodimethylamine	-	74/55	0.48
6	Furans	Furfural	C	97/96/67/51	4.20
7		2(5*H*)Furanone	C	84/70/55	0.69
8	Ketones	1,2-Cyclopentanedione	C	98/69/55	2.19
10		3-Methyl-1,2-cyclopentadione	C	113/112/83/69/55	0.81
9	Others	2,2-Diethyl-3-methyl-oxazolidine	-	114/58	9.02
5		3-Propoxy-1-propene	-	71/58	0.65
13	Aromatics	3-Methoxycathecol	Ca	140/125/97	0.87
14		3-Methylcathecol	Ca	124/106/78	0.66
11		Guaiacol	G	109/124/81/53	2.18
12		4-Methylguaiacol	G	138/123/95	4.31
16		4-Vinylguaiacol	G	150/135/107/77	4.21
15		4-Ethylguaiacol	G	137/152	0.96
18		4-Propenylguaiacol	G	164/77/149	6.96
19		Vanilin	G	151/152/109/81	1.92
21		4-Acetylguaiacol	G	166/151/123	1.07
22		Guaiacylacetone	G	137/180/122	0.68
17		Syringol	S	154/139/111/96	2.07
23		4-Vinylsyringol	S	180/165/137	3.71
20		4-Methylsyringol	S	168/153/125	3.77
25		Syringaldehyde	S	182/181/111	1.50
24		4-Propenylsyringol	S	194/91/151	6.04
			Total S-type		17.09
			Total G-type		22.29
			Lignin S/G ratio		0.77

C: carbohydrate; Ca: catechol; G: guaiacil; S: syringyl.

Glycosidic bonds present in cellulose tend to break down at high temperatures. Therefore, the cellulose structure degrades markedly during the early stages of fast pyrolysis with a reduction in the degree of polymerization (WANG *et al.*, 2017).

The cleavage of β-1,4-glycosidic bonds largely contribute to the formation of furans and levoglucosan (LG) (WU *et al.*, 2016). Studies show that the main glucose-based carbohydrate pyrolysis products were LG, 5-hydroxymethylfurfural (HMF), furfural, methylglyoxal, 2-hydroxyacetaldehyde (HAA) and acetic acid (METTLER *et al.*, 2012).

Räisänen *et al.* (2003) revealed that the pyrolysis product distributions of xylose, arabinose, mannose, and galactose were similar in quality, but different in quantity. Furans, ketones and anhydro-sugars were the main products, with furfural being the most abundant.

The pyrolysis products of hardwood and agricultural residues hemicelluloses present high contents of acids, furfural and five-carbon compounds. Softwood hemicelluloses contained mainly six-carbon compounds, such as glycans, galactans and anhydro-sugars (WANG *et al.*, 2015a; WANG *et al.*, 2015b). It was possible to observe this behavior in the coffee residue, with a high percentage of area of acetic acid (7.01%) and furfural (4.20%).

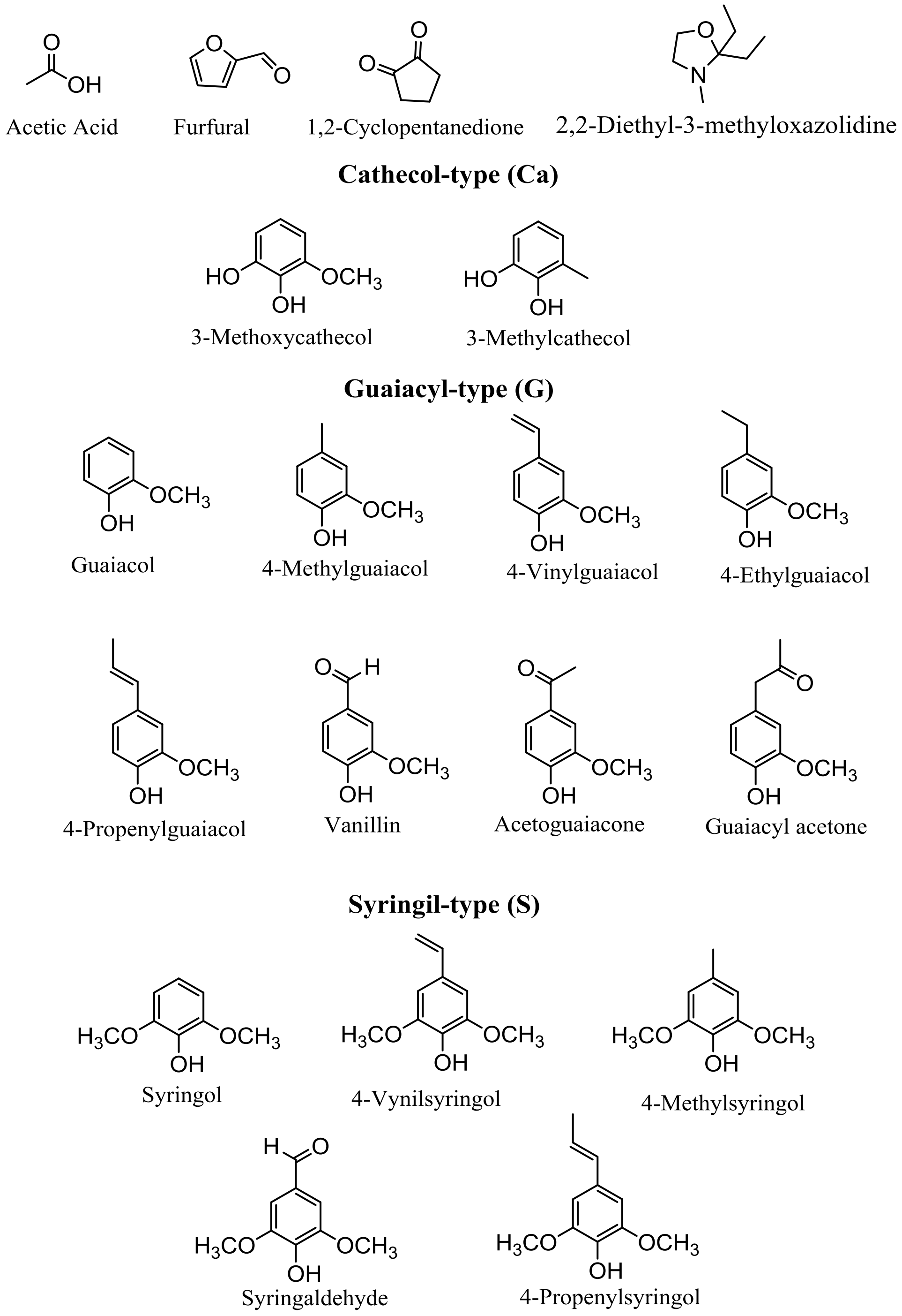
Parchment pyrolysis showed an area percent of 9.02% for compound 2,2-Diethyl-3-methyl-oxazolidine. At high temperatures, there may be a decrease in pyrolysis products with high added value and the formation of O/N-heterocyclic compounds, due to deoxygenation, demethoxylation and deamination reactions, and cracking of lower molecular weight compounds (MISHRA *et al.*, 2020).

The Py-CG-MS analysis provided the identification of 26 compounds (Figure 2), which were categorized into six different groups, such as acids, aldehydes, amines, furans, ketones, others and aromatics from the decomposition of lignin. Based on literature data, the lignin markers were separated into: catechol type (Ca), guaiacyl type (G) and syringyl type (S) (FERNANDEZ-RODRÍGUEZ *et al.*, 2020; SILVA *et al.*, 2020; DEMUNER *et al.*, 2021b). Lignin hydroxyphenyl-type (H) markers were not found (Figure 3).

The decomposition of lignin methoxyl groups can lead to the transformation of S-type phenols into G-type phenols and even into catechol (Ca) and hydroxyphenyl (H). This transformation is potentiated at high reaction temperatures (WANG *et al.*, 2017).

It was observed that the parchment presents 43.4% of S-type lignin and 56.6% of G-type lignin, obtaining a lignin S/G ratio value of 0.77. This S/G ratio value was similar to that found by the oxidation with nitrobenzene methodology (Lignin S/G ratio: 0.78) in this study.

Figure 3 - Main compounds present in Py-GC-MS



3.5 Pulping processes

The kraft pulping process aims to break the bonds of lignin and solubilize it in the cooking liquor, avoiding as much as possible the degradation of carbohydrates. The main chemical reagents in cooking liquor are sodium hydroxide ($NaOH$) and sodium sulfide (Na_2S)

(GOUVÊA *et al.*, 2009; GOMIDE & GOMES, 2015; DEMUNER *et al.*, 2021a; BIJOK *et al.*, 2022). Table 9 shows the results obtained in kraft pulping for the delignification curves.

Table 9 - Results of kraft pulping of parchment

	Effective alkali, %	Kappa number	Screened yield, %	Rejects, %	Total yield, %	Residual effective alkali, g/L
Kappa 25	21.5	26.9	42.6	0.6	43.2	6.0
	22.5	24.5	42.1	0.5	42.6	7.4
	23.5	22.1	40.5	0.6	41.1	8.3
Kappa 60	19.5	68.4	48.1	0.8	48.9	5.9
	20.5	61.4	46.8	0.8	47.6	6.1
	21.5	54.7	45.9	0.6	46.5	8.3

The operational variables of the Kraft process were fixed for each curve (kappa 25 and 60), except for the effective alkali. A delignification curve was obtained using an alkaline concentration between 21.5 and 23.5% for kappa 25 and 19.5 and 21.5% for kappa 60. The objective was to reach an ideal alkaline concentration to obtain a kappa number around 25 and 60, with an adequate yield and a moderate consumption of reagents.

It was observed that an increase in effective alkali resulted in a decrease in kappa number and process yield. The residual effective alkali increased, indicating an excess amount of chemical reagent during the process. The pH of the black liquor for all cooking was kept at 12.9.

Kraft process was suitable for the production of pulp from parchment, requiring 22.5% of effective alkali to obtain a kappa of 24.5 and a total yield of 42.6%. To obtain a kappa of 61.4 and a yield of 47.6% was needed 20.5% of effective alkali.

The increase in the kappa number provided a gain in pulp yield. Compared to the pulp EA 23.5%, there was an increase of 1.5% yield for the pulp EA 22.5%. An increase of 2.1% yield for the pulp EA 21.5% compared to pulp EA 23.5% was also observed. During cooking, some of the carbohydrates are also dissolved by chemical reactions, mainly hemicelluloses. The increase in the delignification intensity, in order to reach lower kappa numbers, causes a decrease in yield and carbohydrate content (VENTORIM *et al.*, 2016).

Usual residual effective alkali values by the pulp and paper industries for both curves were maintained. The total yield obtained was close to the values found in the literature for pine wood (DEMUNER *et al.*, 2020), commonly used in the pulp production.

The residual effective alkali (REA) can be an indicator of the efficiency of the process. A low alkali residual ensures greater conservation of carbohydrates (cellulose and hemicelluloses), resulting in benefits to the process yield (ACHRÉN *et al.*, 1998; SHIN & STROMBERG, 2003; RIBEIRO *et al.*, 2019) and to the quality of the final product (SHIN & STROMBERG, 2005). However, it is necessary to ensure a satisfactory residual at the end of cooking so that lignin does not precipitate on the fibers.

The final pH of the black liquor should be high enough to guarantee a good delignification of the wood and to avoid the lignin precipitation. According to Gomes *et al.* (2001), under normal cooking conditions, precipitation occurs from pH 11.0.

The REA ranged from 6.0 to 8.3 g/L and the pH remained at 12.9 for all cooks, a value that does not allow the precipitation of lignin. The higher the kappa number and the lower REA represents a lower chemical load for the recovery boiler.

The pulps obtained after the kraft process with kappa 24.5 had a brightness of 20.9 %ISO, viscosity of 965 dm^3/Kg and hexenuronic acids (hexA) of 63.5 mmol/Kg. The pulp with kappa 61.4 had a brightness of 15.4%ISO, viscosity of 1013 dm^3/Kg and hexA of 66.4 mmol/Kg.

Almeida (2010) reported kraft pulping of eucalyptus wood for kappa number 25. In comparison with parchment, eucalyptus wood needed less drastic conditions of effective alkali (16.0%) and achieved better results in screened yield (54.5%). It was already expected that the pulping of eucalyptus wood would be easier than that of coffee residue due to the differences in its chemical compositions. Despite having a lignin content close to that found in hardwood, parchment has lower cellulose content and lower lignin S/G ratio.

However, the parchment obtained a yield similar to that obtained by softwood. In general, the yield pulp obtained for softwoods is 40 to 45% and for hardwoods is 45 to 54% (D'ALMEIDA, 1988; SMOOK, 1989; SIXTA, 2006).

3.6 Bleaching process

Bleaching process starts with the oxygen delignification process (O_2-stage). The results of the O_2-stage are shown in Table 10.

Table 10 - Results of oxygen delignification stage

Parameter	Results
Kappa number – unbleached pulp	24.5
Kappa number – O_2-pulp	16.9
Delignification efficiency, %	31.0
Viscosity – unbleached pulp, dm^3/kg	965
Viscosity – O_2-pulp, dm^3/kg	898
Selectivity	4.47
Brightness – unbleached pulp, % ISO	20.9
Brightness – O_2-pulp, % ISO	28.6
Brightness gain, %ISO	7.7
Hexenuronic acid – unbleached pulp, mmol/kg	63.5
Hexenuronic acid – O_2-pulp, mmol/kg	62.8

The oxygen acts preferentially on lignin structures containing free phenols, converting these phenols into dicarboxylic acids, which increase lignin solubility (COLODETTE & MARTINO, 2013). This lignin fraction represents only 50% of the total lignin present in unbleached kraft pulp (WHITE, 1996).

The oxygen delignification efficiency of the parchment pulp was 31.0%, with a reduction in the residual lignin in the pulp. However, it is known that as oxygen is a nucleophilic oxidant, under alkaline conditions it promotes the removal of lignin, but does not react with the hexenuronic acid (Hexa) groups. Therefore, high Hexa content in the brown pulp, negatively affects performance of O_2-stage (VUORINEN *et al.*, 1996). The hexenuronic acid of unbleached parchment pulp was 63.5 mmol/kg.

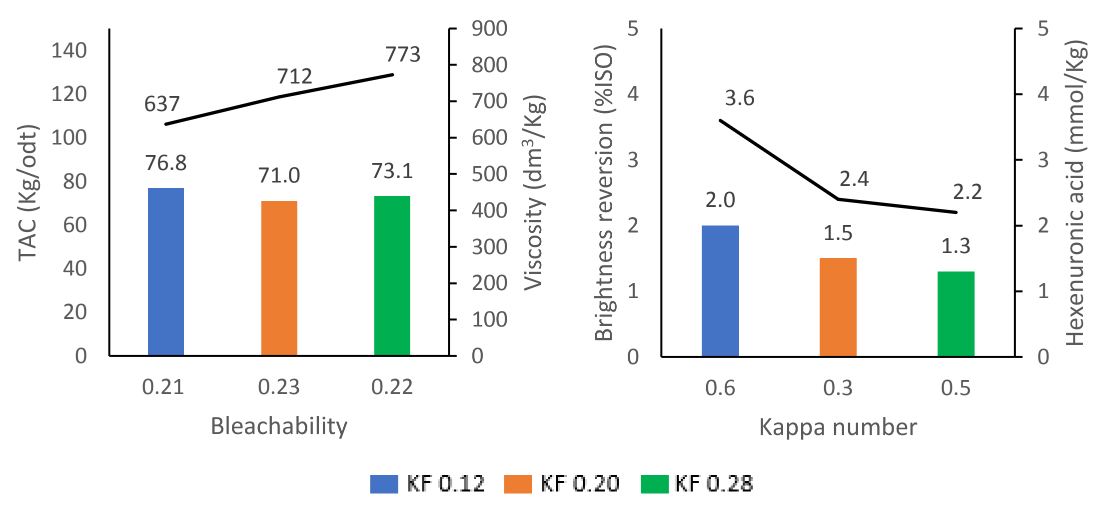
During alkaline pulping, uronic acid groups react with alkali to form HexA, which can be defined as a product of alkaline cooking. The main components of cellulosic pulp kappa number are hexenuronic acids and lignin (FAVARO *et al.*, 2021). There is a linear relationship between the kappa number and the HexA content for both long fiber and short fiber pulps, in which a unit of kappa number is equivalent to 11.6 µmol/g of HexA/kg, depending on the methodology of quantification adopted.

O_2-stage has low selectivity compared to other oxidative processes, presenting high degradation of cellulose and consequent viscosity loss (RABELO, 2006). The use of additives, such as magnesium sulfate, can be applied at this stage to minimize the oxidative cleavage of carbohydrates. Magnesium sulfate reacts with sodium hydroxide to produce magnesium hydroxide, which inactivates the transition metal ions in the pulp (THAKORE *et al.*, 2005). Otherwise, the metal ions would catalyze the decomposition of the peroxides producing free radicals, which would attack the carbohydrate chains and reduce the pulp viscosity.

The drop-in viscosity for the parchment pulp was only 6.9%, resulting in a pulp viscosity of 898 dm^3/kg and oxygen stage selectivity of 4.47. The high selectivity obtained in this step can be due to the magnesium sulfate additive. Besides that, the hexenuronic acids protect the xylans against terminal depolymerization reactions (GOMES *et al.*, 2013; ZANÃO *et al.*, 2019; FAVARO *et al.*, 2021).

The results of the pulp bleaching performance are shown in Figure 4. The pulps bleaching was carried out by QD$_{HT}$(EP)DP sequence, differentiating between them only in the kappa factor of the D$_0$-stage. The total active chlorine (TAC) was lower for the kappa factor 0.20 pulp sample (71 kg/odt), which also presented a higher value of pulp bleachability (0.23).

Figure 4 – Pulp bleaching performance, where: (A) indicates the bleachability, total active chlorine and final pulp viscosity; and (B) indicates final kappa number, brightness reversion and hexenuronic acid content



The coffee tree belongs to the group of angiosperms (hardwood) plants, like eucalypt wood, and its lignin consists of syringyl (S) and guaiacyl (G) units, while in gymnosperms, as pine, guaiacyl units are predominant (SARKANEN & HERGERT, 1971). The relative proportions of S and G units, and the nature of bonds between them are highly variable, influencing the lignin reactivity during the pulping and bleaching process (PINTO *et al.*, 2005).

Lignin S-type have two methoxyl groups at the C-3 and C-5 position, which makes syringyl lignin more reactive than guaiacyl (PINTO *et al.*, 2005). G-type have an aromatic carbon at the C-5 position available to make carbon-carbon bonds, which contributes to a high degree of condensation and, consequently, to a greater resistance to delignification (COLLINS *et al.*, 1990; GUTIÉRREZ *et al.*, 2006).

It was also observed an effect of the kappa factor on the brightness stability and HexA content. When applied Rabelo (2006) in a study with *Eucalyptus globulus* clones confirmed the effect of syringyl lignin units in the pulping and bleaching process when comparing the lignin S/G ratio with the chemical charges used. It was observed that the clone with the highest lignin S/G ratio has the best pulping and bleaching performance. Therefore, it is believed that pulps with a high content of type S lignin are easier to delignify during ECF bleaching (TSUTSUMI *et al.*, 1995; DEL RIO *et al.*, 2005).

4 CONCLUSION

The analysis of the density and chemical properties of the residue from the coffee industry allows us to conclude that this material has the potential to be used as a raw material for the pulp production. Parchment had extractives (4.5%), ash (0.9%) and lignin (25.9%) similar to the raw materials most used in the pulp production, as eucalypt. Despite having a low cellulose content (36.4%), it has a high hemicelluloses content (30.8%), compared to pine and eucalypt wood, which contributes to the 42.1% yield in kraft pulping. ECF bleaching of the parchment with the OQD$_{HT}$(EP)DP sequence proved to be adequate for the production of 90%ISO bleached pulp. Despite the total active chlorine of 71.0 kg/odt, it obtained a bleachability of 0.23, a value similar to that found for eucalypt wood and higher than pine wood. These results are indicative that the waste biomass evaluated has a good potential for the pulp production.

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CAPÍTULO 2: TECHNICAL KRAFT LIGNIN FROM COFFEE PARCHMENT

ABSTRACT

The biomass deconstructed by kraft process and the lignin dissolved in the black liquor are burned to generate energy in a pulp mill. This study used the black liquor from coffee parchment cooking, a residue from the coffee industry, to isolate kraft technical lignin. The parchment was subjected to the kraft pulping process to obtain pulps of kappa number 60 and 25, and the resulting black liquors were used for lignin extraction. Chemical characterization, elemental analysis and heating value of liquors and lignins were performed, as well as FTIR and Py-CG-MS analysis of lignins. The cooking provided liquors with similar characteristics, with lignin content of 31.67 and 32.63% for kappa 60 and 25 liquors, respectively. The extractions resulted in high purity lignin (92.35% for K#60 lignin and 93.96% for K#25 lignin). The higher heating values were 23.8 and 25.4 MJ/Kg for K#25 and K#60 lignins, respectively. FTIR analysis showed characteristic peaks of lignin. Through Py-GC-MS, it was possible to observe the slight predominance of guaiacyl-type lignin, which can be an advantage depending on the application. It is possible to extract lignin from the black liquor obtained from the coffee parchment pulping to generate products with high-added value.

Keywords: Biorefinery. Coffee industry. Coffee waste. Kraft process

1 INTRODUCTION

Coffee is a perennial and dicotyledonous plant, belonging to the Rubiaceae family (SCHEEL *et al.*, 2019). *Coffea arabica* L. and *Coffea canephora* L. are the species with economic importance in Brazil (MARTINS *et al.*, 2022).

Coffee industry is important worldwide, generating annually revenue of around US$ 200 billion (ABDELWARETH *et al.*, 2021). However, the coffee harvest (2020/21) generated 11.4 million tons of solid by-products (SILVA *et al.*, 2022) and a high percentage is considered waste. The parchment represents approximately 12% (dry basis) of the coffee cherry and causes pollution and health ricks if discarded to the environment (MARTINEZ *et al.*, 2021).

Coffee parchment chemical composition is based on cellulose, hemicelluloses, lignin, extractives and inorganics (MARTINEZ *et al.*, 2019). With its high sugars content, it can be a potential raw material for pulp and paper production. Besides that, the parchment structure is also fibrous material, very close to the wood (RAMIREZ-MARTINEZ *et al.* 2013), the main raw material used in pulp mills. The parchment fibers have a length 0.53 mm, width of 23.29 µm and lumen diameter of 12.84 µm, similar to that found by Foelkel (2007) and Zanuncio *et al.* (2016) for eucalypt wood fiber. Then, the parchment lignin can also be extracted and used to produce high value-added products.

Lignin can be extracted from biomass mainly by pulping processes. These processes can be acidic (sulfite process) or alkali (kraft process). Currently, more than 90% of the pulps produced are by the kraft process, and more than 50 million tons of kraft lignin is produce annually (MANDLEKAR *et al.*, 2018; TRIBOT *et al.*, 2019).

In the kraft process, the deconstruction of biomass occurs under conditions of high temperatures (160-170 °C) and pressures, through an aqueous solution of NaOH and Na_2S (POTTHAST, 2006). The aim of the process is to cleave and solubilize the lignin and, as a result, to obtain a pulp basically composed of cellulose and hemicelluloses. This pulp is used for the paper production, as packaging, tissue, printing and writing and special papers.

A residual liquor is generated in the kraft process, called black liquor. This liquor is rich in inorganic and organic components, mainly lignin and hemicelluloses cleaved during the process (KROTSCHECK & SIXTA, 2006). Black liquor is routed to the cooking liquor kraft recovery cycle. In this cycle, the cooking reagents (NaOH and Na_2S) are recovered and steam/energy is generated due to the burning of the liquor in the recovery boiler.

Energy generation is important to meet the needs of the kraft mill itself. However, part of the lignin present in black liquor may be used to produce products with high-added value, without harming energy generation and, inserting the kraft industry into the current concept of biorefinery. Some pilot scale or industrial facilities for using a fraction of the lignin available in kraft pulp mill have been announced in the last decade and are already in operation (STORA ENSO *et al.* 2010; SÖDRA 2022; SUZANO 2023).

The lignin recovery process has been introduced in mills in several countries, such as Canada (Mead-Westvaco), USA (Domtar Plymouth Mill), Finland (Stora Enso) and Sweden (Nordic Paper Bäckhammer) (GORDOBIL *et al.*, 2021). Kraft mills in Brazil (Klabin and Suzano) have also intensified studies with lignin in an industrial scale.

Among the various technologies for the extraction of kraft lignin from the black liquor, the most considered are the LignoBoost™, LignoForce™, membrane-assisted electrochemical and ionic liquids processes (JIN *et al.* 2013; DESSBESELL *et al.* 2020; BAGH *et al.* 2021; DIAZ-BACA & FATEHI 2021; KALLIOLA *et al.* 2022). These processes enable its best use and increase the profitability and sustainability of the kraft mills. In the LignoBoost™ and LignoForce™ processes, which are the most used in pilot scale or industrial operation, the lignin is extracted based on the through acidification of black liquor (HUBBE *et al.* 2019).

Kraft lignin has the characteristics of environment-friendly, biodegradable and sustainable. Besides that, it is a versatile material applied in biomaterials (GIL-CHÁVEZ *et al.*, 2021). Among the various opportunities, lignin has been studied for the production of adhesives, lignosulfonates, carbon fibers, bioplastics, biofuels and chemicals (CHENG & BREWER, 2017; THÉBAULT *et al.*, 2017; BAJWA *et al.*, 2019; DEMUNER *et al.*, 2019; MONGKHONSIRI *et al.*, 2021).

However, challenges are also faced when working with kraft lignin. It is a very heterogeneous polymer due to its variable molecular weights and chemical complexity (inter-unit linkages and functional groups), what affects the solubility and reactivity (VISHTAL & KRASLAWSKI, 2011; LOURENÇON *et al.*, 2021; ZHANG *et al.*, 2022). Then, for better use of this kraft mill waste, a complete characterization of lignin needs to be performed before using it in lignin-based bioproducts.

As eucalyptus and pine woods are widely used in the kraft process, the wood kraft lignins have already been extensively studied (TAGAMI *et al.*, 2019; DEMUNER *et al.*, 2021; GORDOBIL *et al.*, 2021; LOURENÇON *et al.*, 2021; PAANANEN *et al.*, 2021; SUOTA *et* *al.*, 2021). However, the alternative biomasses are being used for the pulp production and it is also necessary to characterize the lignins obtained.

In this study, similarities may be observed between coffee residue kraft lignin and eucalyptus kraft lignin, commonly studied, since both (coffee and eucalyptus) are dicotyledonous plants (GRATTAPAGLIA *et al.* 2012; SCHEEL *et al.* 2019). However, the study of alternative lignins to wood lignin is important because different characteristics such as functional groups and molecular weight can be observed. Lignins with different properties may be suitable for different products, which is critical for the advancement of new lignin products. In addition, it is economically viable and sustainable to use waste to generate high value-added products.

The aim of this study was performed a complete characterization of two kraft technical lignins obtained by different kraft pulping process of coffee parchment. Complete chemical analysis with the use of advanced analytical tools were used to characterize this lignins. This study will provide the basis for the adequacy of these raw materials to produce high-added value products and for advance and diversification of kraft industry bioproducts.

2 MATERIAL AND METHODS

2.1 Material

Pulps and kraft black liquors were obtained from the kraft pulping process of coffee parchment. The parchment is a residue from the coffee industry, from the production of *Coffea canephora* L., popularly known as Conilon. The parchment used in this study comes from Santa Teresa city (19° 55′ 53″ South, 40° 35′ 43″ West), Espírito Santo State, Brazil.

2.2 Kraft Pulping

The kraft pulping process was carried out using previously optimized parameters to obtain cellulosic pulps with kappa 25 and kappa 60. To obtain a pulp with kappa number 60, the effective alkali and the H-factor were 20.5% and 492, respectively. For kappa number 25, the effective alkali was 22.5% and the H-factor was 1040. The maximum cooking temperatures for kappa numbers 60 and 25 were 158 °C and 168 °C, respectively. For both kappa numbers, time to temperature was 60 minutes and time at temperature was 80 minutes. Both cooks were carried out in MK digester using a liquor/biomass ratio of 5/1, 32% sulfidity and effective residual alkali of 6-8 g/L.

The total yield of the kraft process was determined by gravimetry and the pulps were characterized for kappa number (TAPPI T236 cm-85) and viscosity (SCAN CM 15:99).

2.3 Lignin Kraft Extraction

Residual kraft black liquors from coffee parchment cooking were used to extract coffee kraft lignins. The first black liquor was obtained from kraft pulping to reach pulp of kappa number 60, described as BL-KN 60. The second black liquor was obtained from kraft pulping to reach pulp of kappa number 25, described as BL-KN 25.

The black liquors were concentrated to solids content between 30-40% and the first step of lignin precipitation was performed with carbon dioxide until pH 9.0. After, the lignin was suspended in a sulfuric acid solution between pH 2.0-3.0. Precipitated lignin was filtered and washed with acidic water for its extraction and purification. The lignins extracted from BL-KN 60 and BL-KN 25 were named Lignin KN 60 and Lignin KN 25, respectively.

2.4 Analytical Methods

Black liquors and kraft lignins were chemically characterized for acid-insoluble lignin (TAPPI T222 om-02), acid-soluble lignin (TAPPI UM 250) and total lignin (Sum of acid-soluble and acid-insoluble lignins). The sugar content (SCAN-CM 71:09), ash content (TAPPI T211 om-02) and metals (TAPPI T266 om-02) were also measured.

CHNS-O model LECO equipment was used to measure the elemental analysis of the kraft lignins and black liquors. TruSpec CHNS Micro module was used to determinate carbon, hydrogen, nitrogen and sulfur percentages and TruSpec Oxygen Add-On module was used to determinate oxygen percentage. Higher and lower heating value of black liquors and kraft lignins were performed by TAPPI Test T684 om-15 standard.

Functional groups present in each kraft lignin was determined in the range of 400- 4000 cm^{-1} with a resolution of 4 cm^{-1} in the Fourier-transform infrared spectroscopy (VARIAN 600 with GladiATR).

Py-GC-MS technique was used to measure the amount of hydroxyphenyl (H), guaiacyl (G), syringyl (S), and catechol (Ca) types of kraft lignins. A micro-furnace pyrolyzer (Frontier

Laboratories Ltd., Fukushima, Japan) was used to perform the pyrolysis. Connect to the pyrolyzer, the GC-MS apparatus (Shimadzu, model QP2020) had an Ultra-ALLOY® Capillary Column (UA5, 30 m x 0.25 mm ID, 0.25 µm film thickness). The conditions used were report in Demuner *et al.* (2021). A comparison with the GC-MS spectral library (NIST) and the literature (SILVA *et al.* 2020; DEL RIO *et al.* 2005; DEMUNER *et al.* 2021; FERNÁNDEZ-RODRÍGUEZ *et al.* 2020) were performed to identify the compounds. The H-lignin markers were Phenol, *p*-Creosol, *o*-Creosol and Dimethylphenol isomers. The G-lignin markers were Guaiacol, Guaiacyl acetone, 3-Methylguaiacol, 4-Methylguaiacol, Acetoguaiacone, 4-Ethylguaiacol, 4-Propenylguaiacol, 4-Propylguaiacol, 4-Vinylguaiacol, Homovanillic acid, Benzoic acid, Butyrovanillone and Vanilin. The S-lignin markers were Syringaldehyde, Syringol, Syringylacetone, 3,4-Dimethoxyphenol, Acetosyringone, 4-ethylsyringol, 4-Propenylsyringol and 4-Vinylsyringol. The Ca-lignin markers were Catechol, 4-ethylcathecol, 3-Methylcathecol and 3-Methoxycathecol.

3 RESULTS AND DISCUSSION

3.1 Kraft cooking

The coffee parchment was used to produce pulps of kappa number 60 (KN 60) and 25 (KN 25). The kraft pulping processes resulted in a total yield of 42.6% with 0.5% reject and 47.6% with 0.8% reject for kappa 25 and 60, respectively. Some pulping variables remained constant for the two cookings, such as 32% sulphidity and a range of residual effective alkali between 6-8 g/L, however, to obtain kappa 25 a more drastic process was necessary, with H factor of 1140 and effective alkali 22.5%, compared to cooking conditions of kappa 60, H factor of 492 and 20.5% effective alkali.

The characteristics of pulps from parchment kraft pulping are shown in Table 1.

Table 1 - Characterization of kraft parchment pulps

Constituents		**Pulp – KN 60**	**Pulp – KN 25**
Kappa number		61.4	24.5
Soluble lignin, %		0.93	0.78
Insoluble lignin, %		8.75	2.49
Total lignin, %		9.68	3.27
Uronics, %		1.70	1.31
Hexenuronic acids, mmol kg^{-1}		66.4	63.5
Sugars, %	Glucan	62.4	67.3
	Xylan	20.7	21.7
	Mannan	0.0	0.0
	Galactan	0.1	0.2
	Arabinan	0.0	0.1

The kappa number is widely used as a measure of the degree of pulp delignification, but it reflects not only the lignin content but also the hexenuronic acid (HexA) content (LI & GELLERSTEDT 1997). Therefore, the higher the kappa number, a higher percentage of these constituents is expected (Table 1).

Lignocellulosic biomass is formed mainly by cellulose, consisting exclusively of glucan units. Hemicelluloses may be composed of xylan, mannan, glucan, galactan and arabinan units. The main hemicelluloses of hardwoods is the 4-O-methylglucuronic-xylan acetate (SHEN *et al.* 2010; WIEDMANN & LAMPRECHT 1999).

During kraft pulping, polysaccharides may undergo some undesirable reactions, one of which results in the formation of HexA by the elimination of methanol from 4-O-methylglucuronic acid, which are the side groups attached to xylan chains (VUORINEN *et al.*, 1996; CHAKAR *et al.*, 2000). Its formation rate is influenced by some cooking variables, including time, temperature and amount of alkali (ZHANG *et al.*, 2019).

When comparing cooking with 60 and 25 kappa what is expected is that the pulping process with the higher kappa will preserve more carbohydrates. When analyzing the characterization of pulps in percentage (Table 1), it was not possible to observe this trend. But when performing a cooking mass balance (Table 2), we can conclude that the results are consistent. Regarding the pulp quality another important parameter is its strength properties, being the pulp viscosity an indicator of this quality. Pulp viscosity is used for measuring the preservation degree of the carbohydrates, as high pulp viscosity as high the pulp strength (LIN *et al.*, 2014). In this work the observed viscosity was 1013 dm^3/Kg and 965 dm^3/Kg to the pulps KN 60 and KN 25, respectively. These values compared to the commercial eucalypt pulps are quite similar to those reported in the literature (KIM *et al.*, 2018).

It is known that 400 g of absolutely dry parchment was added to the digester for cooking. Through the total yield and tailings content, it is possible to determine the mass of pulp, waste and how much parchment is present in the liquor.

Table 2 - Parchment mass balance

Constituents, g		**Pulp – KN 60**	**Pulp – KN 25**
Pulp Total		187.2	168.4
Reject		3.2	2.0
Pulp	Carbohydrates	153.8	147.8
	Lignin	17.9	5.5
	Uronic Acid	3.1	2.2

3.2 Black liquors characterization

The black liquors obtained from the kraft pulping of coffee parchment to reach a pulp of the kappa number 60 (BL - KN 60) and from the kraft pulping to reach a pulp ofthe kappa number 25 (BL - KN 25) were chemically characterized (Table 3).

Table 3 - Characterization of black liquors as to lignin (acid-soluble, acid-insoluble andtotal), organics, inorganics and sugars

Constituents (%)		**BL – KN 60**	**BL – KN 25**
Soluble lignin		9.64	9.88
Insoluble lignin		22.04	23.25
Total lignin		31.67	32.63
Organics		53.2	51.2
Inorganics		46.8	48.8
Sugars	Glucan	0.8	0.7
	Xylan	2.8	2.2
	Mannan	0.1	0.1
	Galactan	0.6	0.6
	Arabinan	0.9	0.8

The BL-KN 60 and BL-KN 25 presented solids content of 12.5 and 14.0%, respectively. KOUSINI *et al.* (2016) report that black liquor typically has a solids content of around 15%, immediately after being removed from the fibers.

Black liquor consists of organic and inorganic components that were removed from the lignocellulosic biomass during the kraft process (DEMUNER *et al.*, 2019). The BL-KN 60 and BL-KN 25 showed similar chemical characterizations. The organic fraction was 53.2% for BL-

KN 60 and 51.2% for BL-KN 25, consisting mostly of lignin fragments and carbohydrates degraded during pulping.

The total lignin of the liquors was 31.67% (BL-KN 60) and 32.63% (BL-KN 25) and the carbohydrate contents were 5.2 and 4.4%, respectively. Among the carbohydrate fragments, hemicelluloses derivatives are mainly present and at least 50% are xylans.

As expected, the lignin content in BL-KN 25 was higher than in BL-KN 60, a more drastic cooking promotes greater delignification of the biomass. When comparing levels, we have a difference slightly greater than 1%. But analyzing the mass balance we have 66.4 g and 74.8 g of lignin in 60 and 25 kappa liquors, respectively.

The lignin and carbohydrate content in black liquor may vary according to the conditions of the kraft process and the biomass (HUBBE *et al.*, 2019). Some studies obtained between 40.2-44% of total lignin and 2.2-4.1% of carbohydrates, in the characterization of black liquor from the kraft process of eucalypt wood (CARDOSO *et al.*, 2009; COLODETTE *et al.*, 2013; DEMUNER *et al.*, 2021).

The total lignin content of parchment black liquors was lower than that found for eucalypt wood. It is known that lignins with a high content of ether bonds and low degrees of condensation in their chemical structure generally have lower thermal stability (MONTEIL-RIVERA *et al.*, 2013; LI & MCDONALD, 2014). Then, the high lignin content presented in eucalypt kraft liquor may be associated with the content of the syringyl unit (S) in the composition of the lignin present in the biomass.

Normally, a high content of methoxyl groups or a high S/G ratio limit the formation of C-C bonds during the kraft process (SILVA *et al.*, 2020). This could lead to less condensed lignin in the pulp and more lignin fragments in the liquor. As the coffee parchment has mainly lignin of guaiacyl type (G), there is a greater formation of condensed bonds during kraft pulping (SILVA *et al.*, 2020), which justifies the lower lignin content in black liquor.

In addition to lignin and carbohydrate, the organic fraction of the biomass comprises compounds based on extractives, aliphatic carboxylic acids and methanol (HUBBE *et al.*, 2019), which were not quantified in this study.

The content of carbon, hydrogen, nitrogen, oxygen, sulfur and metals in the blackliquor represents its ultimate analysis (Table 4).

Table 4 - Characterization of black liquors as to ultimate analysis and heating value

Parameters		**BL – KN 60**	**BL – KN 25**
Ultimate analysis (%)	Carbon	36.7	36.3
	Hydrogen	3.74	3.73
	Nitrogen	0.517	0.493
	Oxygen	36.8	36.5
	Sulfur	4.88	5.33
	Sodium	16.7	16.8
	Potassium	0.543	0.695
	Chlorine	0.202	0.163
	Calcium	0.0051	0.0043
	Magnesium	0.0126	0.0140
	Iron	0.0403	0.0273
	Manganese	0.0034	0.0026
	Copper	0.0026	0.0029
Heating value (MJ/Kg)	Higher	12.2	14.9
	Lower	11.4	14.0

The main components of the inorganic fraction of the liquor are sodium hydroxide, sodium sulfate, sodium carbonate and any unreacted sodium sulfide (EMPIE, 2009). According to Kevlich *et al.* (2017), it is likely that much of the reduced sulfur is present in the black liquor as thiosulfate, $Na_2S_2O_3$. Other inorganic components such as sodium chloride and trace amounts of some metals are also present (HUBBE *et al.*, 2019). The biomass used in the kraft process is a determining factor in the content of inorganic chemicals in black liquor.

The ultimate analysis of kraft black liquor consists mainly of carbon, oxygen, sodium, sulfur and hydrogen. Both liquors obtained present characteristics consistent with other studies. According to Frederick (1997), kraft black liquor consists of 34 to 39% of carbon, 33 to 38% of oxygen, 17 to 25% of sodium, 3 to 7% of sulfur and 3 to 5% of hydrogen.

The heating value is a property that describes the amount of thermal energy released during the combustion of a specific amount of material. It can be expressed as higher heating value (HHV) or lower heating value (LHV). Both quantify the energy released in the form of heat, but only the HHV considers the energy spent in the vaporization of water that forms in oxidation reaction (BOSCHETTI *et al.*, 2019).

The higher and lower heating values of black liquors were 12.2 and 11.4 MJ/Kg for BL-KN 60 and 14.9 and 14.0 MJ/Kg for BL-KN 25. Close values were presented by Demuner *et al.* (2021) for eucalyptus kraft black liquor: 13.9 MJ /Kg of HHV and 13.2 MJ /Kg of LHV.

While the organic and sulfur content can increase the heating value, the inorganic composition of black liquor can contribute negatively (MAGDELDIN & JÄRVINEN, 2020).

BL-KN 25 showed a higher heating value, which can be explained by the higher lignin and sulfur content compared to BL-KN 60.

3.3 Kraft lignins characterization

Kraft lignins were recovered from black liquors by precipitation with CO_2 until pH 9.0, and later with sulfuric acid until pH between 2-3. After that, filtration and hot acid washing were performed, the last being the critical stage to obtain a lignin with high purity.

The kraft process allows the dissolution of lignin in black liquor through various chemical reactions that partially degrade its structure (CHAKAR & RAGAUSKAS, 2004). Zhu and Theliander (2015) reported that the hydroxyl groups of lignin become ionized in an alkaline medium, and when acid is added to the black liquor, the concentration of protons [H] in the medium increases and the precipitation occurs. The addition of acid to the black liquor promotes the protonation of the ionized phenolic groups in the lignin macromolecule (ZHU & THELIANDER, 2015).

Kraft lignin characterization is important, since the biomass, pulping process conditions and extraction of lignin from black liquor can generate different types of kraft lignin (TEJADO *et al.*, 2007).

3.4 Chemical characterization, elemental analysis and heating value

Chemical characterization of coffee kraft lignins are shown in Table 5.

Table 5 - Characterization of coffee kraft lignins as to lignin (acid-soluble, acid-insolubleand total), ash content and sugars

Constituents (%)		**Lignin KN 60**	**Lignin KN 25**
Soluble lignin		3.85	4.34
Insoluble lignin		88.50	89.62
Total lignin		92.35	93.96
Ash content		1.61	1.26
Sugars	Glucan	0.6	0.6
	Xylan	5.1	3.7
	Mannan	0.0	0.0
	Galactan	0.1	0.1
	Arabinan	0.2	0.2

The purity of the kraft lignins was based on the soluble and insoluble lignin content. The KN 25 lignin showed higher soluble and insoluble lignin content and lower carbohydrate content compared to KN 60 lignin. Then, we can infer that lignin KN 25 is purer. The predominant sugars in the lignins were xylan and glucan, while mannan was not detected.

Studies have published high purity values (94.1-95.3 %) for kraft lignins (CASSALES *et al.*, 2020; DEMUNER *et al.*, 2021a). Demuner *et al.* (2021a) reported total lignin values of 95.3% with 9.8% of soluble lignin, 2.5% of carbohydrate and 2.2% of ash, when characterizing eucalypt kraft lignin. In this study, we obtained lignins with a lower content of soluble lignin and ash, and a higher content of carbohydrate. This difference can be explained by the type of biomass and extraction technique.

It is known that in native wood the presence of lignin-carbohydrate complex (LCC) is already found, most frequently as benzyl ester, benzyl ether and phenylglycosidic bonds. The last two being stable in the kraft process (LAWOKO *et al.* 2004). As carbohydrates are covalently linked with dissolved lignin fragments during the kraft process, studies suggest the formation of ether-type LCC during pulping (LAWOKO *et al.* 2004; DODD *et al.* 2015). Therefore, carbohydrates can precipitate with lignin, making it difficult to eliminate (DODD *et al.* 2015). The extraction process of kraft lignin from black liquor can also influence its purity, as content of carbohydrate and ash (TOMANI, 2010).

3.5 Elemental analysis and heating value

Table 6 presents the results of elemental analysis and higher and lower heating values of kraft lignins.

Table 6 - Characterization of coffee kraft lignins as to elemental analysis and higher heating value

Parameters		**Lignin KN 60**	**Lignin KN 25**
Elemental analysis (%)	Carbon	60.5	62.3
	Hydrogen	5.62	5.62
	Nitrogen	0.989	0.866
	Oxygen	29.4	27.3
	Sulfur	3.02	2.45
Heating value (MJ/Kg)	Higher	23.8	25.4
	Lower	22.6	24.2

HHV and LVH are influenced by the elemental composition of lignin. Lignocellulosic materials that have higher carbon and hydrogen contents have a greater ability to release energy during thermal degradation, that is, they have a higher enthalpy of combustion (BOSCHETTI *et al.*, 2019). According to Turns (2011), hydrogen is the element that releases the most energy during combustion, followed by carbon.

Comparing the two lignins obtained in this study, we can observe that lignin K25 has the same hydrogen content as lignin K60. However, it obtained higher carbon content and lower levels of the other elements, which would explain its higher heating value.

The elemental analysis of lignin from the parchment kraft process was similar to that obtained in studies of eucalyptus kraft lignins, which showed 61.8-63.0 (%C), 4.5-5.8 (%H), 28.2-30.7 (%O), 0.1-0.7 (%N) and 1.7-2.6 (%S) (BOSCHETTI *et al.*, 2019; DOU *et al.*, 2019; TAGAMI *et al.*, 2019; DEMUNER *et al.* 2021a). The lignins sulfur contents are in accordance with the values described in the literature for kraft lignin (between 1 and 3%), which are present as aliphatic thiol groups (DOHERTY *et al.*, 2011).

3.6 FTIR analysis

Functional groups present in parchment kraft lignin KN 60 and KN 25 are presented in Figure 1 and discussed in Table 7. Between the KN 60 and KN 25 lignin samples, no differences were observed between the functional groups and peak intensity.

Figure 1 - FTIR of coffee kraft lignins: Lignin KN 60 and Lignin KN 25

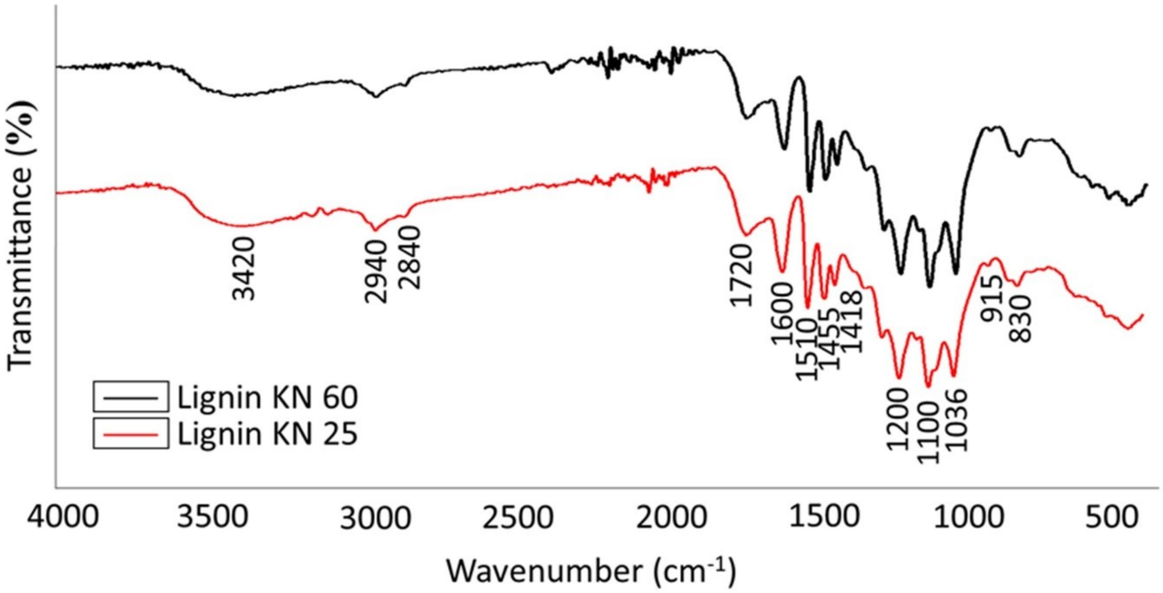


Table 7 - Functional groups in lignin KN 60 and KN 25

Peak (cm^{-1})	Assessment
3420	O-H stretching of phenolic or alcohol groups
2940	C-H stretching of sp^3 and sp^2 methyl and methylene groups
2840	C-H vibration of the $-OCH_3$ groups
1720	C=O stretch in non-conjugated ketone and carboxyl groups
1600	Aromatic skeletal vibrations together with C=O stretching
1510	Aromatic skeletal vibrations
1455	C-H bending of methyl or methylene groups
1418	Aromatic skeletal vibration combined with CH asymmetric deformation of methyl groups
1200	C-O and C=O stretching of the aromatic ring
1100	-CH-OH bonds of secondary alcohols
1036	CH_2-OH bonds of primary alcohols in the molecule
915	C-H out-of-plane bending of syringyl units
830	C-H out-of-plane deformation

These bands have also been observed by other authors for lignin (FAIX, 1991; BOERIU *et al.*, 2004; IBRAHIM *et al.*, 2004; MALUTAN *et al.*, 2008; LISPERGUER *et al.*, 2009; LI & GE, 2011; INWOOD, 2014; HUANG *et al.*, 2016; HUANG *et al.*, 2018; SATHAWONG *et al.*, 2018; MELRO *et al.*, 2020; LATHAM *et al.*, 2021) and the bands found for parchment lignin were similar to those from lignin of eucalyptus and pine.

The absorption in the region 600-700 cm^{-1} may be attributed to the C-S vibrations of the thiolignins, once it has been described in the literature a very weak band at 630 cm^{-1} which was attributed to C-S elongation (MANSOUR *et al.*, 1984). This study showed very weak absorption near the 600 cm^{-1}. On the other hand, no bands were observed at 2600 cm^{-1}, indicating absence of the thiol group (S-H).

3.7 Py-GC-MS

The pyrolysis of kraft lignins resulted in a large number of aromatic compounds with different substituents at various positions on the benzene ring. Barbosa *et al.* (2008) concluded that the temperature that obtained the maximum yield of phenolic compounds was 550 °C, so this was the pyrolysis temperature used in this study.

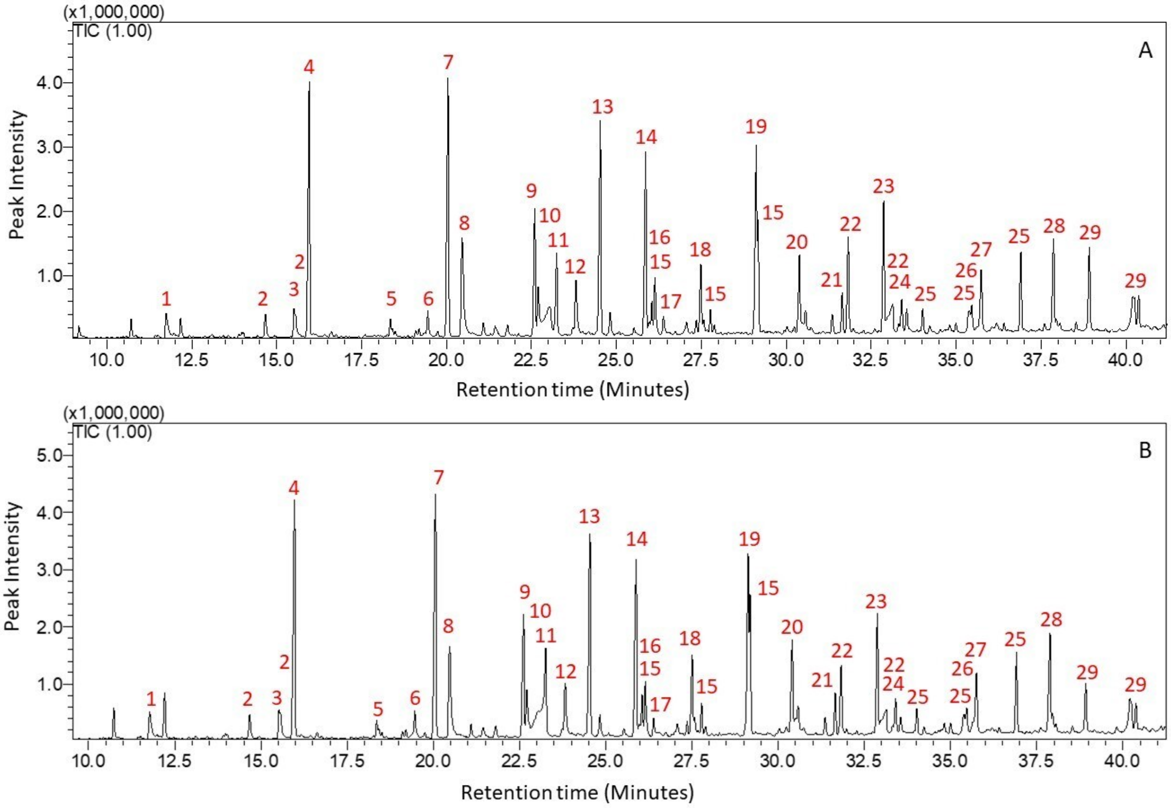
Twenty-nine phenolic products were identified, classified into four categories according to their aromatic structure: compounds type phenolic (H), guaiacyl (G), syringyl (S) and catechol (Ca). The names and area percentages of these compounds obtained from the pyrogram are shown in Table 8.

Table 8 - Py-GC-MS results

Origen	**Compound**	**Lignin KN 60**	**Lignin KN 25**	**Peak number**
H-type lignin	Phenol	0.71	0.88	1
	p-Creosol	0.53	0.54	3
	o-Creosol	0.84	1.00	2
	2,4-Dimethylphenol	0.22	0.35	5
	Total	2.30	2.77	-
G-type lignin	Guaiacol	6.14	6.06	4
	3-Methylguaiacol	0.41	0.54	6
	4-Methylguaiacol	6.12	6.32	7
	4-Vinylguaiacol	4.97	5.02	13
	4-Ethylguaiacol	1.68	1.95	11
	4-Propenylguaiacol	2.80	4.13	15
	Vanillin	1.52	1.90	18
	Acetoguaiacone	1.79	2.37	20
	Guaiacyl acetone	2.85	2.40	22
	4-Propylguaiacol	0.33	0.35	17
	Homovanillic acid	0.66	0.58	26
	Vanillic acid	0.39	0.38	21
	Butyrovanillone	0.44	0.31	24
	Total	30.10	32.31	-
S-type lignin	Syringol	4.41	4.63	14
	4-Vinylsyringol	2.77	2.64	23
	3,4-Dimethoxyphenol	1.02	1.18	16
	4-Methylsyringol	4.49	4.57	19
	Acetosyringone	2.08	2.52	28
	Syringaldehyde	1.38	1.28	27
	Syringylacetone	2.51	1.65	29
	4-Propenylsyringol	2.65	2.81	25
	Total	21.31	21.28	-
Ca-type lignin	Cathecol	3.08	3.08	8
	3-Methoxycathecol	2.87	3.04	9
	3-Methylcathecol	0.96	1.10	10
	4-Methylcathecol	1.23	1.26	12
Total		8.14	8.48	-

Sample pyrograms are shown in Figure 2 and equivalent compounds for peak number are listed in Table 8 and illustrated in Figure 3.

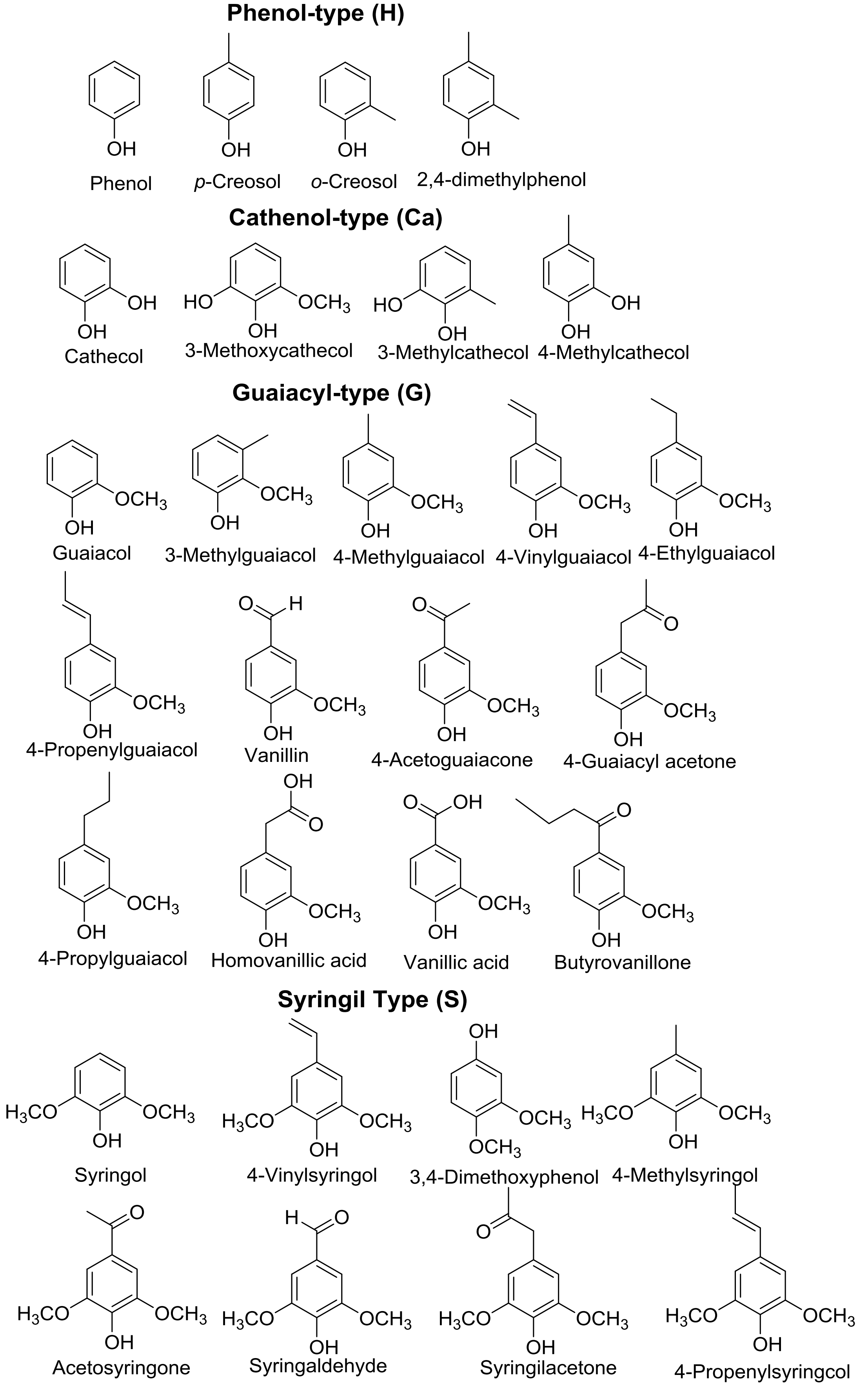
Figure 2 - Pyrogram of kraft lignins: A) Lignin KN 60 and B) Lignin KN 25



The predominance of guaiacyl and syringyl units was observed, which characterizes lignin derived from angiosperms (BARBOSA *et al.*, 2008). Both lignins showed the same markers, differing only in the slightly higher total area percentage of the monomers G, H and Ca for lignin KN-25. As it is a purer lignin, a higher percentage of total area was expected compared to KN-60 lignin.

The lignin syringyl/guaiacyl (S/G) ratio was calculated using analytical pyrolysis (Py-GC-MS) at 550 °C, dividing syringyl-type lignin (S) by guaiacyl-type lignin (G). The values found were 0.71 and 0.66 for KN 60 and KN 25 lignins, respectively.

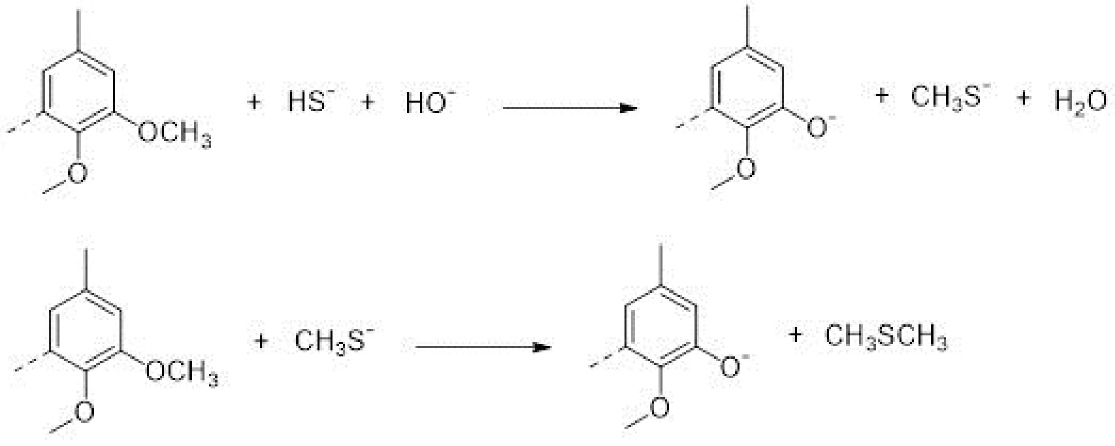
Figure 3 - Main compounds present in Py-GC-MS



In the kraft process, lignin is degraded through these reactions: (1) hydrolysis of α-ethers and breaking of the β-aryl ether bond in the phenolic unit; (2) demethylation reaction; (3) formation of vinyl ethers and stilbene via γ-elimination of the primary alcohol in the phenolic unit; and (4) condensation reaction at the C5 position on the aromatic ring (HU *et al.*, 2016).

The hydrolysis of methyl-aryl ether linkages during kraft pulping occurs by reaction of lignin with hydrosulfide ion (HS-), strongly nucleophilic. This ion cleaves the methoxy group forming methylmercaptan (CH_3SH) and the catechol structure. The anion of methylmercaptan (CH_3S-) is an even stronger nucleophile than the disulfide and also reacts with the methoxy group, thus forming dimethylsulfide (CH_3SCH_3) and other catechol units containing free hydroxyls (GOMIDE & GOMES, 2015; GIERER 1985) (Figure 4). It is known that catechol can be formed through the demethylation reaction from guaiacol (MUKUNDAN *et al.* 2019), which explain the decrease in the lignin G-type and increase in the percentage of Ca-type lignin.

Figure 4 - Cleavage of lignin methoxy groups by hydrosulfide and methylmercaptan ions



Fonte: Adapted of GIERER, 1985.

Lignin has a complex structure that may be modified by some chemical reactions such as oxidation, sulfonation, amination, condensation and may also be graft copolymerization due to the presence of reactive effect groups that may be linked in its structure, such as phenolic and alcohol hydroxyl, methoxyl groups and aldehydes (WANG *et al.*, 2022). This property allows lignin to be transformed into chemical products with high added value and increases the opportunity for its applications.

Due to the large number of phenolic groups in its structure, lignin has been considered as a potential for replacing phenol in resins, such as phenol-formaldehyde (PF) resins (SARIKA *et al.*, 2020). The reaction of formaldehyde in the ortho and para position of phenol forms PF resins (DUVAL & LAWOKO, 2014). However, the phenolic groups of lignin are substituted in the para position by aliphatic chains and in the ortho position may be also occupied by a methoxyl group (type G lignin) and two methoxyl groups (type S lignin), which decreases the reactivity of lignin compared to the phenol (GANDINI & BELGACEN, 2008). Some strategies have been described aiming increase lignin reactivity, including the use of the reactive site at the unsubstituted C5 position of the phenolic ring in G-type lignins, which makes basic parchment lignin more advantageous than eucalyptus lignin due to its lower syringyl/guaiacyl lignin ratio (DUVAL & LAWOKO, 2014; DEMUNER *et al.*, 2021a).

4 CONCLUSION

The kraft pulping of the coffee industry residue in order to obtain a pulp with kappa 60 and 25, behaved in a coherent way. Higher cooking yield and higher lignin content were obtained for the pulp with the highest kappa number. The characterization of black liqueurs were similar to wood kraft liqueurs, they can be divided into organic and inorganic, in which the organic part consists mainly of lignin and carbohydrate. Through a precipitation process, it was possible to precipitate lignin from black liquors which adding more value to the residue. High purity kraft lignins (92.35-93.96%) were obtained, with elemental analysis and heating value similar to those obtained in wood kraft lignin. Through the Py-GC-MS analysis, it was possible to observe the predominance of guaiacyl-type lignin, which can be an advantage depending on the application, as it is more reactive than syringyl-type lignin. Parchment lignin has favorable characteristics for application in biorefinery, such as in the replacement of phenol in the production of phenol-formaldehyde resins considering the presence of G lignin, which is more advantageous, collaborating for generating high value-added products from waste.

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CAPÍTULO 3: STUDY OF MICROFIBRILLATED CELLULOSE PRODUCED FROM KRAFT PULP OF COFFEE PARCHMENT

ABSTRACT

Lignocellulosic biomass is abundant in nature and is currently considered the greatest renewable resource on the planet. The use of agro-industrial waste as a source of lignocellulosic biomass reduces the use of forest resources while adding market value toby-products that were previously discarded, such as parchment, the residue of an important agricultural product, coffee. In the nanotechnology field, the production of nanocellulose, for various applications, has gained prominence due to its excellentproperties. The objective of this study was to produce microfibrillated cellulose (MFC) and microfibrillated lignocellulose (LCMF) from coffee parchment and to perform the characterization of the nanocellulose. The three CMF were produced from the kraft pulps(K#60, K#25 and bleached) and keeping the same process conditions, pulp hydration followed by defibrillation using an ultra-refiner (MasuKo). The chemical, physical and morphological characterization of the CMF was performed through techniques such as elemental analysis, X-ray diffraction, Fourier transform infrared (FTIR), thermogravimetric analysis, zeta potential, water retention index (WRI) and electron microscopy. The cellulosic fibers from parchment, a residue of the coffee industry, provedto be a viable alternative for production of LCMF and CMF, presenting in general comparative properties with the nanocellulose produced through wood. LCMF-K#60, LCMF-K#25 and CMF-Branched showed crystallinity index of 52.5; 58.8 and 65.1%, respectively, and were thermally stable. The FTIR spectra were similar for all nanocellulose showing characteristic peaks of cellulosic polymers. Through the scanningelectron microscopy (SEM) it was possible to confirm that the fibers were deconstructedby the mechanical process of defibrillation.

Keywords: Biomass. Mechanical defibrillation. Nanocellulose. Coffee residue.

1 INTRODUCTION

The growing demand for environmental sustainability has encouraged the development and research of materials produced from inexhaustible and sustainable reservoirs, aiming to minimize the environmental impact caused by the disposal of petrochemical polymers (FRANCO *et al.*, 2019; OWOLABI *et al.*, 2020; MARAKANA *et al.*, 2021). In this context, lignocellulosic biomass is the most attractive raw material, for being considered the largest renewable resource on the planet and being in abundance in nature (SETTER *et al.*, 2020; MARAKANA *et al.*, 2021).

The use of agro-industrial residues as a source of lignocellulosic biomass reduces the use of forest resources, allowing sites with low wood production to produce cellulosic fibers (FRANCO *et al.*, 2019).

Coffee is an important agricultural product and it is estimated that 169.69 million bags of coffee were produced globally in 2020/21 (EMBRAPA, 2021). During the processing of the bean, more than half of the fruit is discarded, which generates considerable waste (ESQUIVEL & JIMÉNEZ, 2012). Thus, finding applications for this waste is attractive because it is possible to add market value to by-products that were previously discarded causing environmental problems (POLIDORO *et al.*, 2018; SETTER *et al.*, 2020).

Cellulose is a biopolymer composed of anhydroglycoside units connected through β-1,4-glycosidic bond, and can be extracted from different agricultural waste such as cotton linter, bagasse, rice husk, wheat straw, coffee waste (OWOLABI *et al.*, 2020; MARAKANA *et al.*, 2021; TANPICHAI *et al.*, 2022). Main component of the cell wall of plants, it has the advantage of being renewable, biodegradable and chemically versatile (FRANCO *et al.*, 2019).

Cellulose chains are joined by intra- and intermolecular hydrogen bonds and van der Waals forces between adjacent hydroxyl groups and oxygenates to form elementary fibrils, which are then held together to form microfibrils with diameters ranging from 5 to 50 nm and lengths of several micrometers (TANPICHAI *et al.*, 2022). Cellulose fibrils are basically surrounded by lignin and hemicelluloses, forming a three- dimensional structure known as lignocellulosic biomass (FRANCO *et al.*, 2019).

In recent years there has been increasing interest in cellulose-based nanoparticles due to their excellent chemical, mechanical and optical properties, in addition to being biocompatible materials, which present excellent mechanical performance with low weight and highly reactive due to the hydroxyl groups present on the surface, making nanocellulose a highly attractive biopolymer for diverse applications (ALBORNOZ-PALMA *et al.*, 2020; M'BAREK *et al.*, 2022; WANG *et al.*, 2022).

Nanocellulose is obtained by processing lignocellulosic biomass. Depending on the extraction method, nanocellulose can be categorized into three: cellulose nanofibrils (CNF), cellulose nanocrystals (CNC) and bacterial cellulose (BC) (OWOLABI *et al.*, 2020). Microfibrillated cellulose (MFC) is considered by some authors as cellulose nanofibrils (CNF), and can be termed as cellulosic material, moderately degraded thus expanding its surface area, obtained through a mechanical disintegration process without the use of hydrolysis (HERRICK *et al.*, 1983; ALBORNOZ-PALMA *et al.*, 2020).

With a wide range of applications in science and technology, nanocellulose can be used in the production of films, automotive components, biomedical devices and food, as well as in water treatment (FRANCO *et al.*, 2019; TANPICHAI *et al.*, 2022).

The effective separation of the constitutional components of biomass constitutes one of the main challenges to the effective use of renewable resources, to obtain nanocellulose requires an association of cellulose isolation process and preparation of nanocellulose from isolated cellulose (FRANCO *et al.*, 2019; MARAKANA *et al.*, 2021).

The present work uses the process of chemical delignification followed by mechanical disintegration to obtain microfibrillated cellulose, which was characterized for a better understanding of its physical and chemical properties, which may be useful to guide its future applications. The efficient conversion of this renewable raw material into a high value-added product such as MFC significantly benefits the agroindustrial sector, in addition to introducing a new alternative fibrous resource, making the coffee agroindustry a more sustainable and competitive sector.

2 MATERIAL AND METHODS

2.1 Materials

The cellulosic pulps used as raw material were obtained from the Kraft pulping process of coffee parchment, a residue of the coffee industry, from the production of Coffea canephora, popularly known as Conilon. The coffee residue was obtained in the city of Santa Teresa (19° 55′ 53″ South, 40° 35′ 43″ West), Espírito Santo State, Brazil.

The Kraft pulping process was conducted based on previously optimized parameters to obtain pulps with two kappa numbers, kappa 25 and kappa 60. In addition, the pulp with kappa 25 was submitted to the ECF bleaching process to obtain bleached pulp with 90%ISO brightness.

The three pulps obtained, with distinct kappa numbers, were used for microfibrillated pulp production and their chemical compositions are described in Table 1.

Table 1 - Characterization of kraft parchment pulps

Constituents		Pulp – K#60	Pulp – K# 25	Pulp – Bleached
Length, mm		0.52	0.51	0.50
Width, µm		23.98	23.81	23.36
Kappa number		61.40	24.50	0.30
Soluble lignin, %		0.93	0.78	0.46
Insoluble lignin, %		8.75	2.49	-
Total lignin, %		9.68	3.27	0.46
Uronics, %		1.70	1.31	0.90
Hexenuronic acids, %		1.20	1.10	0.04
Sugars, %	Glucan	62.40	67.30	70.70
	Xylan	20.70	21.70	22.50
	Mannan	0.00	0.00	0.00
	Galactan	0.10	0.20	0.10
	Arabinan	0.00	0.10	0.10

2.2 Production of microfibrillated cellulose (MFC)

The three MFC suspensions were produced at the Chemical and Textile Industry Technology Center (Senai CETIQT), prepared in the same concentration (1.5% m/m) and volume (10 L). The suspensions were defibrillated using the SuperMassColloider (Masuko, model MKZA10-15J IV) ultrorefining device. The disks (model MKE10-46) are made of ceramic material (aluminum oxide and resin) without porosity to avoid any infiltration of nanometric particles and to allow better fit between the disks.

To prepare the pulp suspension, 150 g (dry basis) of each pulp sample was weighed and dispersed in 50% of the total deionized water used to reach 1.5% consistency. The suspension was left to stand for 72 hours for complete hydration of the pulp. Then, the remaining volume of water was added to complete the volume to 10 L and the pulp suspension was kept under stirring using a mechanical stirrer (Heidoph) fora period of 2 hours at a rotation of 650 rpm. Finally, the cellulose suspension was forwarded to mechanical defibrillation (Masuko). During the operation, one of the disks remained stationary and the other in motion, with rotation of 1500 rpm. The distance between the discs was determined and fixed at 100 µm and 32 cycles were performed for the three suspensions. Briefly, the "zero" position was determined by the noise generated by the contact position between the two discs before loading the suspension. From the "zero" position, the ultrafiner was loaded with the cellulose suspension and the disks were immediately adjusted to the amplitude position of 100 µm between the disks. The ultracleaner was operated with a cooling system using water flow at room temperature.

2.3 Characterization of nanocelluloses

The MFCs produced were analyzed in the Pulp and Paper Laboratory of the Federal University of Viçosa (LCP-UFV) for carbohydrate content (SCAN-CM 71:09), soluble lignin (TAPPI UM250), insoluble lignin (TAPPI T222 om-02), uronic acids (SCOTT, 1979), Hexenuronic acids (TAPPI T282 pm-07), ash content (TAPPI 211 om- 08) and silica content (TAPPI T245 cm-98).

Viscosity analysis, fibre size, elemental composition (CHNS), X-ray diffraction, thermogravimetric analysis (TG/DTG), Fourier transform infrared spectroscopy (FTIR), Zeta potential, water retention index (WRI), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were also performed. The methodologies are described in the following subtopics.

2.3.1 Viscosity

The viscosity analysis of the MFCs suspensions was performed at the Chemical and Textile Industry Technology Centre (Senai CETIQT), by the dynamic viscosity technique, using the Viscometer from Lamy Rheology.

2.3.2 Fiber dimensions

The fiber analysis of the microfibrillated celluloses was performed in the Pulp and Paper Laboratory of the Federal University of Viçosa (LCP-UFV) using the Valmet FS5Analyzer equipment, in order to obtain the fiber length and diameter dimensions. The sample was suspended in demineralized water and analyzed.

2.3.3 Elemental analysis

The percent determination of carbon, hydrogen, nitrogen and sulfur percentages was carried out at the Pulp and Paper Laboratory of the Federal University of Viçosa (LCP-UFV) using the equipment CHNS-O model LECO, TruSpec CHNS Micro module. The percentage of oxygen was determined by difference.

2.3.4 X-Ray Diffraction

X-ray diffraction of the MFC samples was performed at the Chemical and Textile Industry Technology Center (Senai CETIQT) in a Panalytical-Aeris Cu-Kα diffractometer (λ = 154056 Å). For the analysis, films with a weight of 30 g/m^2 were formed and dried at room temperature for 48 hours. The configuration adopted for the analysis was the slit monochromator mode, operating at 40 kV with a current of 30 mA. The scanning speed adopted was 3° min-1 in the range of diffraction angles from 0 to 30°, using Cu-Ka radiation with a wavelength of 0.154 nm. The crystallinity index was determined according to the method proposed by Segal *et al* (1959), that is, by the ratio between the maximum intensity of diffraction and the minimum intensity located between the two crystalline peaks of the diffractogram, according to equation 1.

$$CI\ (\%) = \frac{I_{002} - I_{AM}}{I_{002}} x100 \quad (1)$$

In which:

I_{002} = the maximum diffraction intensity, attributed to the crystalline regions of the sample (2θ between 22-23°);

I_{AM} = the minimum intensity, assigned to non-crystalline regions (2θ between 18-19°).

2.3.5 Thermogravimetric Analysis (TG/DTG)

The thermogravimetric analyses were performed at the Technology Center of Chemical and Textile Industry (Senai CETIQT), using a Hitachi thermal analyzer, model STA 7300. For the analysis, films with a grammage of 30 g/m2 were formed and dried at room temperature for 48 hours. The analyses were performed under nitrogen gas atmosphere, at a constant flow rate of 50 mL/min. Thermogravimetric (TG) curves were obtained from 25 °C to a maximum temperature of 800 °C, using a heating rate of 10 °C/min. The thermal degradation of the samples was obtained through the first derivative of the TG curve, which establishes the mass loss as a function of temperature.

2.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra were performed at the Technology Center of Chemical and Textile Industry (Senai CETIQT), using a Bruker Vertex 80 FTIR spectrophotometer, with ATR configuration. For the analysis, films with a weight of 30 g/m^2 were formed and dried at room temperature for 48 hours. The analyses were performed at room temperature, wavelength from 4000 to 650 cm^{-1} with 32 scans per spectrum at a resolution of 4 cm^{-1}.

2.3.7 Zeta potential

The zeta potential of the MFC samples was performed at the Technology Center of Chemical and Textile Industry (Senai CETIQT), using the Litesizer 500 equipment from Anton Paar. For the analysis, the samples of MFC (2% m/m) were diluted in distilled water to a consistency of 0.1% (m/m) and homogenized in a mechanical agitator at 200 rpm for 60 minutes. The diluted sample was transferred to the appropriate measuring cell and triplicates of each analysis were performed. The analysis was performed at 25 °C and the refractive index of water is used as parameter.

2.3.8 Water retention value (WRV)

The water retention index of the MFC samples was performed in the Pulp and Paper Laboratory (LCP-UFV). The analyses were performed according to the TAPPI UM-256 standard. Briefly, the retention index indicates the capacity of fibers to swell and absorb water. The WRV was calculated according to Equation 2.

$$WRV\ (\%) = \frac{W_{humid} - W_{dry}}{W_{dry}} x100 \qquad (2)$$

In which:

W_{humid} = weight of sample after centrifugation;
W_{dry} = absolute dry weight of the sample.

2.3.9 Scanning electron microscopy (SEM)

Scanning electron microscopy of the MFC samples was performed in the Carlos Alberto Redins Cellular Ultrastructure Laboratory of the Federal University of Espírito Santo, in a JSM610LV model scanning electron microscope. For the analysis, the CMF samples were freeze-dried.

2.3.10 Transmission Electronic Microscopy (TEM)

Transmission electron microscopy of the MFC samples was performed in the Cellular Ultrastructure Laboratory Carlos Alberto Redins of the Federal University of Espírito Santo, in a JEM1400 model scanning electron microscope.

3 RESULTS AND DISCUSSION

3.1 Production of the MFCs

Microfibrillated cellulose (MFC), also called nanofibrillated cellulose (NFC), can be considered as cellulosic material, moderately degraded thus expanding its surface area and obtained through a mechanical disintegration process without the use of hydrolysis (HERRICK *et al.*, 1983).

To verify the variations inherent to the mechanical system of the defibrillation process in relation to the characteristics of each cellulosic pulp, the three suspensions obtained were prepared and defibrillated in the SuperMassColloider under the same conditions, that is, suspension consistency, disc rotation, distance between discs and number of passes. The obtained MFCs were identified as LMFC-K#25, LMFC-K#60 and MFC-bleach, from K#25, K#60 and bleached pulps, respectively.

The yields of the samples were not measured in this work, however it is known that the number of pulp passages through the mill and the use of pulps with or without residual lignin can interfere in the final result, due to the loss of fibers during the bleaching process of pulps.

Ribes *et al.* (2018) obtained the yield of 99.39% and 98.13% for nanofibrillar suspensions of Eucalyptus pulp produced through pulps with and without residual lignin, respectively.

3.2 Characterization of the MFCs

3.2.1 Fiber size and viscosity

Changes in the size distribution profile were expected throughout the defibrillation process, especially in the longitudinal direction of the fiber (WANG *et al.*, 2012). Another expected aspect was the obtaining of highly viscous suspensions, even at very low consistencies (ALBORNOZ-PALMA *et al.*, 2020). In order to understand the dimensions of the fibers, as well as the viscosities obtained for each sample, the length and average diameter of the fibers were measured and the viscosity of the suspensions of MFC presented in Table 2.

Table 2 - Evaluation of nanocelluloses as to their dimensions and viscosity

Parameters,	LMFC-K#60	LMFC-K#25	MFC-Bleached
Length, µm	39	47	47
Width, nm	6820	5600	5280
Viscosity, cP	5357	8336	15587

Microfibrillated cellulose (MFC) generally present diameter in the range of 20 to 100 nm and length of several micrometers (LAVOINE *et al.*, 2012; ALBORNOZ- PALMA *et al.*, 2020; VERA-LOOR *et al.*, 2022). The values obtained in this study showed the length of several micrometers, however the diameter larger than expected.

The instrument used for fibre measurement, Valmet FS5 Analyzer, considered 98.2-99.5% of the MFC suspension as smaller fibre particles (fines), thus making the measurement of only 0.5-1.8% of the samples, thus not dimensions representing MFCs. Mechanical defibrillation produces a material that can be heterogeneous, containing fibers, fibre fragments, fines and fibrils (PÄÄKKÖ *et al.* 2007; PLACKETT *et al.* 2010).

The different pulp delignification and bleaching processes currently used result in pulps with different residual amounts of hemicelluloses and lignin, as well as reduces the degree of polymerization and crystallinity of the pulp, which affects the microfibril properties (ALBORNOZ-PALMA *et al.*, 2020; SPENCE *et al.*, 2010). For example, microfibrillated celluloses (LMFCs) from unbleached cellulosic pulps show moreelongated fibers and form less viscous suspensions than MFCs from bleached cellulosic pulps (IWAMOTO *et al.*, 2014; ALBORNOZ-PALMA *et al.*, 2020). This statement is in agreement with the results found, presented in Table 2.

One explanation for the resulting high viscosity of microfibrillated cellulose suspensions is related to the hygroscopic character of cellulose and the high aspect ratio and high specific surface area of microfibrils, which results in strong interconnections of the fibers, even at low concentrations, generating highly viscous suspensions (ALBORNOZ-PALMA *et al.*, 2020).

3.2.2 Chemical composition

Mechanical fibrillation primarily affects the size of cellulose fibers, without varying their chemical components (ALBORNOZ-PALMA *et al.*, 2020). However, Jiang *et al.* (2018) and Carvalho *et al.* (2019) explain that as the degree of fibrillation increases, lignin migrates out of the fibrils, which implies the separation of lignin from microfibrils, modifying their composition. The presence of residual lignin also adjusts the polarity and hydrophilicity of microfibrillated cellulose, due to the hydrophobicity and less polar character of lignin (CHEN *et al.*, 2018; WEN *et al.*, 2019). The change in MFC properties opens possibilities for other applications.

To evaluate this behavior, the compositional analysis of the MFC suspensions (Table 3) was performed and compared with the initial characterization of the pulps (Table 1).

Table 3 – Compositional analysis of MFC suspensions

Constituent, %		**LMFC-K#60**	**LMFC-K#25**	**MFC-Bleached**
Soluble lignin		0.84	0.64	0.43
Insoluble lignin		8.50	2.40	-
Total lignin		9.34	3.04	0.43
Uronics		1.60	1.25	0.87
Hexenuronic acids, %		1.20	1.10	0.04
Sugars	Glucan	64.40	67.50	70.80
	Xylan	19.20	20.30	22.10
	Mannan	0.00	0.00	0.00
	Galactan	0.10	0.10	0.10
	Arabinan	0.00	0.10	0.10

According to the data in Table 3, the MFC suspensions presented chemical composition similar to the cellulose pulps (Table 1) because they were produced through a mechanical process.

It can be noticed that the higher the kappa number in the pulp of origin, the higher the lignin and Hexa content in the MFC suspension. It is known that lignin and Hexenuronic acids (Hexa) contribute to the measurement of kappa number (LI & GELLERSTEDT, 1997). The results obtained for the total lignin content for the samples LCMF-K#60, LCMF-K#25 and MFC-bleached were 9.34; 3.04 and 0.43%, respectively. The Hexenuronic acids content observed for samples LMFC-K#60, LMFC-K#25 and MFC-bleached were 1.20, 1.10 and 0.04%, respectively.

Regarding the content of carbohydrates, in this study, we obtained higher percentages for glycans and xylans, a result already expected, because both Eucalyptus and coffee belong to the hardwood group, in which xylan is the main hemicellulosess (GIUDICIANNI *et al.*, 2019). These results are in agreement with the results found by Demuner *et al.* (2020), who obtained, in both samples of nanocellulose produced through Eucalyptus kraft pulp, glycans and xylans, with values of 80.6 and 13.8% for LCNF and 83.3 and 14.2% for CNF, respectively. The other sugars were between 0.0 and 0.3%.

The glycan and xylan contents for LMFC-K#60, LMFC-K#25 and MFC-bleached samples were 64.4 and 19.2%; 67.5 and 20.3% and 70.8 and 22.1%, respectively. We can observe that in all samples we obtained a higher xylan content and lower glycan content than those observed by Demuner *et al.* (2020) in Eucalyptus nanocellulose samples, a result that can be explained by the difference in the chemical composition of the raw material used (JARDIM *et al.*, 2017; ZANÃO *et al.*, 2019; REIS *et al.*, 2020; BONDAM *et al.*, 2022).

Hemicelluloses are known to propitiate nanofibrillation, i.e. facilitate the release of individual fibrils and consequently save energy during the mechanical defibrillation process (DIAS *et al.*, 2019).

The proportion of carbohydrate in the sample increases as the other constituents of the sample decrease, so there are higher percentages of carbohydrate in the sample MFC-Branched due to the removal of lignin and Hexa in the bleaching process to which the fiber was submitted, and higher levels of carbohydrate in the sample LMFC-K#25 if compared to LMFC-K#60 due to the more drastic process of kraft pulping to obtain kappa number 25, and consequently lower levels of lignin and Hexa.

The contents of Hexa and uronic acids in the nanocellulose samples were similar to those obtained by Demuner *et al.* (2020). But this study obtained higher residual lignin contents, due to characteristics of chemical composition of the raw material, which despite presenting lower lignin content (10.1-26.6% in coffee against 27.1-31.3% in Eucalyptus wood), its S/G ratio is 0.8 while studies report values of 2.5-3.1 for Eucalyptus wood (NUNES *et al.*, 2010; MARTINEZ *et al.*, 2019; CANGUSSU *et al.*, 2021).

The ratio between the S and G units and the nature of the links between them are highly important, because they influence the reactivity of lignin during pulping (PINTO *et al.*, 2005). The S-type lignin presents two methoxyl groups in the C-3 and C-5 position, making it more reactive (PINTO *et al.*, 2005). The G type lignin has an aromatic carbon in the C-5 position available to make carbon-carbon bonds, which contributes to a high degree of condensation in the cellulose pulp (COLLINS *et al.*, 1990; GUTIÉRREZ *et al.*, 2006).

The MFC samples are composed of organic compounds - cellulose, hemicelluloses and lignin - and a small percentage of inorganic compounds, which can be quantified through the ash content (PURI *et al.*, 2020). In Table 5, we can observe that LMFC-K#60, LMFC-K#25 and MFC-bleached samples presented ash values higher than those found in Eucalyptus nanocellulose samples (0.73-0.81%), due to characteristics of chemical composition of the raw material (DEMUNER *et al.*, 2020). Coffee parchment presents higher ash content (0.5-7%) compared to Eucalyptus (0.1-0.3%) (NUNES *et al.*, 2010; JARDIM *et al.*, 2017; ZANÃO *et al.*, 2019; REIS *et al.*, 2020; CANGUSSU *et al.*, 2021). The silica content was less than 0.41%.

The elemental analysis (Table 4) of lignocellulosic biomass shows carbon, oxygen and in a smaller percentage hydrogen as predominant elements, which are present in the composition of organic substances of cellulose, hemicelluloses and lignin (LUDUEÑA *et al.*, 2011; PURI *et al.*, 2020).

Sulfur and nitrogen are present in lower proportion, and may come from the protein residues present in coffee parchment (CANGUSSU *et al.*, 2021; LITTARDI *et al.*, 2021). Sulfur may also be present due to the kraft pulping process used to obtain cellulose pulps, since it is known that this process uses sodium sulfide as a reagent (BORGES *et al.*, 2018; RIBEIRO *et al.*, 2019).

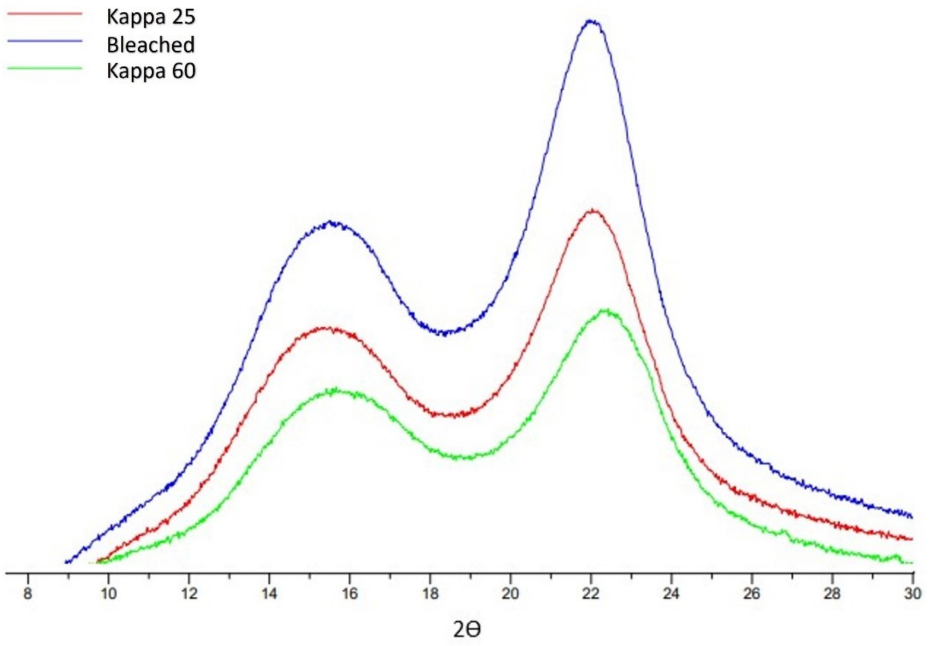
Table 4 - Elemental analysis and inorganic composition of nanocellulose samples

Parameters, %		**MFC-K#60**	**MFC-K#25**	**MFC-Bleached**
Silica		0.41	0.00	0.00
Ash		1.63	1.19	0.85
Elemental analysis	C	49.10	46.30	46.30
	H	6.18	6.34	6.20
	N	0.06	0.02	0.05
	S	0.17	0.16	0.15
	O	44.49	47.18	47.30

3.2.3 X-ray diffraction (XRD)

X-ray diffraction analysis was performed aiming to obtain the crystallinity of the LMFC and MFC samples. The diffractogram presented in Figure 1 shows diffraction intensity peaks around 18.2-18.8 for the amorphous peaks (I_{AM}) and 21.8-22.2 for the crystalline peaks (I_{002}), indicating that the samples present the typical polymorph of cellulose sample I. According to Ass *et al.* (2006), the peak referring to the crystalline fraction at $22° \leq 2\theta \leq 23°$ corresponds to type I cellulose, while for type II cellulose this peak occurs at $18° \leq 2\theta \leq 22°$. Whereas for the regions corresponding to the amorphous fraction for type I cellulose and type II cellulose occur at $18° \leq 2\theta \leq 19°$ and $13° \leq 2\theta \leq 15°$, respectively.

Figure 1 - X-ray diffractogram of the MFC suspensions



The crystallinity of microfibrillated cellulose increases due to the successive dissolution of lignin and hemicellulosess during the pulp extraction step (MARAKANA *et al.*, 2021). The delignification and bleaching processes affect the raw material by modifying the hemicellulosess and lignin content reducing the degree of polymerization and crystallinity of the cellulose (ALBORNOZ-PALMA *et al.*, 2020). The amount of lignin, hemicelluloses and cellulose differs in % in the produced MFCs, which results in varied distribution of crystalline and amorphous parts.

The crystallinity indices obtained in this study was 52.5; 58.8 and 65.1% for the samples LMFC-K#60, LMFC-K#25 and MFC-bleached, respectively. Demuner *et al.* (2019) obtained the values and 82.2 and 82.9% for eucalyptus LCNF and CNF samples, respectively. The values were consistent with those reported by Oliveira (2017), who presented 81.3% for eucalyptus fibers and 49.1 and 53.6% for unbleached and bleached coffee husk fibers respectively.

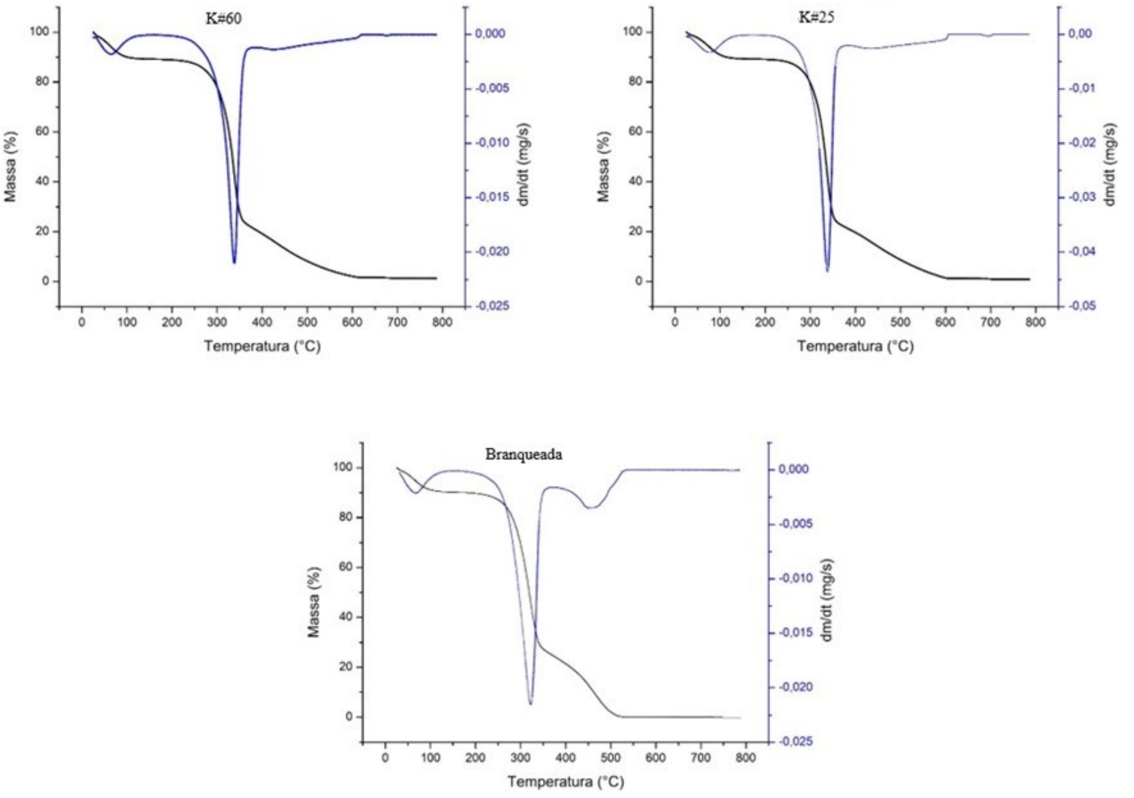
The difference in crystallinity of the samples from Eucalyptus and coffee parchment may be due to the characteristics of each biomass, as it was observed in this study that the coffee parchment pulp has more lignin and hemicelluloses and less cellulose than Eucalyptus pulp, i.e., it contains more amorphous and less crystalline parts in its constitution.

3.2.4 Thermogravimetric analysis (TG/DTG)

The evaluation of the thermal stability of LMFC and MFC is an important parameter for the use of these nanomaterials as reinforcing agents, since, the typical processing temperature of thermoplastic materials is above 200 ºC (REIS *et al.*, 2020; DEMUNER *et al.*, 2020).

The thermal stability of the MFCs samples were tested using thermogravimetric analysis from 25-600 °C (Figure 2). The Figure presents both the thermogravimetric (TG) curves, which shows the mass loss in percentage as a function of temperature, and also the first derivative of TG (DTG) curves, which shows the change in mass with respect to time as a function of temperature (DEMUNER *et al.*, 2020).

Figure 2 - TG/DTG curves of the MFCs suspensions



The thermogravimetric degradation curves were similar for the three suspensions of MFC, and the maximum degradation temperatures of LMFC-K#60 (339 °C) and LMFC-K#25 (339 °C) were slightly higher than that of MFC-Bleached (322 °C), which indicates a slight increase in the thermal stability of LMFCs if compared to MFC. Reis *et al.* (2020) obtained the value of 330 °C for coffee parchment, consistent with that observed in this study.

Thermal degradation occurs in three phases. The first phase occurs around 60-100 °C, in which absorbed waters that may be bound to the microfibrillated cellulose surface are usually released, as well as evaporation of low molar mass volatile compounds (MAHARDIKA *et al.*, 2018; DEMUNER *et al.*, 2020; MARAKANA *et al.*, 2021). The degradation peak of the second phase appears around 250-350 °C, depending on the size and length of the MFC, at this stage it starts to degrade, which usually depends on several factors such as the nature of the feedstock (MAHARDIKA *et al.*, 2018; MARAKANA *et al.*, 2021). After 350 °C the mass loss gradually decreases with increasing temperature. Moreover, an increase in temperature above 450-600 ºC leads to complete degradation of the sample (MARAKANA *et al.*, 2021).

The expressive mass loss of nanocelluloses occurred in the range 300-400 °C (Table 5), this mass loss is attributed to the dehydration of cellulose and then the thermal depolymerization of this polymer (DEMUNER *et al.*, 2020; ASYRAF *et al.*, 2021). The MFC-Bleached lost more mass in the 200-300 °C range if compared to LMFC, which can be explained by the chemical composition of the samples. It is known that the thermal degradation of cellulose occurs later than that of hemicelluloses, due to the greater amount of energy required for depolymerization of the cellulose chain and for the breakdown of its monomers (REIS *et al.*, 2020).

Table 5 - Temperature ranges for loss of mass of the samples

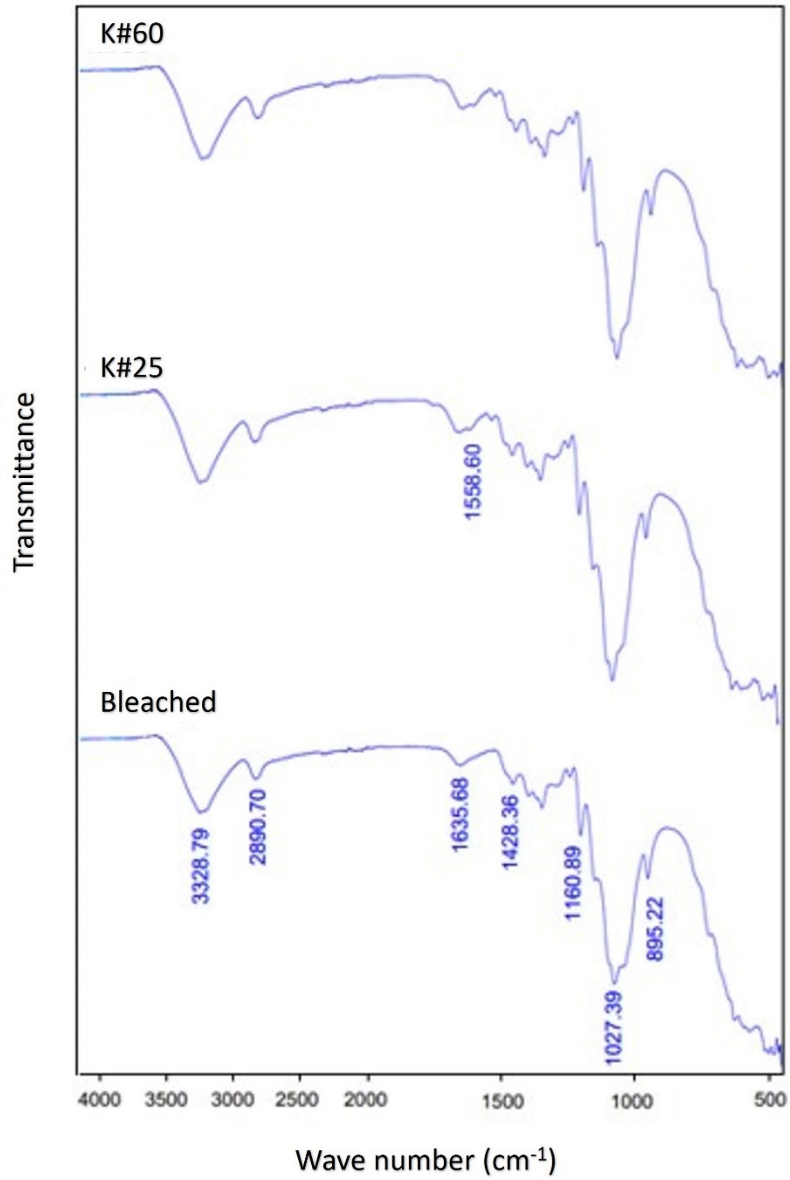
Samples	**Loss of mass (%)**				
	100-200 °C	**200-300 °C**	**300-400 °C**	**400-500 °C**	**500-600 °C**
LMFC-K#60	1.15	10.89	58.78	11.02	6.05
LMFC-K#25	1.83	9.55	59.82	10.95	7.26
MFC-Bleached	1.44	20.31	47.98	19.34	2.05

The higher thermal stability of LMFC can be explained by the presence of lignin in the chemical composition of these samples, since this polymer is thermally more resistant than hemicelluloses and cellulose (ASYRAF *et al.*, 2021).

3.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR characterization can be used to identify the presence of different functional groups and bonds in the nanocelluloses. From the spectra obtained (Figure 3) it can be seen that the microfibrillated cellulose samples presented the same profile in the infrared, with characteristic bands of stretching and C-H, O-H and C-O deformation.

Figure 3 - FTIR spectra of the MFCs suspension samples



Cellulose contains on its surface the hydroxyl group -OH and various bonds such as C-C, C-H and C-O-C. The summary of the bands and corresponding events is presented in Table 6. The wave numbers of the functional groups coincide, but the peak may vary due to the raw material and the methods used (MARAKANA *et al.*, 2021).

Table 6 - FTIR bands attribution of nanocellulose samples

Wave number (cm^{-1})	**Correspondent Assignments**	**References**
3330	Broad band stretching and bond vibration of the O-H groups of cellulose and absorbed water, including hydrogen bonding	DAMÁSIO, 2015; DEMUNER *et al.*, 2020; REIS *et al.*, 2020; MARAKANA *et al.*, 2021; KIM *et al.*, 2021; MHLONGO *et al.*, 2022
2890	Vibration of C-H group bonds CH and CH_2, present in cellulose and hemicelluloses	DAMÁSIO, 2015; DEMUNER *et al.*, 2020; REIS *et al.*, 2020; KIM *et al.*, 2021; MHLONGO *et al.*, 2022
1635	Bond stretching of the carboxylic acid groups, C=O and C-O, can be attributed to some residue of hemicelluloses	DAMASIO, 2015; KIM *et al.*, 2021
1559	Vibration of the benzene ring present in lignin	REIS *et al.*, 2020
1428	Deformation of the symmetric bond of the CH and CH_2 groups of cellulose	DAMÁSIO, 2015; DEMUNER *et al.*, 2020; KIM *et al.*, 2021; MHLONGO *et al.*, 2022
1160	Angular deformation of C-O bonds of primary alcohols existing in cellulose molecules and their polysaccharides	REIS *et al.*, 2020; MARAKANA *et al.*, 2021
1027	C-O-C bonding of asymmetric 1,4-glycosidic bonds of D-glucose	REIS *et al.*, 2020; MARAKANA *et al.*, 2021
895	*β*-Glycosidic linkages between cellulose glucose units	DAMÁSIO, 2015; DEMUNER *et al.*, 2020; MHLONGO *et al.*, 2022

3.2.6 Zeta Potencial

The Zeta Potential analysis is a characterization that evaluates the colloidal stability of suspensions taking into account the density of surface charges. The stability of suspensions is directly linked to the surface forces of particles and the interactions between them (repulsion or attraction). The intensity of these characteristics defines the formation of clusters of particles in suspension and their sizes and, consequently, the sedimentation of suspensions (XU *et al.*, 2021; SHARMA *et al.*, 2021).

The stability and electrostatic repulsion between the fibers increase as the zeta potential decreases, usually considering the system moderately stable when it is lower than -30 mV (XU *et al.*, 2021). On the other hand, values between 10-30 are considered unstable (SHARMA *et al.*, 2021).

The zeta potential values found for LMFC-K#60, LMFC-K#25 and MFC-bleached samples were -19.8 mV, -15.8 mV -27.4 mV, respectively. Some factors influence the zeta potential, such as the length of microfibrils that can result in interlacing of LMC and MFC; the presence of residual hemicelluloses due to their binding capacity; and the sulfur content in the samples that increases surface charges (DAMASIO, 2015; DEMUNER *et al.*, 2020).

3.2.7 Water retention value (WRV)

The water retention index presents a measure of the fibers' ability to absorb water, after centrifugation in standard conditions. This property is associated with the binding capacity of the fibers, since they present highly exposed free hydroxyl groups, and with the higher surface area of their compounds (CHENG *et al.*, 2010; XU *et al.*, 2013; HU *et al.*, 2022).

The WRV values for microfibrils, LMFC-K#60, LMFC-K#25 and MFC-bleached, were 792, 849, 1032%, respectively. The different contents obtained by the samples can be justified by their chemical compositions (Table 3), it is known that a higher content of xylans increases the WRV because they have negative electrical charges arising from the deprotonation of carboxylic groups present in its structure (WINUPRASITH & SUPHANTHARIKA, 2013). A higher lignin content decreases the water retention index due to its hydrophobic character (SPENCE *et al.*, 2010).

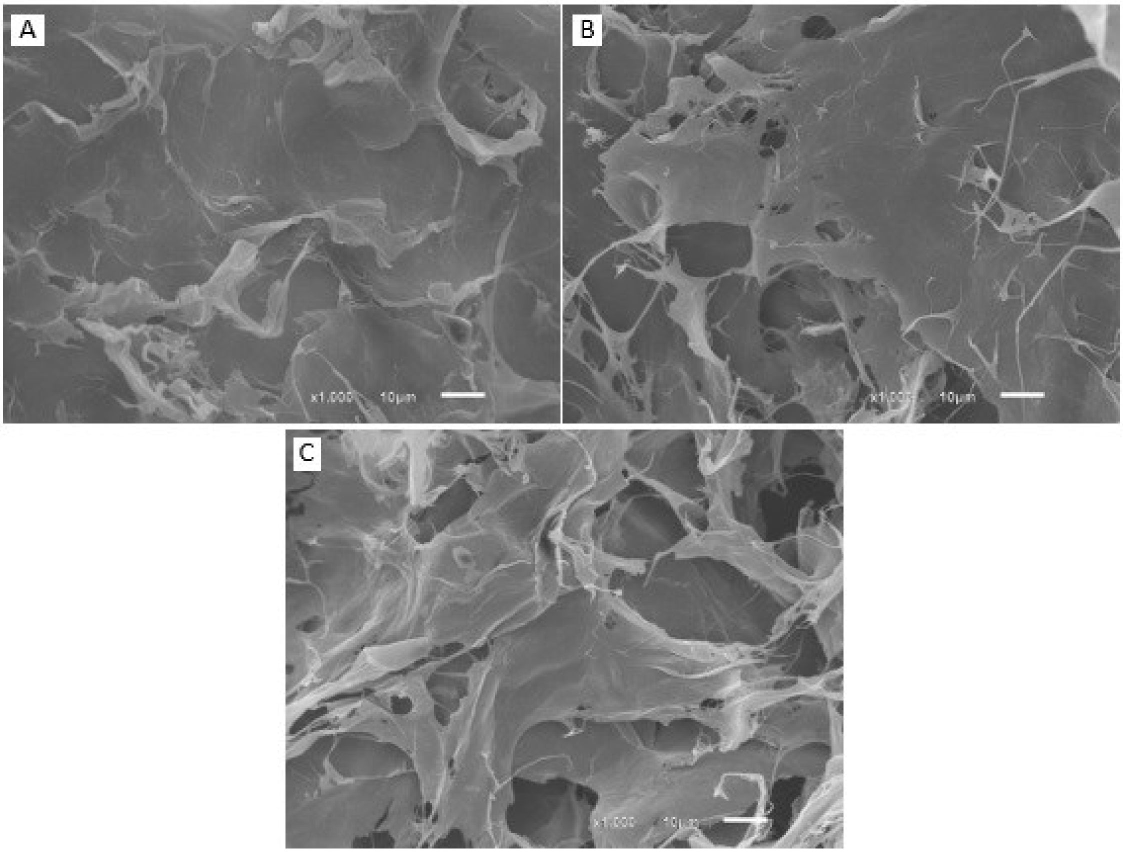
Demuner *et al.* (2020) obtained higher values when compared to coffee parchment for the water retention indices of eucalyptus nanofibrils, 1117 for LCNF and 1496 for CNF, this fact can be explained due to the smaller size and larger surface area obtained in the studies of eucalyptus nanofibrils, which favors greater water retention (CHENG *et al*, 2010).

3.2.8 Electron microscopy

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can be used to characterize the surface and dimensions of nanomaterials (PURI *et al.*, 2020).

Figure 4 presents the SEM images of the samples - LMFC-K#60, LMFC-K#25 and MFC-bleached - we can observe that the three suspensions presented similar superficial structure, being possible to observe through the SEM that the walls of the fibers were deconstructed due to the mechanical process of defibrillation, releasing the microfibrils from the interior of the fibers.

Figure 4 - SEM images at 1000x magnification - 10 µm: A) LMFC-K#60; B) LMFC- K#25 and C) MFC-Bleached



Already through transmission electron microscopy it was expected to observe the structure of the suspensions of MFC as a web, which is formed due to the interweaving of microfibrils because of the exposure of their active binding sites (DAMÁSIO, 2015), thus presenting one of its dimensions on the scale of nanometers, the diameter, and the length on the scale of micrometers.

However, it was not possible to obtain quality images. The MET image is obtained due to the emission of an electron beam towards an ultrafine sample (less than 50 nm), interacting with the sample as it passes through it (INKSON, 2016). To obtain an ideal sample is performed the dilution of the suspension of MFC, but even performing this procedure the image obtained was not satisfactory, which can be justified by the fact that the suspensions of LMFC-K#60, LMFC-K#25 and MFC-bleached are unstable, i.e., have a tendency to agglomerate, proven by the zeta potential analysis.

4 CONCLUSION

Cellulose fibers from the residue of the coffee industry, parchment, have shown to be a viable alternative for the production of microfibrillated cellulose (MFC) and microfibrillated lignocellulose (LMFC), presenting in general comparative properties with the nanocellulose produced from eucalyptus.

Parchment nanocelluloses contain higher lignin and hemicelluloses content compared to eucalyptus nanocelluloses, due to the chemical composition of its original biomass, which influences the decrease in crystallinity.

The zeta potential values found for LMFC-K#60, LMFC-K#25 and MFC- Bleached samples were -19.8 mV, -15.8 mV -27.4 mV, respectively. Which shows us that the suspensions of MFCs are unstable, i.e., present the tendency to agglomerate. LMFC-K#60, LMFC-K#25 and MFC-Bleached showed crystallinity index of 52.5; 58.8 and 65.1%, respectively, and proved thermally stable, with the maximum temperatures of LMFC-K#60 (339 °C), LMFC-K#25 (339 °C) and MFC-Bleached (322 °C). FTIR spectra were similar for all nanocelluloses, showing peaks characteristic of cellulosic polymers, including characteristic peaks of lignin in LMFCand absent in MFC.

Scanning electron microscopy showed that the fibers were deconstructed due to the mechanical defibrillation process in the three samples, whereas in transmission electron microscopy we did not obtain relevant images to confirm the microfibril interweaving and the web-like nanostructure of the MFCs.

The characterization of LMFC and MFC were quite similar, which makes LMFC more advantageous when the application does not require a colorless suspension or even when the presence of lignin adds to the product, as in the case of sunscreen, in which the lignin itself helps in UV protection. Furthermore, the production cost of LMFC is lower than that of MFC, because in addition to needing a lower alkali load and less drastic pulping conditions, which also contributes to higher yield, its production eliminates the bleaching step, used for removal of residual lignin present in the pulp from the cooking process.

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CAPÍTULO 4: MORPHOLOGICAL AND PHYSICAL-MECHANICAL CHARACTERIZATION OF COFFEE PARCHMENT FIBERS FOR PAPER PRODUCTION

ABSTRACT

The use of waste as a raw material for the manufacture of new products adds value, creates opportunities through innovation, reduces the pressure for new resources and stimulates the entrepreneurship. Coffee is one of the most important commodities today. But production generates a large amount of waste. The use of these residues, transforming them into by-products of the industry, becomes an attractive possibility for the market and mainly for the environment. Coffee by-products include husks, skin and pulp, coffee mucilage, coffee parchment and coffee silver foil. The coffee parchment refers to the endocarp that covers the coffee seed and separates the two hemispheres of the seed. In the present work, three types of kraft pulp from the cooking of coffee parchment (unbleached pulp kappa 25, unbleached pulp kappa 60 and bleached pulp) were morphologically characterized and their potential as raw material in paper production were analyzed. The pulps did not present significant morphological differences between them, presenting short fibers and high wall thickness. The coffee parchment fibers had an average length of 0.51 mm, approximately 23 µm in width with a lumen diameter and wall thickness of approximately 12.5 µm and 5.3 µm, respectively. As expected by the results of the morphological analysis and by the relationship between the dimensions of the fibers, and confirmed by the results of the physical tests, the parchment fibers present high rigidity, and consequently difficulty in their interconnections. However, these characteristics can be attractive for papers for cigarettes production and also as a reinforcing material for tissue paper production.

Keywords: Biomass. Coffee industry. Kraft pulp.

1 INTRODUCTION

The world demands real transformations, since there is no more space for an economy based on exploration, production, consumption and waste. Through the circular economy, we need to prioritize the sustainable bio-economy, using resources intelligently. The use of waste as a raw material to manufacture new products adds value, creates opportunities through innovation, reduces pressure for new resources and encourages the entrepreneurship (IBÁ, 2021).

The production and processing of coffee generate a huge amount of waste, including husk, skin, pulp, mucilage, parchment and coffee grounds (REIS *et al.*, 2020). Because it contains organic matter in its composition (tannin, caffeine and polyphenols), which are powerful or highly toxic stimulants, its reuse becomes restricted. Environmental reasons and possible destinations of this huge amount of lignocellulosic biomass, become relevant studies on the reuse of these coffee wastes.

Parchment is the fibrous endocarp that covers and separates the coffee seeds, representing 6.1% by weight of the whole fruit. Currently, its main destination is in the production of briquettes and pellets, to be burned for energy generation (MIRÓN-MÉRIDA *et al.*, 2019).

Among the residues from the coffee industry, parchment has the greatest amount of cellulose. Then, its isolated lignocellulosic fibers could be used as pulp in the production of paper or other high-added value products (REIS *et al.*, 2020).

In the present work, the parchment fibers were morphologically characterized and submitted to kraft pulping for their individualization and lignin removal. After that, the pulp was analyzed as a potential raw material in paper production.

2 MATERIAL AND METHODS

Kraft pulps from the cooking of coffee residues (parchment) from Santa Teresa, ES, Brazil were used. The study was carried out with three types of pulp, two unbleached pulps (kappa numbers 25 and 60) and one bleached pulp.

2.1 Fiber morphology

Parchment pulps from pulping process (brown pulp), delignification with oxygen (O_2 pulp) and final pulp of the bleaching sequence (bleached pulp) were subjected to fiber analysis, using the Valmet FS5 Analyzer equipment, in order to obtain the coarseness value, fibers numbers and fines content. The sample is suspended in demineralized water and analyzed.

Fiber morphology analysis was also performed on the four pulps (brown – kappa 25 and 60 –, O_2 and bleached). For the individualization of the fibers, the samples were placed in a test tube, with a solution of hydrogen peroxide and glacial acetic acid, according to the method recommended by Dadswell (1972). Subsequently, temporary blades were mounted to obtain the length (L), width (W), lumen diameter (D) and wall thickness (T) of the fibers. An optical microscope with a camera attached, an image acquisition system, and the Axio-Vision software were used.

From these parameters, Runkel index, wall fraction, envelope index and flexibility coefficient were calculated according to equations (1), (2), (3) and (4), respectively.

$$\text{Runkel Index} = 2T \div D \tag{1}$$

$$\text{Wall fraction} = \left\{\left[\frac{(2T)}{W}\right] * 100\right\} \tag{2}$$

$$\text{Envelope Index} = L \div W \tag{3}$$

$$\text{Flexibility Coefficient} = \left\{\left[\frac{D}{W}\right] * 100\right\} \tag{4}$$

2.2 Papers production

For paper production, brown pulps (kappa 60 and 25) and bleached pulp from the bleaching process of kappa number 25 pulp were used. Three different refining levels were used, based on the number of revolutions 250, 500 and 750 rpm for kappa 60 pulp; 100, 200 and 300 rpm for kappa 25 pulp and 150, 300 and 450 rpm for bleached pulp. The refining was carried out in a PFI refiner, model MARK VI from Hamar Norway, following the TAPPI T248 sp-08 standard.

The determination of the drainage resistance, in Schopper-Riegler degrees (°SR), was carried out according to the ISO 5267-1:1999 standard. The preparation of laboratory sheets was carried out according to the TAPPI T 205 om-81 standard. The formed sheets were placed in an environment with a relative humidity of 50±2% and a temperature of 23±1 °C. A grammage of 180 g/m^2 was adopted for making the sheets.

2.3 Physical-mechanical tests

The papers produced were evaluated for tensile index (TAPPI 494 om-06), burst index (TAPPI 403 om-02), modulus of elasticity (TAPPI 494 om-06), tear index (TAPPI 414 om-04) and air resistance of paper (TAPPI 536 om-07).

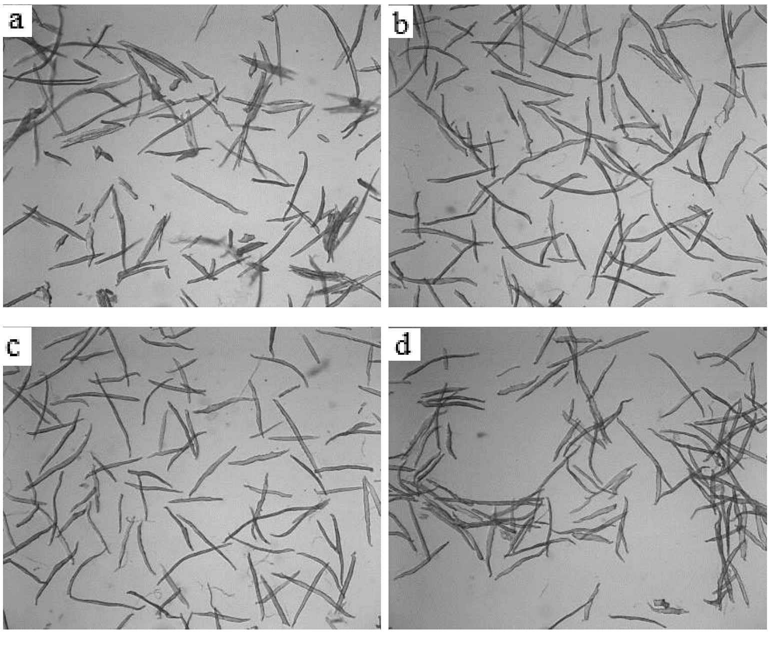
3 RESULTS AND DISCUSSION

3.1 Fiber Morphology

Morphological characteristics are among the first indicators to be evaluated for screening potential raw materials for paper production. It is known that the paper structure and mechanical behavior depend on the specific characteristics of the fiber (BRONKHORST, 2003; CLARK, 1978; RYDHOLM, 1965).

Figure 1 illustrates the electron microscopy of pulps from the kraft pulping of coffee parchment, oxygen delignification and bleaching process.

Figure 1 - Electron microscopy image: (a) brown pulp - kappa 60, (b) brown pulp - kappa 25 (c) O$_2$-pulp and (d) bleached pulp



No significant difference was observed in the pulp fibers from the different stages of the process. In Table 1 are shown the fiber dimensions of the parchment pulps and dimensions of eucalyptus and pine fibers for ease of comparison.

Table 1 - Average values of fiber dimensions

Parameters	Kappa 60	Kappa 25	O_2-pulp	Bleached pulp	*Eucalyptus**	*Pinus taeda***
Length, mm	0.52	0.51	0.51	0.50	0.856	3.50
Width, µm	23.98	23.81	23.03	23.36	17.39	40.55
Lumen diameter,	13.01	12.51	12.61	12.52	10.92	27.73
Wall thickness, µm	5.35	5.23	5.21	5.42	3.23	6.41
Runkel index	0.82	0.84	0.83	0.87	0.59	0.46
Flexibility, %	54.25	52.54	54.75	53.60	62.79	68.0
Wall fraction, %	44.62	43.93	45.25	46.40	37.15	32.0
Envelope index	21.68	21.42	22.15	21.40	49.22	86.0

*MENEGAZZO, 2012
**VIVIAN *et al.*, 2015

From the papermaking point of view, lignocellulosic fibers can be classified as long fibers (average length between 2 and 5 mm) and as short fibers (average length between 0.5 and 1.55 mm) (KUAN *et al.*, 1988). Based on this statement and the values presented in Table 6, the fibers of the parchment can be classified as short fibers.

Fiber length is an important characteristic in determining the properties, quality of paper and its application. According to Foelkel (2007), fiber length affects sheet formation and especially paper mechanical strength (tensile and burst strength). Generally, short fibers favor the formation of sheets, improve surface properties and interfiber bonding, and have high tensile strength. In contrast, long fibers produce papers with high mechanical strength, in addition to affecting the acceptable speed of the paper machine (wet strength of the paper) (DIAS & SIMONELLI, 2013).

Fiber width is a fiber characteristic whose relationship with pulp quality is not yet well defined. However, this dimension affects other properties such as slenderness, flexibility and fiber stiffness (PEGO *et al.*, 2019). The width of the parchment fibers proved to be larger than that of eucalyptus and smaller than that of pine. Usually, longer fibers are also wider. However, for some species, substantial length development is not proportional to the increase in fiber width (OLIVEIRA, 1979).

Cell wall thickness is one of the factors that is most related to the strength of pulp. According to Foelkel and Barrichelo (1977), thick wall fibers have a higher relative content of cellulose, which favors the yield of the pulping process.

Larger lumen diameters and thinner walls facilitate fiber collapse during sheet formation, resulting in greater interfiber bond intensity and higher tensile and burst strength properties. The lumen diameters of the parchment are close to the value found in Eucalyptus wood, however the fiber walls are thicker compared to wood commonly used in paper production. Fibers with greater wall thicknesses and smaller lumen diameters are less flexible, as they present lower degrees of collapse and fewer interfiber connections (SILVA, 1996; FERREIRA & FIGUEIREDO, 2001).

The relationships between the fundamental dimensions of the fibers have been shown to be more important than the dimensions themselves alone (FOELKEL & BARRICHELO, 1977). The Runkel index value for the parchment pulps was classified as good for paper production. Fiber up to 0.25 is considered excellent for paper; from 0.25 to 0.50 is very good; from 0.50 to 1.00 is good; from 1.00 to 2.00 is regular, and above 2.00 should not be used for paper, as they are fibers with very thick walls (RUNKEL APUD PAULA, 1999).

Foelkel and Barrichelo (1977) reported that, generally, the fibrous materials used in production must have a wall fraction ratio of less than 40%, which did not occur with the parchment fibers. This data allows the inference that the pulp produced with parchment may not have good quality, presenting extremely rigid fibers, not very flexible and with difficulties in their interconnection. But these characteristics do not prevent the use of coffee parchment fiber associated with eucalyptus fibers, for example, to give paper greater volume, which is desired for tissue production.

The parchment flexibility coefficient was lower than the other species listed in Table 6. The highest values of this coefficient characterize the more flexible fibers, facilitating the connections between them and adding strength to the paper (FOELKEL & BARRICHELO, 1975). The low bond between fibers can lead to a more porous paper, which can be interesting for the manufacture of cigarette papers.

The low values determined for the envelope index were lower than the pine and eucalyptus indexes, which can affect the physical-mechanical strength of the parchment pulps.

3.2 Paper production and physical-mechanical tests

The properties in paper depend on the fiber properties and the fiber preparation method (pulping, bleaching and fiber processing). The best properties of paper depend on the product being made. However, alternatives such as pulp refining and mechanical treatment of cellulose fibers can be used to develop their ideal papermaking properties.

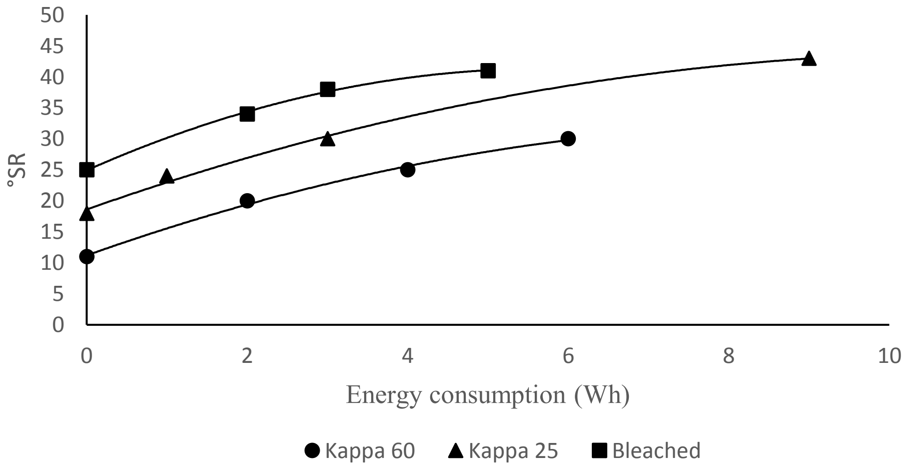
Refining process increases the strength of fiber-to-fiber bonds, the surface area and makes the fibers more flexible. Then, increases the bonding surface area and leads to the formation of a denser sheet. However, the individual fibers are weakened and shortened due to the cutting action and, in most cases, it is an unwanted refining effect (BAJPAI, 2018).

For the refining and physical-mechanical and optical properties of the papers, three types of pulp were analyzed: (1) brown pulp kappa 60; (2) brown pulp kappa 25; (3) bleached pulp from ECF bleaching of brown pulp kappa 25. Properties will be displayed in graphs, as a function of energy consumption (Wh) required for refining.

3.2.1 Drainage Resistance

Pulp drainage resistance was measured using the Schopper-Riegler method (ºSR), which is an important parameter for evaluating fiber entanglement. The greater the pulp drainage resistance, the lower its capacity to drain water. In Figure 2, the relationship between drainage resistance and refining energy consumption is presented.

Figure 2 - Drainage resistance as a function of refining energy consumption



All studied pulps required little energy consumption to significantly change the ºSR values. In the absence of refining (x=0), kappa 25 and bleached pulps already presented greater resistance to drainage compared to pine and eucalyptus pulps, usually used in paper production in Brazil, under the same conditions (DEMUNER, 2017; ZANÃO, 2016).

This high drainage resistance of the pulps can be explained mainly by the high surface area of the parchment fibers. As evidenced in the morphology analysis, the studied biomass presents a very short fiber.

It was observed that with the increase in the lignin content in the pulps, there is a decrease in the drainage resistance. The corrected value of kappa number and residual lignins of the pulps is shown in Table 2. Li and Gellerstedt (1997) propose the correction of the kappa number of the pulps without the participation of the HexA, with 11.6 mmol of HexA/kg of pulp representing a unit of kappa number.

Considering this correction, the residual lignins were 8.36% for kappa 60 pulp, 2.85% for kappa 25 pulp and 0.015% for bleached pulp. It is known that the higher content of residual lignin, a polymer that has hydrophobic properties, contributes to a lower drainage resistance of pulp (SPENCE *et al.*, 2010). Because of that, the pulp with kappa number 60 showed lower drainage resistance when compared to other pulps.

Table 2 - Corrected kappa number and residual lignin

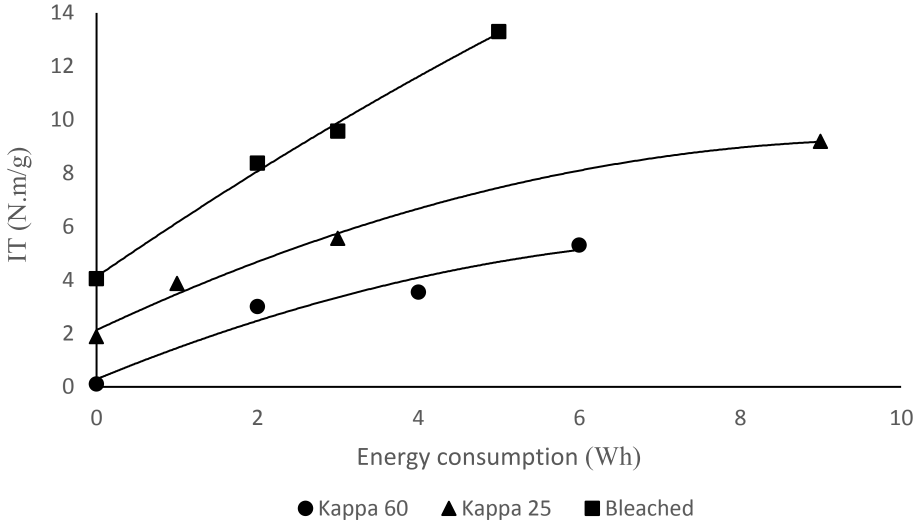
Parameters	**Pulps**		
	Kappa 60	**Kappa 25**	**Bleached**
Kappa number (K)	61.4	24.5	0.3
Hexenuronic acids, mmol kg^{-1} (H)	66.4	63.5	2.4
^{1}Corrected kappa number (Kc)	55.7	19.0	0.1
^{2}Residual lignin (%)	8.36	2.85	0.015

^{1}Correct kappa number (Kc) = K – (H/11.6)
^{2}Residual lignin = Kc*0.15

3.2.2 Tensile index

The tensile index is a very relevant property for pulps for paper production. It indicates the quality of the final product and the probability of a sheet breaking during its production process. In Figure 3, the relationship between the tensile index and the refining energy consumption is presented.

Figure 3 - Tensile index as a function of refining energy consumption



The tensile strength increases with the evolution of refining, but still presents extremely low values compared to the woods commonly used in paper manufacture. The tensile property is influenced by the degree of refinement, fiber connections, sheet structure and fiber length (FERREIRA, 2008).

The low tensile strength of parchment pulps can be explained by the size of the fibers present in the biomass. The presence of residual lignin in the pulps also helps to reduce this property.

3.2.3 Burst index

The burst index is directly related to the number of interfiber connections and the force exerted by these connections (MOREIRA, 2006). It is defined as the pressure necessary to produce the material burst, when a uniformly increasing pressure is applied by an elastic diaphragm with a circular area (D'ALMEIDA, 1981; SILVA, 2015).

Studies show that cellulosic pulp produced from pine has greater mechanical strength compared to eucalyptus. This behavior can be explained by the morphological difference presented by pine fibers, that is, greater length (GOMES & ALVES, 2015).

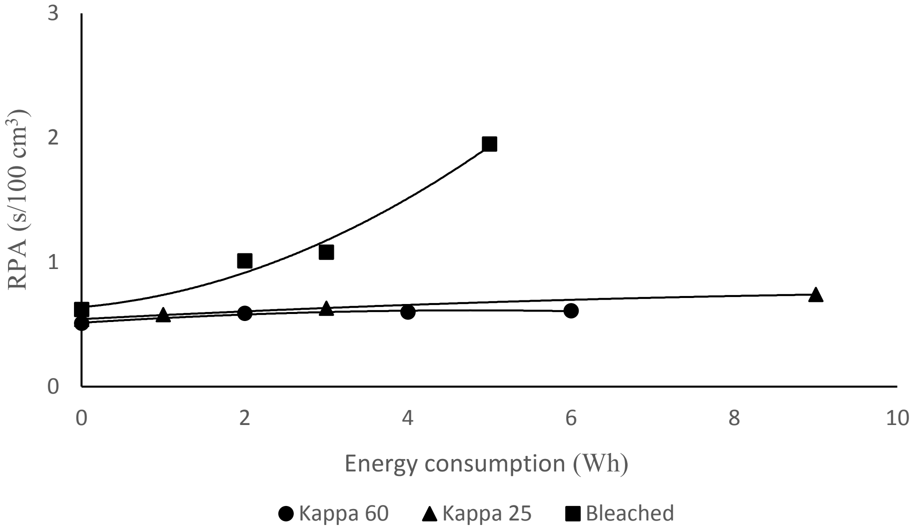
The pulps produced with the parchment showed no resistance to bursting in the absence of refining (x=0). It presented an insignificant gain with refining evolution, obtaining a maximum of 0.04; 0.10 and 0.22 kPa m^2/g for kappa 60, kappa 25 and bleached pulps, respectively. This performance of the pulps can be explained by the fiber morphology of this biomass, fiber with a low value in length and high in width.

The properties of burst index and tensile index are mainly affected by the binding capacity between the fibers, which justifies the similarity in the trend observed for both properties (POTULSKI *et al.*, 2014). This behavior suggests that the pulp produced by the parchment has low fiber binding.

3.2.4 Air resistance

Air resistance is the time that a given volume of gas or vapor flows through a paper under specified conditions. It is a property greatly influenced by the degree of fiber compaction, so that a more porous paper leads to lower strength (GOMES, 2010; SILVA, 2011). Figure 4 shows the relationship between air resistance and refining energy consumption.

Figure 4 - Air resistance as a function of refining energy consumption

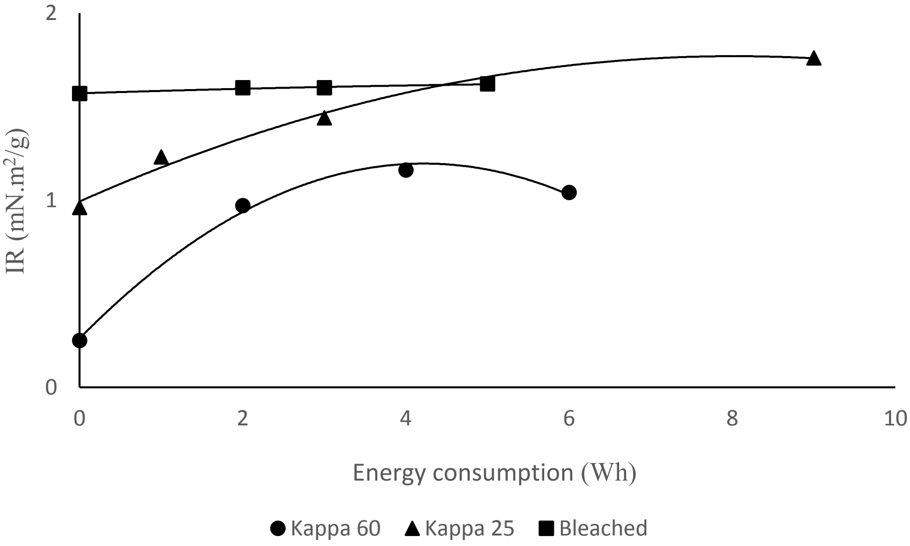


The increase in air resistance with the evolution of refining was only observed for the bleached pulp. However, the values found in the three pulps are extremely low compared to the resistance observed in the wood pulps.

3.2.5 Tear index

Tear index measures the work performed by a pendulum, necessary to tear a set of sheets, after performing an initial cut in the samples up to a predetermined distance (KLOCK, 2000). The main factors influencing the tear index are length, intrinsic strength, fiber wall thickness and interfiber bonds (GOMES, 2010). In Figure 5, the relationship between the tear index and the refining energy consumption is presented.

Figure 5 - Tear index as a function of refining energy consumption



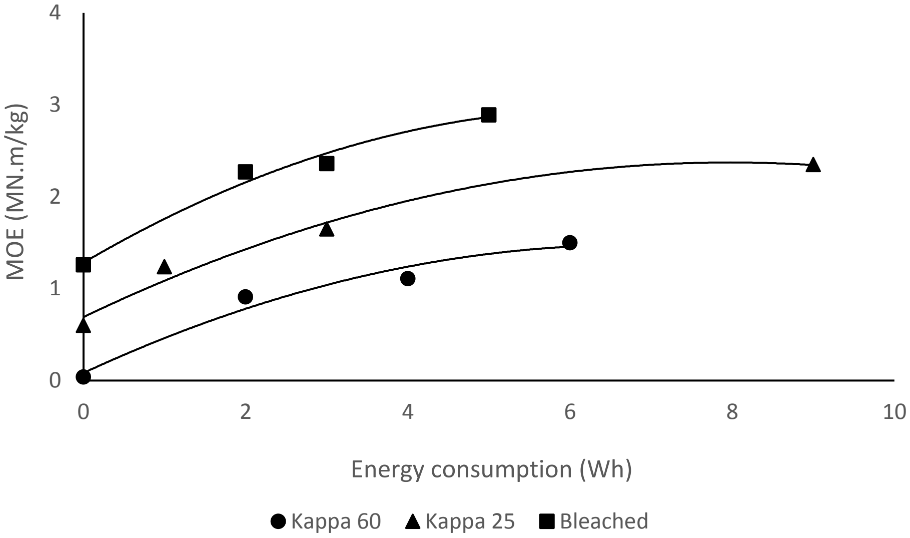
There was no gain in the tear index with refining for the bleached pulp, its value remained constant at around 1.60 mN m^2/g. The brown pulps, kappa 60 and 25, showed a tendency to increase with the evolution of refining, reaching a maximum of 1.04 and 1.76 mN m^2/g, respectively. The values found are much lower compared to wood pulps.

This fact occurs because tear strength is directly related to fiber length (FAVARO *et al.*, 2014; CARVALHO *et al.*, 1997; HAKANEN & HARTLER, 1995). With refining, there may be an increase in interfiber connections, which justifies the gain in strength of brown pulps. However, the reduced fiber length of this biomass also contributes to a significant reduction in the tear index.

3.2.6 Specific modulus of elasticity

The specific modulus of elasticity expresses the ability of a material to resist deformation when subjected to stress. The paper initially presents a linear behavior of elasticity. Then, it assumes a plastic behavior, when subjected to a continuous effort, until reaching the maximum load at breakage (KARLSSON, 2006; SILVA & OLIVEIRA, 2000). In Figure 6 the specific modulus of elasticity is represented as a function of refining energy consumption.

Figure 6 - Specific modulus of elasticity as a function of refining energy consumption



3.3 Possibility of use for paper production

Fiber characteristics such as fiber thickness, wall thickness, and fiber width infer the binding capacity between fibers. A more open fibrous network structure, with fewer interfiber connections, will positively influence softness and negatively influence tensile strength (MORAIS *et al.*, 2019; PIRRALHO *et al.*, 2014). In this way, coffee parchment fibers could add these characteristics to other pulps, forming pulp blends with better properties for the production of tissue paper.

Another possible use would be cigarette papers. It is widely known that increasing the air permeability of paper can minimize the formation of carbon monoxide (HOFFMANN *et al.*, 1979; KOZLOWSKI & O'CONNOR, 2002; ROBINSON & FORBES, 1975; ROSTAMI & HAJALIGOL, 2003; STEPHENS, 2007; SHEN *et al.*, 2014). Therefore, a porous paper with low air resistance can be favorable for the production of cigarette papers. With high air permeability, oxygen levels in cigarettes increase, thus facilitating the conversion of carbon monoxide to carbon dioxide (SHEN *et al.*, 2014).

The characteristics of coffee parchment fibers are unique. Its use is a reality for the pulp industry. In-depth studies on the type of material most suitable for the use of the raw material must be carried out.

4 CONCLUSION

The pulps did not present significant morphological difference among themselves, with short fibers and high wall thickness. As expected by the results of the morphological analysis and by the relationships between the dimensions of the fibers, and confirmed by the results of the physical tests, parchment fibers do not show good interfiber bonding capacity. The analyzed pulps can be used in some types of paper that require fibers with high rigidity and high roughness. The production of cigarette papers is attractive due to its low air resistance. The possibility of using the fiber together with fibers from other raw materials may allow for an increase in bulk, necessary for tissue papers.

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CONSIDERAÇÕES FINAIS

O uso do pergaminho de café, resíduo da indústria cafeeira, para geração de produtos de alto valor agregado é promissor. Durante o processo de desconstrução da biomassa pelo processo kraft, obtém-se tanto a fibra de celulose com residual de lignina, que pode ser usada dessa forma ou seguir para a etapa de branqueamento para remoção de grupos cromóforos, como também o licor negro kraft, que pode ser utilizado para extrair lignina kraft.

Nesse estudo ficou evidenciado que a fibra de celulose de pergaminho, apresenta característica que não são favoráveis para a produção de papel formado exclusivamente por fibras de pergaminho. No entanto, pode ser usada em conjunto com fibras provenientes de outras matérias-primas ou até mesmo na produção de papéis de cigarro.

As fibras de celulose com e sem residual de lignina também podem ser submetidas a um tratamento mecânico para obtenção de nanocelulose com características semelhantes a nanocelulose obtida de fontes madeireiras.

Por fim, esse estudo traz outro produto de alto valor e amplamente estudado atualmente que é a lignina kraft, com alto teor de pureza e com total capacidade de ser utilizada em diversas aplicações, inclusive as que demandam uma lignina com mais sítios ativos livres.

Como possibilidade de novas pesquisas, é possível avaliar o uso das fibras de celulose de pergaminho em misturas com outras fibras e na produção de papéis especiais. Além disso, é viável avaliar aplicações para as suspensões de nanocelulose com e sem residual de lignina obtidos, como também aplicações para lignina kraft extraída.

APÊNDICE

Capítulo 1: COFFEE BIOMASS RESIDUE AS RAW MATERIAL FOR CELLULOSE PRODUCTION AND PY-GC-MS ANALYSIS

Quadro 1 – Resultado da etapa de branqueamento Fator Kappa 0,12

Condições e Resultados	**Rep.**	**MARROM**	**Estágios de Branqueamento**											
			O	**Q**	**D**	**(EP)**	**D(a)**	**D(b)**	**D(c)**	**D(int)**	**P(a)**	**P(b)**	**P(c)**	**P(int)**
Consistência, %	-	-	10	10	10	10	10	10	10	10	10	10	10	10
Temperatura, °C	-	-	90	80	90	90	80	80	80	80	80	80	80	80
Tempo, min	-	-	60	30	120	60	120	120	120	120	60	60	60	60
Pressão, kPa	-	-	350	-	-	-	-	-	-	-	-	-	-	-
O_2, kg/tas	-	-	18,0	-	-	-	-	-	-	-	-	-	-	-
Fator kappa	-	-	-	-	0,12	-	-	-	-	-	-	-	-	-
ClO_2, como ClO_2, kg/tas	-	-	-	-	7,7	-	12,0	14,0	16,0	12,9	-	-	-	-
H_2O_2, kg/tas	-	-	-	-	-	7,8	-	-	-	-	3,0	3,0	3,0	3,0
H_2SO_4, kg/tas	-	-	-	-	2,5	-	-	-	-		-	-	-	-
NaOH, kg/tas	-	-	15,0	-	-	14,5	5,5	7,0	8,5	6,2	6,5	6,5	6,5	6,5
$MgSO_4.7H_2O$, kg/tas	-	-	3,0	-	-	3,0	-	-	-	-	-	-	-	
DTPA, kg/tas	-	-	-	2,0	-	-	-	-	-	-	-	-	-	-
pH final	A	-	11,3	7,0	3,4	10,5	5,0	5,0	5,2	5,2	10,7	10,6	10,6	10,8
	B	-	11,1	7,0	3,4	10,5	5,0	5,0	5,2	5,2	10,7	10,6	10,6	10,8
	Média	-	11,2	7,0	3,4	10,5	5,0	5,0	5,2	5,2	10,7	10,6	10,6	10,8
Consumo de reagentes, %	A	-	-	-	100	68,6	-	-	-	95,6	-	-	-	61,8
	B	-	-	-	100	68,6	-	-	-	95,6	-	-	-	61,8
	Média	-	-	-	100	68,6	-	-	-	95,6	-	-	-	61,8
Número Kappa	A	24,5	16,9	16,8	-	4,1	-	-	-	-	-	-	-	0,6
	B	24,5	16,9	16,8	-	4,1	-	-	-	-	-	-	-	0,6
	Média	24,5	16,9	16,8	-	4,1	-	-	-	-	-	-	-	0,6
Alvura, %ISO	A	20,9	28,6	31,7	39,3	69,3	87,9	88,6	88,6	87,7	89,6	90,5	90,7	90,0
	B	20,9	28,6	31,7	39,3	69,2	87,9	88,6	88,6	87,7	89,6	90,5	90,7	90,0
	Média	20,9	28,6	31,7	39,3	69,3	87,9	88,6	88,6	87,7	89,6	90,5	90,7	90,0
Reversão de alvura, %ISO	A	-	-	-	-	-	-	-	-	-	-	-	-	2,0
	B	-	-	-	-	-	-	-	-	-	-	-	-	1,9
	Média	-	-	-	-	-	-	-	-	-	-	-	-	2,0
Viscosidade, dm3/kg	A	965	894	859	-	-	-	-	-	-	-	-	-	640
	B	965	901	865	-	-	-	-	-	-	-	-	-	633
	Média	965	898	862	-	-	-	-	-	-	-	-	-	637
Hexa, mmol/kg	A	63,5	62,8	-	-	-	-	-	-	-	-	-	-	3,7
	B	63,4	62,8	-	-	-	-	-	-	-	-	-	-	3,5
	Média	63,5	62,8	-	-	-	-	-	-	-	-	-	-	3,6

Quadro 2 – Resultado da etapa de branqueamento Fator Kappa 0,20

Condições e Resultados	Rep.	MARROM	Estágios de Branqueamento											
			O	**Q**	**D**	**(EP)**	**D(a)**	**D(b)**	**D(c)**	**D(int)**	**P(a)**	**P(b)**	**P(c)**	**P(int)**
Consistência, %	-	-	10	10	10	10	10	10	10	10	10	10	10	10
Temperatura, °C	-	-	90	80	90	90	80	80	80	80	80	80	80	80
Tempo, min	-	-	60	30	120	60	120	120	120	120	60	60	60	60
Pressão, kPa	-	-	350	-	-	-	-	-	-	-	-	-	-	-
O_2, kg/tas	-	-	18,0	-	-	-	-	-	-	-	-	-	-	-
Fator kappa	-	-	-	-	0,20	-	-	-	-	-	-	-	-	-
ClO_2, como ClO_2, kg/tas	-	-	-	-	12,8	-	6,0	8,0	10,0	5,6	-	-	-	-
H_2O_2, kg/tas	-	-	-	-	-	7,8	-	-	-	-	3,0	3,0	3,0	3,0
H_2SO_4, kg/tas	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NaOH, kg/tas	-	-	15,0	-	0,5	14,5	0,8	2,1	3,5	1,1	6,5	6,5	6,5	6,5
$MgSO_4.7H_2O$, kg/tas	-	-	3,0	-	-	3,0	-	-	-	-	-	-	-	
DTPA, kg/tas	-	-	-	2,0	-	-	-	-	-	-	-	-	-	-
pH final	A	-	11,3	7,0	3,4	10,6	4,6	4,6	4,6	4,8	10,9	10,7	10,7	10,9
	B	-	11,1	7,0	3,4	10,6	4,6	4,6	4,6	4,8	10,9	10,7	10,7	10,9
	Média	-	11,2	7,0	3,4	10,6	4,6	4,6	4,6	4,8	10,9	10,7	10,7	10,9
Consumo de reagentes, %	A	-	-	-	100	60,8	-	-	-	99,6	-	-	-	54,1
	B	-	-	-	100	60,8	-	-	-	99,6	-	-	-	54,1
	Média	-	-	-	100	60,8	-	-	-	99,6	-	-	-	54,1
Número Kappa	A	24,5	16,9	16,8	-	2,9	-	-	-	-	-	-	-	0,3
	B	24,5	16,9	16,8	-	2,9	-	-	-	-	-	-	-	0,3
	Média	24,5	16,9	16,8	-	2,9	-	-	-	-	-	-	-	0,3
Alvura, %ISO	A	20,9	28,6	31,7	46,8	75,7	86,1	87,8	88,7	86,2	89,9	90,4	90,8	90,0
	B	20,9	28,6	31,7	46,8	75,5	86,1	87,8	88,7	86,2	89,9	90,4	90,8	90,0
	Média	20,9	28,6	31,7	46,8	75,6	86,1	87,8	88,7	86,2	89,9	90,4	90,8	90,0
Reversão de alvura, %ISO	A	-	-	-	-	-	-	-	-	-	-	-	-	1,5
	B	-	-	-	-	-	-	-	-	-	-	-	-	1,5
	Média	-	-	-	-	-	-	-	-	-	-	-	-	1,5
Viscosidade, dm3/kg	A	965	894	859	-	-	-	-	-	-	-	-	-	716
	B	965	901	865	-	-	-	-	-	-	-	-	-	707
	Média	965	898	862	-	-	-	-	-	-	-	-	-	712
Hexa, mmol/kg	A	63,5	62,8	-	-	-	-	-	-	-	-	-	-	2,4
	B	63,4	62,8	-	-	-	-	-	-	-	-	-	-	2,4
	Média	63,5	62,8	-	-	-	-	-	-	-	-	-	-	2,4

Quadro 3 – Resultado da etapa de branqueamento Fator Kappa 0,28

Condições e Resultados	Rep.	MARROM	Estágios de Branqueamento											
			O	**Q**	**D**	**(EP)**	**D(a)**	**D(b)**	**D(c)**	**D(int)**	**P(a)**	**P(b)**	**P(c)**	**P(int)**
Consistência, %	-	-	10	10	10	10	10	10	10	10	10	10	10	10
Temperatura, °C	-	-	90	80	90	90	80	80	80	80	80	80	80	80
Tempo, min	-	-	60	30	120	60	120	120	120	120	60	60	60	60
Pressão, kPa	-	-	350	-	-	-	-	-	-	-	-	-	-	-
O_2, kg/tas	-	-	18	-	-	-	-	-	-	-	-	-	-	-
Fator kappa	-	-	-	-	0,28	-	-	-	-	-	-	-	-	-
ClO_2, como ClO_2, kg/tas	-	-	-	-	17,9	-	1,0	2,0	3,0	1,3	-	-	-	-
H_2O_2, kg/tas	-	-	-	-	-	7,8	-	-	-	-	3	3	3	3
H_2SO_4, kg/tas	-	-	-	-	-	-	1,5	1,0	-	1,4	-	-	-	-
NaOH, kg/tas	-	-	15	-	2,7	14,5	-	-	-	-	6	6	6	6
$MgSO_4.7H_2O$, kg/tas	-	-	3	-	-	3	-	-	-	-	-	-	-	
DTPA, kg/tas	-	-	-	2,0	-	-	-	-	-	-	-	-	-	-
pH final	A	-	11,3	7,0	2,6	10,9	4,8	4,6	5,0	4,7	11,0	11,2	11,1	11,1
	B	-	11,1	7,0	2,6	10,9	4,8	4,6	5,0	4,7	11,0	11,2	11,1	11,1
	Média	-	11,2	7,0	2,6	10,9	4,8	4,6	5,0	4,7	11,0	11,2	11,1	11,1
Consumo de reagentes, %	A	-	-	-	100	53,4	-	-	-	99,6	-	-	-	54,1
	B	-	-	-	100	53,9	-	-	-	99,6	-	-	-	54,1
	Média	-	-	-	100	53,7	-	-	-	99,6	-	-	-	54,1
Número Kappa	A	24,5	16,9	16,8	-	1,9	-	-	-	-	-	-	-	0,5
	B	24,5	16,9	16,8	-	1,9	-	-	-	-	-	-	-	0,5
	Média	24,5	16,9	16,8	-	1,9	-	-	-	-	-	-	-	0,5
Alvura, %ISO	A	20,9	28,6	31,7	53,9	79,3	86,1	88,0	89,0	86,1	89,8	90,4	90,9	90,0
	B	20,9	28,6	31,7	53,9	79,3	86,1	88,0	89,0	86,1	89,8	90,4	90,9	90,0
	Média	20,9	28,6	31,7	53,9	79,3	86,1	88,0	89,0	86,1	89,8	90,4	90,9	90,0
Reversão de alvura, %ISO	A	-	-	-	-	-	-	-	-	-	-	-	-	1,3
	B	-	-	-	-	-	-	-	-	-	-	-	-	1,3
	Média	-	-	-	-	-	-	-	-	-	-	-	-	1,3
Viscosidade, dm3/kg	A	965	894	859	-	-	-	-	-	-	-	-	-	775
	B	965	901	865	-	-	-	-	-	-	-	-	-	771
	Média	965	898	862	-	-	-	-	-	-	-	-	-	773
Hexa, mmol/kg	A	63,5	62,8	-	-	-	-	-	-	-	-	-	-	2,3
	B	63,4	62,8	-	-	-	-	-	-	-	-	-	-	2,1
	Média	63,5	62,8	-	-	-	-	-	-	-	-	-	-	2,2